European Commission

Combined Draft Renewal Assessment Report prepared according to Regulation (EC) N° 1107/2009
and
Proposal for Harmonised Classification and Labelling (CLH Report) according to Regulation (EC) N° 1272/2008

Glyphosate

Volume 3 – B.8 (AS)

Rapporteur Member State: Assessment Group on Glyphosate (AGG) consisting of FR, HU, NL and SE

Version History

When	What
2021/06	Initial RAR

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B.8.5. MONITORING DATA CONCERNING FATE AND BEHAVIOUR OF THE ACTIVE SUBSTANCE, METABOLITES, DEGRADATION AND REACTION PRODUCTS

B.8.5.1. Summary of monitoring data for all compartments

An extensive review of existing monitoring data have been submitted, including collection of public monitoring data (raw data and aggregated data from national authorities and any regional/national agencies - note that aggregated data refers to information provided in publicly available reports, *e.g.* from environmental agencies or research institutes) and review of open literature. For the current approval renewal, there are 10 new applicant studies, 7 existing applicant studies and several published peer-reviewed papers (considered reliable or reliable with restrictions) covering the monitoring of glyphosate and its principal metabolite AMPA in soil, groundwater, surface water, transitional water, sediment, drinking water and air.

Two new applicant studies relate to collection and analysis of public monitoring data for soil, groundwater, surface water, transitional water, drinking water and sediment. These are [redacted] (2020, CA 7.5/001) which describes the collection process of public monitoring data (from regional/national environment agencies) for European countries for glyphosate, AMPA and HMPA and the report by [redacted] (2020, CA 7.5/002) which assesses the data collected by [redacted] (2020, CA 7.5/001). These two studies were designed to be more comprehensive than previous studies by considering additional metabolites, compartments and time periods.

In addition to these, further studies or papers were collected:

- For soil monitoring there are a further five published peer-reviewed papers presented.
- For groundwater monitoring there are three new applicant studies, four existing studies and eighteen published peer-reviewed papers presented.
- For surface water monitoring there are seven new applicant studies and forty seven published peer-reviewed papers presented.
- For transitional water monitoring there are two new applicant studies and one published peer-reviewed paper presented.
- For drinking water monitoring there is one new applicant study, two existing applicant studies and two published peer-reviewed papers presented.
- For sediment monitoring there is one existing applicant study and seven published peer-reviewed papers presented.
- For air monitoring, there are no applicant studies. Three published peer-reviewed papers are presented.

The studies and publications assessed cover a number of different spatial extents ranging from pan-EU and country, to regional/provincial, and even specific locations/fields. Similarly, they cover a range of temporal scales ranging from a single sampling occasion to multi-monthly and annual sampling schemes.

The data have been collated and analysed by applicant with regard to compliance of regulatory triggers, considering that the whole EU data set was large enough to capture a range of agronomic, geographical, pedoclimatic and hydrogeological situations, as well as providing a good temporal coverage allowing assessment of the state of a compartment in different seasons and hydrological regimes.

However, if the collected data indeed covers a wide variety of situations (as the public monitoring programs are aimed at), RMS highlights that further information and analysis are precisely missing to get a clear picture of what the overall data set really captures, notably in terms of relation to use pattern of the active substance and temporal percentile.

Reasoning on the whole data set to get a rate of compliance to regulatory triggers or to calculate any 90th, 95th or 99th percentile concentration as proposed by applicant is *de facto* biased; these should be taken with caution as they do not cover consistent situations, and cannot be compared to those considered in risk assessment.

Summary table of main results taken from the literature data have been provided by applicant for each compartment, and have been reported by RMS in the corresponding section summaries below.

The overall rates of compliance of the collated data with different RACs and thresholds as well as maximum reported concentrations in each compartment are provided in Table 8.5-1. RMS higlights that only maximum values from EU public monitoring data set and from literature data that could be assimilated to EU public monitoring data (notably in terms of scale, compartment of interest for EU approval) are included in the following table. Literature data relying on specific experiment (specific conditions, flux concentration rather than environmental compartment concentration), although may be considered reliable, are not considered in the table below. Details of results from all submitted studies are reported in table results in corresponding compartment summaries.

Table 8.5-1: Summary of minimum reported rates of quantification, of compliance with regulatory acceptable concentrations (RAC) or relevant thresholds and reported maximum concentrations for glyphosate (GLY) and AMPA in each environmental compartment

		GLY				AMPA			
	Dataset Size	Quantif (% samples	RAC[1]/ Threshold (µg/L)	Compliance (%)	Max Conc. (µg/L unless stated)	Quantif (% samples)	RAC[1]/ Threshold (µg/L)	Compliance (%)	Max Conc. (µg/L unless stated)
Soil	Small	~21%	94.6* mg/kg	100	2.05 mg/kg	~42%	26.4 mg/kg	100	1.92 mg/kg
Ground water	Very Large	~2%	0.1	99.38	1005 39.21[4]	~2.9%	10.0[2]	99.99	19.0
Surface Water	Very Large	~40%	100	99.99	3400[¤]	~64%	1200	99.99	3369[¤]
Tidal Water	Very Small	~7%	100	100	1.2	~33.1%	1200	100	0.9
Drinking Water	Small/ Medium	-[$]	0.1	99.84	0.92	-[$]	0.1[3] 10.0[2]	99.78 100	3.0
Sed	Small/ Medium	-	NA	-	2.84 mg/kg <4.0	-	NA	-	9.56 mg/kg <4.0
Air	Very Small	~7% to ~56%	NA	-	1.225 ng/m3	~1.3%	NA	-	-

NA – Not available
1 - Regulatory acceptable concentration
2 - Threshold for non-relevant metabolite
3 - Threshold value chosen to allow statistical comparisons only
4 – Maximum excluding outliers
* The value of 94.6 mg/kg is a RAC derived for soil macroorganisms, and correspond to the NOEC divided with a safety factor of 5. For microorganisms, no significant effect is observed for a tested NOEC (highest tested concentration) of 33.1 mg/kg.
[$] Frequency of quantification not available for a EU combined data, data from individual MS only
[¤] Maximum concentration to be confirmed once additional data are provided by applicant on outlier exclusion procedure.

In conclusion, it is an extended data set for most compartments that have been collected by applicant, although not always equally spatially distributed throughout EU (see summary for each compartment below). RMS emphasizes very few exceedance of the regulatory triggers are detected for each compartment but it often remains many uncertainties to set into context these results.

Particular attention should be paid to the results in surface water and air.
The number of detection above LOQ (respectively ~40% and ~64% samples EU-wide for GLY and AMPA) tend to indicate that the active substance is widely and regularly found in surface water. This indeed reflects the spread and diversity of use of glyphosate containing products, but it still cannot be evaluated on which extend actual peak concentration and exceedance of the RAC in relation to pesticide use of glyphosate is caught by these monitoring programs. These levels of quantification highlight the necessity of implementing better-reasoned practices for glyphosate containing products, in order to limit environmental contamination.
The few available data in air also shows a high frequency of quantification of glyphosate in air, despite its

intrinsic properties which indicate no significant potential of volatilization. Further data would be necessary to confirm these observations.

Summary of soil monitoring data

Regarding the collection of public monitoring data; according to [redacted] (2020, CA 7.5/001) and [redacted] (2020, CA.5/002) which deals with these public data, for soil compartment, there were hardly any official programs in place targeting monitoring of glyphosate or its metabolites residues in soil. Raw data for glyphosate and AMPA were collated by applicant for the German federal state of Brandenburg only. In addition, aggregated monitoring data at the EU level for soil were obtained in the form of a research article (Silva *et al.*, 2018). These data are included in the review made in [redacted] (2020, CA 7.5/002).

Data from the German federal state of Brandenburg: The small number of raw data (57 samples from 29 sites, covering 9 years period) of GLY and AMPA analyses from agricultural soils were assessed against the soil regulatory acceptable concentration (RAC) of 94.6 mg/kg for GLY and 26.38 mg/kg for AMPA. Analysis indicates that GLY is quantified in ~30% of samples (total 43 samples) and AMPA is quantified ~86% of the samples (total 14 samples) No analyses exceeded the RAC with the maximum measured concentration being 0.25 mg/kg for GLY and 0.975 mg/kg for AMPA. However, these samples cannot be related to land use (not reported) although study authors suggested it was largely agricultural land (visual assessment of locations in GIS), neither to a specific soil layer depth, since sampling method is not described.

In the aggregated report (Silva *et al*., 2018, CA 7.5/004) results stem from data that are well distributed across the EU and sample a range of different cropping systems. 300 of the samples have been collected as part of the LUCAS topsoil project between April and October of 2015 and 17 samples are from three independent vineyards in north-central Portugal taken in September 2015. Results from these data indicate GLY is quantified in ~21% of 317 soil samples, AMPA is quantified in ~42% of 317 soil samples. None exceed the RAC, or come close to doing so, with the maximum concentration being 2.05 mg/kg for GLY and 1.92 mg/kg for AMPA, associated with permanent crops (vineyards) in central Portugal. However, the measured concentration should be regarded with caution since the exact sampling depth is unknown (15/20cm), and in any case higher than the one that would be considered for risk assessment in permanent crops (5cm). Also, the glyphosate application amounts, as well as the time passed since last application are not known.

Within the open literature review, there are five published peer-reviewed papers for soil monitoring data. These papers report concentrations that are partly not directly comparable with the soil compartment that is typically assessed as part of the approval process, *e.g.* concentrations in soil pore water, or unconsistent soil layer depth sampling compared to what is considered in risk assessment.They were identified in the formal literature search conducted for the current submission and cover a wide range of use settings, predominantly agricultural, including rotational and permanent crops.

Karanasios *et al*. (2018, CA 7.5/003) reports monitoring data for glyphosate and AMPA in Greek agricultural soils associated with olive production, but the residues are measured in 30 cm depth samples, which is much higher than the standard depth for risk assessment purpose for perennial crops. Napoli *et al.* (2016, CA 7.5/005) describes a runoff experiment with glyphosate in a vineyard in Italy, where soil residues after 12 months were additionally assessed (5cm depth samples). Daouk (2013b, CA 7.5/053) assesses glyphosate and AMPA in soil after application of the parent to a vineyard soil in Switzerland but it only relates to porewater concentration, measured through the soil profile, at depths not relevant for risk assessment purpose (40, 60 and 80 cm).
Silva *et al*. (2018, CA 7.5/004), previously mentioned above and included in [redacted] (2020 CA7.5/002) as aggregated report, describes the result from a field study to measure the distribution of glyphosate and AMPA in European topsoils and results were included in review of [redacted] (2020). Székács *et al.* (2014, CA 7.5/006) reports measurements of glyphosate in soils in Hungary from agricultural and industrial settings, but the results cannot be set into context of the use pressure of

glyphosate.Contaminant concentrations of soil profiles from topsoil to subsoil were characterised down to ground water table, creating one sample in every 30 or 50 cm.
Measurements from these published papers are reported in table below. However, it should be kept in mind that they are only valid for the time and place they represent, and are not equivalent to the PECsoil calculated for risk assessment purpose.

Table 8.5-2: Summary of reported maximum concentrations of glyphosate (GLY) and AMPA in soil

Reference	**Use Setting**	**Maximum Concentration (mg/kg unless indicated)**	
		GLY	**AMPA**
[redacted] 2020, CA 7.5/001 [redacted] [redacted] [redacted] [redacted] 2020[1], CA 7.5/002	Various incl. rotational and permanent crops (15/20cm depth samples)	2.05[1]	1.92[1]
Karanasios, E. *et al.* 2018, CA 7.5/003	Olive (30cm depth samples)	0.35	0.65
Silva, V. *et al.* 2018, CA 7.5/004	Various incl. rotational and permanent crops (15/20cm depth samples)	2.05	1.92
Napoli, M. *et al.* 2016, CA 7.5/005	Vineyards (5cm depth sample)	<LOD	0.065 ±.006
Székács, A. *et al.* 2014, CA 7.5/006	Agricultural (unspecified); Industrial (30/50 depth samples)	0.56 ± 0.26	NA

[1] Silva *et al.* 2018 was included in this study as an aggregated report, and provides the mximum concentration values of the overall dataset.
NA – Not applicable

All reported soil concentrations are well below the RACs for soil macroorganisms of 94.6 mg/kg for glyphosate (GLY) and 26.4 mg/kg for AMPA. Concentrations are also well below the NOEC of 33.1 mg/kg (highest tested concentration) for soil microorganisms. However, it should be kept in mind that the measured concentration from these monitoring programs or literature articles are only valid for the time and place they represent, and are not equivalent to the PECsoil calculated for risk assessment purpose.

Summary of ground water monitoring data

Regarding the collection of public monitoring data, an extended monitoring data set was collected throughout 14 EU countries and analysis of these data have been proposed by the study authors to assess what they call “the state of all environmental compartments” and “consider the impacts this state might have on biota, ecosystems and human health via drinking water” ([redacted] (2020, CA 7.5/001),[redacted] (2020, CA 7.5/002). Results are given for each country, and for the whole combined EU data set. These include all the samples after removal of unvalidated data (unavailable data, analysis not completed, uncertain data or not validated data), and represents >251 000 samples collected from >37 800 sampling sites for glyphosate and >230 000 samples collected from >34 400 sampling sites for AMPA.

The EU combined monitoring dataset was dominated by French data (~79.1%/82.4% of the samples for GLY/AMPA) with smaller contributions from Denmark (~5.8%/6.4% for GLY/AMPA), Germany (~5.7%/5.2%) and Austria (~3.8% for GLY).

Detection of GLY above the limit of quantification (>LOQ) in GW samples of EU combined data set was ~2% ranging from as low as 0.2% in AT to as high as 10.3% in ES. Compliance of the combined EU data set with the 0.1 µg/L threshold was 99.4% of samples from 97% of sites, indicating few exceedances (~0.6% of samples from ~3.0% of sites). The assessment of outliers identified 10 outliers in the dataset and if these are excluded the maximum concentration is reduced to 39.2 µg/L which is well below the SW RAC (for groundwater fed ecosystems) Case studies exploring elevated rates of groundwater detection in ES and the UK, suggest these findings are most likely a function of direct contamination, like spray drift into open wells.

Detection of AMPA above the limit of quantification (>LOQ) in GW samples of EU combined data set was ~2.9%, ranging from as low as 0.4% in ES to as high as 19.5% in BE. Compliance with the regulatory threshold of 0.1 µg/L was very high (99.3% of samples) with few exceedances (~0.7% of samples) indicated. Compliance with the 10 µg/L regulatory threshold for a non-relevant metabolite was 99.998% of samples from 99.994% of sites, indicating rare exceedances (~0.002% of samples from ~0.006% sites). A maximum concentration of 16 µg/L is reported from the review of [redacted], 2020, while a maximum value of 19 µg/L was reported in previous review of [redacted], 2016. Although they exceed the regulatory threshold for a non-relevant metabolite of 10 µg/L, a consumer risk assement based on the maximum value of 19 µg/L indicate that the exposure via drinking water for the most vulnerable consumers (infants) was estimated representing less than 1% of the ADI. In addition, these maximum concentrations are below the SW RAC (for groundwater fed ecosystems).

Data from this review compares well with results from the previous data collection, ([redacted], 2012) that was reviewed in the RAR 2015, and which indicated that glyphosate has been detected in Europe with 0.64 % above the limit concentration 0.1 µg/L; and AMPA with 0.77 % above 0.1 µg/L. The maximum measured concentration for AMPA from previous data collection is 19 µg/L ([redacted], 2016, CA7.5/010).

However, it should be kept in mind that these conclusions based on % of compliance toward regulatory triggers cannot be related to a consistent groundwater type, or to any clear temporal or spatial percentile, either to any actual use pattern of the active substance. This because key information on description of monitoring locations are often missing in such public monitoring data and were thus not included in the applicant's analysis. It is neither possible to evaluate the vulnerability to leaching of the sampling sites. Frequency and regularity of sampling have also not been included as criteria in the data analysis, although the sampling effort can clearly be very different from a site to another. Indeed, [redacted] (2016), focusing on the results from the French public monitoring between 1999 and 2013, showed that more than half of stations for which sampling results are available were in fact monitored for one single year over the 15 year period studied, while less than 15% of the stations have been monitored for 5 years or more over the period. With regard to the frequency of sampling within a year in groundwater, [redacted] (2016) reports a frequency varying between once and twice a year, with a majority of measurements being carried out once a year. The exception to this is 2012, where 4 or 5 measurements per year were conducted for more than 40% of stations. This means the temporal distribution of the overall data set in [redacted], (2020) is unknown, but also that the spatial distribution of the sampling results might be affected by this heterogeneous sampling effort.

RMS notes that further information on use and detailed data on sampling sites may be available in underlying reports available at national level not collated here, or from the open literature. For instance several publication - Rosenbom et al. (2015, 2019, 2020 CA 7.5/016 and CA7.5/099), Norgaard et al. (2014, CA 7.5/021) - describe a well controlled monitoring program in DK with regard to use pattern and soil vulnerability (see paragraph on literature hereunder). However, these are often relating to a reduced number of sampling sites, and at such specific scale that they cannot be taken into account to set into context the huge EU scale monitoring results provided in [redacted], (2020). Additional information may be requested and analysed at MS level for product registration.

Regarding the exceedance of the 0.1µg/L trigger, there are 1496 samples >0.1 µg/L for glyphosate, distributed on 1128 sites, with maximum number of samples >threshold at single site being 13. For AMPA they are 1511 samples >0.1 µg/L distributed on 994 sites, with maximum samples >threshold at single site being 37.

The exceedances were therefore considered as non-systematic given that very small proportion were consecutive sampling. However, too little information are given on this analysis to confirm applicant conclusions (the number of consecutive sampling at one site are not related to the total number of sampling at this site) and too little information is given in general on the samples exceeding the triggers and reported in [redacted] (2020). For instance, the number of exceedance and the maximum values are given for each MS for the whole period, but not given per year. Some of the maximum concentration can be recovered from [redacted], 2016 but these might not be exhaustive (not covering the same overall period). It also remains unclear whether the exceedance can be related to specific conditions (vulnerable context, shallow groundwater only, higher pressure of use or misuses of glyphosate containing product….). Additional assessment could be performed on this point to confirm the exceedance are not related to long-term contamination in some locations. This is a data gap identified for applicant. On the contrary, it cannot be evaluated on which extent the high percentile of compliance with regulatory triggers indicated by study authors (0.1 µg/L triggers represents the 98.976th percentile concentration for glyphosate) is influenced by a total absence of use of the active substance in the catchment areas of the sampling locations. However, this influence might be limited in the case of glyphosate, considering the spread and diversity of uses of glyphosate containing products (including agricultural and non-agricultural uses, professional and non professional uses).

Specific elucidation was nevertheless performed in Spain and the UK in [redacted] (2020) since these two MS showed lower compliance rates with the 0.1 µg/L threshold (Spain 93.6% and the UK 93.0%).

- For Spain it was found that 128 out of 137 sites showing glyphosate exceedances are situated in the region of Andalucía. Eleven sites which showed the most consecutive exceedances are located in rural areas dominated by agricultural use and that the all 11 monitoring sites show deficiencies, mostly due to inappropriate well construction or at location which makes them susceptible to overspray. Assumption is also made that the combination of depleted soil OC that are typical of southern Spain (thus reducing adsorption of glyphosate) together with repeated high dosage applications in orchards may cause leaching of glyphosate to shallow groundwater.
- For the UK the vast majority of glyphosate exceedances >0.1 µg/L, and all multiple exceedances, relate to a small area near Hereford in west-central England. All detections in this area relate to the time period 2000-2009, as monitoring for glyphosate discontinued in 2010. Most detections, and the highest glyphosate concentrations, relate to the vicinity of a large plant nursery, with some further detections, lower in concentration and less frequent, in the urban area of Hereford. The local focus on glyphosate analyses together with a dense monitoring network and frequency may indicate that a problem with glyphosate occurred in the area and that the contamination spread and temporal course was examined. A possible scenario may have been an accident with glyphosate containing products.

[redacted] (2016) also provides a review of glyphosate and AMPA monitoring for groundwater across EU. It is an update of previous review from [redacted] (2012) that was included in the RAR 2015. The raw data collected in this report overlaps the data from [redacted], 2020. However, in some cases it gave further information on some findings above 0.1 µg/L.

- In AT, no further data compared to the previous review of [redacted] 2012. Glyphosate was detected in isolated cases. AMPA was detected somewhat more frequently and at higher concentrations. There is no information about the type of groundwater, although the results, as presented, related to pore groundwater only, not the springs from fractured aquifers. Traces of AMPA were also found in two spring water samples and it was considered unclear at the time whether these findings were related to glyphosate or to aminophosphonates from detergents.
- In DK, there is no information on samples data above 0.1 µg/L, other than the depth being less than 15 metres in all samples analysed since 2004. Study author however indicate that "a recent study ([redacted], 2011) reported the investigation of four of the wells where glyphosate and AMPA had been detected in the GEUS groundwater survey. It was concluded that the occurrence of glyphosate and AMPA was unlikely to be caused by agricultural and other approved usages."
- In FR, investigations (ISL, 2007; [redacted] 2015) relating to a small number of detections of glyphosate in drinking waters, most of which were derived from groundwater, revealed that the detections were most likely due to sample contamination, analytical problems or short-term contamination of small private or community wells. From the findings of another study (Anonymous, SCE, 2012, CA 7.5/011) to analyse the potential contamination of groundwater with glyphosate (and AMPA) at 27 sites from 2007-2010, it is concluded that none of the glyphosate detections could be attributed to long-term contamination of typical groundwater. The majority of detections occurred once only, and the small number of multiple detections occurred in shallow groundwater (spring water) or wells unsuitable for groundwater monitoring, suggesting superficial short-term contamination. However, the heterogeneity of the data, the absence of information on glyphosate use in this study constituted a limited approach, as this was noted in the previous review from RAR 2015.

- In IT, Glyphosate in groundwater was detected in 9 samples (0.6%) (detection limit of 0.1 µg/L), of a total of 1497 samples, taken from at least 359 sites from 2005-2008, and 2011-2012 (no data for 2009-2010). The maximum concentration was 1.2 µg/L.In the period 2005-2008 all the detections were in May 2007. AMPA was detected in 14 samples (1.2%) of a total of at least 1156 samples from at least 359 sites in the years 2007-2008 and 2011-2012. The maximum concentration was 1.3 µg/L. Further investigation of the May 2007 detections of glyphosate revealed that the conditions of the wells were not suitable for collection of groundwater quality samples, and that contamination was attributable to superficial influences, such as inflow of surface water and/or mud and point source contamination; in all except one of the wells which remained under investigation.
- In DE, Groundwater data is collated at Federal level and glyphosate and AMPA data has been obtained for the years 1996-2008 (though 2008 data was incomplete, and no more recent data has become available). Glyphosate and AMPA have been reported for a small number of sites, with AMPA at higher frequency and concentrations. However, an investigation (up to 2004) of sites with glyphosate detections showed all these to have been due to invalid analyses or contaminated observation wells ([redacted], 2006).
- In NL no more data available compared to [redacted], 2012. Both glyphosate and AMPA have been detected in a small number of groundwater samples (once each in 10 different wells). These were investigated in detail and it was concluded that 5 of the results (all at levels below 0.15 µg/L were uncertain (high margins of error) whilst overall, all sampling points with positive detections were in cultivation areas with sandy or highly sandy soils, and samples were taken mainly from shallow groundwater.
- In ES, Glyphosate monitoring data for groundwater have become available for 2009-2012. Glyphosate was frequently detected (34% of samples) in groundwater, and above 0.1 µg/L in 8.9% of samples, with a maximum concentration of 25 µg/L in 2012. There was no information on the type or depth of groundwater, or whether the focus was on particularly vulnerable sites as it was the case in an earlier study on the 2007-2010 study (Sanchís et al., 2012), where glyphosate was detected in a number of groundwater samples taken during glyphosate application periods (detected in 47.3% of the samples analysed and the average concentration was reported as 0.202 µg/L, and the range as <LoQ – 0.624 µg/L). No further investigations of these detections is given in the report.

The individual report for detailed monitoring studies cited in [redacted], 2016, from Italy ([redacted], 2011), Germany ([redacted], 2006), The Netherlands ([redacted]., 2010), Sweden ([redacted], 2005), France (Anonymous, 2012) and Spain (Sanchís et al., 2012), have already been reviewed in the RAR 2015 but are submitted for completeness. These sites investigations confirm the difficulty of interpreting groundwater monitoring data without site specific context. The review from RAR 2015 is reported here: "In some cases, clarification could be presented by the authors; e.g. causes for glyphosate findings in groundwater aquifers > 0.1 µg/L were point source contamination, affection by waste deposit, deficient analysis, no fully protected wells, potential for direct hydrological connectivity between surface water and shallow groundwater via artificial drainage systems and short-term contamination of shallow groundwater or spring water. However, it remains often unclear if findings above the authorisation limit originate from a technically correct and regulation compliant use of the respective plant protection products in agricultural areas, or misuses or if construction defects on the groundwater abstraction points are reasonable for the limit exceedances etc. Another emerging issue is that other sources of glyphosate than agricultural applications, e.g. the control of weeds on streams and drains, around railways, roads, sports fields and industrial areas have to be considered as well. Regarding the pathways of glyphosate into groundwater when used for agricultural purposes as intended, RMS considers that groundwater contamination > 0.1 µg/L via direct leaching is generally not expected as the substance is strongly adsorbed to soil particles. Exceptions may be made, e.g. for preferential flow. Sanchís et al. (2012) describe that surface waters exist in 10 out of 11 sampling sites where glyphosate was (at least partly) detected".

Within the open literature review, groundwater monitoring data were obtained from several published peer-reviewed papers, that provides additional information of various interest and reliabiliy

Rosenbom et al. (2019, CA 7.5/016, 2020, CA7.5/099), Rosenbom et al. (2015, CA 7.5/019) and Norgaard et al. (2014, CA 7.5/021) present data interpretations from the Danish Pesticide Leaching Assessment Programme which comprises 6 highly instrumented field sites. These monitoring programs at field scale are well documented with regard to use pattern, depth of sampling and soil vulnerability. Results from Rosebom et al (2015) indicate a potential for leaching of many pesticides and degradation products (among which Glphosate and AMPA) to shallow groundwater via preferential flow in the loamy soils compared to the sandy soils among the 6 instrumented field sites. While Norgaard et al. (2014) demonstrated, based on a 12 year monitoring serie from the shallow drainage system of one of the loamy site, that the timing of precipitation in relation to glyphosate application is a controlling factor for glyphosate leaching at this site.

Di Guardo and Finizio (2016, CA 7.5/018) does not generate monitoring data but relies on monitoring data collated from the ARPA Lombardia (IT). It aimed at developing tools for risk manager to identify groundwater vulnerable areas to pesticides and undertake mitigation actions at regional scale. 95th percentile monitoring values from 2005 to 2009 in 320 montoring stations, indicate that the groundwater concentrations of glyphosate ranged between 0.04 – 0.06 µg/L in 280 wells (98%) and greater than the parametric drinking water limit of 0.1 µg/L in 5 wells (2%). It thus provides additional results from public monitoring programs that were apparently not collated within [redacted], 2020. These results can however considered outdated now.

Some articles provide additional data from grab sample monitoring at regional scale: Poiger et al. (2017, CA 7.5/017) for specific regions of Switzerland, Mörtl, M. et al. (2013, CA7.5/024) reports results from analysis of 36 ground water samples collected from Békés county in Hungary at 14 sampling sites in 2010. However, these results cannot be directly related to the use of glyphosate within the cathment areas and the results from HU may be outdated.

McManus et al. (2014, CA 7.5/020) explores the associations of pesticide occurrence in groundwater in Ireland and the geological characteristics of the monitoring points (MPs) contributing area. However, the physical characteristics of the monitoring points are tested with regard to the overall pesticide detection and therefore no conclusions are specific to glyphosate. It seems that glyphosate is not detected at level above 0.1 µg/L, however no further quantitative conclusions on glyphosate use and its presence in GW can be made.

Sanchis et al. (2012, CA 7.5/025 and CA 7.5/026) presents regional data for Catalonia, Spain; Glyphosate was investigated in 139 samples between May and September 2007 to 2010, from sites qualified of high risk of contamination (parly due to intensive agriculture). Concentrations ranged from LOQ to 2.6 µg/L. However, the pathways of glyphosate into groundwater are not investigated by the authors. In this article also, due to the fact that surface waters exist in 10 out of 11 sampling sites, surface run-off and/or drainage into these waters with subsequent bank filtration into groundwater cannot be excluded.

Some articles present site investigations focused on locations with groundwater quality issues: [redacted] (2011, CA 7.5/028) investigated 5 sampling location in Lombardia, were glyphosate exceeded the limit concentration of 0.1 µgL in May 2017. Until now, the findings could not be correlated with the normal and proper use of glyphosate in the field. [redacted] (2010, CA 7.5/029) elucidates findings of glyphosate and AMPA in groundwater in 14 sites in the Netherlands. The investigation showed that the protection of the well was poor at 2 sites and medium at 5 sites, and that surface water inflow or contamination by spray drift cannot be excluded at these locations, while no explanation could be found during this investigation for 6 of the sites at which glyphosate was detected. .

Bruchet et al. (2011, CA 7.5/027) present data in shallow boreholes exploited for drinking water following bank filtration.

Some of the datasets likely overlap with those in existing applicant studies presented e.g. [redacted] (2020, CA 7.5/002). Concentration values from these papers, when available are reported in table below.

An overview of maximum concentrations of glyphosate (GLY) and AMPA in groundwater reported by the applicant studies and publications is presented in table below while the maximum reported rates of exceedance of various thresholds by these datasets are summarized in table after.

Table 8.5-3: Summary of reported maximum concentrations of glyphosate (GLY) and AMPA in groundwater

Reference	Location	Context	Maximum Concentration (µg/L)	
			GLY	AMPA
[redacted], 2020, CA 7.5/002	EU	Summary (large scale monitoring)	1005.0 39.2[1]	16.0 16.0[1]
[redacted], 2019a, CA 7.5/008	FR	Summary (large scale monitoring)	1005.0 10.7[5]	9.3 2.5[5]
[redacted], 2016, CA 7.5/010	EU	Summary (large scale monitoring)	28.0	19.0
[redacted], 2016, CA 7.5/009	FR	Summary (large scale monitoring)	1005.0 8.9[5]	19.0 2.2[5]
Anonymous, 2012, CA 7.5/011	FR	Site investigation of highly vulnerable sites	12.9	3.4
[redacted], 2012, CA 7.5/013	EU	Summary (large scale monitoring)	24.0	19.0
[redacted], 2006, CA 7.5/014	DE	Site investigation	0.32[2]	0.5
[redacted], 2005, CA 7.5/015	SE	Site investigation	0.18	NA
Rosenbom, A. et al., 2019, CA 7.5/016 Updated in Rosenbom, A. et al., 2020, CA 7.5/099	DK	Soil pore water in saturated zone - PLAP Sites	8.60	1.30
	DK	Groundwater in saturated zone - PLAP Sites	0.13	0.02
Poiger, T. et al., 2017, CA 7.5/017	CH	Investigation of 14 vulnerable sites, including karst	0.025	0.65
Di Guardo A., Finizio A., 2016, CA 7.5/018	IT	Lombardy, investigations base on regional monitoring data.	NR	NR
Rosenbom, A. et al., 2015, CA 7.5/019	DK	Soil pore water ~1 m - PLAP Sites	31.0	1.6
	DK	Groundwater - PLAP Sites	0.67	0.08
McManus, S., et al., 2014, CA 7.5/020	IE	Global site investigation	<0.1[3]	<0.1[3]
Norgaard, T., et al., 2014, CA 7.5/021	DK	Drainflow at 1.1 m depth	31.0	~1.6[3]
Mörtl, M., et al., 2013, CA 7.5/024	HU	36 ground water samples; 14 sampling sites in Békés county, Hungary	0.98	NA
Sanchís, J., et al., 2012, CA 7.5/025	ES	139 samples from 69 site, regional monitoring program	2.56	NA
Bruchet, A., et al., 2011, CA 7.5/027	FR	Groundwater following bank filtration	<0.1[7]	<0.1[7]
[redacted], et al., 2011, CA 7.5/028	IT	Site investigation of 5 sites in Lombardy	1.375[6]	NA
[redacted], et al., 2010, CA 7.5/029	NL	Site investigations	4.74	0.23[4]

NR/NA – Not reported/Assessed

[1] - Excluding outliers

[2] - Wastewater from sewage plant

[3] - Inferred from graph

[4] - Was not target of the investigation

[5] - 99th percentile

[6] - Confirmed point source contamination

[7] - Bank infiltration

Table 8.5-4: Summary of reported exceedance of various thresholds for measured concentrations of glyphosate (GLY) and AMPA in groundwater

Reference	Location	Context	Exceedance threshold and rate		
			Threshold (µg/L)	GLY (%)	AMPA (%)
[redacted], 2020, CA 7.5/002	EU	Summary (large scale monitoring)	0.1	0.62	0.68
			10	NA	0.002
[redacted], 2019a, CA 7.5/008	FR	Summary (large scale monitoring)	0.1	0.7[4]	1.1[4]
			2	<0.1[4]	<0.1[4]
[redacted], 2016, CA 7.5/010	EU	Summary (large scale monitoring)	0.1	0.6	0.75

[redacted], 2016, CA 7.5/009	FR	Summary (large scale monitoring)	0.1	3.0[2]	11.4[2]
			2	<0.1[2]	<0.1[2]
Anonymous, 2012, CA 7.5/011	FR	Site investigation of highly vulnerable sites	NR	NR	NR
[redacted], 2012, CA 7.5/013	EU	Summary (large scale monitoring)	0.1	0.64	0.77
[redacted], 2006, CA 7.5/014	DE	Site investigation	NR	NR	NR
[redacted], 2005, CA 7.5/015	SE	Site investigation	NR	NR	NR
Rosenbom, A. et al., 2019, CA 7.5/016 Updated in Rosenbom, A. et al., 2020, CA 7.5/099	DK	Soil pore water in saturated zone - PLAP Sites	0.1	0.0	3.1[6]
	DK	Groundwater in saturated zone - PLAP Sites	0.1	0.9[5]	0.0
Poiger, T. et al., 2017, CA 7.5/017	CH	Investigation of 14 vulnerable sites, including karst	NR	NR	NR
Di Guardo A., Finizio, A., 2016, CA 7.5/018	IT	Lombardy, investigations base on regional monitoring data.	0.1	1.75[1]	NR
Rosenbom, A. et al., 2015, CA 7.5/019	DK	Soil pore water ~1 m - PLAP Sites Groundwater - PLAP Sites	0.1	NR	NR
McManus, S. et al., 2014, CA 7.5/020	IE	Global site investigation	0.1	0.0	NR
Norgaard, T. et al., 2014, CA 7.5/021	DK	Drainflow at 1.1 m depth	NA	NA	NA
Mörtl, M. et al., 2013, CA 7.5/024	HU	36 ground water samples; 14 sampling sites in Békés county, Hungary	0.1	100[3]	NA
Sanchís, J. et al., 2012, CA 7.5/025	ES	139 samples from 69 site, regional monitoring program	NR	NR	NA
Bruchet, A. et al., 2011, CA 7.5/027	FR	Groundwater following bank filtration	0.1	0.0	0.0
[redacted] [redacted] [redacted] [redacted], 2011, CA 7.5/028	IT	Site investigation of 5 sites in Lombardy	NR	NR	NR
[redacted] [redacted] [redacted] [redacted], 2010, CA 7.5/029	NL	Site investigations	NR	NR	NR

NA/NR – Not Assessed/Reported

[1] - 5 out of 285 samples

[2] - Maximum annual value of 14/15 years (AMPA/GLY) and influenced by small sample sizes

[3] - atypical results from a very small study focussing on contaminated industrial sites

[4] - Maximum annual value of 7 years

[5] - 1 out of 116 samples

[6] - 2 out of 65 samples

Summary of surface water monitoring data

Regarding the collection of public monitoring data for surface water, an extended monitoring data set was collected throughout 8 EU countries and 2 large transboundary catchments relating to the Rhine and Danube river basins. Analysis of these data have been proposed by the study authors to assess what they call "the state of all environmental compartments" and "consider the impacts this state might have on biota, ecosystems and human health via drinking water" ([redacted] (2020, CA 7.5/001, [redacted] (2020, CA 7.5/002). These were analyzed for compliance with a range of regulatory endpoints and thresholds. The SW data were assessed against RAC values for GLY and AMPA. Additional analyses against MS specific Environmental Quality Standard was also undertaken. Compliance with annual average (AA) and Maximum Allowable Concentration (MAC) EQS values are proposed for MS where such thresholds are defined.

The whole combined EU monitoring data set for surface water represents >291 000 samples collected from >13 800 sampling sites for glyphosate and >269 000 samples collected from >12 400 sampling sites for AMPA.

It was dominated by French data (~65%/68% for GLY/AMPA) with smaller contributions from Belgium (9% for both GLY and AMPA), Germany (~8.5%/9% for GLY/AMPA), the Netherlands (~5.6%/5.0 for GLY/AMPA) and Spain (~4.9% for GLY).

Detection of GLY above the limit of quantification (>LOQ) in SW samples was ~40%. Detection of AMPA >LOQ in SW samples was ~64%.

This compares well with results from the previous data collection, ([redacted], 2012) that was reviewed in the RAR 2015, and which indicated that glyphosate has been detected in Europe with ~31% of samples for glyphosate and ~50% of samples for AMPA. The apparent increase is likely to be a function of improving LOQs.

Glyphosate quantification

Compliance of the concentration results with the GLY RAC was 99.994% of samples; 99.90% of sites and the exceedances (0.006% of samples; 0.10% of sites) were on separate non-consecutive occasions (0.003% of samples being consecutive). Note that this analysis was performed based on a RAC of 400 µg/L initially proposed by applicant, while RMS final proposed RAC is 100 µg/L. However, this does not significantly impact the compliance rates (see below).

A small number (58) of high maximum concentrations in the dataset were considered to be outliers by study authors and once excluded a maximum concentration of 57 µg/L was retained, and compliance of 100% with any of the RAC values. However, very few justification on the value considered outliers was provided in the report. Some maximum values over the RAC (up to 558 µg/L) considered outliers should be further justified. Also the report of [redacted], 2016 reports higher maximum concentrations (3400 µg/L for glyphosate and 393 µg/L for AMPA) that were apparently not considered outliers. This is identified as a data gap for the applicant, to clarify the outlier exlusion procedure to check which maximum concentration should be retained for surface water (within data from [redacted], 2020 and [redacted] 2016). In any case, maximum values including outliers above the RAC were mainly located in UK (13 exceedances on 3 sites), BE (10 exceedances on 5 sites), FR and SE (both 3 exceedances on 3 sites). It was eventually concluded that assessment of the spatial distribution of locations that exceed the GLY RAC did not indicate any specific pattern or bias.

Since detailed results of maximum concentrations are not available, the analysis and the % compliance cannot be updated by RMS based on the RAC of 100 µg/L. However, considering that about 58 samples considered “outliers” by applicant are above 57 µg/L, the overall compliance with the lower RAC of 100 µg/L would not be significantly different than the one presented by applicant.

Regarding Environmental Quality Standard (EQS), no EU-wide EQS values, annual average (AA) or maximum allowable concentration (MAC), were available for assessment as broader ecosystem endpoints. Consideration of the MS GLY surface water data against MS EQS values indicates that the presence of GLY is not expected to have any adverse impacts on ecosystems with a near total compliance (99.987%) across the large EQS-MAC dataset (~228 000 samples from ~9 000 sites) with very few exceedances (0.013% of samples; 0.22% of sites) identified. Similarly, 100% compliance for the large EQS-AA dataset (~11 000 years from ~1 600 sites) is indicated with no exceedances identified.

Regarding the threshold of 0.1 µg/L, detection for glyphosate above the threshold of 0.1 µg/L was ~23% of samples (~54.0% of sites), ranging from 3.4% in AT to 57.5% in BE. These results compare well with the previous data collection ([redacted], 2012; 2016) where ~21% of samples were found to exceed 0.1 µg/L. Note that this comparison is reported for information and is only relevant for locations where the surface water is actually intended to supply drinking water production. The proportion of sampling locations potentially intended to supply drinking water is unknown.

AMPA quantifications

Compliance of the concentration with the AMPA RAC of 1200 µg/L was very high (99.999% of samples; 99.976% of sites) with infrequent exceedances (0.001% of samples from 0.024% of sites) occurring on 3 separate non-consecutive occasions. A small number of high maximum concentrations were confirmed to be outliers and once excluded indicated a maximum concentration of 224.4 µg/L, which is below the RAC.

Assessment of the spatial distribution of locations of AMPA exceedance of the RAC did not indicate any specific pattern or bias.

Regarding Environmental Quality Standard (EQS), no EU-wide EQS values, AA or MAC, were available for assessment as broader ecosystem endpoints. Consideration of the MS AMPA surface water data against MS EQS values indicates that no sites showed average annual concentration >EQS-AA in the MS where such trigger is defined.

Assessment against the threshold of 0.1 µg/L was also undertaken; detection above the threshold of 0.1 µg/L was ~47.5% of samples (~67.6% of sites), ranging from 16.3% in AT to 77.7% of samples in BE.

Note that this comparison is reported for information. The proportion of sampling location potentially intended to supply drinking water is unknown.

The conclusions of the study authors is that GLY and AMPA residues are frequently detected in surface water, but that they do not pose risk to the environment. If indeed the results show very few exceedance of the RAC and other Environmental Quality Standard, any straightforward risk assessment conclusions based on these findings should be regarded with caution, as key information are lacking to get a clear picture of what these data capture in terms of use pressure and temporal percentile. The number of detections above LOQ (respectively ~40% and ~64% samples EU-wide for GLY and AMPA) tends to indicate that the active substance is widely and regularly found in surface water. This indeed reflects the spread and diversity of use of glyphosate containing products, but it still cannot be evaluated on which extent actual peak concentration and exceedance of the RAC in relation to pesticide use of glyphosate is caught by these monitoring programs.

Frequency and regularity of sampling have not been included as criteria in the data analysis, although the sampling effort can clearly be very different from a site to another. Indeed, [redacted] (2016), focusing on the results from the French public monitoring between 1999 and 2013, showed that more than third of stations for which sampling results are available were in fact monitored for one single year other the 15 year period studied (36 % and 32% for AMPA and glyphosate, respectively). Less than 15% of the stations have been monitored for 7 years or more out of 15.

Regarding use of active substance, the surface water sampling sites cannot be related to any use pattern of the active substance. No sufficient information is available to evaluate the proportion of sampling sites that are really located down gradient of area where the active substance is used, or even just likely to be used. However RMS notes that this might have less importance in the case of glyphosate, considering the wide spread and diversity of uses of glyphosate containing products (including agricultural and non-agricultural uses, professional and non professional uses).

Further investigation were available in studies specific to French monitoring data but no clear straightforward conclusions could be drawn from these. The study [redacted] (2019b, CA 7.5/032) focuses the findings of GLY and AMPA in surface water for this 7 years period in the area of six vineyards across France, but the representativeness of stations and associated analysis results presented for the 6 vineyard areas are very limited (there are three areas where less than 3 stations monitor the water quality) and the regularity of inter- and intra-annual sampling is not always met.

The two studies of [redacted] (2018a, CA 7.5/033 and 2018b, CA 7.5/034) provide details on respectively 8 and 10 stations from the French public monitoring stations where elevated concentrations of glyphosate and AMPA were found during the period 2008-2014. However, the selection criteria of the stations are not detailed. The study gives good description of the findings and of the monitoring sampling site and catchment area, but no further sensitivity analysis is provided. Maximum peak concentration from these stations were respectively 13.2 µg/L for GLY and 61.4 µg/L for AMPA.

Finally, [redacted] (2019, CA 7.5/031) which details a multi-year investigation of farmer engagement strategies on water quality for a catchment in Belgium, has highlighted these difficulties of interpreting monitoring data in the absence of a detailed understanding of the monitoring location and practices in the upstream catchment. This study provides very detailed results on glyphosate loads on a small pilot catchment dominated by agriculture, and the effects of mitigation measures to reduce the glyphosate loads. The measurements allowed distinction of runoff sources from point source losses. Maximum concentration of 153 µg/L and 218 µg/L for glyphosate and AMPA respectively were identified as resulting from point source contamination (i.e. high concentration during dry period). After implementation of mitigation measures (buffer strip, water management, information on point source contamination…), the number and intensity of point sources losses, so as runoff event concentration were reduced, while the baseflow loads were not significantly different.

Within the open literature review, surface water monitoring data were obtained from several published peer-reviewed papersproviding data at different scales.

Some articles do not generate experimental or monitoring data on themselves but provide additional work relying on existing public monitoring data. These articles report in some cases measured concentration results from national/regional monitoring campaign, but those cannot be related to specific context neither to known uses of glyphosate. Di Guardo and Finizio (2018, CA 7.5/0036) aimed at developing tools for risk manager to identify priority zones and undertake mitigation actions at regional scale. Schreiner et al. (2016, CA7.5/046) also aimed at identifying at large scale the most frequently detected substance and mixture of substances, but does not report any raw data of concentration measurements. Busetto et al. (2010) (CA7.5/066 and 067) report detailed results from local stations in the Brianza region in Lombardia (IT), but the measured concentration cannot be related to agricultural or urban pressure of use of glyphosate. Szésaks (2014, CA 7.5/006 and 2015, CA 7.5/048) report monitoring results from different part of HU, however results are reported globally and in some cases for unspecified (SW/GW) water body. Desmet, N. et al. (2016, CA7.5/044) relies on monitoring data from RIVA-Maas on the river Meuse and its tributaries for calibrating a river model. Stenrød (2015, CA 7.5/047) relies on monitoring data compiled by the Norwegian Agricultural Environmental Monitoring Programme, in which however only occasional analysis were performed for glyphosate. Martin, J. et al. (2013, CA7.5/022), reviews results from 10 years of monitoring in the specific tropical context of Reunion Island (FR) but no concentrations are reported.

Some articles provide additional data from grab sample monitoring at regional scale. These are Masiol *et al.* (2018, CA 7.5/038) for North East IT, Poiger *et al.* (2017, CA 7.5/017) for specific regions of Switzerland, Houtman, C. *et al.* (2013, CA7.5/054) for the Dutch part of the river Meuse, and Mörtl, M. *et al.* (2013, CA7.5/024) for the Danube river and a lake in HU. For all these articles, the same limitation as met when dealing with public monitoring data are encountered, i.e. they give a picture of the contamination at the particular place and time they represent, but the results cannot be related to the pressure of use of glyphosate or any particular flow event. No temporal or spatial percentile can be determined from these results.

Smaller scale monitoring, based on river flow proportional sampling are reported in several articles for different periods. These are Reoyo-Prats *et al.* (2017, CA 7.5/043) for the River Tet in FR, Petersen *et al.* (2012, CA 7.5/059) for 3 catchments in DK, Meyer *et al.* (2011, CA 7.5/065) for a single catchment in Luxembourg. Bruchet *et al.* (2011, CA 7.5/027) focused on river bank filtration, but also reports raw surface water concentrations. Hanke *et al.* (2010, CA 7.5/069) relates to a small catchment in Switzerland. However, only the articles from Petersen *et al.* (2012) and Hanke *et al.* (2010) report known uses of glyphosate within the catchment and are considered reliable. For all other studies, the pressure of use of glyphosate within the catchment is not known, and the peak concentrations, when described, cannot be related to detailed agricultural use of glyphosate.

Urban dominated catchment concentrations (or from wastewater treatment plant) are reported by Botta *et al.* (2012, CA 7.5/057) and Botta *et al.* (2009, CA 7.5/070) for the Orge river in FR. Peschka *et al.* (2006, CA 7.5/072) relates to the Rhine and two tributaries in Hesse DE. Augustin (2003, CA 7.5/073) relates to the river Selz DE. It is noticeable however that these articles report data from before 2010.

Urban runoff concentrations prior to entry into surface water bodies are reported by Gasperi *et al.* (2014, CA 7.5/050), Vialle *et al.* (2013, CA 7.5/056), Zgheib *et al.* (2012, CA 7.5/060), Birch *et al.* (2011, CA 7.5/061) and Lamprea and Ruban (2011, CA 7.5/062). These are presented for completeness and context. Tang *et al.* (2015, CA 7.5/049) and Ramwell *et al.* (2014, CA 7.5/052, focus on the contribution of residential use of glyphosate to storm water contamination. Household use of glyphosate is determined through survey in those studies and the concentrations recovered in the storm drain at the outlet of the catchment were determined to correspond to less than 1% of the applied amount.

Finally, there are articles that deal with field scale monitoring. RMS highlights that all these studies, whose advantage is that context and methodology are well described, are all related to flux concentration measured in drain flow or surface runoff flow, before entry into surface water compartment. These therefore cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009, and should not be directly compared to ecotox risk assessment PEC and RAC but sill provides reliable additional information. Theses studies are as follow:

Several articles report results from flow proportional monitoring in an artificial storm water wetland catching surface runoff from a small vineyard in France, Alsace (42, 7 ha). These are Maillard and Imfeld (2014, CA 7.5/051), Imfeld *et al.* (2013, CA 7.5/055), Coupe *et al.* (2012, CA 7.5/058), Maillard *et al.* (2011, CA 7.5/064) and Gregoire *et al.*, (2010, CA7.5/068). These can be assimilated to field experiments, focusing on specific agricultural uses of pesticides in vineyards (including glyphosate and AMPA) and on the ability of a constructed wetland to attenuate runoff-carrying pesticides from large rainfall events. Not all those articles provide the same level of information regarding use amounts of glyphosate but give concentration results at the inlet and outlet of the wetland from different periods. From the 2003-2006 years monitoring, the pesticide loss from the catchment (to the inlet of the wetland) was quite stable and represented less than 0.033% of the applied amount of glyphosate. The evaluation of this loss is however based only on the collected run-off events which represent 29% of the flow during the study period (which itself does not cover the all year (March-Oct)). The transport of glyphosate through the wetland was found to differ both on seasonal and yearly time scale, and attenuation efficiencies of the wetland were also various. Imfeld *et al.* (2013) reports concentrations decrease at the outlet of the wetland from 36 to 263 times for glyphosate and from 3 to 31 times for AMPA for the period 2003-2006.

Dairon, R. et al. (2017) describes a field study at experimental station of La Jaillère (FR) on the influence of reduced tillage practices on water and pesticide balance. Amount applied of glyphosate are higher on the reduced tillage plot, and the study reports higher quantification rates of glyphosate in the drained flow under reduced tillage. However maximum concentration is recorded in the drainflow from conventional tillage. Over the long term, 0.052 and 0.025% of glyphosate applied dose were losses in drainage for CT and RT, respectively.

Lefrancq, M. et al. (2017, CA7.5/040), also described glyphosate concentration in surface runoff in a small vineyard catchment, with flow based sampling of runoff events, monitored from 2009 to 2012. Results are related to use of glyphosate.

Napoli, M. et al. (2016, CA7.5/005) studied the influence of grass cover on concentration in surface runoff before entering surface water during 4 years in vineyard, where glyphosate is applied every year in March. Results indicates higher concentration of both glyphosate and AMPA in runoff water from the harrowed plot compared to the grass covered plots. Concentration recovered in the runoff water intercept at the lower side of the plots are in any case are quite high, in this context or vineyard with great slope.
Daouk, S. et al. (2013b, CA7.5/007) reports reliable information on glyphosate and AMPA concentration in runoff to surface water after application of the parent to 2 parcels of a vineyard soil in Switzerland. However, there is no indication on the pressure of use of glyphosate within the catchment.

Finally, Larsbo, M. et al. (2016, CA7.5/045) monitored pesticides (among which glyphosate) concentration in surface runoff from a clay loam field with known application of glyphosate in Eastern Sweden. The application pattern of glyphosate is known and the maximum concentration reported for glyphosate and AMPA are respectively 7.4 µg/L and 2.7 µg/L (aqueous phase). This article however describes runoff in the particular context of snowmelt.

An overview of the concentration results recovered from the applicant studies and the literature review are provided in table below. It is reminded that measured concentrations collated are not all related to surface water as defined in Regulation 1107/200, i.e. some are measured in drain or surface runoff flow before entry into surface water. This has been indicated in the column “context” for clarity.

Table 8.5-5: Summary of reported maximum concentrations of glyphosate (GLY) and AMPA in surface water

Reference	Location	Context	Maximum Concentration (µg/L)	
			GLY	**AMPA**
[redacted], 2020, CA 7.5/002	EU	Surface water (large scale monitoring)	91600 57.0[1]	230000 224.4[1]
[redacted], 2019, CA 7.5/031	BE	Surface water (catchment study)	153.0[7]	218.0[7]
[redacted], 2019a, CA 7.5/008	FR	Surface water (large scale monitoring)	2237 2.1[4]	3369 4.2[4]
[redacted], 2019b, CA 7.5/032	FR	Surface water associated with vineyards	21	106
[redacted], 2018a, CA 7.5/033 and 2018b, CA 7.5/034	FR	Surface water, site investigations	13.1	106
[redacted], 2016, CA 7.5/010	EU	Surface water (large scale monitoring)	3400	393
[redacted], 2016, CA 7.5/009	FR	Surface water (large scale monitoring)	3257 2.8[4]	3369 4.6[4]
[redacted], 2012, CA 7.5/013	EU	Surface water (large scale monitoring)	370	>200
Di Guardo and Finizio, 2018, CA 7.5/036	IT	Surface water, Lombardy (large scale monitoring)	108	NA
Huntscha, S. *et al.* 2018, CA 7.5/037	CH	Lake case study – surface water Tributaries	1.43	0.42
		Lake case study - Lake	0.15	0.10
Masiol, M. *et al.* 2018, CA 7.5/038	IT	Surface water	1.4	1.4
		Tidal Water (venice lagoon?)	2.1	1.4
Dairon, R. *et al.* 2017, CA 7.5/039	FR	Drainflow before entering SW	12	NR
Lefrancq, M. *et al.* 2017, CA 7.5/040	FR	Surface runoff before entering SW	386.9	47.0
Lerch, R.N. *et al.*, 2017, CA 7.5/041	US	Surface runoff from field, before entering SW	Expressed as input normalised loads	NA
Poiger, T. *et al.*, 2017, CA 7.5/017	CH	Surface water from various region	<50[2] 2.1[5]	<10[2] 2.6[5]
Reoyo-Prats, B. *et al.*, 2017, CA 7.5/043	FR	Surface water	1.5	1.1
Desmet, N. *et al.*, 2016, CA 7.5/044	NL	Surface water (Meuse river moniroting)	12.0	130.0[8]
Larsbo, M. *et al.*, 2016, CA 7.5/045	SE	Surface runoff from field, before entering a SW	7.4[6] 2.7[9]	2.7[6] 0.85[9]
Napoli, M. *et al.* 2016, CA 7.5/005	IT	Surface runoff from field, before entering SW	128.9	151.9
Stenrød, M., 2015, CA 7.5/047	NO	Surface water, small agricultural catchments	4.0	NA
Székács, A., *et al.*, 2015, CA 7.5/048	HU	Surface water (large scale monitoring)	1.0	NA
Tang, T. *et al.*, 2015, CA 7.5/049	BE	Urban runoff before entry into SW	6.1	5.8
Gasperi, J. *et al.*, 2014, CA 7.5/050	FR	Urban stormwater before entry into SW	0.2[3]	0.47[3]
Maillard E., Imfeld G., 2014, CA 7.5/051	FR	Surface runoff, before entering wetland for vineyard catchment	Expressed as loads	Expressed as loads
Norgaard, T. *et al.*, 2014, CA 7.5/021	DK	Drainflow before entry into SW, PLAP site	31.0	~1.6[2]
Ramwell, C. *et al.*, 2014, CA 7.5/052	UK	Urban runoff (storm drain, drain flow from domestic usage) before entering	8.99	1.15

		SW		
Székács, A., *et al.*, 2014, CA 7.5/006	HU	Surface water (large scale monitoring)	0.98	NA
Daouk, S. *et al.*, 2013a, CA 7.5/053	CH	Surface water associated with vineyards - River	0.80	0.30
		Surface water associated with vineyards - Lake	<LOQ (10 ng/L)	0.067
Daouk, S. *et al.*, 2013b, CA 7.5/007	CH	Surface runoff from vineyard, before entry into SW	110.0	14.0
Houtman, C. *et al.*, 2013, CA 7.5/054	NL	River Meuse	0.21	2.28
Imfeld G. *et al.*, 2013, CA 7.5/055	FR	Surface runoff, before entering wetland for vineyard catchment	150	19.0
Vialle, C. *et al.*, 2013, CA 7.5/056	FR	Roof runoff	6.0	0.9
Botta F. *et al.*, 2012, CA 7.5/057	FR	Surface water, urban dominated catchment	NR	5.1
Coupe, R. *et al.*, 2012, CA 7.5/058	FR	Surface runoff, before entering wetland for vineyard catchment	86	44
Petersen, J. *et al.*, 2012, CA 7.5/059	DK	Surface water, runoff event sampling in 3 catchments	2.80	0.54
Zgheib, S. *et al.*, 2012, CA 7.5/060	FR	Storm water from urban area of Paris, before entering SW	232	9.37
Birch H. *et al.*, 2011, CA 7.5/061	DK	Storm water from urban area of Copenhagen, before entering SW	1.3	1.3
Bruchet, A. *et al.* 2011, CA 7.5/027	FR	Surface water - river and bank filtration	0.12	0.65
Lamprea, K., Ruban, V., 2011, CA 7.5/062	FR	Storm/wastewater, before entry in SW, urban area	71.0	1.45
Litz, N.T. *et al.*, 2011, CA 7.5/063	DE	Surface water, River Havel, Berlin. Slow sand filter	5.0	NR
Maillard, E. *et al.*, 2011, CA 7.5/064	FR	Surface runoff, before entering wetland for vineyard catchment	15.0	21.0
Meyer, B. *et al.*, 2011, CA 7.5/065	LU	Surface water (stream), small catchment runoff events	6.22	1.12
Busetto, M. *et al.*, 2010, CA 7.5/066	IT	Surface water, Lombardy	2.20	16.0
Gregoire, C. *et al.*, 2010, CA 7.5/068	FR	Surface runoff, before entering wetland for vineyard catchment	86.0	44.0
Hanke I. *et al.*, 2010, CA 7.5/069	CH	Surface water, Urban dominated catchments	4.2	1.11
Botta, F. *et al.*, 2009, CA 7.5/070	FR	Surface water, Urban dominated catchments	1.7	1.93
Peschka, M. *et al.*, 2006, CA 7.5/072	DE	Surface water (Rhine and 2 tributaries), waste water.	0.4	NR
Augustin, B., 2003, CA 7.5/073	DE	Surface water, (Selz river)	1.8	NA

‡ - Maximum annual value of 7 years
^{1} - Excluding outliers
^{2} - Inferred from graph
^{3} – 80th Percentile
^{4} - 99th Percentile
^{5} – 95th percentile value
^{6} – aqueous phase
NR – Not reported;
^{7} - Point source pollution
^{8} – highly influenced by waste water emission
^{9} – particle bound phase
NA – Not applicable/analysed

Summary of transitional/tidal water monitoring data

Regarding the collection of public monitoring data, concentrations of glyphosate (GLY), AMPA and HMPA in transitional water arising from public monitoring datasets have been collected from regional/national environment agencies. Since tidal water is usualy not specifically considered in regulatory assessment for active substance approval, these data are considered as supportive. Only few data were collated.

Raw data from monitoring in tidal water are reported for a limited number of sites (~800 samples from 22 sites) from DE and UK. These include a variety of tidal water bodies including estuaries, lagoons and near shore brackish areas.

The bulk of the data (~46% for GLY and 100% for AMPA) came from the DE dataset which comprises 15 sites located along the Baltic Sea coastline of Germany in the Bundesland of Mecklenburg-Vorpommern. This dataset covered 9 years spanning the period 2009 – 2018.
Within the 260 samples, GLY was quantified in 6.9% of samples, and AMPA was quantified in 33.1%. The maximum measured concentrations were 0.18 µg/L for GLY, and 0.9 µg/L for AMPA, which are below the RAC and EQS thresholds.

The dataset from the UK comprised 8 sites distributed unevenly along the east coast of England. It covered 9 years spanning the period 2000 to 2009. Within the 303 samples, GLY was quantified in 8.9% of samples. The maximum measured concentrations was 1.2 µg/L for GLY which is below the RAC and EQS thresholds.

Within the open literature review, a single study from literature review was considered reliable with restriction by RMS (Skeff et al., 2015). This study aimed at optimizing an analytical method, which was further validated on Baltic Sea estuaries water samples. Samples from 10 locations along the Baltic Sea coastline of Mecklenburg-West Pomerania, Germany were collected in 2012 and analysed in order to study the presence of the herbicide glyphosate, AMPA and their potential transport to the marine environment. Maximum concentration of 1.690 µg/ and 4.256 µg/L are reported respectively for glyphosate and AMPA.

Summary of drinking water monitoring data

Regarding the collection of public monitoring data, concentrations from public monitoring datasets of glyphosate (GLY), AMPA and HMPA in drinking water have been collected from regional/national environment agencies as well as published peer reviewed publications from literature searches.

Public monitoring data were collated by applicant in two main reports: [redacted], 2020 (CA7.5/002), which analyse the data collated according to the methodology described in [redacted], (2020, CA7.5/001) for the period 2008-2018 and [redacted], 2015 (CA7.5/074) for period 2008-2015. The data from [redacted], 2020 should in principle overlap those from [redacted], 2015, but it is not the case and data seem to come from different sources. In any case, it should be noted that the data collated either from [redacted], 2020 or [redacted], 2015 are very limited and outdated for many countries. It is also worth noting that the process of determining the reliability of the data is not clearly described in [redacted], 2015, so as the definition of drinking water taken into account, which is not always clear. Results from different water supplies (groundwater, surface water and “other sources”) are gathered for each country and it is sometimes unclear whether the data reported in the summary tables and the statement indicated in the conclusions refer to raw or treated water. In the report of [redacted], 2020 which provides the most recent review methodology, there is no precise indication on the the origin of raw data for drinking water (i.e. ground water, surface water..) although this was part of the information to be collected in the described methodology; RMS aknowledges that few information is usually publicly available on the sampling location and the origin of raw water cannot be further indicated when collecting raw data.

A data gap is however set for the applicant to clarify the definition of “drinking water” considered in these studies, at least from the aggregated data that may be clearer on the origin of the water types taken as supply for drinking water.

Additional data may be requested for completness at MS level for product registration.

Very little un-aggregated drinking water data was available for analysis in [redacted], 2020 (~8000 samples for GLY, ~7000 for AMPA). Bulk of the data (~86% for GLY and 99% for AMPA) came from Sweden (SE). Only data for GLY were available in Ireland (IE) (14% of the data). A small dataset from Germany (DE) is limited to the federal state of Schleswig-Holstein.
The SE dataset comprises records from 1998 to 2014, the DE data set covers 2012 to 2018 while that from IE are from 2017 only.

For DE, results indicated 3 exceedance of 0.1 µg/L for GLY and 1 for AMPA, likely being isolated cases although the overall number of analysis is very limited. Aggregated data provides information on a wider set of data. Exceedances were very marginal representing less than 0.2% of samples.

For SE, raw data collected indicated 5 sampling >0.1 µg/L for GLY and 6 for AMPA, with maximum concentration of 0.17 µg/L for GLY and 0.680 µg/L for AMPA. All exceedances are indicated to be old (≤2007) and significant strides have been made in SE since the introduction of the water protection regulations in 2004 through delineation of water protection zones. This is consistent with data from [redacted], 2015 that does not further report any detection above 0.1 µg/L for the period 2008-2015.

For FR, no raw data neither aggregated data were collected in [redacted], 2020. Data were collected in [redacted] 2015 and comes from different sources with variable degree of detail and are limited to the periods 2001-2003 and 2010-2012. There is very few details on the samples exceeding the trigger. As in previous review of [redacted], 2008, the report indicates that further investigations failed to establish any coherent relationships between these detections and factors, such as seasonal occurrence, raw water quality, type of aquifer, analysis and water treatment. In fact, several of the samples with glyphosate were found in chlorinated waters; although it has been shown that chlorine effectively remove glyphosate. Overall, the evidence points to isolated detections, most likely due to contamination at the sampling stage or problems with analyses, rather than any indication of a persistent presence in drinking water. RMS supplements this overview with published data at FR level on glyphosate and AMPA measurements in drinking water[1]: Through the period 2007-2016, for glyphosate the annual number of analyses for drinking water were between 4 293 and 15 003, and the proportion of yearly observed exceedance of 0.1 µg/L were between 0.09% and 0.30%. For AMPA in the same period the number of annual analyses was between 4138 and 14422, and the observed yearly exceedance of 0.1 µg/L were between 0.08% and 0.27%.

In BE, detection above >0.1 µg/L are reported from aggregated data for year 2016 in [redacted], 2020 (2 for GLY, 1 for AMPA) representing less than 0.2 % of total samples. [redacted], 2015 collated data from Flanders in 2013, with no excedence for 17 samples collected.

In DK, single detection above >0.1 µg/L for GLY is reported from aggregated data [redacted], 2020) for period 2014-2016, representing 0.07% of total samples. No detection above >0.1 µg/L have been reported in the data set for the period 2011-2013 from [redacted], 2015.

For NL, a maximum concentration for glyphosate of 3.0 µg/L from aggregated report is reported in [redacted], 2020 but no further details are given (number of sample, time of sampling). In [redacted], 2015, results are not clear and are mixing results from raw water intakes and treated water (see comments on [redacted], 2015).

In Spain, the sampling which exceeded 0.1 µg/L seem to be isolated cases (2 in 2013, 1 in 2012, 4 in 2011). However, the report indicates that there is no detail on the samplings such as actual concentrations found, whether they occurred at one or more sampling points. Data indicates that glyphosate was monitored in a relatively small proportion of water supply zones; the number of sites and sampling frequency is not known, as only the total number of analyses per year has been reported.

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[1] Glyphosate. Phytopharmacovigilance : Synthèse des données de surveillance. Appui scientifique et technique n°2017-04. ANSES. Octobre 2018

In the UK, there is no further details on the sampling found above 0.1 µg/L. They are isolated cases, representing 0.030 % of the analyses performed during the 2008-014 period

Glyphosate has not been found at concentrations at or above 0.1 µg/L in Austria, the Czech Republic and Switzerland.

Within the open literature review, two publications are also presented outlining concentrations found in drinking water:

Malaguerra *et al*. (2012, CA 7.5/077) decribes the use of data from the Danish National Borehole Database to predict drinking water well vulnerability to contamination by pesticides, and to identify the dominant mechanisms leading to well pollution in Zealand, Denmark. It constructed a statistical model to assess factors influencing GLY concentrations in drinking water abstracted from local groundwater sources and concluded that distance from surface water was a driving factor. Glyphosate and its metabolite AMPA are the most common compounds found in Danish streams at concentrations over 0.1 µg/L, with 26.7% and 38.2% respectively of samples in Danish streams recording such high concentrations They postulated that infiltration from SW sources or slower degradation due to prevalence of anaerobic conditions in riparian areas close to surface water were possible reasons for this observation.

Bruchet *et al.* (2011, CA 7.5/027) demonstrate that bank filtration, the lateral movement of groundwater through the phreatic aquifer, removed GLY and AMPA very effectively resulting in no detectable residues in drinking water.

An overview of the concentration results recovered from the applicant studies and literature review are provided in table below.

Table 8.5-6: **Summary of reported maximum concentrations of glyphosate (GLY) and AMPA in drinking water**

Reference	**Location**	**Context**	**Maximum Concentration (µg/L)**	
			GLY	**AMPA**
[redacted], 2020, CA 7.5/002	EU	SW, GW, Large scale monitoring,	0.61	0.85
			0.92[1]	3.0[1]
[redacted], 2015, CA 7.5/074	EU	SW, GW, Large scale monitoring	NR	NR
[redacted], 2008, CA 7.5/075	EU	SW, GW, Large scale monitoring	NR	NR
Malaguerra, F. *et al.*, 2012, CA 7.5/077	DK	Zealand	NR	NR
Bruchet, A. *et al.*, 2011, CA 7.5/027	FR	GW, In situ bank filtration	<0.1	<0.1

[1] Aggregated report values

Table 8.5-7: **Summary of reported rates of concentrations of various thresholds for measured concentrations of glyphosate (GLY) and AMPA in drinking water**

Reference	**Context**	**Exceedance threshold and rate**		
		Threshold (µg/L)	**GLY (%)**	**AMPA (%)**
[redacted], 2020, CA 7.5/002	EU Summary	0.1	0.10	0.13
		10	NA	0.00
		0.1[1]	0.16[1]	0.05[1]
[redacted], 2015, CA 7.5/074	EU Summary	0.1	0.09	0.22
[redacted], 2008, CA 7.5/075	EU Summary	0.1	NR	NR

Malaguerra, F. *et al.*, 2012, CA 7.5/077	Zealand, DK	0.01	9.3	8.4
		0.1	NR	NR
Malaguerra, F. *et al.*, 2012, CA 7.5/077	FR following bank filtration	0.1	0.00	0.00

[1] Aggregated report values

Summary of sediment monitoring data

Regarding the collection of public monitoring data for sediment compartment, a small number (~2 700 analyses from ~550 sampling sites) of GLY and AMPA analyses from riverine sediment were collected as raw data from public data base. These were from two MS, FR and SE.

The bulk of the data (~91% for GLY and ~99% for AMPA) comes from the FR dataset which comprises ~541 sites, primarily in the north of France from a subset of departments. This dataset covers 13 years spanning the period 2005 – 2017. Monthly sampling effort for both GLY and AMPA is limited to the months of May through December and appears to be unimodal with lower sampling intensities in the early/latter months

The dataset from SE comprises ~12 sites distributed around the country targeting research catchments and locations. The GLY dataset covers 10 years spanning the period 2003 to 2012 while the AMPA data is restricted to 2006. Monthly sampling effort appears to be inconsistent and targets predominantly September.

The maximum measured concentrations were 2.84 mg/kg (FR) and 0.9 mg/kg (SE) for GLY, 9.56 mg/kg (FR) and 0.15 mg/kg (SE) for AMPA. No RAC are available for sediment and no comparison could be done.

Within the open literature review, sediment monitoring data are reported in several publications. Lerch *et al.* (2017, CA 7.5/041), Napoli *et al.* (2016, CA 7.5/005), Maillard and Imfeld (2014, CA 7.5/051), Sabatier *et al.* (2014, CA 7.5/078), Imfeld *et al.* (2013, CA 7.7/55), Zgheib *et al.* (2012, CA 7.5/060) and Maillard *et al.* (2011, CA 7.5/064) report sediment concentrations that are however not directly comparable with the sediment compartment that is typically risk assessed as part of the approval process, e.g. sediments in runoff water prior to entering a surface water body or entering/retained by artificial wetlands. Others report the concentrations in units that make it difficult to interpret the results e.g. as loads in mg or as concentrations ng/cm^2/yr.

The overall monitoring data presented in this section are summarised in Table 8.5-8.

Table 8.5-8: Summary of reported maximum concentrations of glyphosate (GLY) and AMPA in sediment

Reference	**Location**	**Context**	**Maximum Concentration (mg/kg or µg/L)**	
			GLY	**AMPA**
[redacted] [redacted] [redacted] [redacted], 2020, CA 7.5/002	FR and SE	Predominantly riverine	2.84 mg/kg <4.0 µg/L	9.56 mg/kg <4.0 µg/L
Lerch, R.N., 2017, CA 7.5/041	US	Sediment in field runoff attenuated by a buffer strip	Expressed as input normalised loads in %	NA
Napoli, M. *et al.* 2016, CA 7.5/005	IT	Sediment in field runoff (before entering SW)	0.68 mg/kg	0.71 mg/kg
Maillard, E., Imfeld, G., 2014, CA 7.5/051	FR	Suspended sediment entering/exiting artificial wetland	All sediment data expressed as loads e.g. mg	All sediment data expressed as loads e.g. mg

Sabatier, P. *et al.*, 2014, CA 7.5/078	FR	Lake sediment	NA	Concentrations given as ng/cm^2/yr
Imfeld G. *et al.*, 2013, CA 7.5/055	FR	Artificial wetland sediment	<LOD (LOQ stated as 10 µg/kg)	<LOD (LOQ stated as 10 µg/kg)
Zgheib, S. *et al.*, 2012, CA 7.5/060	FR	Suspended sediment in urban storm runoff before entering SW	8.3 mg/kg	4 mg/kg
Maillard, E. *et al.*, 2011, CA 7.5/064	FR	Suspended sediment entering artificial wetland	0.045 mg/kg	0.021 mg/kg

NA – Not applicable

Summary of air monitoring data

Regarding the collection of public monitoring data for the air compartment, no data was identified by the applicant from requests to and from searches of online data of regional/national environment agencies for the compartment air.

RMS however reports the results from a FR national exploratory pesticide campaign[2] that was likely not published at the time the applicant conducted its review. This sampling campaign lasted 12 months, from June 2018 to June 2019 and focused on the monitoring of 74 substances and 1 metabolite (AMPA). It included 50 sites, but for glyphosate and AMPA, due to specific material needed to sample these substances, sampling was performed on 8 sites. There were 3 urban/peri-uban areas and 5 rural areas. Six sites had different agricultural profile (field crops, vineyards, orchards, market gardening and breeding). Two sites were indicated without agricultural profile, due to the very low proportion of surfaces agricultural fields within a radius of 1 and 5 km.

Overall, Glyphosate was quantified in 56% of the analyses (LOQ 0.009 ng/m^3). AMPA was quantified in 1.3% of the analyses (LOQ 0.009 ng/m^3). In details within the different agricultural typology, the frequency of quantification was as follow: 65% of quantification for field crops areas, 75.5% for orchards, 76.9% in vineyards areas, 24.5% in breeding areas, 41.2% in market gardening areas and 54.1% for areas without agricultural profile.

Maximum concentration for glyphosate was 1.225 ng/m3. The 25th percentile concentration is 0.004 ng/m^3 and 95th percentile concentration is 0.088 ng/m^3. Most of the concentrations (99.5th percentile) are below 0.25 ng/m^3 and mainly in vineyard sites. The maximum concentration of 1.25 ng/m^3 is observed on the orchard site of Cavaillon and is a unique high value.
RMS reminds that these results were obtained in a national exploratory campaign on a limited number of sites and duration. Although the frequency of quantification for glyphosate is quite high and unexpected when considering its intrinsic properties (vapour pressure, DT50 in air), further data would be necessary to confirm these observations.

Within the open literature review for the air compartment, a publication by Ravier *et al.* (2019, CA 7.5/079) describes the results of a monitoring exercise of glyphosate and AMPA in the air of four different sites in the southeast of France where glyphosate is applied intensively. AMPA was not found in the samples.
Glyphosate was detected at a global frequency of 7% with frequencies ranging from 0% (Nice) to 23% (Cavaillon), according to the sampling site.

These results highlight a higher detection frequency of glyphosate in rural areas than in urban areas, i.e., 3/13 analysis against 2/58 analysis, respectively.

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[2] Résultats de la Campagne Nationale Exploratoire des résidus de Pesticides dans l’air ambiant (2018-2019) - DRC-20-172794-02007A – Ineris, Juin 2020

Glyphosate concentration reached a maximum level of 1.04 ng/m3 in the rural site of Cavaillon. This is despite the physicochemical characteristics of glyphosate, which are not favourable to its passage into the atmosphere. The absence of simultaneous detection of glyphosate and AMPA suggests that drift during spraying operation is the main atmospheric source of glyphosate and that resuspension from soil particles is minor.

B.8.5.2. Monitoring data in soil

New studies/assessments

Data point:	CA 7.5/001
Report author	[redacted]
Report year	2020
Report title	Collection of public monitoring data for European countries for the compartments soil, water, sediment and air for Glyphosate, AMPA and HMPA
Document No	110057-1
Guidelines followed in study	Methodology is based on the Groundwater Monitoring guideline document (Gimsing *et al*., 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations') Minimum quality criteria of monitoring data described by the FOCUS Ground Water Work Group chapter 9.5 (European Commission, 2014)
Deviations from current test guideline	None
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

The report provides information about the outcome of a search for readily accessible and available monitoring data in European countries at a regional/national level for the time period 1995-2019. The main focus was on the time period 2012-2019 while earlier years are already covered by existing data. The search included raw data, requested from regional/national authorities or downloadable from their websites, as well as aggregated data extracted from reports compiled by authorities.

Data from 14 European countries were considered: Austria, Belgium, Denmark, France, Germany, Hungary, Ireland, Italy, The Netherlands, Poland, Romania, Spain, Sweden and the United Kingdom. The countries represent the major markets of products containing glyphosate sold in the EU. The data compilation included the active substance glyphosate and its metabolites AMPA and HMPA, in the soil, groundwater, surface water, tidal water, drinking water, sediment and air environmental compartments.

As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities and other bodies of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were actually not included in any of the monitoring programs.

Soil Compartment Conclusion

There were hardly any official programs in place targeting monitoring of glyphosate or its metabolites residues in soil. Raw data for glyphosate and AMPA were available for the German federal state of Brandenburg. Aggregated monitoring data at the EU level for soil were obtained in the form of a research article.

I. MATERIALS AND METHODS

The general methodology of data collection of public monitoring data and minimum quality criteria is based on existing guideline documents for groundwater monitoring programs. The underlying principles have been applied to all environmental compartments, especially where no specific guidance is at hand. Data search, acquisition and processing approaches are described below. The same approach was applied for each country, compartment and substance. Country specific adaptations to the general procedure were made

in order to generate a harmonized database. The data collected for this report refers to third party organization data regarding all environmental compartments (SOIL, GW, SW, TD, DW, SD, AIR) and was further differentiated into the two different data types, i.e. raw data and aggregated data. Aggregated data refers to information provided in publicly available reports, e.g. from environmental agencies or research institutes. Such reports might hold only summary information on substance findings over space and time and may intersect with the raw data. Raw data refers to mid to long term time series of data that are provided on request by e-mail or by database from governmental authorities and are therefore recognized as official monitoring data. These datasets hold the information of sampling values, quality information (sampling, treatment, limit of detection - LOD, limit of quantification - LOQ) as well as information of location and time of sampling.

The following data source types were taken into account in order to collect monitoring data:

- E-mail requests: a general e-mail was sent to the national responsible authorities with regard to the required information.

- Governmental webpages: the official webpages of the national responsible authorities were searched for information regarding available reports and datasets.

- Public online databases: available data from online databases were downloaded as provided by the webpages of governmental authorities and other institutions.

- Professional contacts: information indicated by experts in frequent professional contact to governmental authorities and other institutions were considered in order to complement data sources and datasets.

The data search resulted in a very heterogeneous collection of tabular data and reports in different formats and structure. Data were processed into a harmonized tabular format by selecting relevant information and adapting data organisation. In general, the complete datasets were included in the final harmonized database as provided by the authorities, but obvious duplicates were deleted. In general, all entries for the digital database were checked for consistency and plausibility. For the raw data it was assumed that information was already subjected to critical scrutiny by the respective organization. For the aggregated data the same assumption was made with quality assurance of the data (mostly summaries) being the responsibility of the authors of the respective reports.

II. RESULTS AND DISCUSSION

The final data collection of raw data and aggregated data is summarised for each compartment and each country in Table 8.5-9.

Soil

Raw monitoring data from national authorities for soil were provided by the regional authorities of Brandenburg. Aggregated monitoring data at the EU level for soil were obtained in the form of a research article.

Table 8.5-9: Overview of public monitoring data availability of raw data (R) and aggregated data (A)

Country	Soil	Water				Sediment	Air
		Ground	Surface	Tidal	Drinking		
Austria	-	R, A	R, A	-	A	-	-
Belgium	-	R	R	-	A (Flanders)	-	-
Denmark	-	R, A	A	-	A	-	-
France	-	R	R	-	A	R	-

Germany	R (Brandenburg)	R, A	R, A	R	R (Schleswig-Holstein), A	-	-
Hungary	-	A (one research article)	A (one research article)	-	-	-	-
Ireland	-	R, A	R, A	-	R, A	-	-
Italy	-	R (Lombardia), A	R, A	-	-	-	-
The Netherlands	-	R, A	R, A	-	R	-	-
Poland	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Romania	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Spain	-	R, A	R, A	-	A	-	-
Sweden	-	R, A	R	-	R, A	R	-
UK England	-	R	R	R	A	-	-
UK Northern Ireland	-	R	-	-	-	-	-
UK Scotland	-	-	R	-	-	-	-
UK Wales	-	-	R	-	A	-	-

R raw data available; A aggregated data from reports available; - no raw or aggregated data available

III. CONCLUSIONS

The collection of public monitoring data for glyphosate, AMPA and HMPA in soil, groundwater, surface water, drinking water, tide water, sediment and air resulted in a comprehensive database of ‘raw monitoring data from national authorities’ and ‘aggregated monitoring data from reports published by national authorities’. As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were actually not included in any of the monitoring programs.

There were hardly any official programs in place targeting monitoring of glyphosate or its metabolites residues in soil. Raw data for glyphosate and AMPA were available for the German federal state of Brandenburg. Aggregated monitoring data at the EU level for soil were obtained in the form of a research article.

Assessment and conclusion by applicant:
The study describes the collection process of public monitoring data for European countries for the compartment soil, water, sediment and air for Glyphosate, AMPA and HMPA
The study is considered valid.

Assessment and conclusion by RMS:
This report describes the methodology employed for collection of monitoring data for Glyphosate, AMPA and HMPA. The data collection refers to third party organization data regarding all environmental compartments (Soil, GW, SW, TD, DW, SD, AIR).

Two different data types could in principles be collected, i.e. raw data from national authorities and aggregated data from publicly available reports (from environmental agencies or research institute).

The general search strategy was similar for each compartment, country and substance. All details of data acquisition are given in the report, and all data sources are carefully listed and described.
Although the process can clearly not be reproduced, and cannot be checked in details for exhaustiveness, the search strategy is clearly exposed and considered acceptable.

For soil compartment, there were hardly any official programs in place targeting monitoring of glyphosate or its metabolites residues in soil. Raw data for glyphosate and AMPA were available for the German federal state of Brandenburg only. Aggregated monitoring data at the EU level for soil were obtained in the form of a research article.

Results of these data collection and corresponding analysis are given in a separate report; see [redacted] 2020 below.

The study (soil part) is acceptable.

Data point:	CA 7.5/002
Report author	[redacted]
Report year	2020
Report title	Glyphosate (GLY) and the primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA): Public monitoring data assessment and interpretation
Report No	EnSa-20-0322
Document No	-
Guidelines followed in study	Groundwater monitoring guideline document (Gimsing *et al.*, 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations'); Article 5 of Directive 2009/90/EC - Technical specifications for chemical analysis and monitoring of water status.
Deviations from current test guideline	Not relevant
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary

The report provides information about the outcome of an analysis of public monitoring data comprising environmental concentrations of glyphosate (GLY) and its primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA) collated from readily available public monitoring databases held by national/regional environment agencies. This data collection and analysis was designed to expand previous reviews to include other compartments and supplement them for surface water, groundwater and drinking water. Public monitoring data from the following Member States (MS) were assessed for the water, sediment and soil compartments: Austria (AT), Belgium (BE), Denmark (DK), France (FR), Germany (DE), Ireland (IE), Italy (IT), Netherlands (NL), Spain (ES), Sweden (SE) and the United Kingdom (UK). Three MS, namely Poland (PL), Hungary (HU), and Romania (RO) confirmed that they do not conduct analyses for GLY, AMPA and HMPA in any environmental compartment. No data for HMPA was identified for any MS or compartment. Note that at the time the study was started the UK was a Member State and is referred to as a Member State throughout the report.

Analyses of the large spatial and temporal dataset of measured concentrations occurring in several environmental compartments, namely surface water, groundwater, drinking water, tidal water, sediment and soil, were conducted to assess their state. This analysis not only sought to assess the state of the environmental compartment but also to consider the potential impacts this might have on biota, ecosystems and human health by using regulatory endpoints and thresholds from a range of European (EU) Directives. These included the Water Framework Directive (Directive 2000/60/EC) and associated Groundwater (2006/118/EC), Drinking Water (1998/83/EC) and Priority Substances (2008/105/EC28) Directives in addition to the Plant Protection Products Directive (1107/2009/EC).

Soil

A small number (57 samples from 29 sites) of GLY and AMPA analyses from agricultural soils were collected and analysed. These were from a single MS, namely DE, in the Bundesland of Brandenburg. The data were assessed against the soil regulatory acceptable concentration (RAC) of 94.6 mg/kg for GLY and 26.38 mg/kg for AMPA.

Compliance was 100% with no exceedances of the RAC indicated by the data for both GLY and AMPA. The maximum measured concentrations of 0.25 mg/kg for GLY and 0.975 mg/kg for AMPA are well below the RAC. These are comparable with data from a much larger published pan-European dataset where the maximum measured concentrations were 2.05 mg/kg for GLY and 1.92 mg/kg for AMPA, which are also well below the RAC.

Soil Compartment Conclusions

While limited in number, spatial and temporal scope, the available soil data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in this environmental compartment.

I. MATERIALS AND METHODS

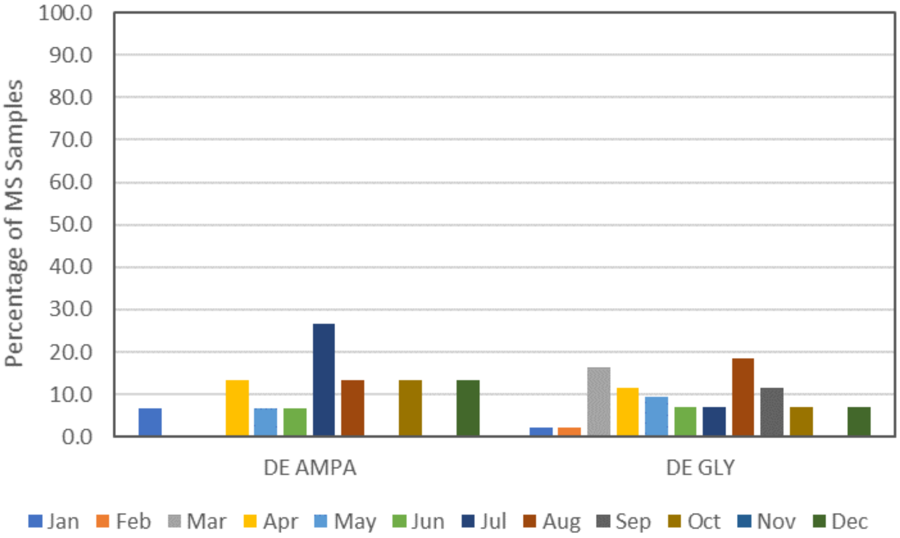
The dataset analysed comprised individual sediment analysis records as well as existing aggregated analyses extracted from reports sourced from regional/national environment agencies (see [redacted], 2020, CA 7.5/001). The approach taken for the data processing encompassed a precautionary approach that preserved samples in the analysis where there was any doubt regarding their reliability. As such no soil records were excluded from the analysis. Similarly, no attempt to remove outliers was undertaken. Analysis and assessment of the data against thresholds was undertaken in Excel and was evaluated against the following thresholds and endpoints:

- Ecotoxicological endpoint: Regulatory acceptable concentration (RAC) of 94.6 mg/kg for GLY and 26.38 mg/kg for AMPA.

II. RESULTS AND DISCUSSION

The data analysed was very limited (57 samples) and as such is biased both spatially and temporally. While it is not stated which kinds of landuse were sampled, visual assessment of monitoring locations in GIS suggest that the samples were largely of arable agricultural land. All of the data comes from a DE dataset which comprises 29 sites located in the Bundesland of Brandenburg. This dataset covers 9 years spanning the period 2008 – 2018. Monthly sampling effort for both GLY and AMPA appears to be variable (see Figure 8.5-1).

Figure 8.5-1: **Bar chart of soil monthly glyphosate (GLY) and AMPA sampling effort**



Analysis of the GLY soil dataset indicates that GLY is quantified in ~30% of samples (see Table 8.5-10), albeit the number of samples is quite limited at 43. Compliance was 100% given no analyses exceeded the RAC or came close to doing so with the maximum measured concentration being 0.25 mg/kg.

Comparison with the larger aggregated report dataset suggests agreement (see Silva *et al*., 2018). These published aggregated results stem from data that are well distributed across the EU and sample a range of different cropping systems, however, they are temporally limited with 300 of the samples being collected as part of the LUCAS topsoil project between April and October of 2015 and 17 samples from three independent vineyards in north-central Portugal taken in September 2015. Aggregated data from EU MS reports are presented in Table 8.5-11 which suggest GLY is quantified in ~21% of 317 soil samples, however none exceed the RAC, or come close to doing so, with the maximum concentration being 2.05 mg/kg associated with permanent crops (vineyards) in central Portugal.

Analysis of the AMPA soil dataset indicates that AMPA is quantified in ~86% of samples (see Table 8.5-10), albeit the number of samples is very limited at 14. Compliance was 100% given no analyses exceeded the RAC or come close to doing so with the maximum measured concentration being 0.975 mg/kg. Aggregated data from a report are presented in Table 8.5-11 which suggests AMPA is quantified in ~42% of 317 soil samples, however none exceed the RAC, or come close to doing so, with the maximum concentration being 1.92 mg/kg associated with permanent crops in central Portugal.

Table 8.5-10: Summary results of glyphosate (GLY) and AMPA analyses in soil

Substance	Number of Sites	Number of Samples	Years	LOQ	Detected >LOQ		Detected >RAC		Measured Concentration (mg/kg)
				Mean (min - max)	Samples	%	Samples	%	Median (min - max)
AMPA	13	14	2011 - 2018	0.1 mg/kg (0.1 - 0.1)	12	85.7	0	0	0.059 mg/kg (0.029 - 0.975)
GLY	29	43	2008 - 2018	0.025 mg/kg (0.001 - 0.5)	13	30.2	0	0	0.0125 mg/kg (0.001 - 0.25)

Table 8.5-11: Summary of soil monitoring data aggregated in reports for glyphosate (GLY) and AMPA in soil

MS	Substance	Number of reports identified	Reports with data relating to threshold						Maximum value (mg/kg)
			Number of reports	Date range	Number of samples	Threshold LOQ (mg/kg)	Samples above threshold	% samples above threshold	
EU	AMPA	1	1	2015	317	0.05	133	42	1.92
	GLY	1	1	2015	317	0.05	67	21	2.05

III. CONCLUSIONS

Compliance for the soil compartment was 100% with no exceedances of the RAC indicated by the data for both GLY and AMPA. The maximum measured concentrations of 0.25 mg/kg for GLY and 0.975 mg/kg for AMPA are well below the RAC. These are comparable with data from a much larger published pan-European dataset where the maximum measured concentrations were 2.05 mg/kg for GLY and 1.92 mg/kg for AMPA, which are also well below the RAC. While limited in number, spatial and temporal scope the available soil data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in this environmental compartment.

Assessment and conclusion by applicant:

The study describes the analysis of public monitoring data for European countries for the compartment soil, water and sediment for Glyphosate and AMPA. Maximum measured soil concentrations were 2.05 mg/kg for GLY and 1.92 mg/kg for AMPA. The available soil data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in the soil compartment.

The study is considered valid.

Assessment and conclusion by RMS:

The present summary focuses on soil results, and analysis for other compartments can be found in the relevant corresponding sections.

The small number of raw data (57 samples from 29 sites, covering 9 years period) of GLY and AMPA analyses from agricultural soils were assessed against the soil regulatory acceptable concentration (RAC) of 94.6 mg/kg for GLY and 26.38 mg/kg for AMPA. Analysis indicates that GLY is quantified in ~30% of samples (total 43 samples) and AMPA is quantified ~86% of the samples (total 14 samples) No analyses exceeded the RAC and maximum measured concentration is 0.25 mg/kg for GLY and 0.975 mg/kg for AMPA. However, it should be underlined that these samples cannot be related to any soil depth since no information on the sampling conditions are reported, neither to any land use (not reported) although study authors suggested it was largely agricultural land (based on visual assessment of locations in GIS). RMS notes that the value of 94.6 mg/kg is a RAC derived for soil macroorganisms, and correspond to the NOEC divided with a safety factor of 5. For microorganisms, no significant effect is observed for a tested NOEC (highest tested concentration) of 33.1 mg/kg.

In the aggregated report (Silva et al., 2018, CA 7.5/004), results stem from data that are well distributed across the EU and sample a range of different cropping systems. 300 of the samples have been collected as part of the LUCAS topsoil project between April and October of 2015 and 17 samples are from three independent vineyards in north-central Portugal taken in September 2015. Results from these data indicate GLY is quantified in ~21% of 317 soil samples, AMPA is quantified in ~42% of 317 soil samples. None exceed the RAC with the maximum concentration being 2.05 mg/kg for GLY and 1.92 for AMPA, associated with permanent crops (vineyards) in central Portugal. However, the measured concentration should be regarded with caution since the exact sampling depth is unknown (15/20cm), and in any case higher than the one that would be considered for risk assessment in permanent crops (5cm). Also, the glyphosate application amounts, as well as the time passed since last application are not known. Please refer to Silva et al., 2018, CA 7.5/004 for further comments on this study.

The study (soil part) is acceptable.

Existing studies/assessments

There was no monitoring data in soil reported in RAR (2015)

Relevant literature articles

Data point	Study (Author, year)	Study type	Substance(s)	Type of measured data	Status
RELEVANT LITERATURE ARTICLES					
CA 7.5/003	Karanasios, E. *et al.*, 2018	Monitoring of glyphosate and AMPA in soil samples from two olive cultivation areas in Greece	Glyphosate AMPA	Soil concentration, 30 cm depth.	Reliable with restrictions
CA 7.5/004	Silva *et al.*, 2018	Distribution in European agricultural topsoils	Glyphosate AMPA	Soil concentration, 15/20 cm depth	Reliable with restrictions

Data point	**Study (Author, year)**	**Study type**	**Substance(s)**	**Type of measured data**	**Status**
CA 7.5/005	Napoli, M. *et al.,* 2016	A runoff experiment in a vineyard in Italy	Glyphosate AMPA	Soil concentration, 5 cm depth	Reliable
CA 7.5/006	Székács, A. *et al.,* 2014	Monitoring and biological evaluation of surface water and soil micropollutants in Hungary	Glyphosate	Soil concentration	Reliable with restrictions
CA 7.5/007	Daouk, S. *et al.,* 2013b	The role of infiltration and surface runoff	Glyphosate AMPA	Pore water concentration	Reliable with restrictions

Data point:	CA 7.5/003
Report author	Karanasios, E. *et al.*
Report year	2018
Report title	Monitoring of glyphosate and AMPA in soil samples from two olive cultivation areas in Greece: aspects related to spray operators activities
Document No	Environ Monit Assess (2018) 190: 361
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The persistence of glyphosate and its primary metabolite AMPA (aminomethylphosphonic acid) was monitored in two areas in Southern Greece (Peza, Crete and Chora Trifilias, Peloponnese) with a known history of glyphosate use, and the levels of residues were linked to spray operators' activities in the respective areas. A total of 170 samples were collected and analysed from both areas during a 3-year monitoring study. A new method (Impact Assessment Procedure - IAP) designed to assess potential impacts to the environment caused by growers' activities, was utilised in the explanation of the results. The level of residues was compared to the predicted environmental concentrations in soil. The ratio of the measured concentrations to the predicted environmental concentrations (MCs/PECs) was >1 in Chora the first 2 years of sampling and <1 in the third year, whilst the MCs/PECs ratio was <1 in Peza, throughout the whole monitoring period. The compliance to the instructions for best handling practices, which operators received during the monitoring period, was reflected in the amount of residues and the MCs/PECs ratio in the second and especially the third sampling year. Differences in the level of residues between areas as well as sampling sites of the same area were identified. AMPA persisted longer than the parent compound glyphosate in both areas.

Materials and methods

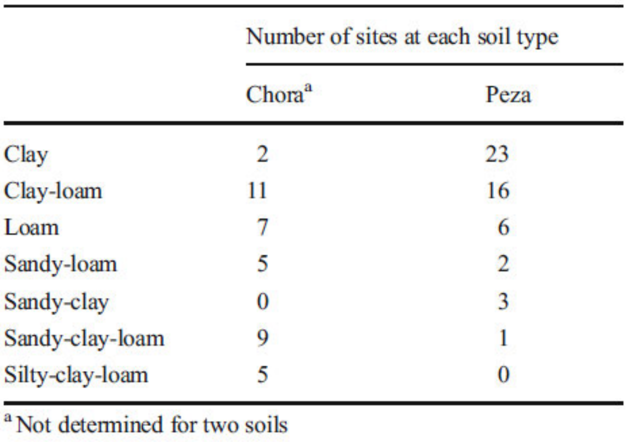
Field sites

Sampling was carried out between 2012 and 2014 in two typical olive-growing areas of Southern Greece (Peza, Crete and Chora Trifilias, Peloponnese). The first year of the monitoring program, sampling was carried out at each site in order to quantify the background pollution levels. A total of 51 sites were selected in Peza, 16 of which did not receive any glyphosate during the 3-year sampling period. Further, soil from 27 sites from conventional farms (6 of which were not treated with glyphosate) and 13 sites from organic farms in Chora Trifilias were collected and analysed. The selection of the study sites was based on the following criteria: (i) the spatial distribution within the studied areas and the landscape variability, (ii) the soil texture and properties and (iii) the farming practices/production schemes. Soil types varied between target areas and within sampling sites of the same area (Table 8.5-12). The physiochemical characteristics of soils are presented in Table 8.5-13.

Soil samples

Samples for residual analysis were taken from the 0 to 30-cm topsoil layer using a soil sampler. At least four soil sub-samples were collected per plot and pooled to obtain a representative sample for each site. Each soil sample consisted of 1 kg stored in labelled clean plastic bags and sent for analysis to the Laboratory of Chemical Control of Pesticides of Benaki Phytopathological Institute in portable containments under low temperature conditions and constant darkness. For practical reasons, sampling was carried out at variable dates after application of glyphosate (Table 8.5-14).

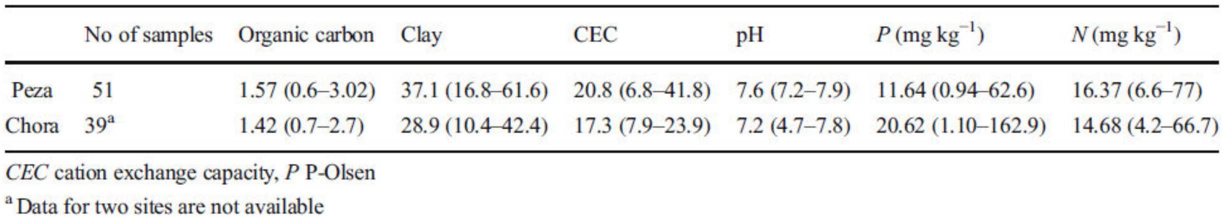
Table 8.5-12: Characterisation of soil in sampling sites in Chora and Peza



	Number of sites at each soil type	
	Chora[a]	Peza
Clay	2	23
Clay-loam	11	16
Loam	7	6
Sandy-loam	5	2
Sandy-clay	0	3
Sandy-clay-loam	9	1
Silty-clay-loam	5	0

[a] Not determined for two soils

Table 8.5-13: Physicochemical characteristics of soils

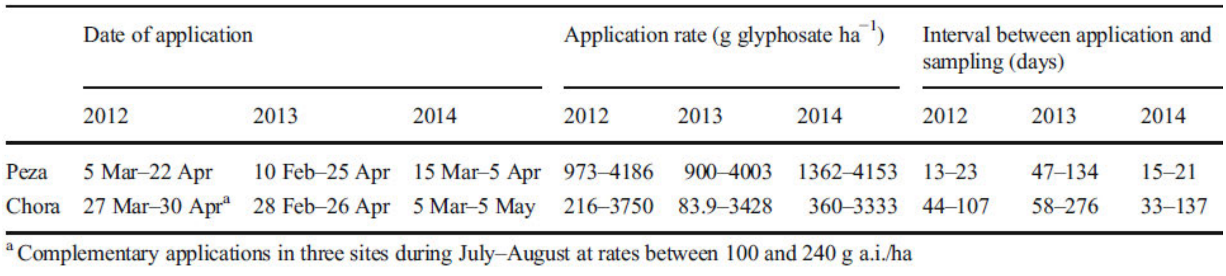


	No of samples	Organic carbon	Clay	CEC	pH	*P* (mg kg^{-1})	*N* (mg kg^{-1})
Peza	51	1.57 (0.6–3.02)	37.1 (16.8–61.6)	20.8 (6.8–41.8)	7.6 (7.2–7.9)	11.64 (0.94–62.6)	16.37 (6.6–77)
Chora	39[a]	1.42 (0.7–2.7)	28.9 (10.4–42.4)	17.3 (7.9–23.9)	7.2 (4.7–7.8)	20.62 (1.10–162.9)	14.68 (4.2–66.7)

CEC cation exchange capacity, *P* P-Olsen

[a] Data for two sites are not available

Table 8.5-14: Application of glyphosate in the two target areas



	Date of application			Application rate (g glyphosate ha^{-1})			Interval between application and sampling (days)		
	2012	2013	2014	2012	2013	2014	2012	2013	2014
Peza	5 Mar–22 Apr	10 Feb–25 Apr	15 Mar–5 Apr	973–4186	900–4003	1362–4153	13–23	47–134	15–21
Chora	27 Mar–30 Apr[a]	28 Feb–26 Apr	5 Mar–5 May	216–3750	83.9–3428	360–3333	44–107	58–276	33–137

[a] Complementary applications in three sites during July–August at rates between 100 and 240 g a.i./ha

Glyphosate applications
Glyphosate was applied once after the onset of rainfalls in both regions between mid-February and early May, after weeds had emerged or were actively growing at the time of spraying, except for three soil sampling sites in Chora where a complementary application of glyphosate, at a much lower dose, was carried out in the middle of summer (Table 8.5-14).

Application rate of glyphosate varied between and within areas due to differences in the target weeds and local practicalities. Weed management differed among olive groves and depended on weed species present, parcel's soil type, application of irrigation and various other factors related to the farming system applied. At least two weed surveys per year (late winter and end of spring) were conducted by agronomists and included identification of the weed species and determination of weed density. These surveys were the basis for weed management advices provided by agronomists to operators related to herbicide choice and practices on rational handling, spraying and herbicides remnants management. In few olive groves, combinations and/or sequential applications of herbicides were required to provide effective weed control.

Analytical standards
High purity analytical standards of glyphosate (98 %) and aminomethyl phosphonic acid (AMPA) (99.8 %) were purchased from ChemService (USA). Analytical standards of glyphosate-FMOC (97 %) and aminomethyl phosphonic acid-FMOC (97.5 %) were obtained from Dr. Ehrenstorfer. Individual stock solutions of glyphosate and AMPA were prepared by gravimetric weighing of high purity standards at concentrations of approximately 1000 mg L^{-1} in water (HPLC grade).Working solutions of individual compounds, their mixtures and spiked samples were prepared at different concentration levels, by appropriate dilutions of the stock solutions in water. Glyphosate and AMPA mixture working solutions were used for the estimation of recovery. Individual stock solutions of glyphosate-FMOC and AMPA-FMOC were prepared by gravimetric weighing of the high purity analytical standards at concentrations 492.76 and 970 μg/mL respectively, in an appropriate mixture of water:methanol (75:25) (HPLC grade). Working solutions of their mixtures were prepared in methanol at the concentrations of 0.01, 0.05, 0.1, 0.5 and 1 μg/mL and were used for establishing the linearity of the chromatographic system. All the standard and working solutions were stored in amber nonsilanized glasses at 0-1°C in dark. Before each use, the standard solutions were equilibrated at room temperature and weighed to check for evaporation losses.

Solvents and reagents
Analytical reagent-grade sodium tetraborate decahydrate of 100 % purity and 9-fluorenylmethylchloroformate (FMOC-Cl) of 98 % purity were obtained form LACHNER (Czech Republic) and ACROS ORGANICS respectively. Reagent grade hydrochloric acid and potassium hydroxide (KOH) was purchased from Panreac Quimica S.A. (Spain), and ammonium acetate from (NH_4Ac) of 98 % purity was obtained from Merck (Germany). Hydrochloric acid 11.65 N, LC-MS grade water and acetonitrile and HPLC water used in this study were supplied by Fisher Scientific (UK). Solution of 5 % borate buffer at approximately pH 9 in water of HPLC grade and solution containing 12,000 mg/L of FMOC-Cl in acetonitrile were used for the derivatization step of the samples. Argon (Ar), used as collisioninduced gas (CID gas) in the triple quadrupole, was obtained from Air Liquid (Greece).

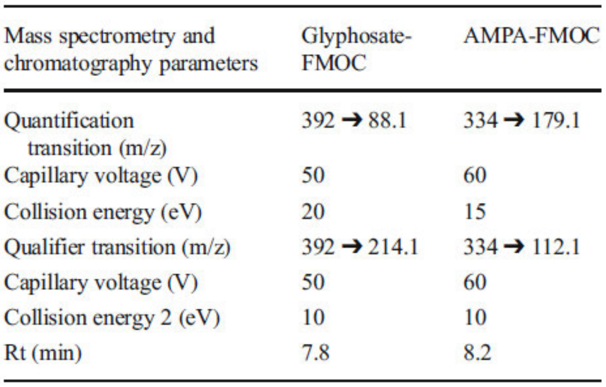
Sample preparation and extraction method
Sample preparation was based on the method proposed by Ibanez *et al.* (2005) with minor modifications as described below. Soil samples were air dried at room temperature in the dark, sieved through 2-mm sieve and frozen at - 40°C till extraction. Soil samples were allowed to reach ambient temperature and after thorough mixing of the sample, a subsample of 5 g (± 0.1) was transferred to a centrifuge tube (50 mL) with 10 mL of 0.6 M KOH, shaken mechanically in a horizontal shaker for 30 min and then centrifuged at 3000 rpm for 30 min. The alkaline supernatant was separated and neutralised by adding drops of 6 N and 0.6 N HCl until approximately pH 7.0. After that, the neutralised supernatant was tenfold diluted with water of HPLC grade. The next step concerns the derivatisation step in which 2 mL of the tenfold diluted supernatant was pipetted into a glass tube together with 120 μL HPLC water, 120 μL of borate buffer (pH 9) and 120 μL of FMOC-Cl reagent (12,000 mg/L). The tube was swirled and left overnight at room temperature, and then the samples were acidified with hydrochloric acid until pH 1.5, filtered through 0.45 μm syringe filter and injected directly to LC-ESI-MS/MS system. It should be mentioned that the

tenfold dilution of soil samples with water was assayed as a simple and fast way to minimize matrix interferences.

Instrumental
The high-performance liquid chromatograph used for the separation glyphosate and AMPA was a Varian (USA) system (working pressure maximum 400 bar), composed of two Prostar pumps (VARIAN, Prostar 210), a vacuum degasser (Metachem Technologies Inc), an autosampler (Varian, Prostar 420) with a 10-µL sample loop and a column oven (Varian, Prostar 510). The analytical column employed was a reversed phase C18 of 50 mm × 2 mm × 5 µm particle size (Agilent Zorbax Eclipse Plus). The mobile phases, A and B, consisted of water 5 mM acetic acid/ammonium acetate adjusted at pH 4.6 and acetonitrile at a ratio 10:90 respectively. The flow rate was set at 0.2 mL/min and the column gradient program consisted of 90 vol. % of A and 10 vol. % of B where it remained for 5.06 min. Next, at 5.1 min, it was reversed to 10 vol. % of A and 90 vol. % of B where it remained for 10 min. At 10.01 min, the gradient was returned to the initial conditions (90 vol. % A) where it maintained up to the end of the analysis at 20 min. After the 20 min run time, the column was re-equilibrated for 10 min at the initial mobile phase composition. The column temperature was maintained at 30°C during all runs and the injection volume was 5 µL. In order to avoid carry over, the autosampler was purged with a mixture methanol/water (50:50 v/v) before sample injection.

The triple quadrupole system used was a Varian 1200 L (VARIAN, USA) Quadrupole MS-MS spectrometer fitted with an electrospray ionisation (ESI) interface. The ESI-MS interface was operated in the positive ion detection mode. The ESI source conditions were capillary voltage, 5000 V in positive-ion (PI) mode; drying gas temperature, 300°C; nebuliser gas pressure, 45 psi (both nebuliser and drying gas were high purity nitrogen, produced by a high purity generator) and electron multiplier voltage, 1600 V. MS/MS experiments were carried out with Argon (purity 99.9 %) at pressure of approximately 1.5 mTorr in the collision cell. Cone voltage and collision energy values optimised for each of the two compounds selected, were used. For selected ion monitoring (SIM) experiments, both Q1 and Q3 were set at fixed m/z values. For each analyte, the most abundant and characteristic fragment ion was chosen for quantization and two fragment ions selected for confirmation (Table 8.5-15). Dwell times of 0.1 ms were set. For instrument control, data acquisition and processing, the Varian MS Workstation software version 6.8 was used. The selected ion monitoring (SIM) mode was applied, and the selected characteristic ions are presented at Table 8.5-15. The transition of the most abundant product ion was used for quantitation and the second one in abundance for identification. The first step involved selection of the precursor ion for each compound.

Table 8.5-15: **Mass spectrometry parameters for glyphosate and AMPA**



Mass spectrometry and chromatography parameters	Glyphosate-FMOC	AMPA-FMOC
Quantification transition (m/z)	392 ➔ 88.1	334 ➔ 179.1
Capillary voltage (V)	50	60
Collision energy (eV)	20	15
Qualifier transition (m/z)	392 ➔ 214.1	334 ➔ 112.1
Capillary voltage (V)	50	60
Collision energy 2 (eV)	10	10
Rt (min)	7.8	8.2

For both compounds, glyphosate and AMPA and in the positive-ion electrospray full scan spectrum, the protonated derivatized molecule [M + H] + was recorded at m/z 392 and 334, respectively. In the case of glyphosate, the MS/MS spectra showed two abundant fragments at m/z 214 and 88, whereas in the case of AMPA the respective abundant fragments were at m/z 112 and 179.

Validation study
The method has been fully validated following the European Union SANCO guidelines. The precision (repeatability, in terms of % RSD) and the accuracy (percentage recoveries) of the method were estimated by recovery experiments in soil which was free of glyphosate and AMPA at three fortification levels.

Linearity
Linearity for glyphosate and AMPA was evaluated using calibration curves at five concentration levels covering concentrations at three orders of magnitude: 0.01 - 1 µg/g, based on the linear regression and squares correlation coefficients, R^2. Regression analysis exhibited an excellent relationship, as correlation coefficients (R^2) were 0.9987 for AMPA and 0.9978 for glyphosate.

Precision
The repeatability of the method was determined at the concentration level of 0.05 µg/g dry weight, by the analysis of five spiked matrix extracts ($n = 5$). The calculated RSDs ranged between 5 and 15 %. Inter-day RSDs were calculated for 5 days and varied between 7 and 19 %. According to "Guidance document on pesticide residue analytical methods", these results were considered to be acceptable and demonstrated a satisfactory repeatability of the method and therefore its effectiveness for quantitative purposes. The accuracy of the method was verified by measuring from spiked blank samples at three concentration levels, i.e. at 0.01, 0.05 and 0.5 µg/g dry weight. All experiments were performed five times, and the relative standard deviation (RSD %) was calculated, and the values obtained were used for the estimation of the precision of the extraction method.

Recovery and limit of quantitation
The accuracy of the method was verified by measuring recoveries form spiked blank samples at three concentrations levels, i.e. at 0.01, 0.05 and 0.5 µg/g dry weight. All experiments were performed five times, and the relative standard deviation (RSD) was calculated. Recovery ranged between 89.6 and 118.8 % for glyphosate and between 67.9 and 94.6 % for AMPA whereas the RSD was 15.35 % for glyphosate and 11.9 % for AMPA in all cases.

The validated LOQs were defined as the lowest validated spike level (expressed in µg/g dry weight) for which a recovery in the 70-120 % range could be obtained, with a corresponding RSD $\leq$20 %, according to the EU SANCO document on validation and QC procedures. Based on the EU SANCO, the validated LOQs were defined as the lowest calibrated spiked level and were 0.01 µg/g soil dry weight for both compounds. Recoveries for the studied compounds were in the range 75.62-113.65 %, thus, the concentration of pesticides in soil samples was not corrected for recovery.

A soil sample free from glyphosate and AMPA residues was used for recovery experiments. The specific sample was previously analysed to ensure that it did not contain the studied compounds and was used as blank soil sample. This blank soil sample used for the estimation of recovery was treated as follows: 10 g of the sample (blank soil sample) was placed in a centrifuge tube (50 mL) along with 1 mL of the standard mixture of the desired pesticide concentration in water. It was homogenised by mechanical shaking for 60 min for better analyte distribution, and the bulk of the solvent was left to evaporate at ambient temperature and controlled by weight. This is a procedure able to mimic weathered residues. Then, spiked samples were extracted in the same way as described in the sample preparation and extraction method.

Predicted environmental concentration
The concentration of glyphosate and AMPA in soil was estimated with the soil persistence model of the Soil Modelling Work group of FOCUS:

$$\mathrm{PEC}_s(t_0) = \frac{A \times (1 - f_{\mathrm{int}})}{100 \times \ \mathrm{depth} \times \ \mathrm{bd}} \qquad (1)$$

$$\mathrm{PEC}_s(\text{after n applications}) = \mathrm{PEC}_s(t_0) \times \ \frac{1 - e^{-\mathrm{nki}}}{1 - e^{-\mathrm{ki}}} \ (2)$$

$$k = \frac{\ln 2}{\mathrm{DT}_{50}} \qquad (3)$$

where A is the application dose (g/ha); f_{int} is the fraction intercepted by crop canopy; depth is the mixing depth (cm) and bd is the dry soil bunk density (g/cm^3); k is the dissipation rate constant and DT_{50} the time for disappearance of half the chemical. The following assumptions were made: the f_{int} was set to 0, the mixing depth to 15 cm, the DT_{50} of glyphosate and AMPA were 8.2 and 137.2 days, respectively (geomean of available EU data); and the formation factor of AMPA was set to 27.5 %.

Scoring of environmental impact-IAP method

The results of the IAP (Impact Assessment Procedure) method (under publication), which was implemented in the two target areas (Chora and Peza) in the context of the LIFE09 ENV/GR/000302 SAGE10 project, were used to explain the results from the soil monitoring studies. According to the IAP concept, each impact is expressed as a combination of three elements (called in IAP *Triplet*): *Aspect* (growers' activities)-*Impact*-*Compartment* (soil, water, humans, biodiversity). Several parameters were utilised for the assessment of the environmental impacts in the two target areas. Parameters, which can be related to the farmers' practices and choices or to the resilience of the environment to contamination, were recorded and weighted. Each of the 200 olive-groves which were randomly selected in each area received a score, was based on data collected by agronomists. Data for the value or class of parameters were collected annually for three consecutive years (starting 1 year prior to the initiation of the monitoring). The score of each triplet was normalised to a 0-1 scale, where 0 represents the absence of expected impact and 1 the possibility of significant impact. The four triplets which are related to point source pollution with pesticides are the handling of wastewater loads from pesticide use (emptying, filling and cleaning of equipment), the management of empty containers, the transport and the storage of agrochemicals. In each of these triplets, the impact was pollution and the compartment was the abiotic environment. Groves under organic farming system or groves where chemicals were not used for weed control were excluded.

Results

Monitoring of glyphosate and AMPA residues in conventional olive farms of Chora and Peza with long history of glyphosate use

The analysis of the soil residues was restricted to glyphosate which was extensively used in both studied areas. Its major metabolite AMPA was also determined in all analysed soil samples. The analyses results for glyphosate and AMPA in soil samples during the three sampling years (2012-2014) are given in Table 8.5-16 and Table 8.5-17. For practical reasons (workload, distance between parcels, number of sampling sites etc), sampling was conducted at various intervals after glyphosate application as presented in Table 8.5-14, thus, the side-by-side comparison of the residue levels between years and sampling sites is not possible. In order to compare the level of glyphosate and AMPA residues in different sites, the measured concentration in soil (MCs) was associated with the estimated PECs which corresponds to the time of sampling, using the initially applied dose and the theoretical dissipation rate constants for glyphosate and AMPA (MCs/PECs ratio; Figure 8.5-2).

Glyphosate and AMPA concentrations from soil samples collected in Peza ranged from <LOQ to 240 µg/kg and from <LOQ to 100 µg/kg, respectively. Glyphosate residues exceeding the LOQ were determined in 6 out of 35 glyphosate-treated sites. Concentrations of glyphosate and AMPA were generally far lower than the theoretically estimated levels (PECs) except for three sampling occasions (Table 8.5-16), which suggest that glyphosate was rapidly degraded in this area. The MCs/PECs ratio was 0.35 in the first sampling event and reduced further at subsequent samplings (Figure 8.5-2). The decrease of the MCs/PECs ratio can be linked to the reduction of glyphosate losses from improper pre- and post-application handling as suggested

by the improvement of the triplet score through the application of IAP Method. The targeted training that operators received led to the lowering of the mean score for two of the four examined aspects (remnant handling and transport) (Table 8.5-18). The change in score was significant in groves which received the highest score in the baseline year (score class 0.3-0.4). The reduction of transport distance, the selection of zero-slope spots for handling and disposal of spay leftovers and the frequency of use of spraying equipment are the associated parameters which were refined in the 2012-2013 period. The adoption of environmentally sound practices was mirrored in the slight improvement of specific indicators: the proportion of operators which accurately performed the triple rinsing of empty containers (increase from 55 % in the baseline year to 63 % in 2013; data not shown) and the proportion of spraying equipment without visible leakages (increased by 9.5 % in the same period). It is noticeable that glyphosate remained one of the prevalent weed control practices in the area as the total glyphosate load was reduced by only 9.9 % between 2011 and 2013 in the area.

Based on the results of the first sampling year in Peza, an estimation of the rate of degradation of glyphosate was done, assuming that residue decline follows simple first-order kinetics. Residues of glyphosate reached the limit of quantification (LOQ) within 2-3 weeks after application in 15 out of 18 samples in 2012. In the three remaining sites from the 2012 sampling, some glyphosate residues were traced (31-240 µg/kg). If first order degradation is assumed, the estimated half-lives for AMPA in these three soils could be approximated to range from 3.6 to 5.7 days. Thus, DT_{50} can be anticipated to be close to the lowest recorded values for this active substance. The absence of substantial residual amounts of glyphosate and AMPA indicates that built-up of residues after repeated use of glyphosate products is not expected in this area.

The concentration of glyphosate and AMPA in soil received from Chora ranged from <LOQ to 350 µg/kg and <LOQ to 650 µg/kg, respectively. The variation in the level of residues between sites may be explained by differences in the application rates, the frequency of application events and the interval between last application and sampling. The analysed concentrations of glyphosate and AMPA in Chora exceeded the theoretically estimated values in a number of sites, especially at the first sampling year. The maximum measured concentration of AMPA is soil (650 µg/kg) is, however, lower than the theoretical worst-case plateau concentration of AMPA in permanent crops (4140 µg/kg) after 10 years of continuous glyphosate applications. The proportion of sampling sites with residues exceeding the theoretically estimated values was reduced from 88 % in 2012 to 36 % in 2013 and 21 % in 2014. To be noted that residual AMPA residues from applications before 2012 were not included (the baseline concentration of AMPA was not set). Various sources of contamination linked to the handling of pesticide equipment and the management of the application leftovers are possible to have contributed to the exceeding of the theoretical values.

The results of a survey in Chora showed a perceivable improvement in mean score of triplets and more specifically for aspects linked to point source contamination of soil with pesticides in 2012 and especially 2013 compared to 2011 (Table 8.5-18). The adoption of environmentally friendlier aptitude at the second and especially the third year of monitoring is mirrored in the steep decrease of MCs/PECs values in Chora between 2013 and 2014 (Figure 8.5-2). The mean MCs/PECs ratio was 6.95 in the first sampling year and reduced to <1 in the third year. The aspects which were improved are the handling of remnants from application, the safe transport of pesticide loads and the management of obsolete containers. On the contrary, the safety of storage practices was not practically improved in the monitoring period. The improvement of the environment impact score between 2011 and 2013 is directly linked to the training which operators received by experts during the same period in the context of the program SAGE10. Further scrutiny of the parameters linked to the triplet score revealed that the most significant contributing factors to the year-by-year decrease of the score in the area are the quantity of pesticides in transport and the transport distance, the lowering of the distance between handling areas and surface water bodies and the improvement in the frequency of the visual examination and calibration of spraying equipment before use. Further, in-site inspections and interviews revealed a shift to environmentally friendlier practices. The number of operators which are considered to accurately perform the triple-rinsing increased from 57 to 64 %, and the proportion of spraying equipment without visible leakages increased from 60 to 64 % in the same period (data not presented). Other contributing factor is the reduction of total glyphosate load in the catchment between 2011 and 2013. The total amount of glyphosate was reduced by 61.2 %, due to the gradual shifting to other chemical solutions (oxyfluorfen, glufosinate-ammonium) as part of the Conyza spp. resistance management.

The mean level of AMPA residues in Chora for all sampling years was higher compared to Peza despite the fact that the mean application dose was higher in Peza, and the interval between application and sampling was narrower (Table 8.5-14). Differences were more striking in the first year of application. Variances in residue levels may reflect differences in pesticide residue management or the dissipation potential of soils. Further, differences in the application technique may have influenced the residual amount of glyphosate in soil. In a significant proportion of olive groves in the Peza Region (46.9-63.5 %, depending on the year), glyphosate is carried out as spot application, whilst most spray operations in Chora are usually performed by broadcast spraying (73.0-99.1 % of groves in the 2001-2003 period). Further, the two regions belong to different climatic zones: Chora has a subhumid climate whilst Peza belongs to the semi-arid zone, which may affect the dissipation potential. Compared to Chora, a more favourable environmental profile was observed in Peza as regards the handling of pesticide leftovers and the management of empty containers. On the contrary, a lower mean score was recorded for Chora as regards storage, irrespectively of the year and transport in 2012-2013. However, it should be noted that the initial mean score was generally low in both areas as only a few triplets received a score of higher than 0.3.

Only slight differences in the physicochemical characteristics of soils in the two sites were seen, except for Olsen-P content. The presence of phosphate in soil has been reported to compete with glyphosate and AMPA for sorption sites and thus can affect the bioavailability of the both substances as well as stimulate the glyphosate degradation. However, due to the lack of relevant data, it is not possible to correlate the higher levels of P in the Chora region with the presence of naturally occurred phosphates and/or phosphate fertilisation. Despite the significant number of samples taken for analysis, correlation analysis performed did not reveal association between detected residue levels and pH, soil type or any of the physicochemical soil properties probably due to the fact that the interval between application and sampling differed significantly between sites.

Monitoring of glyphosate and AMPA in organic farms in Chora and conventional farms in Chora and Peza where glyphosate is not used

A number of soil samples were collected from certified organic farms of Chora (OF1-OF13) and conventionally cultivated groves in both target areas, where glyphosate is not used for weed control. The analysis of soil samples aimed at the examination of possible occurrence of glyphosate residues transferred from bordering sites, where glyphosate is used for weed control, or from other unpredictable routes of entry. Except for one site in which glyphosate was traced at levels of 27 µg/kg in 2013, no glyphosate was detected at any sampling event in the OF sites. The metabolite AMPA was detected in five sites, in at least one sampling event, and at concentrations ranging from 13 to 440 µg/kg (Figure 8.5-3). It is possible that glyphosate and AMPA residues were derived from neighbouring sites via drift and run-off. Glyphosate and AMPA have been previously found in soil environments in which glyphosate had never been used as a result of surface run-off from zones where it was initially applied. However, this route of entry cannot explain the elevated concentrations of AMPA in OF5 and OF7 sites. Further scrutiny revealed that the two sites were used as spots for washing of application equipment after use in nearby fields in 2012. The high AMPA levels can thus be considered as a result of point source pollution. The improper disposal of spraying remnants was not repeated at subsequent years. The quantified levels of AMPA in these two sites significantly decreased in 2013, resulting in 93-100 % dissipation of the initial amount within 1 year.

Except for one site in which AMPA amounted to 25 µg/kg, no glyphosate or AMPA residues was traced in the 16 sites in Peza in which no chemical weed control was carried out the year of sampling. Furthermore, AMPA residues ranging from 16 to 21 µg/kg were quantified in the six sites in Chora where glyphosate was not used for weed control.

Figure 8.5-2: **The measure concentration (MCs) to predicted environmental concentration (PEC) ratio of AMPA residues in 2012-2014 in 11 sites from Chora and four sites in Peza (only sites for which data on all 3 years are presented)**

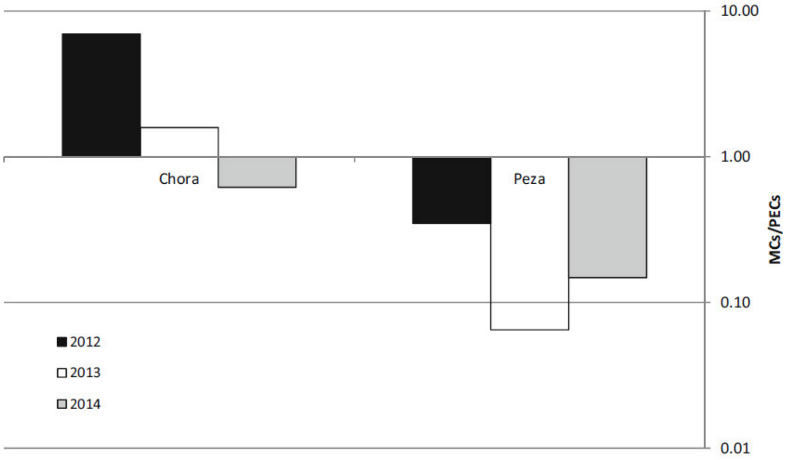
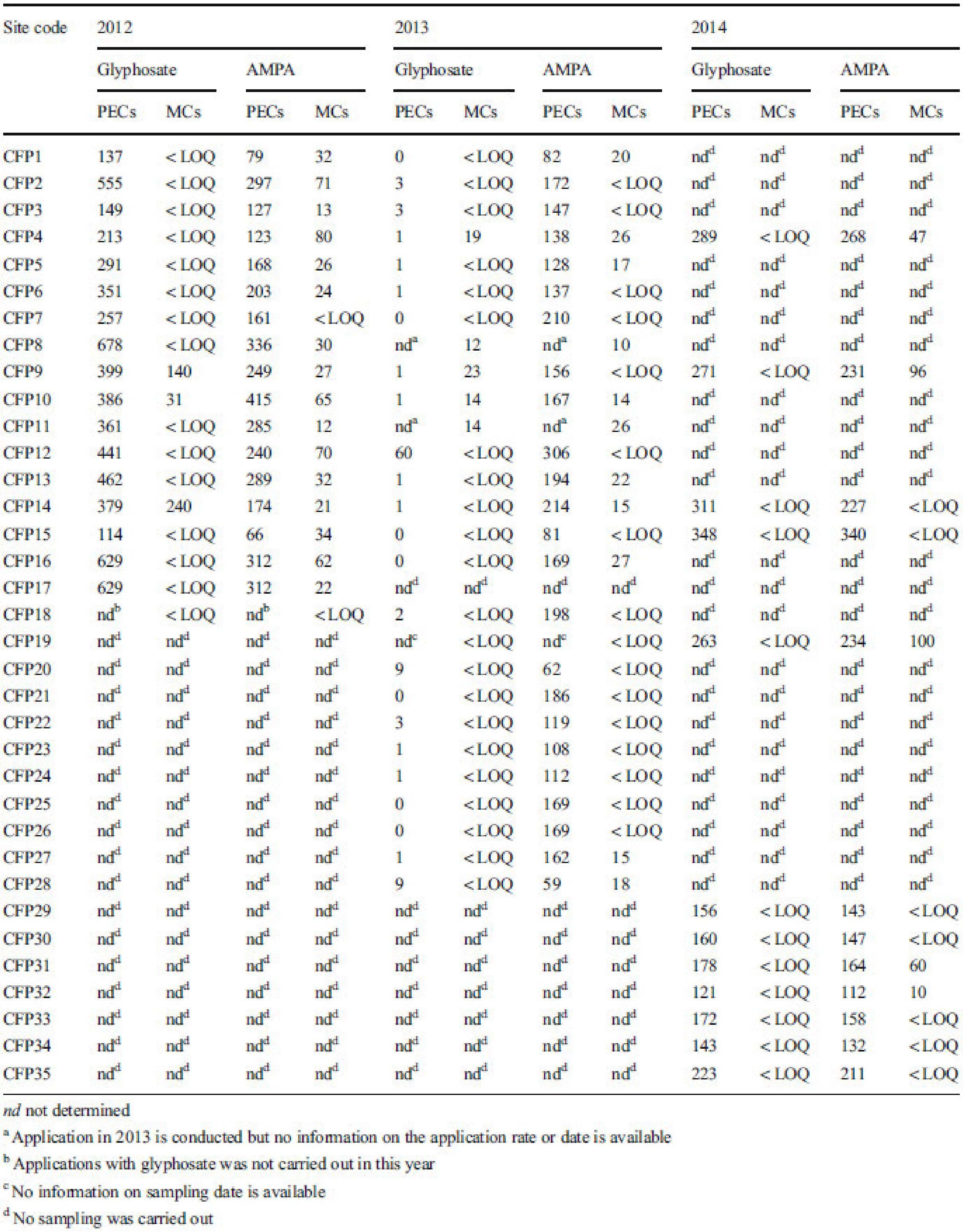


Table 8.5-16: **Measured concentrations (MCs; µg/kg) and predicted environmental concentration (PECs; µg/kg) of glyphosate and AMPA in treated sites in Peza**



Site code	2012				2013				2014			
	Glyphosate		AMPA		Glyphosate		AMPA		Glyphosate		AMPA	
	PECs	MCs	PECs	MCs	PECs	MCs	PECs	MCs	PECs	MCs	PECs	MCs
CFP1	137	< LOQ	79	32	0	< LOQ	82	20	nd[d]	nd[d]	nd[d]	nd[d]
CFP2	555	< LOQ	297	71	3	< LOQ	172	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP3	149	< LOQ	127	13	3	< LOQ	147	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP4	213	< LOQ	123	80	1	19	138	26	289	< LOQ	268	47
CFP5	291	< LOQ	168	26	1	< LOQ	128	17	nd[d]	nd[d]	nd[d]	nd[d]
CFP6	351	< LOQ	203	24	1	< LOQ	137	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP7	257	< LOQ	161	< LOQ	0	< LOQ	210	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP8	678	< LOQ	336	30	nd[a]	12	nd[a]	10	nd[d]	nd[d]	nd[d]	nd[d]
CFP9	399	140	249	27	1	23	156	< LOQ	271	< LOQ	231	96
CFP10	386	31	415	65	1	14	167	14	nd[d]	nd[d]	nd[d]	nd[d]
CFP11	361	< LOQ	285	12	nd[a]	14	nd[a]	26	nd[d]	nd[d]	nd[d]	nd[d]
CFP12	441	< LOQ	240	70	60	< LOQ	306	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP13	462	< LOQ	289	32	1	< LOQ	194	22	nd[d]	nd[d]	nd[d]	nd[d]
CFP14	379	240	174	21	1	< LOQ	214	15	311	< LOQ	227	< LOQ
CFP15	114	< LOQ	66	34	0	< LOQ	81	< LOQ	348	< LOQ	340	< LOQ
CFP16	629	< LOQ	312	62	0	< LOQ	169	27	nd[d]	nd[d]	nd[d]	nd[d]
CFP17	629	< LOQ	312	22	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]
CFP18	nd[b]	< LOQ	nd[b]	< LOQ	2	< LOQ	198	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP19	nd[d]	nd[d]	nd[d]	nd[d]	nd[c]	< LOQ	nd[c]	< LOQ	263	< LOQ	234	100
CFP20	nd[d]	nd[d]	nd[d]	nd[d]	9	< LOQ	62	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP21	nd[d]	nd[d]	nd[d]	nd[d]	0	< LOQ	186	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP22	nd[d]	nd[d]	nd[d]	nd[d]	3	< LOQ	119	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP23	nd[d]	nd[d]	nd[d]	nd[d]	1	< LOQ	108	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP24	nd[d]	nd[d]	nd[d]	nd[d]	1	< LOQ	112	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP25	nd[d]	nd[d]	nd[d]	nd[d]	0	< LOQ	169	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP26	nd[d]	nd[d]	nd[d]	nd[d]	0	< LOQ	169	< LOQ	nd[d]	nd[d]	nd[d]	nd[d]
CFP27	nd[d]	nd[d]	nd[d]	nd[d]	1	< LOQ	162	15	nd[d]	nd[d]	nd[d]	nd[d]
CFP28	nd[d]	nd[d]	nd[d]	nd[d]	9	< LOQ	59	18	nd[d]	nd[d]	nd[d]	nd[d]
CFP29	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	156	< LOQ	143	< LOQ
CFP30	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	160	< LOQ	147	< LOQ
CFP31	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	178	< LOQ	164	60
CFP32	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	121	< LOQ	112	10
CFP33	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	172	< LOQ	158	< LOQ
CFP34	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	143	< LOQ	132	< LOQ
CFP35	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	nd[d]	223	< LOQ	211	< LOQ

nd not determined

[a] Application in 2013 is conducted but no information on the application rate or date is available

[b] Applications with glyphosate was not carried out in this year

[c] No information on sampling date is available

[d] No sampling was carried out

Table 8.5-17: **Measured concentrations (MCs; µg/kg) and predicted environmental concentration (PECs; µg/kg) of glyphosate and AMPA in treated sites in Chora Trifilias**

Site code	2012				2013				2014			
	Glyphosate		AMPA		Glyphosate		AMPA		Glyphosate		AMPA	
	PECs	MCs	PECs	MCs	PECs	MCs	PECs	MCs	PECs	MCs	PECs	MCs
CFC1	41	190	72	210	0	< LOQ	16	140	22	< LOQ	227	< LOQ
CFC2	39	150	70	180	0	< LOQ	40	< LOQ	1	< LOQ	81	80
CFC3	0	< LOQ	74	< LOQ	0	< LOQ	50	< LOQ	1	< LOQ	102	29
CFC4	nd[a]	< LOQ	nd[a]	< LOQ	nd[b]	nd[b]	nd[b]	nd[b]	0	< LOQ	67	100
CFC5	0	< LOQ	176	250	0	< LOQ	62	10	0	< LOQ	44	150
CFC6	0	230	176	260	0	< LOQ	62	19	0	< LOQ	35	34
CFC7	0	350	177	650	0	< LOQ	63	14	0	< LOQ	35	16
CFC8	0	< LOQ	6	260	0	< LOQ	27	26	35	< LOQ	152	10
CFC9	0	< LOQ	35	100	0	< LOQ	58	26	0	< LOQ	109	< LOQ
CFC10	0	< LOQ	32	330	0	< LOQ	58	170	0	< LOQ	107	< LOQ
CFC11	0	< LOQ	87	310	nd[b]	nd[b]	nd[b]	nd[b]	42	< LOQ	118	< LOQ
CFC12	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]	< LOQ	11	< LOQ	0	< LOQ	102	< LOQ
CFC13	0	< LOQ	93	180	0	70	18	30	0	< LOQ	162	< LOQ
CFC14	10	140	52	310	nd[b]	< LOQ	25	50	0	< LOQ	76	47
CFC15	0	nd[b]	11	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]	0	< LOQ	36	< LOQ
CFC16	0	< LOQ	53	< LOQ	nd[b]	nd[b]	nd[b]	nd[b]	0	< LOQ	60	34
CFC17	nd[b]	nd[b]	nd[b]	nd[b]	0	< LOQ	26	70	nd[c]	< LOQ	nd[c]	< LOQ
CFC18	39	< LOQ	54	320	nd[b]	nd[b]	nd[b]	nd[b]	0	< LOQ	22	80
CFC19	28	< LOQ	40	140	nd[b]	nd[b]	nd[b]	nd[b]	0	< LOQ	16	140
CFC20	0	< LOQ	19	20	0	< LOQ	3	< LOQ	nd[c]	< LOQ	nd[c]	20
CFC21	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]	0	< LOQ	35	18

nd not determined

[a] Application with glyphosate was not carried out in this year

[b] No sampling was carried out

[c] No information on glyphosate application is available

Figure 8.5-3: **Glyphosate and AMPA residues in 2012-2014 in nine sites from organic farms in Chora (only samples with data on more than 1 year are presented)**

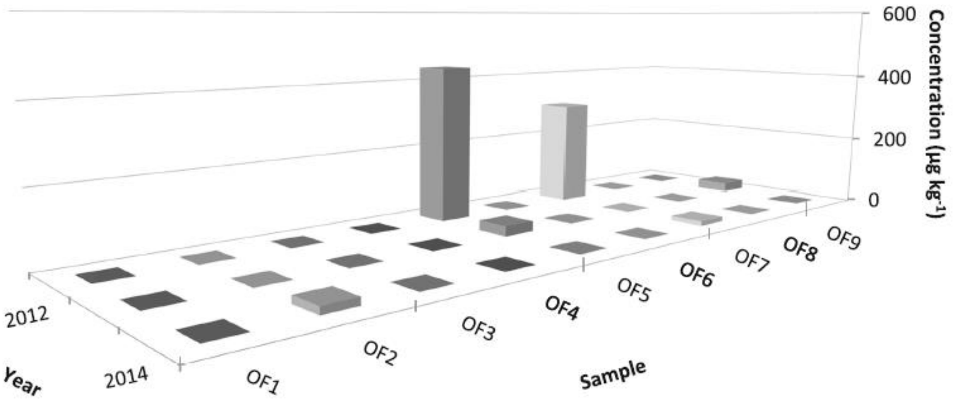
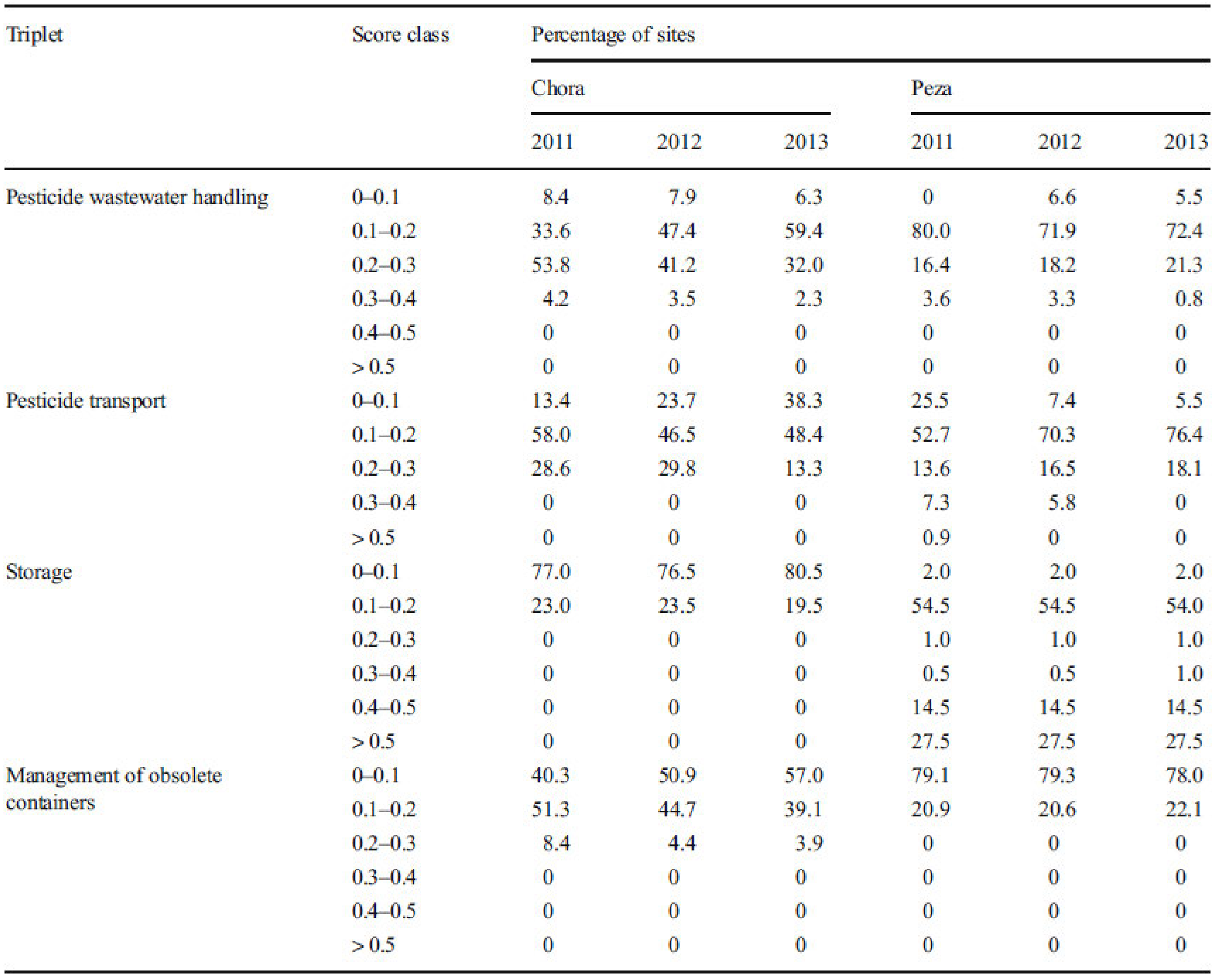


Table 8.5-18: **Percentage of parcels in Chora and Peza in various score classes for each of the three triplets which are associated with the pesticide handling and the risk for contamination of the environment via point sources in the years 2011 to 2013**



Triplet	Score class	Percentage of sites					
		Chora			Peza		
		2011	2012	2013	2011	2012	2013
Pesticide wastewater handling	0–0.1	8.4	7.9	6.3	0	6.6	5.5
	0.1–0.2	33.6	47.4	59.4	80.0	71.9	72.4
	0.2–0.3	53.8	41.2	32.0	16.4	18.2	21.3
	0.3–0.4	4.2	3.5	2.3	3.6	3.3	0.8
	0.4–0.5	0	0	0	0	0	0
	> 0.5	0	0	0	0	0	0
Pesticide transport	0–0.1	13.4	23.7	38.3	25.5	7.4	5.5
	0.1–0.2	58.0	46.5	48.4	52.7	70.3	76.4
	0.2–0.3	28.6	29.8	13.3	13.6	16.5	18.1
	0.3–0.4	0	0	0	7.3	5.8	0
	> 0.5	0	0	0	0.9	0	0
Storage	0–0.1	77.0	76.5	80.5	2.0	2.0	2.0
	0.1–0.2	23.0	23.5	19.5	54.5	54.5	54.0
	0.2–0.3	0	0	0	1.0	1.0	1.0
	0.3–0.4	0	0	0	0.5	0.5	1.0
	0.4–0.5	0	0	0	14.5	14.5	14.5
	> 0.5	0	0	0	27.5	27.5	27.5
Management of obsolete containers	0–0.1	40.3	50.9	57.0	79.1	79.3	78.0
	0.1–0.2	51.3	44.7	39.1	20.9	20.6	22.1
	0.2–0.3	8.4	4.4	3.9	0	0	0
	0.3–0.4	0	0	0	0	0	0
	0.4–0.5	0	0	0	0	0	0
	> 0.5	0	0	0	0	0	0

Conclusion

Glyphosate and the primary metabolite AMPA were present at maximum concentrations of 350 and 650 µg/kg, respectively, in soil sampled from olive groves in two monitoring areas in Greece. The residual amount of both contaminants differed between areas. Reduction of pesticide losses in the environment, which was one of the objectives of the SAGE10 project, was achieved by a combination of reduced glyphosate loads (especially in Chora, Trifilias, Peloponnese) and decreased glyphosate point source entries. The steep reduction of MCs/PECs values at the second and third year of monitoring was mirrored in the IAP Method triplet score, where aspects related to point source contamination were decreased, which in turn can be considered as a result of the targeted training of operators.

Assessment and conclusion by applicant:

The article reports monitoring data for glyphosate and AMPA in Greek agricultural soils associated with olive production. Glyphosate and AMPA were present at maximum concentrations of 350 and 650 µg/kg, respectively.

The article is therefore considered reliable.

Assessment and conclusion by RMS:

The study describes a monitoring program in the soils of two olive growth areas of Southern Greece (Peza, Crete and Chora Trifilias, Peloponnese). A total of 51 sites were selected in Peza, 16 of which did not receive any glyphosate during the 3-year sampling period. Further, soil from 27 sites from conventional farms (6 of which were not treated with glyphosate) and 13 sites from organic farms in Chora Trifilias were collected and analysed.

The analysis of the soil residues was restricted to glyphosate which was extensively used in both studied areas. Its major metabolite AMPA was also determined in all analysed soil samples.

Sampling strategy and analytical method are well described. However, the following points should be noted.

The actual residue levels were measured in a 0-30 cm soil layer, which is not the conventional depth considered in regulatory risk assessment (5 cm considered for perennial crops). Therefore, the measured residue level is somehow "diluted" and intrinsically lower than the one that would be considered for risk assessment purpose.

Sampling was also conducted at various intervals after glyphosate application as presented in Table 8.5-14.

In order to compare the level of glyphosate and AMPA residues in different sites, the measured concentration in soil (MCs) was associated with the estimated PECs which corresponds to the time of sampling, using the initially applied dose and the theoretical dissipation rate constants (the geomean of EU data is reported to be used by the study author) for glyphosate and AMPA (MCs/PECs ratio; Figure 8.5-2).

However, is should be noted that the theoretical estimated PECs are calculated considering a mixing depth of 15 cm, while the actual residue levels are measured in 0-30 cm soil layer samples. Also the choice of a geomean DT_{50} for the estimated PECs could be questionable, as may not represent the actual dissipation conditions at the sites. RMS also notes that the DT50 for glyphosate and AMPA and the maximum occurrence of AMPA used for the calculation are quite different from the ones selected for PECsoil calculation for EU approval (both in EFSA Journal 2015;13(11):4302 and in current dossier for renewal).

The direct comparison between actual and estimated PECs performed in the study should should not be considered further.

For these reasons, this study is considered reliable with restrictions.

Data point:	CA 7.5/004
Report author	Silva, V. *et al.*
Report year	2018
Report title	Distribution of glyphosate and aminomethylphosphonic acid (AMPA) in agricultural topsoils of the European Union
Document No	Science of the Total Environment 621 (2018) 1352–1359
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes
Acceptability/Reliability:	Reliable with restrictions

Approval for glyphosate--based herbicides in the European Union (EU) is under intense debate due to concern about their effects on the environment and human health. The occurrence of glyphosate residues in European water bodies is rather well documented whereas only few, fragmented and outdated information is available for European soils. We provide the first large-scale assessment of distribution (occurrence and concentrations) of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) in EU agricultural topsoils and estimate their potential spreading by wind and water erosion. Glyphosate and/or AMPA were present in 45 % of the topsoils collected, originating from eleven countries and six crop systems, with a maximum concentration of 2 mg/kg. Several glyphosate and AMPA hotspots were identified across the EU. Soil loss rates (obtained from recently derived European maps) were used to estimate the potential export of glyphosate and AMPA by wind and water erosion. The estimated exports, result of a conceptually simple model, clearly indicate that particulate transport can contribute to human and environmental exposure to herbicide residues. Residue threshold values in soils are urgently needed to define potential risks for soil health and off-site effects related to export by wind and water erosion.

Methods

The soil samples

Glyphosate and AMPA distributions were assessed in 317 topsoil samples: 300 samples from the LUCAS 2015 survey Land Use/Cover Area Frame Survey, a harmonized assessment of topsoil characteristics across EU Member States, and 17 samples from three independent vineyards in northcentral Portugal, where a parallel study on transport of pesticide residues by water erosion was conducted. The samples from the LUCAS 2015 survey were collected between April and October of 2015 as described in ESTAT (2015a) and represent the uppermost 15/20 cm of soil. The samples selected for this work followed two main criteria: they were collected in i) the countries of each EU region with the highest percentage of agricultural area and pesticide use per hectare of arable and permanent croplands and ii) the crops with the highest pesticide use per hectare or highest extension of cultivated area in those countries. Pesticide use included, but was not restricted to, glyphosate-based herbicides (GlyBH) use since other pesticide residues were also analyzed in the samples. These sample selection criteria provide a worst case estimate of distribution of multiple pesticide residues in EU agricultural topsoils.

The countries selected by EU region were, from largest to smallest in order of pesticide use per hectare, in the northern region: United Kingdom (UK) and Denmark (DK); southern region: Italy (IT), Greece (EL) and Spain (ES); eastern region: Hungary (HU) and Poland (PL); western region: The Netherlands (NL), France (FR) and Germany (DE). The crops selected were cereals (wheat, barley, rye, maize, triticale, oats), root crops (potatoes, sugar beet), non-permanent industrial crops (sunflower, rapeseed), dry pulses and fodder crops (floriculture, alfalfa, temporary grassland), permanent crops (citrus, vines, olives, other fruit trees and berries), vegetables (tomatoes, other fresh vegetables). Additionally, some bare soils, which were croplands in the previous LUCAS 2009 and 2012 surveys, were included in the category others. The exhaustive list of crops within each LUCAS category is available in ESTAT (2015b). Not all the crops of each category were covered by the samples selected for this study; the covered ones are listed between brackets. Preference was then given to samples having the same land cover in previous LUCAS surveys and from different regions. All EU Member States are subdivided into regions, according to the Nomenclature of Territorial Units for Statistics (NUTS) classification, to ensure comparable regional statistics. The NUTS classification includes three hierarchical levels: NUTS 1 - major socio-economic regions, NUTS 2 - basic regions for the application of regional policies, and NUTS 3 - small regions for specific diagnoses. In this study, results are presented for basic regions (NUTS 2), defined according the NUTS 2013 classification.

The samples from the LUCAS 2015 survey were air dried and stored in the Joint Research Centre (JRC) installations in Ispra, Italy. The 300 LUCAS samples selected for this study were homogenized (by stirring the soil with a spoon until obtain a visually homogeneous sample) and sub-samples (of approximately 50 g dry weight) were collected for pesticide analysis. The sub-samples were sieved with a 2-mm sieve and frozen until chemical analysis. The Portuguese (PT) soil samples were collected in September of 2015, also following method described in ESTAT (2015a), and treated as the LUCAS (sub-) samples, i.e. air dried, 2-mm sieved and frozen until chemical analysis.

Glyphosate and AMPA analysis

The day before the analytical determinations, the soil samples were thawed and homogenized as described above for the selected LUCAS samples. Two aliquots of 2 g were collected from each sample. Glyphosate and AMPA concentrations were determined in the aliquots through HPLC-MS/MS using the same extraction and derivatisation method (see the Supporting Information for full details), chemicals, mobile phases, column characteristics and instrumentation conditions as described in Bento *et al.* (2016) and Yang *et al.* (2015).

All the validation parameters and quality control criteria were in line with those described in the guidance document for pesticides residues analysis in food and feed. Briefly, glyphosate and AMPA analytes were identified according to the retention time and peak shape of isotopically-labelled internal standards, glyphosate (1,2-^{13}C, ^{15}N) and AMPA (^{13}C, ^{15}N). Two transitions were measured by analyte [the quantification (Qn) and confirmation transitions (Ql)], and all positive results/samples presented an ion ratio of the two transitions within ± 30 % of the mean ion ratio of the solvent standards. The responses of the analytes were normalized according to the response of the isotopically-labelled internal standards. Glyphosate and AMPA concentrations were calculated based on one-point calibration, the solvent standard of 0.1 µg/mL, which analyzed every 10-15 injections/samples. A calibration curve (of the solvent standards 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2 µg/mL) was injected at the start, middle and end of the sample sequences. All calibration curves presented satisfactory linearity of response versus concentration, with correlation coefficients ≥0.99 and individual residuals within ± 20 %. Blank soil standards fortified with a mixture of glyphosate and AMPA standards (0.25 µg/g) presented a recovery of both analytes between 70 and 120 %. Similar recovery values (75-120 %) were observed in soil samples fortified with the same mixture of glyphosate and AMPA standards (a third aliquot was prepared from approximately 10 % of the soil samples). The concentration of glyphosate and AMPA measured in each of the two aliquots (replicates) collected per sample was typically within ± 30 %, and always within ± 35 %, the mean concentration of both aliquots. The mean concentrations of glyphosate and AMPA of aliquots were adopted as the concentrations of the sample. The limit of detection (LoD) of glyphosate and AMPA were 0.02 and 0.03 mg/kg, respectively, while the limit of quantification (LoQ) of both compounds was 0.05 mg/kg.

Data analysis

Only measurements/samples with glyphosate or AMPA (≥the LoQ 0.05 mg/kg) were considered in data analysis. Distribution of the concentrations of glyphosate and AMPA in the soils was presented in box-and-whisker plots per country and crop systems. Normality and homogeneity of variances of glyphosate and AMPA concentrations were tested with, respectively, Shapiro-Wilk W and Levine's tests. As the parametric assumptions were not met, even after log, ln, square root or arcsine transformation, differences among EU regions, countries and crop systems were tested with Kruskal-Wallis H tests. At the presence of significant differences (p <0.05), Pairwise Mann-Witney U test with Bonferroni corrections were performed to test differences between each two EU regions, countries or crop systems. The box-and-whisker plots and the statistical analyses were performed using SPSS 22.0.

Wind erosion rates in European agricultural soils were estimated by Borrelli *et al.* (2017) using a GIS version of the Revised Wind Erosion Equation model (GIS-RWEQ) while Panagos *et al.* (2015) used a modified version of the Revised Universal Soil Loss Equation (RUSLE) model to estimate water erosion rates in Europe. The complete wind and water erosion datasets are available via the European Soil Data Centre. Glyphosate and AMPA concentration data is represented at the basic region NUTS 2 level and not on exact locations due to privacy issues, and plotted together with erosion rates (although the different time scales; the erosion maps are annual maps and the soil samples were from a single time point) to indicate immediately if high concentrations in soil appear in areas vulnerable to wind and water erosion, to present a first idea of the dimension of the potential problem which was relevant to be further studied. Since the application pattern of GlyBH in croplands is similar each year, it is expected that concentration data is representative of a normal, recurrent soil situation. The maps of frequency of detection and maximum concentration of glyphosate and AMPA by NUTS 2 region were produced in ArcGIS 10.4.1. To estimate the potential export of glyphosate and AMPA to other locations, glyphosate and AMPA concentrations in top soils were multiplied by the potential annual soil loss rates from wind and water erosion at the sample collection points (extracted with ArcGIS from soil loss by wind and water erosion datasets). Export values were obtain for individual soil sampling points, if glyphosate or AMPA concentration in soil ≥0.05 mg/kg and there was a risk of wind or water erosion >0 Mg/ha year. Export rates of individual soil sampling points were then aggregated by (i) content of residues in soil, i.e. low to medium (defined in this study as 0.05-0.5 mg/kg) or high glyphosate or AMPA contents (>0.5 mg/kg), (ii) EU region, (iii) country, (iv) NUTS 2 region and (v) crop system. The threshold of 0.5 mg/kg used in this work corresponds to the 80th and 85th percentile of glyphosate and AMPA overall concentrations, respectively.

The proportion of AMPA to glyphosate in soil was determined for each sample containing glyphosate and/or AMPA ($\geq$0.05 mg/kg), as the ratio of AMPA concentration in soil to the combined glyphosate and AMPA concentration in the soil, [AMPA / (Glyphosate + AMPA)] $\ast$ 100.

Results

Overall distribution of glyphosate and AMPA in topsoils
Glyphosate and/or AMPA were present ($\geq$0.05 mg/kg) in nearly half (45 %) of the soil samples, with 18 % of the tested soils containing both compounds. AMPA was the predominant form, being present in 42 % of the soils while glyphosate was present in 21 %. Both compounds were present at higher frequencies in northern soils, while eastern and southern regions generally had the most glyphosate- and AMPA- free soils (<0.05 mg/kg), respectively. At national levels, the frequency of soils with glyphosate ranged from 7 % in Poland to 53 % in Portugal, while the frequency of soils with AMPA ranged from 17 % in Italy and Greece to 80 % in Denmark (Figure 8.5-4A and Table 8.5-19). Samples from permanent crops and root crops had the highest frequency of soils with glyphosate and AMPA (30 and 52 %, respectively), and dry pulses and fodder crops the lowest for both compounds (5 and 29 %, respectively, see Figure 8.5-4B and Table 8.5-19).

The highest concentrations of glyphosate and AMPA in soil were observed in southern parts of the EU (Figure 8.5-4C and Table 8.5-19), suggesting higher application rates of GlyBH in this region. Nevertheless, only concentrations of glyphosate were significantly higher in this region [glyphosate: Kruskal-Wallis (H) = 3.03, degrees of freedom (df) = 3, p <0.001, n = 67; AMPA: H = 20.50, df = 3, p = 0.387, n = 133].

Table 8.5-19: Distribution of glyphosate and AMPA in agricultural topsoils (015/20 cm) by EU region, country and crop system

	N	Glyphosate				AMPA				AMPA prop.
		pos. Samp.	Range (mg/kg)	Median		positive Samples	Range (mg/kg)	Median		Mean (%)
Overall	317	67 (21 %)	0.05 - 2.05	0.14		133 (42 %)	0.05 - 1.92	0.15		77
EU Reg.										
North	60	16 (27 %)	0.05 - 0.34	0.12	b	42 (70 %)	0.05 - 0.61	0.14		87
South	107	24 (22 %)	0.07 - 2.05	0.48	a	30 (28 %)	0.06 - 1.92	0.19		54
East	60	6 (10 %)	0.05 - 0.57	0.11	b	20 (33 %)	0.06 - 0.73	0.15		91
West	90	21 (23 %)	0.05 - 0.59	0.1	b	41 (46 %)	0.05 - 1.03	0.14		79
Country										
United Kingdom	30	8 (27 %)	0.05 - 0.21	0.15	ab	18 (60 %)	0.07 - 0.59	0.15	b	89
Denmark	30	9 (27 %)	0.06 - 0.34	0.11	ab	24 (80 %)	0.05 - 0.61	0.14	b	85
Portugal	17	9 (53 %)	0.43 - 2.05	1.14	a	9 (53 %)	0.42 - 1.92	0.73	a	42
Italy	30	5 (17 %)	0.09 - 0.18	0.13	ab	5 (17 %)	0.06 - 1.38	0.1	ab	54
Greece	30	3 (10 %)	0.39 - 0.63	0.54	ab	5 (17 %)	0.16 - 0.38	0.21	ab	61
Spain	30	7 (23 %)	0.07 - 0.95	0.22	ab	11 (37 %)	0.06 - 0.27	0.09	b	60
Hungary	30	4 (13 %)	0.05 - 0.57	0.1	ab	6 (20 %)	0.06 - 0.73	0.23	ab	79
Poland	30	2 (7 %)	0.08 - 0.23	0.16	ab	14 (47 %)	0.06 - 0.42	0.14	b	96
The Netherlands	30	7 (23 %)	0.05 - 0.59	0.13	ab	12 (40 %)	0.05 - 1.03	0.13	ab	75
France	30	9 (30 %)	0.05 - 0.27	0.08	b	15 (50 %)	0.06 - 0.78	0.13	ab	77
Germany	30	5 (17 %)	0.07 - 0.24	0.13	ab	14 (47 %)	0.07 - 0.54	0.15	b	83
Crop system										
Cereals	112	18 (16 %)	0.05 - 0.60	0.11		46 (41 %)	0.05 - 0.62	0.13		84
Root crops	27	6 (22 %)	0.05 - 0.59	0.33		14 (52 %)	0.05 - 1.03	0.12		80

Non-permanent industrial crops	23	5 (22 %)	0.05 - 0.21	0.07	11 (48 %)	0.06 - 0.59	0.16	86
Dry pulses and Fodder crops	21	1 (5 %)	0.06		6 (29 %)	0.07 - 0.17	0.11	86
Permanent crops	101	30 (30 %)	0.07 - 2.05	0.17	41 (41 %)	0.06 - 1.92	0.21	64
Vegetables	9	2 (22 %)	0.13 - 0.14	0.14	3 (33 %)	0.07 - 0.32	0.17	75
Others	24	5 (21 %)	0.05 - 0.95	0.15	12 (50 %)	0.06 - 0.74	0.08	79

Only samples containing glyphosate or AMPA (≥0.05 mg/kg) were considered for the range, median concentrations. For the AMPA proportion, samples containing only glyphosate or AMPA (≥0.05 mg/kg), with respectively an AMPA proportion of 0 or 100 %, were considered in mean values. Different letters represent significant differences [(p <0.05): a >b] between regions, countries or crop systems. N - number of topsoil samples tested, Range - minimum - maximum concentrations, AMPA Prop. - AMPA proportion = [AMPA / (Glyphosate + AMPA)]*100.

Soils from southern parts of the EU also presented the lowest proportion of AMPA (Table 8.5-19), suggesting more recent GlyBH applications and/or slower degradation of glyphosate into AMPA under drier conditions. Portuguese topsoils (all from vineyards) presented significantly higher amounts of glyphosate ($H = 31.97$, $df = 10$, $p < 0.001$, $n = 67$) and AMPA ($H = 27.73$, $df = 10$, $p = 0.02$, $n = 133$) than the other countries, with both compounds reaching concentrations as high as 2 mg/kg (Figure 8.5-4 and Table 8.5-19). NUTS 2 regions such as FR71, EL51, NL23, ES24 or ITC4 seem to contain low herbicide residues or be residue free (<0.05 mg/kg). Other NUTS 2 regions, including DK04, HU10, ES62, PT16 and ITH1, appear to have hotspots of glyphosate and/or AMPA contamination (N 0.5 mg/kg; Table 8.5-20).

Table 8.5-20: Distribution of glyphosate and AMPA in agricultural topsoils (0-15/20 cm) by NUTS 2 region. Only NUTS 2 with at least one sample containing glyphosate and/or AMPA (≥0.05 mg/kg)

NUTS 2	N	Glyphosate			AMPA			AMPA prop.
		positive Samples	Range (mg/kg)	Median	positive Samples	Range (mg/kg)	Median	Mean (%)
UKE3	1	0	-		1 (100 %)	0.07		100
UKF1	1	1 (100 %)	0.15		1 (100 %)	0.29		65
UKF3	2	1 (50 %)	0.21		1 (50 %)	0.57		73
UKG1	2	1 (50 %)	0.14		1 (50 %)	0.31		69
UKG2	3	0	-		3 (100 %)	0.07 - 0.08	0.07	100
UKJ1	1	0	-		1 (100 %)	0.13		100
UKK1	3	0	-		1 (33 %)	0.07		100
UKK2	2	0	-		1 (50 %)	0.09		100
UKM2	6	3 (50 %)	0.05 - 0.18	0.05	4 (67 %)	0.16 - 0.59	0.33	86
UKM3	1	0	-		1 (100 %)	0.07		100
UKM5	1	1 (100 %)	0.19		1 (100 %)	0.44		69
UKN0	2	1 (50 %)	0.07		2 (100 %)	0.09 - 0.43	0.26	93
DK02	6	0	-		5 (83 %)	0.07 - 0.17	0.11	100
DK03	7	1 (14 %)	0.10		5 (71 %)	0.06 - 0.54	0.17	96
DK04	15	6 (40 %)	0.06 - 0.33	0.12	13 (87 %)	0.05 - 0.61	0.13	77
DK05	2	1 (50 %)	0.06		1 (50 %)	0.26		82
PT16	17	9 (53 %)	0.43 - 2.05	1.14	9 (53 %)	0.42 - 1.92	0.73	42
ITC1	5	1 (20 %)	0.09		2 (40 %)	0.07 - 0.15	0.11	71
ITF3	1	1 (100 %)	0.12		0	-		0
ITG1	5	1 (20 %)	0.13		1 (20 %)	0.06		50
ITH1	1	1 (100 %)	0.13		1 (100 %)	1.38		91
ITH5	5	0	-		1 (20 %)	0.10		100
ITI1	3	1 (33 %)	0.18		0	-		0
EL52	10	1 (10 %)	0.39		3 (30 %)	0.16 - 0.38	0.18	83
EL61	2	1 (50 %)	0.53		1 (50 %)	0.20		28
EL65	7	1 (14 %)	0.63		1 (14 %)	0.26		29
ES11	3	1 (33 %)	0.22		1 (33 %)	0.07		50
ES23	3	2 (67 %)	0.07 - 0.43	0.25	3 (100 %)	0.12 - 0.27	0.15	69

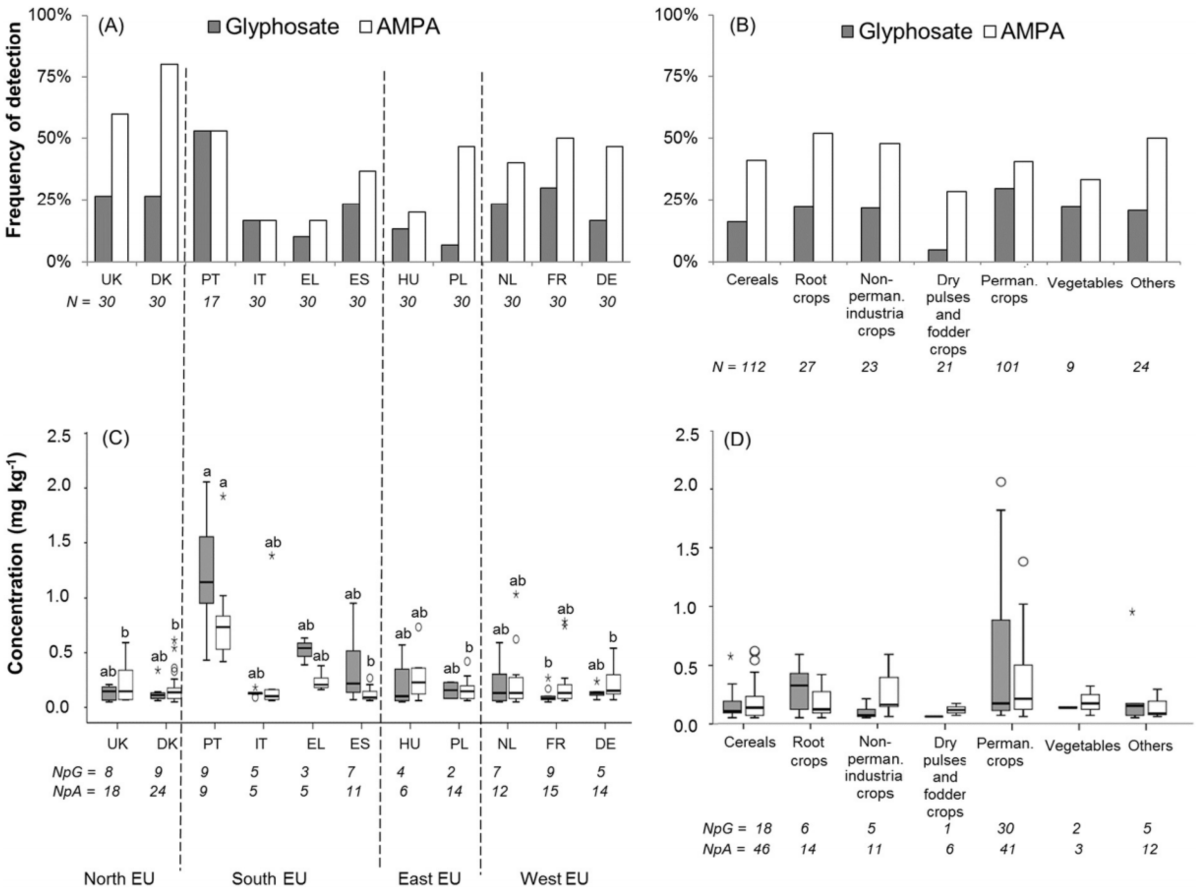
Table 8.5-20: Distribution of glyphosate and AMPA in agricultural topsoils (0-15/20 cm) by NUTS 2 region. Only NUTS 2 with at least one sample containing glyphosate and/or AMPA (≥0.05 mg/kg)

NUTS 2	N	Glyphosate			AMPA			AMPA prop.
		positive Samples	Range (mg/kg)	Median	positive Samples	Range (mg/kg)	Median	Mean (%)
ES41	4	0	-		1 (25 %)	0.08		100
ES42	5	1 (20 %)	0.11		2 (40 %)	0.06 - 0.09	0.08	69
ES61	2	1 (50 %)	0.16		1 (50 %)	0.14		47
ES62	8	2 (25 %)	0.6 - 0.95	0.78	3 (38 %)	0.06 - 0.21	0.08	45
HU10	2	1 (50 %)	0.57		1 (50 %)	0.73		56
HU21	2	0	-		1 (50 %)	0.23		100
HU22	8	1 (13 %)	0.07		1 (13 %)	0.23		77
HU32	9	2 (22 %)	0.05 - 0.13	0.09	2 (22 %)	0.12 - 0.36	0.24	71
HU33	8	0	-		1 (13 %)	0.06		100
PL12	2	0	-		1 (50 %)	0.08		100
PL22	2	0	-		1 (50 %)	0.06		100
PL31	9	2 (22 %)	0.08 - 0.23	0.16	7 (78 %)	0.06 - 0.42	0.15	92
PL33	2	0	-		1 (50 %)	0.08		100
PL41	5	0	-		1 (20 %)	0.10		100
PL51	4	0	-		1 (25 %)	0.20		100
PL52	1	0	-		1 (100 %)	0.21		100
PL61	1	0	-		1 (100 %)	0.07		100
NL11	5	2 (40 %)	0.07 - 0.59	0.33	4 (80 %)	0.06 - 1.02	0.18	85
NL13	4	3 (75 %)	0.05 - 0.42	0.19	4 (100 %)	0.09 - 0.62	0.22	70
NL21	4	0	-		2 (50 %)	0.08 - 0.08	0.08	100
NL23	9	1 (11 %)	0.05		1 (11 %)	0.05		50
NL34	4	1 (25 %)	0.13		1 (25 %)	0.17		57
FR22	1	1 (100 %)	0.17		1 (100 %)	0.74		82
FR25	1	1 (100 %)	0.06		0	-		0
FR51	1	0	-		1 (100 %)	0.23		100
FR52	6	2 (33 %)	0.09 - 0.10	0.10	4 (67 %)	0.09 - 0.16	0.12	79
FR53	3	2 (67 %)	0.05 - 0.07	0.06	2 (67 %)	0.06 - 0.27	0.16	66
FR61	2	0	-		1 (50 %)	0.13		100
FR81	7	3 (43 %)	0.07 - 0.27	0.08	5 (71 %)	0.06 - 0.78	0.09	80
FR82	4	0	-		1 (25 %)	0.07		100
DE11	3	0	-		1 (33 %)	0.11		100
DE91	1	1 (100 %)	0.24		1 (100 %)	0.38		62
DE92	1	1 (100 %)	0.11		1 (100 %)	0.31		73
DE93	1	0	-		1 (100 %)	0.13		100
DE94	3	0	-		2 (67 %)	0.10 - 0.16	0.13	100
DEA3	4	0	-		2 (50 %)	0.13 - 0.19	0.16	100
DEA4	1	0	-		1 (100 %)	0.07		100
DEA5	1	0	-		1 (100 %)	0.54		100
DEB1	1	1 (100 %)	0.13		1 (100 %)	0.30		70
DEB2	2	0	-		1 (50 %)			100
DEB3	6	2 (33 %)	0.07 - 0.14	0.10	2 (33 %)	0.12 - 0.21	0.16	49

Only samples containing glyphosate or AMPA were considered for the range and median concentrations. For the AMPA proportion, samples containing only glyphosate or AMPA (≥0.05 mg/kg), with respectively an AMPA proportion of 0 or 100 %, were considered in mean values. N - number of topsoil samples tested, Range - minimum and maximum concentrations, AMPA Prop. - AMPA proportion = [AMPA/(Glyphosate + AMPA)]*100.

Glyphosate and AMPA contents in soil were highest under permanent crops and lowest with dry pulses and fodder crops (Figure 8.5-4D and Table 8.5-19), yet no significant effect of the crop system was observed (glyphosate: $H = 10.29$, $df = 6$, $p = 0.113$, $n = 67$; AMPA: $H = 11.57$, $df = 6$, $p = 0.72$, $n = 133$). Vineyards presented the highest concentrations of glyphosate, yet at lower levels than those expected in soils of this crop, with maximum predicted environmental concentration (PEC) of 3.0646 mg/kg. On the other hand, the measured glyphosate concentrations in cereals occasionally exceed the respective maximum PEC value of 0.30 mg/kg. Maximum PEC values for AMPA, of 3.0862 mg/kg, available only for the worst-case scenario of a single application of 4.32 kg glyphosate/ha, were never been exceeded. Discrepancies between field measured concentrations and maximum PEC values probably result of an application regime by the farmers different from the recommended (in terms of number of treatments and on the amounts applied), of the growth stage (and interception) of the crop or of different edaphic, management or environmental conditions. In the calculation of PEC values, a worst case interception of 90 (cereals) and 0 % (orchards and vineyards), a fixed bulk density of 1.5 g/cm^3, a tillage depth of 5 cm (permanent crops) or of 20 cm (annual crops) and a halflife time (DT_{50}) of 143.3 days for glyphosate and of 514.9 days AMPA are assumed.

Figure 8.5-4: **Overall distribution of glyphosate and AMPA in EU topsoils (0–15/20 cm). Frequency of detection of glyphosate and AMPA (≥0.05 mg/kg) in soils from different (A) EU countries and (B) crop systems. Box-and-whisker plot representation of the distribution of glyphosate and AMPA contents in soils by the same factors: (C) country and (D) crop system.**

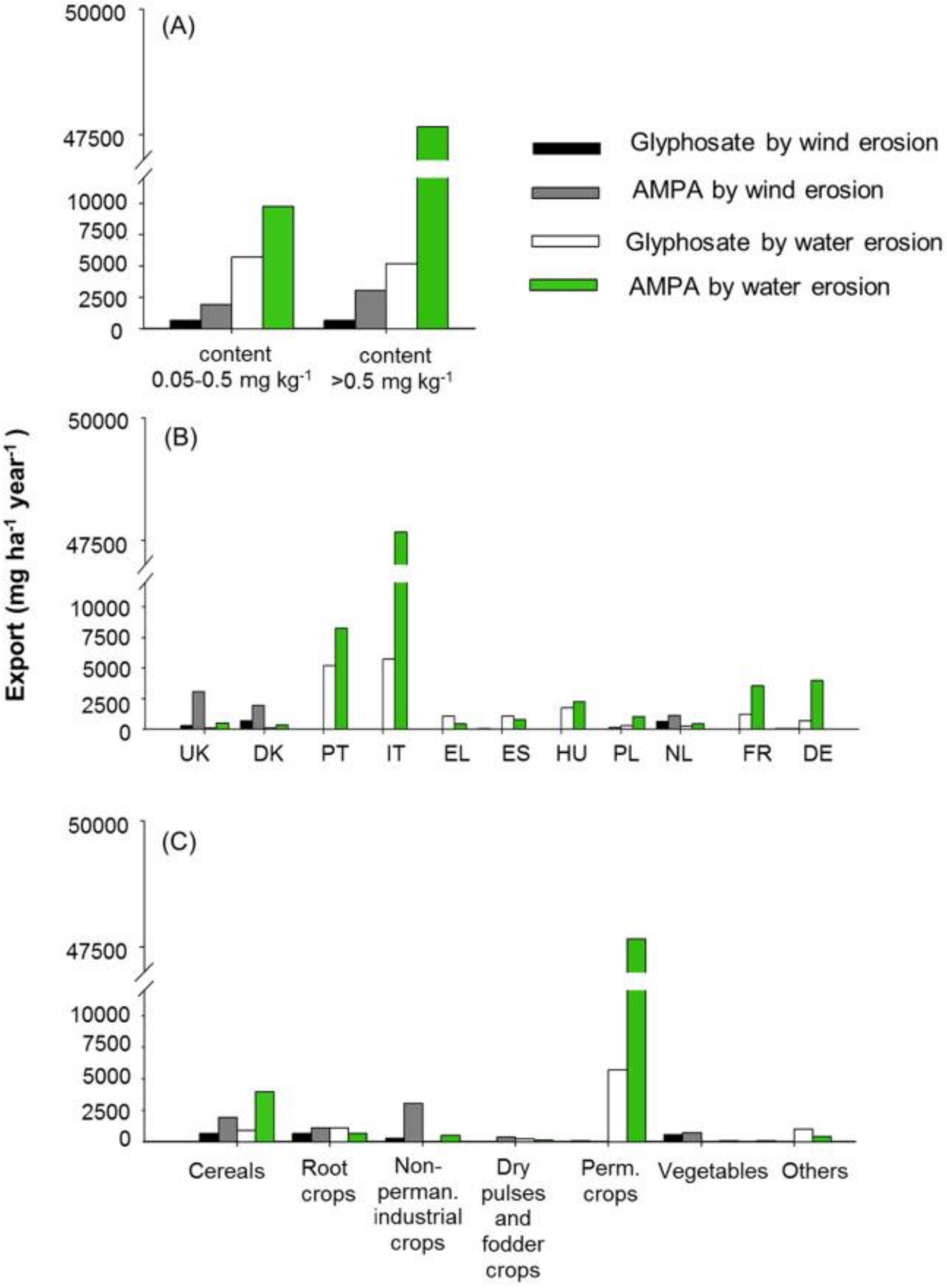


Only measurements ≥0.05 mg/kg were considered in the box-and-whisker plots. Each box represents the 25th percentile, median and 75th percentile. Whiskers represent 1.5 times the interquartile range or minimum and maximum concentrations of glyphosate or AMPA. Outliers (1.5–3 times the interquartile range) are marked with points and extreme outliers (N3 times the interquartile range) with asterisks. Different letters represent significant differences [($p < 0.05$): a > b] in glyphosate or AMPA concentrations between countries or crop systems. N – number of samples tested, Np = number of positive samples ≥0.05 mg/kg, G – glyphosate, A – AMPA.

Off-site transport by wind and water erosion

In areas with low to medium glyphosate or AMPA contents in soil (0.05-0.5 mg/kg), estimated glyphosate and AMPA removal by wind erosion reaches 1941 mg/ha year, while in areas with contents > 0.50 mg/kg it could exceed 3000 mg/ha year. Water erosion could lead to higher potential losses/exports of glyphosate and AMPA, with estimated maximum exports of 9753 mg/ha year in soils with low to medium herbicide contents, and of 47,667 mg/ha year in soils with higher contents (Figure 8.5-5A). The highest export potentials are observed in Southern parts of the EU (Figure 8.5-5B), in areas highly vulnerable to water erosion. Different crop systems, with different soil covers, lead to different transport potentials of glyphosate and AMPA: non-permanent industrial crops and root crops show the highest potential exports through wind erosion, while permanent crops and cereals present the highest exports through water erosion (Figure 8.5-5C).

Figure 8.5-5: **Potential export of glyphosate and AMPA by wind and water erosion. Maximum export estimations according to (A) glyphosate or AMPA content in topsoil, (B) country and (C) crop system. Perm. – Permanent**



A ratio between these potential exports and the typical GlyBH application rates (the exact application rates in the soil sampling points are not known) could provide an indication of the % of the initially applied products lost by erosion processes, potentially reaching water systems and atmosphere. The highest estimated potential export of glyphosate by water erosion (5715 mg/ha year), for example, would correspond to loss 0.13 % of the recommended maximum application rate of 4.32 kg glyphosate/ha year. As only glyphosate is applied to fields, no ratio can be calculated for AMPA, the most common compound in soils. Furthermore, such ratio can led to misleading results because glyphosate and AMPA are persistent compounds in soil, and their concentrations in soil (the ones used to estimate the potential exports by wind and water erosion) often result of more than one year of treatments. Therefore, the ratio should consider not only the amount applied but also the amount accumulated from previous treatments.

Recent experimental and monitoring studies confirm wind-driven transport of glyphosate and AMPA. Bento *et al.* (2017) demonstrated in a wind tunnel experiment that contents of AMPA and especially of glyphosate were particularly high (respectively > 0.6 and > 15 µg/g) in the finest soil particle fractions (<10 µm), which can be inhaled by humans directly. In addition, both glyphosate and AMPA were often (> 50 %) detected in air samples collected from agricultural areas in the U.S.A, reaching concentrations of respectively 9.1 and 0.97 ng/m^3. The presence of glyphosate in atmosphere can result of spray drift during the application and/or wind erosion of contaminated soil particles. However, for AMPA, which is formed in soil, wind erosion is the only source. The contribution of wind erosion to the atmospheric concentration of glyphosate is still unknown. In a comprehensive environmental survey conducted in the U.S.A., Battaglin *et al.* (2014) observed the presence of glyphosate and AMPA in over 70 % of the precipitation samples analyzed, at maximum concentrations of respectively 2.5 and 0.5 µg/L. In Europe, lower frequencies of detection are reported, with glyphosate and AMPA present in respectively 10 and 13 % of the rainwater samples, but with higher maximum concentrations, 6.2 and 1.2 µg/L, respectively. Glyphosate is supposed to degrade rapidly in the atmosphere by photochemical oxidative degradation, but the results from air and rain analyses indicate that glyphosate and AMPA can persist in the atmosphere and can be washed out and redistributed by rain (wet deposition).

Particulate transport via water erosion is an important pathway for glyphosate and AMPA towards surface water bodies. In fact, after a 60 min rain simulation at a rain intensity of 1 mm/min, Yang *et al.* (2015) observed that 4-5 % of the initially applied glyphosate was lost/transported by runoff in the dissolved phase while 8-11 % of the applied glyphosate was transported by the suspended load. Glyphosate and AMPA are frequently detected in U.S. large rivers (53-89 %, respectively), streams (53-72 %, respectively), lakes, ponds and wetlands (34-30 %, respectively) at maximum levels of respectively 300 and 48 µg/L. In Europe, glyphosate and AMPA have been analyzed in respectively 75,350 and 57,112 surface water samples, and detected in 33 % and 54 % of the samples at levels up to 370 µg/L and > 200 µg/L. Correlations between these concentrations in waters and the concentrations measured in this study in soils would be too speculative given the different time collection and location between the information that is available for glyphosate in streams and the soil samples analyzed for this study. However, the spatial relationship between erosion rates and pesticide distribution in soils and water bodies should be further explored. Particulate transport processes are particularly important for the off-site transport of pesticides strongly adsorbed to soil particles, just like glyphosate and AMPA. Quantification of the extent of transport off the field to surface waters (or to the atmosphere) should be explored, too. It should be noted that current EU legislation presents environmental quality standards in the field of water policy for only some pesticides, not including glyphosate or AMPA.

Conclusion

Within the context of this study, some considerations can be made. First, soil samples used in this study were collected during the spring and summer of 2015. No information is available regarding prior GlyBH application dates and rates per sample location, indicating that the 317 samples represent a mixture of real-field conditions, ranging from samples with no trace of glyphosate and/or AMPA to samples with very high levels. Despite the European Commission (EC) recommendations on the frequency of treatments and application rates, information on the actual use/sales of GlyBH in the EU, or of the active substance glyphosate, is not available and the amounts applied per crop system is confidential in almost all countries.

The half-life times of glyphosate and AMPA, also of importance in the respect of the amounts found in soils, are highly variable, ranging from a few days up to one or two years, depending on edaphic and environmental conditions, namely temperature and soil moisture. AMPA is more persistent than glyphosate, and the degradation of both compounds is slower at colder and dryer conditions. The drier soils in southern EU might then explain the lower AMPA proportion found there. Second, it is well-known that glyphosate and AMPA strongly adsorb and accumulate in the top centimeter(s) of soils. As glyphosate and AMPA contents determined in this study are average values for entire topsoil layers up to 15/20 cm depth (a consequence of using topsoil samples from an already established survey), actual contents in the surface layer could be higher than the determined average, implying that the presented potential erosion-driven transport rates of glyphosate and AMPA could be underestimated. The distribution of glyphosate and AMPA at the surface layer (the region most prone to soil erosion) and within topsoil should be considered in future work and should cover different soil management practices, as tillage results in the incorporation/redistribution of contaminants accumulated in surface into deeper layers. Third, pesticide residue transported by wind and water erosion do not necessarily end up in the atmosphere and surface water systems alone; other land and even ocean regions can be reached by such phenomena, with deposition of transported compounds as a result. This stresses the need for better monitoring of the occurrence and spatial distribution of glyphosate and AMPA across the interlinked environmental domains of soil, water and air. Fourth, from a regulatory and legislation perspective, greater effort is needed to more thoroughly assess glyphosate and AMPA contents in soils, to define critical limits to protect soil quality and soil biodiversity, and to minimize the risk of further distribution of these compounds by wind and water erosion. Some EU countries have legislation and screening values for pesticide residues in soil but they are mainly limited to persistent organochloride pesticides. Air quality monitoring programs should also target pesticide residues in transported soil dust, in particular glyphosate and AMPA, and the potential risk of inhalation by humans. Finally, despite its limitations, the results of this study are concerning; high levels of glyphosate and of its main metabolite AMPA have been often detected in agricultural soils across the EU. The presence of glyphosate and AMPA in agricultural soils may not only form a risk for soil health but also a potential risk of further spreading of these compounds across land, water, and air domains. Indeed, besides potential effects on local edaphic communities and on humans, that can be exposed to these substances by inhalation of contaminated dust particles, dermal contact or ingestion of contaminated surface water, wind and water erosion have the potential to transport contaminants to all the environmental compartments: atmosphere, other soils and surface waters. This information should be fully accounted for in reconsidering approval and use of GlyBH. Additional efforts should be made to fully quantify the extent of soil contamination by glyphosate residues in agricultural soils worldwide, and to assess the related risk for humans and the environment.

Assessment and conclusion by applicant:
The article describes the result from a field study to measure the distribution of glyphosate and AMPA in European topsoils. The study should give a basis for the understanding of glyphosate loss from soils via wind and water erosion, i.e. experimental information from the sample sites were extrapolated to the EU area. A detailed and tabulated overview on the results is given in the supporting information. The maximum measured concentrations of 2.05 mg/kg for glyphosate and 1.92 mg/kg for AMPA were from vineyards in central Portugal.
The article is therefore considered reliable with restrictions.

Assessment and conclusion by RMS:
This study describes a large-scale assessment of distribution of glyphosate and its main metabolite AMPA in EU agricultural topsoils (from 11 countries). 300 soil samples were taken from the LUCAS topsoil 2015 survey data base, and 17 soil samples from three independent vineyards in north-central Portugal. The spatial distribution is illustrated in the figure below.

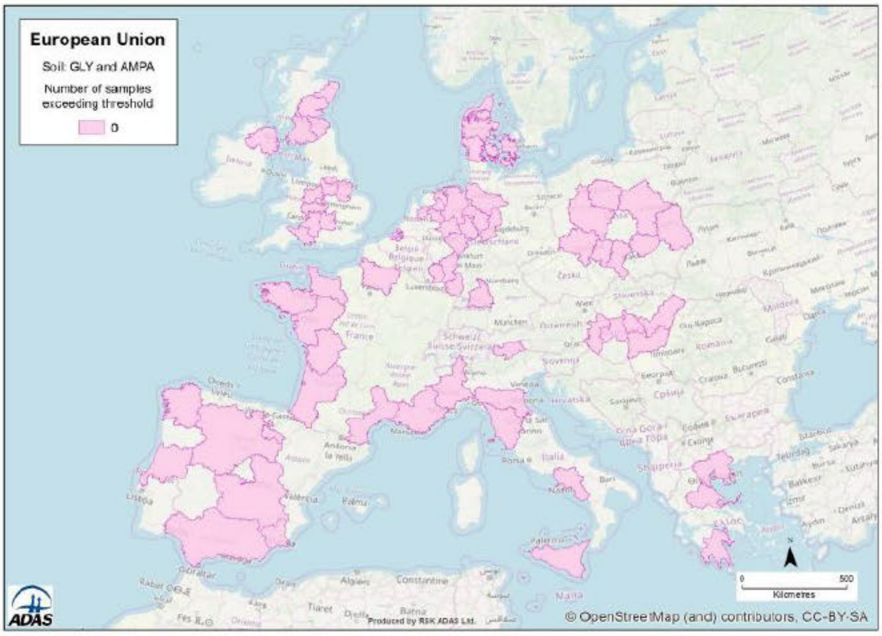


Figure 53: Spatial distribution of the NUTS2 regions included in the glyphosate (GLY) and AMPA monitoring conducted by Silva *et al.*, 2017. The number of analyses that exceed the RAC are indicated for each monitoring location aggregated to NUTS2 region.

All samples were analysed with the same analytical method, with recovery values in a satisfactory range of 70-120%. RMS however notes that no information on the date of analysis is given in the study and it is therefore not known how much time went by between soil collection (LUCAS 2015 survey) and analysis.

Glyphosate and/or AMPA were present (≥0.05 mg/kg) in nearly half (45 %) of the soil samples, with 18 % of the tested soils containing both compounds.
Frequency of detection and concentrations distribution were also statistically analysed per "region" (southern, northern, Eatern, western EU) and per crop cover. However, the following should be noted to set into context the results:

- The statistical analysis is only carried out on the detections so values < LOQ were left out.
- Soil samples are collected in the 15/20 cm topsoil: as underlined in the study conclusion, "the glyphosate and AMPA contents determined in this study are average values […], actual contents in the surface layer could be higher than the determined average". RMS further notes that if the sampling depth is not consistent between all samples (from 15 to 20cm), there might be a bias in the statistical analysis due to variable dilution of the active substance.
- Soil samples were collected between April and October and, as stated in the study conclusion, "no information is available regarding prior GlyBH application dates and rates per sample location". The results therefore cannot be related to any use pattern of the active substance, and "represent a mixture of real-field conditions"

The highest concentrations of glyphosate and AMPA in soil were observed in southern parts of the EU suggesting higher application rates of glyphosate in this region. Nevertheless, only concentrations of glyphosate were significantly higher in this region.
Soils from southern parts of the EU also presented the lowest proportion of AMPA, suggesting more recent GlyBH applications and/or slower degradation of glyphosate into AMPA under drier conditions.

Glyphosate and AMPA contents in soil were highest under permanent crops and lowest with dry pulses and fodder crops. Vineyards presented the highest concentrations of glyphosate, with maximum measured concentration of 2.05 and 1.92 mg/kg respectively for glyphosate and AMPA in Portuguese vineyard. Study author indicate that these where however lower than those expected in soils of this crop, with maximum predicted environmental concentration (PEC) of 3.0646 mg/kg. However the direct

comparison with expected PECsoil is uncertain since the exact sampling depth is unknown (15/20cm), as well as the application rate and time passed since last application, compared to what is considered in the PEC calculation.
On the other hand, the measured glyphosate concentrations in cereals occasionally exceed the respective maximum PEC value of 0.30 mg/kg. However, it is unknown how much was applied in comparison to the dose rate on which the PECsoil is based. It is also not exactly clear how PECsoil was calculated (PEC was calculated over 20 cm for tillage crops, but the seasonal PEC should still be calculated over 5 cm). And finally, the corp interception of 90% considered for the PECsoil calculation for cereals may be considered overestimated for many time of applications.

Evaluation of the glyphosate loss from soils via wind and water erosion is less clear to conclude on. Wind erosion is however not specific for glyphosate and currently not part of the assessment framework.

Overall, the study provides reliable data with restrictions. The results from this study should not be directly compared to risk assessment PEC, since cannot be related to use pattern of the active substance (application rate, time passed since last application….) neither to consistent soil depth. As stated by the study author, this "represent a mixture of real-field conditions"

Data point:	CA 7.5/005
Report author	Napoli, M. *et al.*
Report year	2016
Report title	Transport of Glyphosate and Aminomethylphosphonic Acid under Two Soil Management Practices in an Italian Vineyard
Document No	Journal of Environmental Quality 45:1713-1721 (2016)
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

Worldwide, glyphosate is the most widely used herbicide in controlling the growth of annual and perennial weeds. An increasing number of studies have highlighted the environmental risk resulting from the use of this molecule in aquatic and terrestrial ecosystems. The objective of the study was to determine the transport of glyphosate and its degradation product, aminomethylphosphonic acid (AMPA), through runoff and transported sediment (TS) from a vineyard under two different soil management systems: harrowed inter-row (HR) and permanent grass covered inter-row (GR). The study was performed over a period of 4 yr. Glyphosate and AMPA concentrations were found to be higher in runoff and in transported sediment from HR compared with GR, regardless of the amount of runoff and transported sediment. The mean annual percentages of glyphosate loss, via runoff and transported sediment, were about 1.37 and 0.73 % for HR and GR, respectively. Aminomethylphosphonic acid represented approximately 30.9 and 40.0 % of the total glyphosate losses in GR and HR, respectively. Moreover, results suggested that rains occurring within 4 wk after treatment could cause the transport of glyphosate and AMPA in high concentrations. Soil analyses indicated that glyphosate content was below detection within 1 yr, whereas AMPA remained in the soil profiles along the vine row and in the inter-row. Results indicated that GR can reduce soil and herbicide loss by runoff in vineyard cropping system.

Materials and Methods

Vineyard Plots Set-up and Herbicide Application

The activity was performed in Montepaldi-San Casciano Val di Pesa, Italy. The experiment was conducted over a period of 4 yr from March 2007 to February 2011. According to a nearby weather station, during the decade 1995 to 2014, the pluviometric pattern was sub-Mediterranean, with an average annual rainfall of 854 mm and an average annual temperature of 14.9°C (Napoli *et al.*, 2013).

Runoff and soil loss measurements were performed in 25yr old trained vines (*Vitis vinifera* L.) of the Sangiovese red variety cultivated on a southsouthwest facing convex slope (average slope, 16 %) and located approximately 550 m from the weather station. The soil was classified as a siltyclay, with 16 % sand, 43 % silt, 41 % clay, organic matter content of 0.8 %, total carbonate content of 15 %, and pH of 8.0. The vine rows were 89.5 m long oriented up and down the slope. Vines were planted in a 0.8 m by 2.7 m pattern and lowcordon trained. The interrows were colonized by spontaneous herbaceous species (C*ynodon dactylon* L., >90 %). Every year, a commercial formulation of glyphosate was distributed in the middle of March (360 g/L a.i.) in a 1m wide strip along each vine row at a dose of 2 L/ha (34.8 g of a.i. for plot). Within the vineyard, four plots of about 283 m^2, each including two inter-rows and three rows (about 5.4 m in length), were delimited with a 0.2m high earth bank, forming the plot boundaries. Two management systems were applied: harrowed interrow (HR) and interrow permanent grass covered (GR). The soil in HR was superficially harrowed (810 cm) once a year in late April. In GR, the interrow soil remained undisturbed. Grass height on both HR and GR interrows was kept below 0.15 m with periodical shredding. The average monthly ground cover was 17.6 % (range, 433 %) and 22.2 % (range, 639 %) for HR and GR, respectively.

Water and Soil Core Sampling and Herbicide Residues Analysis

On 26 Feb. 2007 and then at the end of each consecutive year (i.e., the last week of February), a total of 54 undisturbed soil cores (0.05 × 0.05 m) were collected on each plot. The sampling was performed on three transects within each plot (at 15, 45, and 75 m from the top). Within each transect, samples were taken from three sampling areas: on the vine row, at 0.675 m from the vine row (on the tractor wheels traces on soil), and at the center of the inter-row (at 1.35 m apart from the vine row). The samples were collected in duplicate at depths of 0 to 0.05, 0.20 to 0.25, and 0.35 to 0.4 m, respectively. The soil samples were air-dried, weighed, sieved, and then used for analyses according to Napoli *et al.* (2015). Runoff and associated sediment from each plot were intercepted by a Gerlach trough placed along the lower side of the plot. A downstream automated runoff gauge was used for measuring the runoff volume (RV) for separate rainfall events. The runoff gauges collected runoff aliquots of about 0.2 L every 300 L of RV. These aliquots were then poured into a single external poly(p-phenylene oxide) tank to produce a single sample of the entire runoff event. The runoff samples were collected after each rainfall from 1 Mar. 2007 to 28 Feb. 2011. To limit degradation, runoff samples were immediately analyzed for determining TS weight and then preserved in the dark at -20ºC for a maximum of 25 days until analysis. An aliquot of each sample, corresponding to approximately 10 % of the sample volume (0.2 L minimum), was decanted and dried at 105°C and then weighed to determine the TS concentration in each runoff sample.

Water samples were filtered through 1-mm glass fiber filters. The liquid was immediately derivatized with fluorenemethoxycarbonyle. The herbicide residues in TS were determined only when the amount of material collected in the sieve of the suspended solid samples was sufficient (>5 g of sediment) to perform reliable measurements. Then the herbicide residues in TS, along with the residues in the soil samples, were extracted first by ultrasonic extraction in methanol and then using the derivatization procedure. Water and soil samples were dispensed in parallel into plastic vials to reduce the adsorption of glyphosate and AMPA from the methanol-extracted solutions onto glassware surfaces. After derivatization, glyphosate and AMPA were quantified using liquid chromatography electrospray ionization tandem mass spectrometry with a TSQ Vantage triple quadrupole mass spectrometer. The lower limits of glyphosate and AMPA quantification in water and soil samples (method detection limit) were 0.1 mg/L and 10 mg/kg, respectively. Therefore, the glyphosate and AMPA concentrations were set to zero for calculating the occurrence and loading when lower than the quantification limit. The glyphosate lost by runoff as a percentage of the annual amount applied was calculated as reported in Imfeld *et al.* (2013).

Statistical Analysis

Time series were used to evaluate the measured data. Samples with herbicide concentrations less than the detection limits were assigned a value of zero when calculating flow weighted average concentrations and transport amounts. Statistical comparisons of tillage treatments on glyphosate and AMPA concentration in RV and TS were made with Student's *t* test. Statistical comparisons of soil core samples were made with ANOVA. Thereafter, pairwise comparisons were performed using the post hoc Tukey test.

Results and Discussion

Rainfall, Runoff, Soil Loss, and Dissolved Herbicide Concentrations in Runoff and Transported Sediment
Daily rainfall, runoff volumes, soil losses, and glyphosate and AMPA concentrations in RV and TS from HR and GR for the first, second, third, and the fourth year of the experiment are presented in Figure 8.5-6, Figure 8.5-7, Figure 8.5-8 and Figure 8.5-9, respectively. The cumulative rainfall amounts over the period extending from 1 March to 28 February of the subsequent year were 524, 751, 678, and 1043 mm for the first, second, third, and the fourth year of the experiment, respectively. In the observation period, a total of 145 and 146 separate runoff events were recorded and sampled for each replicate on HR and GR fields, respectively. The RV for separate events differed within tillage treatments ($p = 0.02$). In particular, the RV for separate events ranged from 0.001 to 16.26 mm (average, 2 ± 2.7 mm) and from 0.004 to 14.07 mm (average, 1.6 ± 2.3 mm), respectively, for HR and GR plots, thereby generating a total volume of 286.6 ± 1.7 and 238.4 ± 0.9 mm for HR and GR plots, respectively. The annual RV during the first, second, third, and fourth year of the experiment were 14 ± 0.3, 62.1 ± 0.8, 68.8 ± 1.4, and 142.6 ± 0.8 mm for HR fields, respectively, and 18.8 ± 0.1, 56.8 ± 1, 72.3 ± 0.9, and 91.9 ± 1.2 mm for GR fields, respectively.

In the same period, TS were sampled in 130 ± 2.8 and 123 ± 1.4 separate runoff events from the HR and GR fields, respectively. The sediment concentration in RV differed within tillage treatments ($p = 0.003$). The soil losses for separate events ranged from 0.001 to 8.364 *t*/ha (average, 0.27 ± 0.91 *t*/ha) and from 0.001 to 1.029 *t*/ha (average, 0.07 ± 0.12 *t*/ha), respectively, for HR and GR plots. The annual soil loss during the first, second, third, and fourth year of the experiment were 0.34 ± 0.01, 3.21 ± 0.06, 5.53 ± 0.03, and 26.49 ± 0.41 *t*/ha for HR fields, respectively, and 0.15, 0.63 ± 0.02, 2.25 ± 0.01, and 5.04 ± 0.01 *t*/ha for GR fields, respectively. Regardless of the inter-annual variability observed during the study period, results showed that permanent grass cover reduced the average annual RV and the average annual soil loss with respect to HR treatment.

Figure 8.5-6: **Rainfall, runoff, soil losses, and glyphosate and aminomethylphosphonic acid (AMPA) concentration in runoff and in transported sediment from harrowed (HR) and permanent grass-covered (GR) plots during the first year**

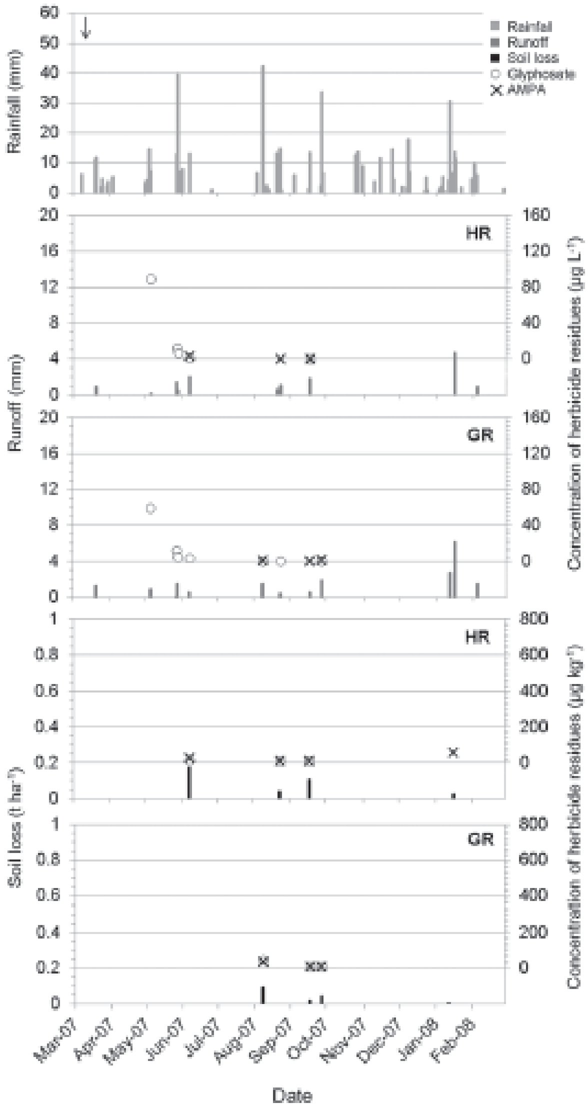
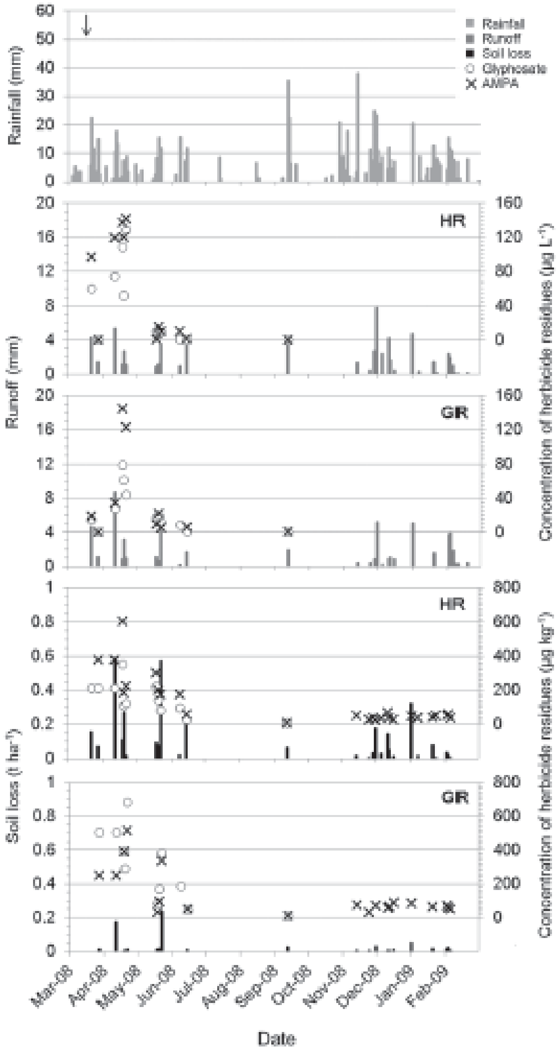


Figure 8.5-7: Rainfall, runoff, soil losses, and glyphosate and aminomethylphosphonic acid (AMPA) concentration in runoff and in transported sediment from harrowed (HR) and permanent grass-covered (GR) plots during the second year

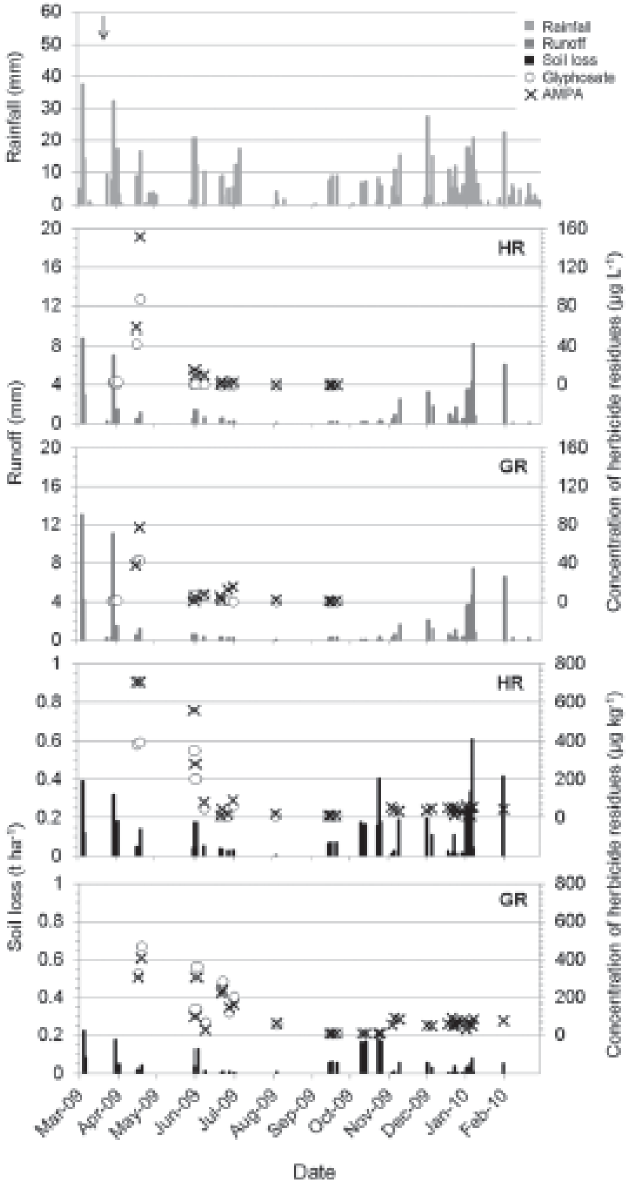


Glyphosate and Aminomethylphosphonic Acid Dissolved in Runoff

Glyphosate was detected in 33.6 ± 1 and 40.4 ± 0.6 % of the RV from HR and GR, respectively. Glyphosate concentrations ranging from 1 to 10 µg/L were detected in 8.2 ± 0.3 % of the RV from HR. Glyphosate concentrations ranging from 10 to 128.9 µg/L were detected in 10.9 ± 0.3 % of the RV from HR. Moreover, concentrations ranging from 1 to 10 µg/L were detected in 8.3 ± 0.2 % of the RV from GR, whereas concentrations ranging from 10 to 78.4 µg/L were detected in 13.7 ± 0.7 % of the RV from GR. After approximately 25.1 ± 13.8 d from the most recent application (days after application [DAA]), glyphosate appeared at high concentrations of about 68.1 ± 20.7 and 37.8 ± 19.3 µg/L in the RV from HR and GR, respectively. In 2008, the highest glyphosate concentrations in the runoff were measured after 37 DAA in HR and 34 DAA in GR. In the same year at 27 DAA, the highest glyphosate losses in runoff were about 3932.7 and 2388.9 mg/ha for HR and GR, respectively. Glyphosate was detected in the RV at concentrations exceeding 1 µg/L over a period of 68.8 ± 4.3 DAA (average, 34.0 ± 13.0 µg/L) and 76.5 ± 11.4 DAA (average, 21.0 ± 6.5 µg/L), respectively, after treatments on HR and GR. During the latter, an average RV of 11.2 ± 7.4 mm (cumulative rainfall amount, 164.4 ± 33.5 mm) and 13.8 ± 10.6 mm (cumulative rainfall amount, 180.8 ± 46.6 mm) was measured for HR and GR, respectively. Thereafter, the final glyphosate peaks appeared in the RV between early August and late September after approximately 173.5 ± 13.9 DAA and 186.8 ± 17.6 DAA in HR and GR, respectively.

Aminomethylphosphonic acid was detected in 33.6 ± 2.1 and 32.9 ± 1.6 % of the RV measured in HR and GR, respectively. In particular, AMPA at concentrations of 1 to 10 and 10 to 151.9 µg/L were detected in 7.5 ± 0.2 and 11.6 ± 0.2 % of the RV from HR, respectively.

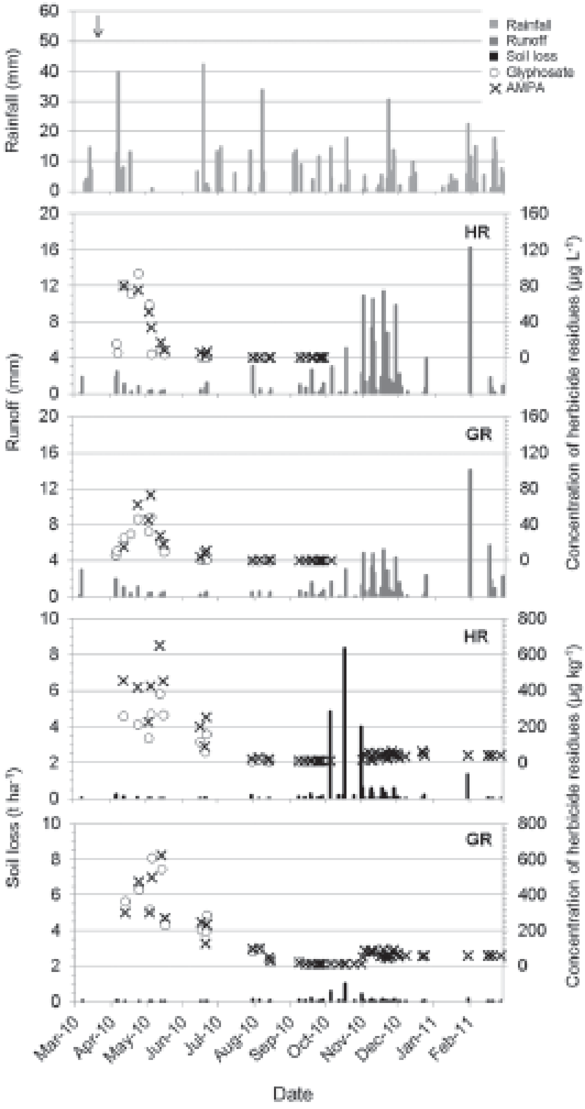
Figure 8.5-8: Rainfall, runoff, soil losses, and glyphosate and aminomethylphosphonic acid (AMPA) concentration in runoff and in transported sediment from harrowed (HR) and permanent grass-covered (GR) plots during the third year



Aminomethylphosphonic acid concentrations of 1 to 10 µg/L were detected in 10.3 ± 0.3 % of the RV from GR, whereas concentrations of 10 to 144.8 µg/L were detected in 11 ± 0.2 % of the RV from GR. After about 33.5 ± 27.7 DAA, AMPA appeared at high concentrations (approximately 59.7 ± 40.6 µg/L) in the RV from HR. In the RV from GR, AMPA appeared at a concentration of about 18.3 ± 15.5 µg/L after about 49 ± 57.6 DAA after the annual treatment. In the RV from GR, AMPA was detected at concentrations exceeding 1 mg/L for about 127.5 ± 39.4 DAA, with an average concentration of about 22.8 ± 17.0 µg/L. Instead, AMPA was detected for 90.8 ± 14.0 DAA, with an average concentration of 31.4 ± 24.1 µg/L in the RV from HR. During the latter, an average RV of 13.7 ± 9.1 mm (cumulative rainfall amount, 200.8 ± 52.9 mm) and 14.9 ± 11.0 mm (cumulative rainfall amount, 218.1 ± 51.6 mm) was measured for HR and GR, respectively. The final AMPA peaks in the RV appeared after approximately 184.3 ± 10.1 and 188.5

± 11.1 DAA in HR and GR, respectively. The average glyphosate and AMPA concentrations in RV were significantly (*p* <0.001) greater in the HR than in the GR. No significant correlations were found between the glyphosate and AMPA concentration in RV and either seasonal or annual rainfall.

Figure 8.5-9: Rainfall, runoff, soil losses, and glyphosate and aminomethylphosphonic acid (AMPA) concentration in runoff and in transported sediment from harrowed (HR) and permanent grass-covered (GR) plots during the fourth year



Results indicate that glyphosate concentrations in the runoff peaked shortly after each application, similar to results observed by Shipitalo and Owens (2011) and Shipitalo *et al.* (2008). Moreover, the appearance of AMPA within the first week of monitoring in 2008 was consistent with the degradation rate of glyphosate reported by Landry *et al.* (2005) and Screpanti *et al.* (2005). Runoff events that occurred in autumn and winter did not produce any detectable concentrations of glyphosate and AMPA in RV as previously observed (Screpanti *et al.,* 2005; Shipitalo and Owens, 2011). When considering the glyphosate and AMPA concentrations in RV, both substances may have significantly contaminated surface waters only under conditions where runoff occurs shortly after herbicide application (Screpanti *et al.*, 2005).

Glyphosate and Aminomethylphosphonic Acid Bound to Transported Sediments
During the study period, glyphosate load associated with TS was detected in 38.1 ± 1.4 and 41.2 ± 0.7 % of the TS samples in HR and GR, respectively. Glyphosate was detected in 19.2 ± 0.6 % of the TS in HR

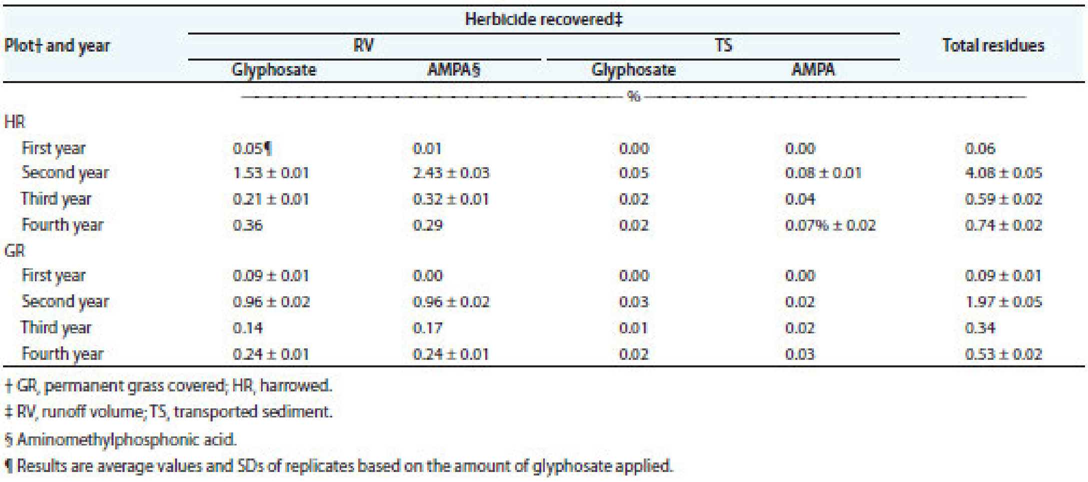
at concentrations lower than 50 mg/kg and in 18.9 ± 0.3 % of the TS at concentrations ranging from 50 to 390 µg/kg. Instead, glyphosate concentrations lower than 50 µg/kg and from 50 to 680 µg/kg were detected in 21.1 ± 0.4 and 4.2 ± 0.1 % of the TS in HR, respectively. The glyphosate associated with TS appeared after about 33.3 ± 27.8 DAA in HR at a concentration of about 220 ± 150 µg/kg. In GR, glyphosate associated with TS appeared after about 50.3 ± 56.3 DAA at a concentration of approximately 310 ± 190 µg/kg. The highest glyphosate concentrations in TS were determined after 30 DAA in the HR in 2009 and after 37 DAA in the GR in 2008. The highest glyphosate losses in TS were about 126.2 and 91.1 µg/ha for HR and GR, respectively, after 27 DAA in 2008. With the exception of the first year, glyphosate was detected in the TS at concentrations exceeding 10 times the method detection limit (100 µg/kg) for a period of 61.3 ± 14.6 DAA (average concentration, 260 ± 70 µg/kg) and 77.3 ± 29.3 DAA (average concentration, 330 ± 80 µg/kg), respectively, after treatments on HR and GR. During the latter, about 1009.5 ± 341.0 and 392.7 ± 159.8 kg/ha of TS were measured on HR and GR, respectively. Thereafter, the final glyphosate peaks appeared in TS in late September, after approximately 184.0 ± 8.3 and 188.3 ± 9.2 DAA in HR and GR, respectively.

Aminomethylphosphonic acid load associated with TS was detected in 85.4 ± 6.6 and 90.2 ± 3.4 % of the TS measured in HR and GR, respectively. Aminomethylphosphonic acid concentrations of 10 to 50, 50 to 500, and >500 µg/kg were detected in 51.5 ± 1.2, 30.0 ± 1.4, and 3.8 ± 0.1 % of the TS from HR, whereas these levels were detected in 28.5 ± 1.9, 60.2 ± 2.2, and 1.6 ± 0.1 % of the TS from GR. Aminomethylphosphonic acid load associated with TS appeared at concentrations of about 390 ± 290 mg/kg after approximately 34.8 ± 25.9 DAA after the treatments in HR and at concentrations of about 220 ± 130 µg/kg after approximately 50.3 ± 56.3 DAA after the treatment in GR. The highest AMPA concentration in TS from HR (710 µg/kg) was measured after 30 DAA in 2009, whereas the highest AMPA concentration in TS from GR (630 µg/kg) was measured after 37 DAA in 2008. The highest AMPA losses in TS from HR (223 µg/ha) and from GR (80.3 µg/ha) were measured in 2008 after 27 and 68 DAA, respectively. Except for the first year, AMPA was detected in TS at concentrations exceeding 100 µg/kg for a period of 85.7 ± 13.0 DAA (average concentration, 400 ± 140 µg/kg) in HR and 104.7 ± 38.1 DAA (average concentration, 260 ± 40 µg/kg) in GR. During the latter, about 1320.6 ± 574.8 and 514.7 ± 59.2 kg/ha of sediment losses were measured on HR and GR, respectively. Thereafter, the final AMPA peaks appeared in TS in late February, after approximately 321.8 ± 22.2 and 294.5 ± 74.9 DAA on HR (average concentration, 50 ± 10 µg/kg) and GR (average concentration, 50 ± 30 µg/kg). The average glyphosate and AMPA bound to TS was significantly ($p < 0.001$) greater from HR than from GR. This was attributable to higher soil losses from HR in comparison to GR. During the study period, no significant correlations were found between seasonal and annual rainfall and the glyphosate (and AMPA) load associated with TS. Unlike AMPA, no detectable concentrations of glyphosate in TS were found in runoff events that occurred in autumn and winter.

Percentage of Applied Glyphosate Lost by Runoff

The amounts of glyphosate and AMPA, in terms of applied glyphosate, measured in RV and TS were summed on a yearly basis (Table 8.5-21). Results indicated that tillage increased herbicide loss. On average, approximately 1.37 ± 0.03 and 0.73 ± 0.07 % of the total glyphosate applied was lost annually from HR and GR, respectively. Results indicated that AMPA represents about the 30.9 and 40.0 % of the total glyphosate losses on GR and HR, respectively. Glyphosate and AMPA bound to TS in runoff is able to reach the bed sediments of streams, lakes, and reservoirs.

Table 8.5-21: The annual glyphosate and aminomethylphosphonic acid amount recovered in runoff volume and transported sediment from harrowed and permanent grass-covered plots for the four experimental years



Plot† and year	Herbicide recovered‡				Total residues
	RV		TS		
	Glyphosate	AMPA§	Glyphosate	AMPA	
	%				
HR					
First year	0.05¶	0.01	0.00	0.00	0.06
Second year	1.53 ± 0.01	2.43 ± 0.03	0.05	0.08 ± 0.01	4.08 ± 0.05
Third year	0.21 ± 0.01	0.32 ± 0.01	0.02	0.04	0.59 ± 0.02
Fourth year	0.36	0.29	0.02	0.07% ± 0.02	0.74 ± 0.02
GR					
First year	0.09 ± 0.01	0.00	0.00	0.00	0.09 ± 0.01
Second year	0.96 ± 0.02	0.96 ± 0.02	0.03	0.02	1.97 ± 0.05
Third year	0.14	0.17	0.01	0.02	0.34
Fourth year	0.24 ± 0.01	0.24 ± 0.01	0.02	0.03	0.53 ± 0.02

† GR, permanent grass covered; HR, harrowed.

‡ RV, runoff volume; TS, transported sediment.

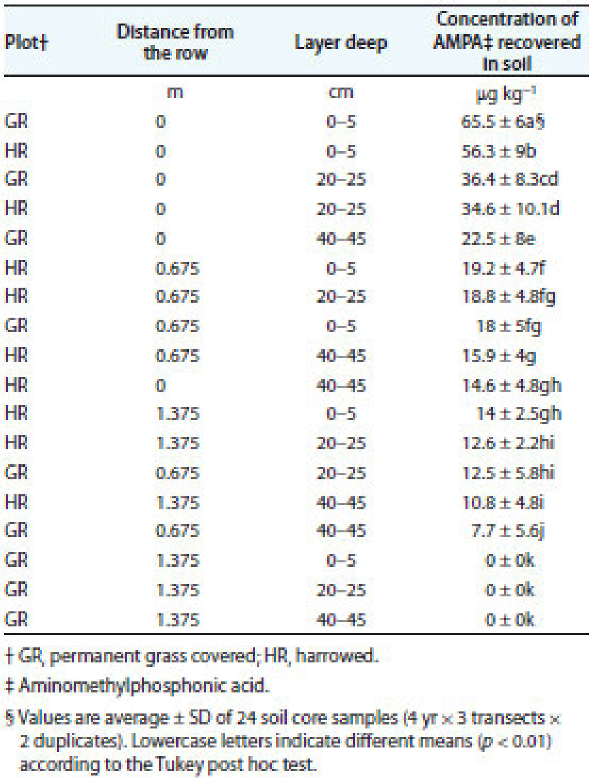
§ Aminomethylphosphonic acid.

¶ Results are average values and SDs of replicates based on the amount of glyphosate applied.

Glyphosate and Aminomethylphosphonic Acid Distribution in the Soil Profile

No extractable glyphosate was detected in the soil profiles. This result is in agreement with the degradation rate of glyphosate (DT_{50} = 10 ÷ 27 d) and its persistence of <1 yr measured in outdoor conditions (Feng and Thompson, 1990; Newton *et al.*, 1994). On the contrary, AMPA was found as deep as 45 cm in the soil profile of both HR and GR plots (Table 8.5-22). Some authors reported a reduced mobility of AMPA caused by absorption onto organic matter and clay in the soil (Grunewald *et al.*, 2001; Newton *et al.*, 1994). During the 4-yr study period, no statistically significant variation in the concentration of AMPA in any layers of the profile was noted. Thus, the measured inter-annual variation cannot be attributed to an accumulation effect but rather is due to different weather conditions. In the same way, the variations observed along the slope were not statistically significant and did not indicate any trend. Along the vine rows, the first and the third layers in GR contained significantly ($p < 0.01$) more AMPA in comparison to the corresponding layers in HR, whereas no significant differences were observed for the second layers. Results indicated that the amounts of AMPA recovered decreased significantly ($p < 0.01$) with depth both for HR and GR, as observed by Landry *et al.* (2005).

Table 8.5-22: Concentration of aminomethylphosphonic acid in the soil 1 yr after the application on the harrowed and permanent grass-covered plots



Plot†	Distance from the row	Layer deep	Concentration of AMPA‡ recovered in soil
	m	cm	µg kg^{-1}
GR	0	0–5	65.5 ± 6a§
HR	0	0–5	56.3 ± 9b
GR	0	20–25	36.4 ± 8.3cd
HR	0	20–25	34.6 ± 10.1d
GR	0	40–45	22.5 ± 8e
HR	0.675	0–5	19.2 ± 4.7f
HR	0.675	20–25	18.8 ± 4.8fg
GR	0.675	0–5	18 ± 5fg
HR	0.675	40–45	15.9 ± 4g
HR	0	40–45	14.6 ± 4.8gh
HR	1.375	0–5	14 ± 2.5gh
HR	1.375	20–25	12.6 ± 2.2hi
GR	0.675	20–25	12.5 ± 5.8hi
HR	1.375	40–45	10.8 ± 4.8i
GR	0.675	40–45	7.7 ± 5.6j
GR	1.375	0–5	0 ± 0k
GR	1.375	20–25	0 ± 0k
GR	1.375	40–45	0 ± 0k

† GR, permanent grass covered; HR, harrowed.

‡ Aminomethylphosphonic acid.

§ Values are average ± SD of 24 soil core samples (4 yr × 3 transects × 2 duplicates). Lowercase letters indicate different means ($p < 0.01$) according to the Tukey post hoc test.

At a distance of 0.675 m from the vine rows, no significant differences were observed between the first layer in GR and HR. In contrast, significantly (p <0.01) more AMPA was recovered from the second and the third layers in HR with respect to the corresponding layers in GR. The AMPA recovered decreased significantly (p <0.01) with depth for GR, whereas no statistical differences were observed between the first and the second layer for HR. According to these results, soil tillage could have contributed to the distribution of AMPA within the soil profile. To the contrary, the grass cover in GR seemed to favor the adsorption of AMPA in the soil surface, as was suggested by Landry *et al.* (2005). In the middle of the inter-rows, AMPA concentrations were below the detection limit for all layers in GR, whereas AMPA was recovered from all layers in HR. Although not statistically significant, results indicated that AMPA decreased with depth for HR. Moreover, significantly (p <0.01) less AMPA was recovered from the all the layers in HR compared with the corresponding layer in GR measured at a distance of 0.675 m from the row. Results indicated that AMPA amounts decreased significantly (p <0.01) with depth for HR and GR. Similar results were observed by Veiga *et al.* (2001), who found that the concentration of AMPA reduced with increasing depth on a 0.35-m profile. According to these results, AMPA was distributed throughout the soil profiles, as observed previously (Landry *et al.*, 2005; Napoli *et al.*, 2015). Leaching of AMPA by preferential flow in macropores may have contributed to the deep penetration of this substance in the soil layers (de Jonge *et al.*, 2001, Fomsgaard *et al.*, 2003; Gjettermann *et al.*, 2009).

Conclusions

Results from this study indicate that transport of glyphosate and AMPA on a hillslope varies over time and according to the soil management practices. The concentrations of glyphosate and AMPA tended to be higher in RV and TS from HR plots than from GR plots. This was evident regardless of the amount of RV and TS. The mean annual glyphosate loss percentages via RV and TS were about 1.37 ± 0.03 and 0.73 ± 0.07 % in HR and GR, respectively. Aminomethylphosphonic acid represented approximately 30.9 and 40.0 % of the total glyphosate losses in GR and HR, respectively. Moreover, results suggested that rainfall, occurring within 4 wk after the treatment, can cause the transport of high concentrations of glyphosate and AMPA. Maximum glyphosate concentrations of 128.9 and 78.4 µg/L were transported from HR and GR, respectively. Maximum AMPA concentrations of 151.9 and 144.8 µg/L were similarly transported from

HR and GR, respectively. Soil analyses indicated that glyphosate was below detection within 1 yr, whereas AMPA was recovered in the soil profiles along the vine rows and in the inter-rows. Overall, results indicated that GR can be used in a vineyard cropping system to reduce soil and herbicide loss by runoff.

Assessment and conclusion by applicant:
The article describes a runoff experiment with glyphosate in a vineyard in Italy. The runoff was measured for glyphosate and AMPA residues. Maximum concentrations of glyphosate and AMPA dissolved in runoff were 128.9 µg/L and 151.9 µg/L, respectively. Maximum concentrations of glyphosate and AMPA associated with runoff sediment were 680 µg/kg and 710 µg/kg respectively.

Soil residues after 12 months were also assessed. No extractable glyphosate was detected in the soil profiles. The maximum AMPA concentration was 65.5 ± 6 µg/kg measured in the top 5 cm of a permanently grassed vineyard soil 0 m from the row.

The article is therefore considered reliable

Assessment and conclusion by RMS:
The study is considered reliable to provide information on Glyphosate and AMPA residues in soil after 12 months under the conditions of the study. This is in the context of the vineyard with great slope (16%), indicating important losses through run-off, while the results also indicate that transport of glyphosate and AMPA on a hillslope varies over time and according to the soil management practices (harrowed plot vs grass covered plot).

No extractable glyphosate was detected in the soil profiles after 12 months. The maximum AMPA concentration was 65.5 ± 6 µg/kg measured in the top 5 cm of a permanently grassed vineyard soil 0 m from the row.

Data point:	CA 7.5/006
Report author	Székács, A. *et al.*
Report year	2014
Report title	Monitoring and biological evaluation of surface water and soil micropollutants in Hungary
Document No	Carpathian Journal of Earth and Environmental Sciences, August 2014, Vol. 9, No. 3, p. 47 - 60
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

In the development of a complex soil contamination monitoring system including the detection of agriculture-related micropollutants, heavy metal contamination and ecotoxicity, a survey has been carried out in Békés county and at certain water catchment areas in Hungary, using different techniques for the characterisation of soil and surface water status. Besides the representativity optimisation of the sampling technique, instrumental analysis, biological tests (soil biology and aquatic toxicity) were also applied, and results obtained were presented in a spatial informatics system. The target analyte group, indicators and methodology is in compliance with recommendations of the European Environment Agency monitoring working group. Contaminant concentrations of soil profiles have been characterised down to the ground water table. Pesticide residues were monitored by using gas chromatography coupled with mass spectrometry and enzyme-linked immunosorbent assay. Target analytes included triazine, phenoxyacetic acid, acetanilide, dinitroaniline and phosphonomethylglycine type herbicides, chlorinated hydrocarbons (CHCs), organophosphate and carbamate insecticides, an insect hormonal agonist and a triazole fungicide. Besides banned persistent CHC insecticides (DDT, HCH, etc.), atrazine and acetochlor herbicides are common contaminants in Hungary, reaching 200 ng/g and 300 ng/mL concentration in the soil and surface water samples studied, and trifluralin, glyphosate and metolachlor were also detected in some cases. Heavy metal and other microelement contamination was detected by inductively coupled plasma atomic emission spectroscopy, and within-plot heterogeneities were studied throughout soil profiles. Nickel has been found as a relatively common contaminant in arable lands in the area, however, relation of the contamination pattern to fertiliser usage in the region could not be confirmed. Total microbiological activity was analysed by using fluoresce in diacetate (FDA) hydrolysis. The results of this measurement did not show correlation with heavy metal content or with land use types. Toxic effects of water and soil samples were determined on *Daphnia magna* Straus (Cladocera, Crustacea) according to the ISO 6341:1996 standard. The vast majority of the samples exerted no observable toxicity on this bioindicator organism. Overall toxicity often occurred not as the sum of the reported toxicity of the individual contaminants found: cases of antagonistic and synergistic effects in toxicity were both observed.

Materials and methods

Chemicals; Chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Sigma Chemical Co. (St. Louis, MO), unless otherwise stated. Analytical standards of the target analyte pesticides were provided by the Hungarian Central Agricultural Office, Plant Protection, Soil Conservation and Agri-environment Directorate, from official standard reference materials received from the manufacturers/distributors of acetochlor, atrazine (Nitrokémia Rt., Fűzfőgyártelep, Hungary), carbofuran (Agro-Chemie Kft., Budapest, Hungary), diazinon, fenoxycarb, prometryn (Syngenta Kft., Budapest, Hungary), metribuzin (Bayer HungáriaKft., Budapest, Hungary), phorate (BASF HungáriaKft., Budapest, Hungary), terbutryn (Agrosol Bt., Gödöllő, Hungary) and trifluralin (BudapestiVegyiművek Rt., Budapest, Hungary). Solvents purchased from Merck KGaA (Darmstadt, Germany) were of analytical grade. CarboPrep-90 (500 mg, 6 mL) and Carbograph (200 mg, 6 mL) columns were purchased from Restek (Bellefonte, PA, USA) and Alltech Associates, Inc. (Deerfield, IL, USA), respectively. HPLC grade distilled water was prepared on a MilliQ RG ion-exchanger from Millipore (Bedford, MA, USA). MN (MachereyNagel) 640W filter paper was obtained from Reanal Rt. (Budapest, Hungary).

Sampling and sample extraction

Sample collection

In the scope of a national monitoring program, 423 soil samples and 202 surface and ground water samples were collected between 2008 and 2013, in uneven annual distribution, from agricultural fields and industrial sites. Contamination in arable lands and industrial areas has been investigated on 13 plots in 5 replicates. Among agricultural areas, three types of land usage have been involved: arable lands under intensive cultivation, organic farming and pasture. The study area in the case of contamination of agricultural origin covered 4 settlements in Békéscounty (Köröstarcsa, Medgyesegyháza, Csorvás, Battonya). Both intensive and organic parcels were chosen in all 4 settlements (4 organic and 4 intensive), the pasture was designated in Csorvás. Contamination of industrial origin was examined in 3 settlements (Orosháza, Gyomaendrőd, Békéscsaba), at 5 sites (Orosháza - Linamar, Public Road Manager Corp., Glass Factory; Gyomaendrőd - Nagylapos; Békéscsaba - Sludge Desposition Site). Spatial setting of sampling accuracy was supported by a global positioning system. Soil sampling was carried out according national standard MSZ 21470-1:1998 (Hungarian Standards Institution 1998) during the April-May period by using a motorised Eijkelkamp soil drilling equipment. Contaminant concentrations of soil profiles from topsoil to subsoil were characterised down to ground water table, creating one sample in every 30 or 50 cm. Parcels of diffuse agricultural load were further narrowed to define a 5 ha Representative Parcel Part (RPP), preferably as a quadrat. RPP was designed on the representative, homogeneous part of the parcel. This was carried out to characterise the nutrient content of the surface soil layer. In our study, a sampling allocation in regular design was used for the mechanical drillings, thus a parcel of 50 m x 50 m territory was designated in one corner of the RPP. The soil samples were taken from drillings in the corners and in the centre point of this part of the RPP, in five replications each. Water sampling was carried out according to national standard MSZ ISO 5667 (Hungarian Standards Institution 1995), twice a year, before and after agricultural pesticide applications, during the months of April-May and June-September. Surface water samples (from depths not exceeding 50 cm) were collected by immersion of a sampling vessel, while groundwater samples were taken from the soil drillings or from already existing groundwater monitoring wells. Both kinds of water samples were transferred into clean, 2.5 litre volume dark glass bottles sealed with a watertight screw-cap insulated with teflon lining, and were transported in cool boxes to the laboratory.

Sample preparation
To provide appropriate sample preparation for gas chromatography - mass spectrometry (GC-MS) determinations, solvent extraction and solid phase extraction (SPE) methods were applied. Soil samples were air-dried, ground on a Retsch GM 200 cutting mill (Retsch GmbH, Haan, Germany), and subjected to solvent extraction. Thus, 10 g dried soil was extracted with 15 mL of hexane/acetone (1:1) and centrifuged at 4000 rpm. Finally, 10 mL of the supernatant was evaporated and resuspended in 1 mL of ethyl acetate. Water samples were filtered in a suction filtration apparatus using MN 640W filter paper to remove floating particles, stirred for 1 min, left to settle for 10 min, and then subjected to SPE using graphitized carbon based SPE cartridges. SPE columns (CarboPrep-90, 500 mg, 6 mL) were conditioned, applying low eluent flow velocity, with 5 mL of dichloromethane/methanol (8:2), 2 mL of methanol, and 10 mL of distilled water containing 10 mg/mL ascorbic acid. After the conditioning step, 1000 mL of the water sample was passed through the column at a flow rate of 10-15 mL/min. The column was rinsed with 7 mL of distilled water, air-dried for 10 min with suction by vacuum, washed with 1 mL of methanol/distilled water (1:1), and air-dried again. Neutral and alkaline components absorbed into the column were eluted, at a low eluent flow velocity, with 1 mL of methanol and 1 mL of dichloromethane/methanol (8:2). Combined eluates were concentrated to 0.1 mL under nitrogen gas flow. Then 2 mL of isooctane was added to the extract, and the solution was evaporated to a final volume of 1 mL. Extract samples were applied for measurement with GC-MS.

In order to evaluate the SPE/GC-MS process, water samples were spiked with standards of the target compounds at concentrations between 0.001 and 25 ng/mL, and subjected to the above SPE protocol and to instrumental analysis. Analytical standards of the active ingredients were added to HPLC grade distilled water (MilliQ) in methanol stock solutions, except for phorate, where stock solution was prepared in acetone. Spike levels included 2- and 5-fold values of the limit of detection (LOD), except for fenoxycarb. Five parallel detections were carried out at these levels for each active ingredient.

Instrumental analysis

GC-MS
GC-MS analyses were carried out on a Saturn 2000 workstation (Varian Inc., Walnut Creek, CA, USA), consisting of a Chrompack CP 3800 gas chromatograph and a Saturn 2000R ion-trap detector. The gas chromatograph was equipped with a Varian 1079 split/splitless injector and a CP 8200 autosampler. GC-MS determinations were carried out using electron impact (EI) or chemical ionization (CI) ion sources, detecting total ion count (TIC) in full scan mode or selected ion(s) in selective ion monitoring (SIM) mode. A capillary column CP-Sil 8 CB filled with 5 % diphenyl polysiloxane and 95 % dimethyl polysiloxane (30 m, 0.25 mm, film thickness 0.25 µm) (Chrompack, Middelburg, the Netherlands) was used. The carrier gas was helium 5.0 at a flow rate of 1.0 mL/min. The mode of injection was splitless (0-1.5 min), then the split ratio set to 50. Both isothermal injection (ITI) and temperature programmed injection (TPI) were applied. During ITI, the injection temperature was set to 230°C. The injection volume was 1 µL. The corresponding column temperature, following an initial period of 120°C for 1 min, was increased to 270°C at 10°C/min, and kept at 270°C for 14 min. During TPI, the injection temperature was 60°C for 0.50 min, raised to 260°C at 200°C/min rate, held for 5 min, raised further to 60°C at 200°C/min rate, held for 20.00 min. The injection volume was 5 µL. Solvent venting was not applied. The corresponding column temperature, following an initial period of 70°C for 0.5 min, was increased to 100°C at 60°C/min, further increased to 240°C at 10°C/min and kept finally at 240°C for 20 min. The transfer line temperature was 270°C. The mass spectrometer was operated in electron impact (EI) or chemical ionization (CI) mode using methanol as reagent gas with CI storage level of 19.0 m/z. The temperature of the ion trap was 150°C. The maximum ionization time was 2000 µs, the maximum reaction time 40 ms, the ionization level 25 u, the reaction level 40 amu, reagent reaction time 9000 µs, scan time 0.60 s/scan, between 45 and 400 amu in full-scan mode. Chlorophenoxyacetic acid type herbicides (2.4-D, dichloprop, MCPA, etc.) were determined upon derivatization with trimethylsilyl N,N-dimethyl carbamate and t-butyldimethylsilyl N,N-dimethyl carbamate.

Enzyme-linked immunosorbent assay (ELISA)
The determination of herbicide active ingredient glyphosate was carried out by the validated commercial immunoassay (PN 500086 by Abraxis LLC, Warminster, PA, USA) using antibodies specific for glyphosate. Measurements were carried out in 96-well microtiter plates according to manufacturer instructions. Acyl-derivatized samples or analytical standards were incubated with glyphosate-specific antibodies immobilized on the walls of the microtiter wells, and an enzyme conjugate of glyphosate was added. Upon washing, the bound enzyme quantity was determined by a colorimetric reaction providing optical signals at 620 nm and 450 nm wavelengths. Glyphosate concentrations were determined using standard calibration curves of linear or sigmoid fit.

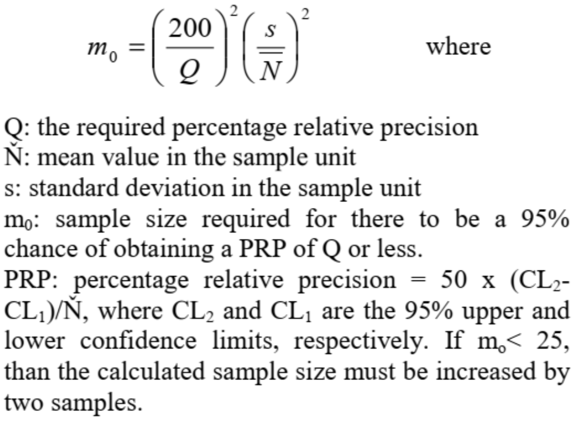
<u>Toxicity tests</u>

Soil microbiology
Microbial enzymatic activity in the soil was measured by fluorescein diacetate (FDA) hydrolysis, optimised for soil samples. Samples were stored at the temperature of 4°C until analysis. FDA reagent (stock solutions at 1 and 10 g/L FDA in acetone) was added to 1 g of soil per replication in 15 mL phosphate buffer (pH 7.6). Upon shaking for 2 hours at 30°C. Then, the reaction was terminated by acetone (1:1 suspension in the solvent), applying a 1.5 hour long glass bead pre-shaking step to reach a proper level of suspension. Upon centrifugation of the suspensions at 3000 rpm), the amount of fluorescein developed was measured from the supernatant of each sample on a spectrophotometer at 490 nm. Statistical analyses of FDA data have been performed using one-way analyses of variances (ANOVA), effects of pesticides residues, soil humus content and soil texture have been analysed by multiple regression.

Immobilization test on Daphnia magna
Aquatic biotests using the giant water flea (*Daphnia magna* Straus) were carried out on soil and water samples with highest contamination rates detected. Immobilization tests were performed according to the ISO 6341:1996 standard (International Organisation for Standardisation 1996). Test animals were kept in 16/8 hr light/dark photoperiod with the testing atmosphere kept at 20-22°C and free from poisonous vapours or dusts. The breeds and the controls were kept in aqueous solution containing $CaCl_2$, $MgSO_4$, $NaHCO_3$ and KCl at concentrations of 220.5, 61.6, 64.8 and 5.75 mg/L, respectively. The bioanalytical accuracy of the test was assessed in potassium dichromate test: the mortality caused by $K_2Cr_2O_7$ was measured at 0.25, 0.5, 0.75, 1 and 1.25 mg/L concentrations, and the sensitivity of the test animals was considered proper according to the standard protocol if the EC_{50} value obtained for potassium dichromate fell between 0.6 and 1.7 mg/L. Water samples and aqueous soil extracts were applied directly to the test in volumes of 10 mL per replication. Floating matter when occurred was removed from the water samples by centrifugation for 5 min at 3000 rpm. For extraction of soil samples 300 g of soil was extracted with 500 mL of distilled water, the mixture was ultrasonicated for 10 min, and filtered in a suction filtration apparatus through MN 640W filter paper. Tests were carried out at the first larval stage (6-24 hours) for 48 hours, when the immobilization of the subject animals was recorded (10 animals per test) in quadruplicates. Mortality (immobilisation) rates were calculated by the Henderson-Tilton formula, correcting the measured mobility inhibition with that detected for untreated control and eliminating the effect of varying number of test individuals applied at the repetitions. Therefore, percentage mortality/immobilisation refers to values corrected with the Henderson-Tilton formula. EC_{50} values were calculated using probit transformation and log-linear regression, the data were statistically evaluated by one way ANOVA.

<u>Computing accurate sample sizes</u>

Reliability of estimates depends on both accuracy and precision. Accuracy is about how close the estimate is to its true value on average. Precision is about how similar repeated estimates are to each other. Percentage relative precision (PRP) of the estimation at heavy metal and pesticide residues contamination, i.e. was used to estimate precision of the measurements. PRP is the difference between the estimated mean of the measurements and its 95 % confidence limits, expressed as a percentage of the estimate. However, because confidence limits are sometimes asymmetrically distributed around the estimate, the mean difference between them and the estimate was used. Estimation of sample sizes needed to attain a fixed percentage relative precision has been calculated on the basis of the following equation:



$$m_0 = \left(\frac{200}{Q}\right)^2 \left(\frac{s}{\bar{N}}\right)^2 \qquad \text{where}$$

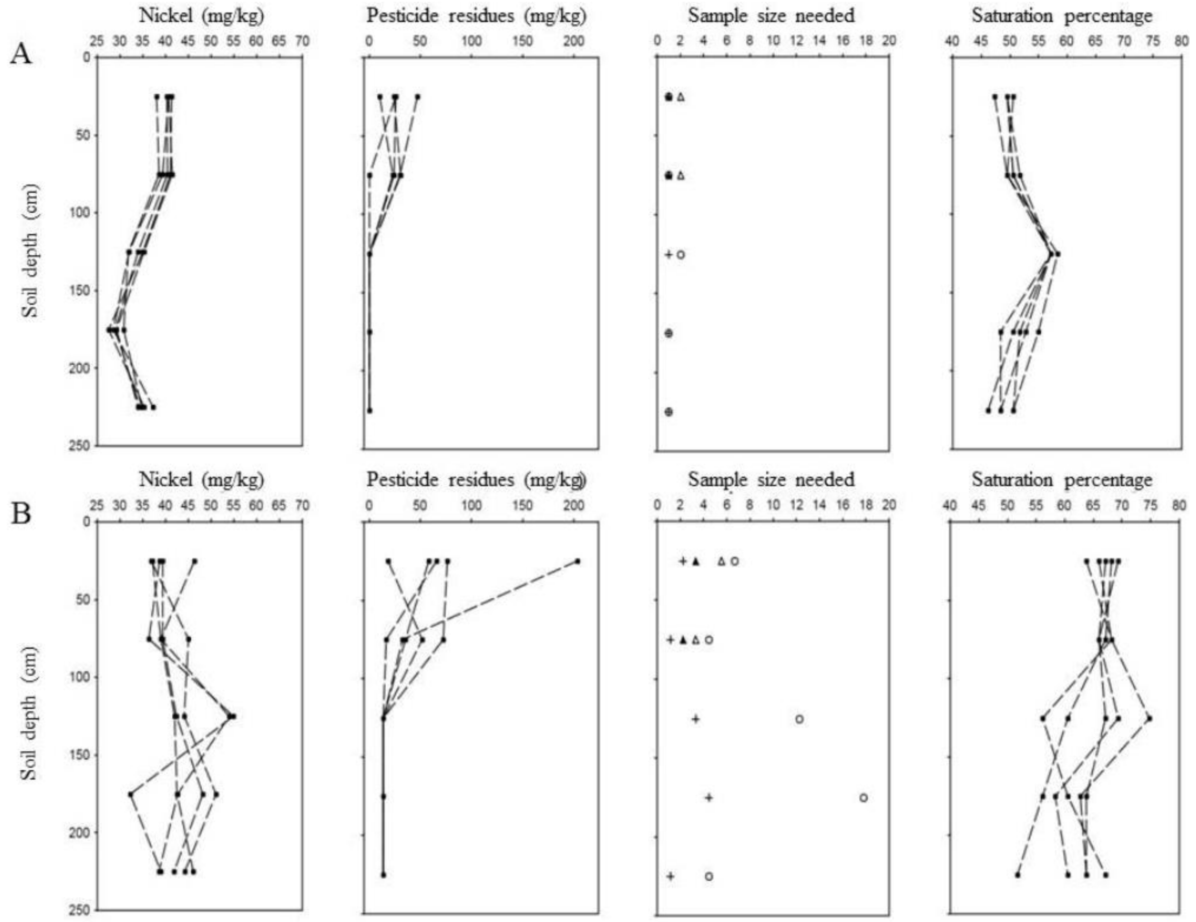
Q: the required percentage relative precision
Ň: mean value in the sample unit
s: standard deviation in the sample unit
m_0: sample size required for there to be a 95% chance of obtaining a PRP of Q or less.
PRP: percentage relative precision = 50 x (CL_2-CL_1)/Ň, where CL_2 and CL_1 are the 95% upper and lower confidence limits, respectively. If $m_o < 25$, than the calculated sample size must be increased by two samples.

Results and discussion

Examination of sampling effort
For reliability assessment, percentage relative precision of the pollution level estimation was calculated at each site. As expected, precision was highly influenced by the heterogeneity of the sites and thus directly depended on the variance of the data. To show the consequences of small-scale heterogeneity of sites, contamination characteristics of a homogeneous and a heterogeneous site are presented on Figure 8.5-10, showing the curves of nickel concentration, pesticide residue levels and soil texture with soil depth. Similar slopes in saturation percentage indicated identical soil textures among the five samples at the homogeneous site (Figure 8.5-10A), whereas soil textures differed substantially in the heterogeneous set (Figure 8.5-10B), probably due to complex sedimentation. Sample sizes needed for 10 % and 20 % precision in nickel concentration varied between 3-4 drillings and 3-16 drillings at the homogeneous and heterogeneous sites, respectively. For pesticide residues, appropriate sample sizes have been determined between 3-8 drillings, considering the higher percentage values of the precision (50 % and 100 %). 100 % percentage relative precision actually indicates only the occurrence of the contamination. This result pointed out that the level of site heterogeneity highly influences the required sample sizes for a given precision, and also indicated the extreme importance of the composite sampling design and homogenisation in the course of sample preparation in environmental monitoring.

Figure 8.5-10: Contamination profiles at a homogenous (site A, Battonya 1) and a heterogeneous (site B, Köröstarcsa 2) sampling site

Nickel concentration was proven to exceed the “B” limit value (40 mg/kg) in both cases. The amount of total pesticide residues at site *B* is regarded to be significant; 10 % PRP (percentage relative precision) at nickel (open circle); 20 % PRP at nickel (cross); 50 % PRP at pesticide residues (open triangle), 100 % PRP at pesticide residues (closed triangle) are shown in the last column.



Chemical analysis

Pesticides

Thirty-three active ingredients and metabolites (acetochlor, alachlor, aldrin, atrazine, butylate, carbofuran, carbofuran phenol, DDD, DDE, DDMU, DDT, diazinon, dibutilphtalate, dieldrin, endrin, endrin ketone, EPTC, α-, β- and γ-HCH, heptachlor, heptachlor epoxide, isodrin, metolachlor, phenkapton, phorate, prometryn, propachlor, sulfotep, TBP (tributil phosphate), terbutryn, trifluralin) and 14 related compounds (AMPA, 2,4-D, 2,4-DB, dichloprop, dimetachlor, fenoxycarb, glyphosate, MCPA, MCPB, mecoprop, metribuzine, propisochor, simazine) or compound groups (camphechlor) were monitored by GC-MS. Of the 423 soil samples analysed, 77 samples contained detectable contamination by one or more target compounds (contamination was marginal in four cases). Therefore, contamination rate found was 17-19 %. Of the 202 water samples analysed, 76 samples contained detectable contamination by one or more target compounds (contamination was marginal in 11 cases). Therefore, contamination rate found was 18-67 %. The most common soil contaminants appeared to be atrazine (10-580 ng/g), trifluralin (3-200 ng/g), acetochlor/metolachlor (5-80 ng/g), as well as DDT/DDE (38-460 ng/g) and lindane/HCH (7-103 ng/g); the most common water contaminants were acetochlor (0.02-3900 µg/L), atrazine (0.5-100 µg/L), metolachlor (0.001-56 µg/L), trifluralin (0.8-9 µg/L) and diazinon (0.001-0.85 µg/L). The found contamination levels are in certain cases alarming as the corresponding harmonised EC Directive effective in Hungary as well sets the maximum residue limit of 100 ng/L for a given pesticide compound and 500 ng/L for all pesticide residues in subsurface water. The herbicide active ingredient glyphosate was detected as water contaminant at concentrations of 0.54-0.98 ng/mL by a commercial ELISA method, at very high or high levels in 5 and 16 cases, respectively (relative to the substantial background signal level of the immunoanalytical method). As the reported cross-reactivity of the commercial ELISA kit used with the main glyphosate metabolite aminomethyl phosphonic acid (AMPA) is reported to be below 0.0002 %, the method only detected the parent compound and not its degradation product. Frequent occurrence of glyphosate is of major concern due to the high water contaminating potential of glyphosate, and due to its known ecotoxicological (cytotoxic, endocrine disruptive and mutagenic/teratogenic) effects, particularly when exerted in co-exposure or synergy with polyethoxylated tallowamine often used as adjuvant for this herbicide active ingredient.

Toxicity testing

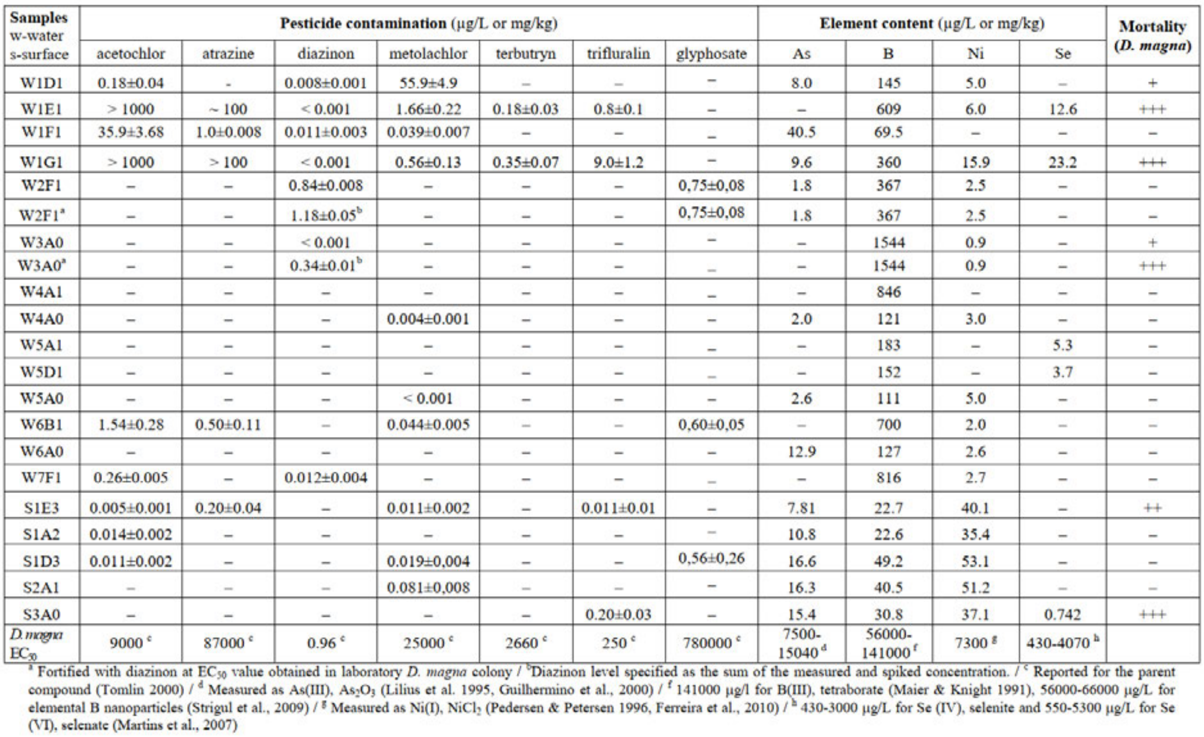
Soil microbial activity

Soil microbial activity on arable lands (nine sites) and industrial locations (four sites) were measured by using FDA analysis with 5 replicates per site (65 drillings). Soil microbial activity differed significantly between arable lands and industrial sites ($F_{(1, 63)} = 74.5$, $p < 0.001$), arable soils showed 14 times higher microbiological activities than industrial ones ($F_{(1, 38)} = 0.39$, $p > 0.05$). Such pattern can be explained by the more favourable ecological conditions for the soil microflora occurring in arable lands than those of industrial sites. FDA activity correlated with humus content in the upper soil layer ($R^2 = 0.6$), constituting another sign for the effect of biotic conditions on soil microbiological activity. However, agricultural land use practice (intensive vs. organic farming) did not affect FDA activity. The reason for such phenomenon may be the fact that the overall duration of organic farming practices at these locations after decades of intensive agriculture was too short for the spontaneous development of a mature microbiological community with higher biomass. Soil microbiological activity is influenced by numerous biotic and abiotic environmental factors, of which contamination is only one driving force. We examined how abiotic soil factors and contamination affected soil microbiological activity. By using multiple linear regression modelling humus content, soil texture and soil pesticide residues were set as independent variables against FDA, as a dependent variable. The partial regression coefficients were obtained respectively -0.08 at herbicide and insecticide residues, 0.4 at soil texture and 0.84 at humus content, ($R^2 = 0.7$). This result showed a statistically not significant, weak negative effect of herbicide and insecticide pollution on FDA, whereas humus content and soil texture did influence microbial activities in soils. Therefore, such a general microbiological activity pattern generated from FDA analysis alone cannot be regarded as a predictor for examined soil contamination.

Aquatic toxicity detected on Daphnia magna indicator organism

There apply strict regulations in pesticide registration regarding aquatic toxicity of the candidate compounds. If the pesticide preparation is dangerous for aquatic organisms, specific protective distances (200, 50 or 20 metres) apply from water courses. As a result, toxicity exerted on *D. magna* is required to be determined for each registered pesticide active ingredient and is listed among the chemical and biological features of pesticides. Zooplankton, *Daphnia* is widely used as a test organism in order to evaluate the toxicity of several contaminants as well as their mixture. A recent report of the effects of herbicides on zooplanktons gives a comprehensive overview of the highly varying EC_{50} values on *D. magna* and other daphnids, revealing possible deviation patterns. Organisms in the environment are permanently exposed to complex mixtures of low concentrations of contaminants from mainly anthropogenic sources. Particularly aquatic organisms are endangered by toxicants since they spend their life entirely or majorly in their aquatic media, and therefore, may suffer exposure to single or multiple water contaminants all over their lifetime. The evaluation of the additive effects of multiple contaminants (e.g. pesticides) in water at low concentrations has received great attention lately. Addition and synergism were observed among sublethal concentrations of diazinon, malathion and chlorpyrifos on coho salmon (*Oncorhynchus kisutch*). A recent review reports a number of combined toxicological interactions of pesticide mixtures such as pyrethroids, carbaryl and triazine herbicides at molecular level. Exposure to pesticides at sublethal doses not only exert combined toxitity to affected organisms, but may also induce their increased sensitivity to other stress factors such as predator stress, parasite infection or UV-radiation. As reported in the scientific literature, toxic effects of low concentration pesticide mixtures on zooplanktons (including *D. magna*) and on algae are typically close to the sum of the effects for each pesticide compound applied independently, therefore, overall toxicity levels are estimated on the basis of toxicity exerted by single compounds. Such phenomenon has been reported not only for insecticides, but for herbicide (acetochlor, metolachlor, glyphosate, 2,4-D, atrazine) mixtures as well. As expected, no toxic effect was observed in the *D. magna* immobilization test in the case of the vast majority of the water samples. In contrast, significant or salient aquatic toxicity was detected in all soil and water samples heavily contaminated with pesticide residues and/or toxic heavy metals (Table 8.5-23), indicating that these contaminants do cause toxicity on *D. magna*. Nonetheless, a clear superposition of the individual toxicity of the contaminants tested was not seen in the statistical analysis of the aquatic toxicity results. Among pesticide type organic micropollutants, mostly insecticides are expected to be considered toxic to *D. magna*: compounds designed to have toxic effects on insects are more likely to cause similar effects on other arthropods, than substances optimized for their effects on plants or on fungi. This is well reflected among the target analyte pesticides in the present study by the outstandingly low EC_{50} value of diazinon on *D. magna* (0.96 µg/L). The toxicity of microelements on *D. magna* is highly dependent on element speciation, therefore, toxicity values reported in the literature commonly refer to the most abundant forms of the given elements. Besides, the toxicity of metals in aquatic environment varies widely, depending both on environmental conditions and on the sensitivity of the exposed organisms. Most prevalently found contaminating microelements in this study (As, B, Ni and Se) exert minor toxicity of *D. magna*. As a result, significant toxicity was expected only from the most contaminated surface water samples or aqueous soil sample extracts, particularly from those contaminated with insecticides. Dibutyl phthalate, commonly reported as ubiquitous water contaminant, has been found in certain water samples, in some cases at concentrations as high as 100 ng/mL (e.g. W4A1, W5D1), yet no toxicity on *D. magna* was observed, in accordance with the reported marginal toxicity of the compound on *D. magna* (EC_{50} = 3.0-5.2 mg/L). Samples W1E1 and W1G1 heavily contaminated with acetochlor and atrazine and containing elevated levels of boron caused full mortality in the *D. magna* biotest, when applied undiluted. These two water samples were measured in 5-, 10- and 25-fold dilutions as well, and it was found that 50 % mortality (EC_{50}) was reached when the samples were applied at dilutions of 6.4- and 13.3-fold, respectively. The strong mortality caused by these samples was a clear result of the synergistic effect of the individual contaminants, as the actual (although apparently high) levels were far below of the individual EC_{50} values. Sample W1D1 represented a similar case with slight diazinon and acetochlor, and considerable metolachlor contamination (the latter still not reaching even 1 % of the EC_{50} value of metolachlor) and causing 65 % mortality on *D. magna*. As toxicity of that high magnitude would not be expected on the test animal neither from the pesticide residue, nor from the microelement contamination detected in the sample, the observed biological effect is either due to an unidentified component or caused by synergistic interactions among the detected contaminants. In contrast, a case of low or no toxicity, when significant effect on *D. magna* was expected, was also recorded: sample W2F1 caused no immobilisation *of D. magna* larvae. This was rather intriguing, because the measured diazinon content of the sample was close to the EC_{50} value of the compound on the test animal. In such case at least limited mortality would have been expected to be observed. To test whether the *D. magna* population used in these experiments shows sufficient sensitivity to diazinon the EC_{50} value of the compound was experimentally determined and was found to be 0.34 µg/L (0.27 to 0.39 µg/L).

Table 8.5-23: Toxicity of water and soil samples contaminated with pesticides and heavy metals on *Daphnia magna* as indicator organism



Samples w-water s-surface	**Pesticide contamination** (µg/L or mg/kg)							**Element content** (µg/L or mg/kg)				**Mortality (*D. magna*)**
	acetochlor	atrazine	diazinon	metolachlor	terbutryn	trifluralin	glyphosate	As	B	Ni	Se	
W1D1	0.18±0.04	-	0.008±0.001	55.9±4.9	–	–	–	8.0	145	5.0	–	+
W1E1	> 1000	~ 100	< 0.001	1.66±0.22	0.18±0.03	0.8±0.1	–	–	609	6.0	12.6	+++
W1F1	35.9±3.68	1.0±0.008	0.011±0.003	0.039±0.007	–	–	–	40.5	69.5	–	–	–
W1G1	> 1000	> 100	< 0.001	0.56±0.13	0.35±0.07	9.0±1.2	–	9.6	360	15.9	23.2	+++
W2F1	–	–	0.84±0.008	–	–	–	0,75±0,08	1.8	367	2.5	–	–
W2F1[a]	–	–	1.18±0.05[b]	–	–	–	0,75±0,08	1.8	367	2.5	–	–
W3A0	–	–	< 0.001	–	–	–	–	–	1544	0.9	–	+
W3A0[a]	–	–	0.34±0.01[b]	–	–	–	–	–	1544	0.9	–	+++
W4A1	–	–	–	–	–	–	–	–	846	–	–	–
W4A0	–	–	–	0.004±0.001	–	–	–	2.0	121	3.0	–	–
W5A1	–	–	–	–	–	–	–	–	183	–	5.3	–
W5D1	–	–	–	–	–	–	–	–	152	–	3.7	–
W5A0	–	–	–	< 0.001	–	–	–	2.6	111	5.0	–	–
W6B1	1.54±0.28	0.50±0.11	–	0.044±0.005	–	–	0,60±0,05	–	700	2.0	–	–
W6A0	–	–	–	–	–	–	–	12.9	127	2.6	–	–
W7F1	0.26±0.005	–	0.012±0.004	–	–	–	–	–	816	2.7	–	–
S1E3	0.005±0.001	0.20±0.04	–	0.011±0.002	–	0.011±0.01	–	7.81	22.7	40.1	–	++
S1A2	0.014±0.002	–	–	–	–	–	–	10.8	22.6	35.4	–	–
S1D3	0.011±0.002	–	–	0.019±0,004	–	–	0,56±0,26	16.6	49.2	53.1	–	–
S2A1	–	–	–	0.081±0,008	–	–	–	16.3	40.5	51.2	–	–
S3A0	–	–	–	–	–	0.20±0.03	–	15.4	30.8	37.1	0.742	+++
D. magna EC_{50}	9000 [c]	87000 [c]	0.96 [c]	25000 [c]	2660 [c]	250 [c]	780000 [c]	7500-15040 [d]	56000-141000 [f]	7300 [g]	430-4070 [h]	

[a] Fortified with diazinon at EC_{50} value obtained in laboratory *D. magna* colony / [b]Diazinon level specified as the sum of the measured and spiked concentration. / [c] Reported for the parent compound (Tomlin 2000) / [d] Measured as As(III), As_2O_3 (Lilius et al. 1995, Guilhermino et al., 2000) / [f] 141000 µg/l for B(III), tetraborate (Maier & Knight 1991), 56000-66000 µg/L for elemental B nanoparticles (Strigul et al., 2009) / [g] Measured as Ni(I), $NiCl_2$ (Pedersen & Petersen 1996, Ferreira et al., 2010) / [h] 430-3000 µg/L for Se (IV), selenite and 550-5300 µg/L for Se (VI), selenate (Martins et al., 2007)

Diazinon was spiked into water sample W2F1 at this concentration, verified to cause substantial mortality, yet mortality still not appeared in the *D. magna* immobilisation test. This observation indicates a clear antagonist effect among contaminants such as sub-lethal concentrations of diazinon and copper. Similar antagonistic patterns observed when crustacean *Ceriodaphniadubia* or mayfly *Ephoronvirgo* were exposed to a mixture of copper and diazinon. Another critical water sample (W3A0) of high boron content and of limited (40 %) toxicity on *D. magna* was also spiked with diazinon at 0.34 µg/L concentration, and resulted in full (100 %) mortality in the *D. magna* immobilization test. This verified assay sensitivity to diazinon, and indicated a slight synergism between diazinon and the boron content of the sample. Sample S1E3 contained various pesticide and microelement contaminants, primarily nickel at a substantially high level of 40.1 mg/kg. The aqueous extract of this soil sample caused 95 % immobilisation on *D. magna*. Soil sample S3A0,containing (along with other microelements) high level (15.4 mg/kg) of arsenic, the aqueous soil extract caused 100 % immobilisation, and required a 2.54-fold dilution to reach EC_{50}. Detectable toxicity to *Daphnia magna* has not been observed on water samples with detected content of glyphosate residues. This is in accordance with the known toxicity of glyphosate and AMPA to *D. magna* (780 and 690 mg/L, respectively), escalated by polyethoxylated tallowamine detergents used as formulating agents. Nonetheless, recent literature data indicate sublethal effects of glyphosate and its formulations on aquatic organisms. They may cause reduction of juvenile size and affect the growth, fecundity and abortion rate of daphnids and inhibit cholinesterase activity of mussel and fish as well.

Conclusion

The present study combines chemical analysis of pesticide residues and microelements from topsoil and subsoil, as well as surface and ground water samples with biotests on total soil microbiological activity using fluorescein diacetate (FDA) hydrolysis and on aquatic toxicity using the ISO 6341:1996 standard immobilisation protocol on *Daphnia magna* Straus. Contamination by organic micropollutants, mainly pesticide residues occurred more frequently in surface water (18-67 %), than in soil (17-19 %); the most contaminated samples arrived from an identified illegal contamination site scheduled for remediation. Residues of herbicide active ingredients atrazine, acetochlor/metolachlor and trifluralin were found both as water and as soil contaminants at various concentrations up to 3900 ng/mL and 580 ng/g, respectively. In addition, residues of the insecticide active ingredients diazinon also occurred as water contaminant below 1 ng/mL. Of the 14 microelements monitored, 18 % and 53 % contamination frequencies above the legal threshold value was detected for soil and water samples, respectively, with Ni, As and Ba as most common soil contaminant microelements, and B and Se as major water contaminant microelements. While a clear correlation between detected soil contamination and microbiological activity determined by FDA analysis could not be established, toxicity tests with *D. magna* showed substantial toxicity in 6 cases. The survey indicated that biotests are worthwhile to be carried out even if analytical measurements reveal sublethal level contamination to the given test organism, because contaminant interactions may result in lethal effects. Interactions may appear synergistic, antagonistic and additive.

Assessment and conclusion by applicant:
The article reports measurements of glyphosate among other pesticides, organic pollutants, heavy metals and other microelements in soils, surface waters and groundwater bodies in Hungary from agricultural and industrial settings. The effect of the found concentrations of the different substance on *D. magna* was investigated. The reported glyphosate findings cannot be assigned to the respective sampling site. Furthermore, no comprehensive list of glyphosate findings is presented. A maximum concentration of glyphosate at 0.98 µg/L was reported as an unspecified (SW/GW) water contaminant. The maximum glyphosate soil concentration reported was 0.56 ± 0.26 mg/kg.
The article is therefore considered reliable with restrictions.

Assessment and conclusion by RMS:
This articles reports results from monitoring program in Hungary.
In the scope of a national monitoring program, 423 soil samples and 202 surface and ground water samples were collected between 2008 and 2013, in uneven annual distribution, from agricultural fields and industrial sites. Contamination in arable lands and industrial areas has been investigated on 13 plots in 5 replicates. Among agricultural areas, three types of land use have been involved: arable lands under intensive cultivation, organic farming and pasture.
The findings are not detailed and as indicated by applicant, the reported glyphosate findings cannot be assigned to any respective sampling site. The maximum glyphosate soil concentration reported was 0.56 ± 0.26 mg/kg, but no further information is given on the context.

The study is considered reliable with restrictions.

Data point:	CA 7.5/053
Report author	Daouk, S. *et al.*
Report year	2013b
Report title	The herbicide glyphosate and its metabolite AMPA in the Lavaux vineyard area, western Switzerland: Proof of widespread export to surface waters. Part II: The role of infiltration and surface runoff
Document No	Journal of Environmental Science and Health, Part B (2013) 48, 725–736
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

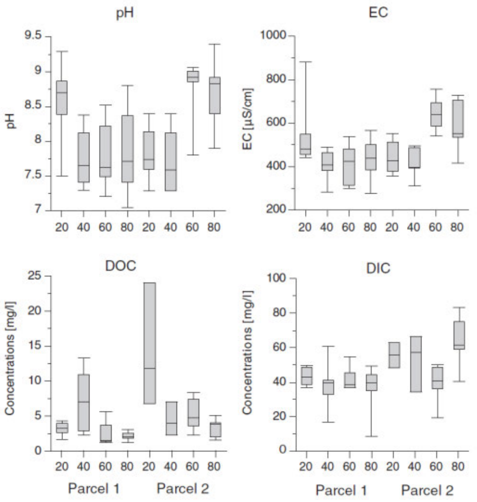
Two parcels of the Lavaux vineyard area, western Switzerland, were studied to assess to which extent the widely used herbicide, glyphosate, and its metabolite aminomethylphosphonic acid (AMPA) were retained in the soil or exported to surface waters. They were equipped at their bottom with porous ceramic cups and runoff collectors, which allowed retrieving water samples for the growing seasons 2010 and 2011. The role of slope, soil properties and rainfall regime in their export was examined and the surface runoff/throughflows ratio was determined with a mass balance. Our results revealed elevated glyphosate and AMPA concentrations at 60 and 80 cm depth at parcel bottoms, suggesting their infiltration in the upper parts of the parcels and the presence of preferential flows in the studied parcels. Indeed, the succession of rainy days induced the gradual saturation of the soil porosity, leading to rapid infiltration through macropores, as well as surface runoff formation. Furthermore, the presence of more impervious weathered marls at 100 cm depth induced throughflows, the importance of which in the lateral transport of the herbicide molecules was determined by the slope steepness. Mobility of glyphosate and AMPA into the unsaturated zone was thus likely driven by precipitation regime and soil characteristics, such as slope, porosity structure and layer permeability discrepancy. Important rainfall events (>10 mm/day) were clearly exporting molecules from the soil top layer, as indicated by important concentrations in runoff samples. The mass balance showed that total loss (10–20%) mainly occurred through surface runoff (96%) and, to a minor extent, by throughflows in soils (4%), with subsequent exfiltration to surface waters.

Materials and Methods

Study area and soil features

The Lavaux is a vineyard area located in western Switzerland. This landscape is composed of moraine deposits and, with its steep slopes from 13 to 43% and the light reflection on the Lake of Geneva, it represents a very suitable environment for the growth of grapevines. The bedrocks are composed of Tertiary molasse deposits, which include conglomerates, sandstones and marls from the upper Oligocene epoch. Soils of both parcels are colluvial calcosols, according to the French classification. Both soils showed a silt loam texture and light differences were observed between plots and depths.

Figure 8.5-11: **pH, electrical conductivity (EC), dissolved organic and inorganic carbon (DOC/DIC) contents in soil water samples at 20, 40, 60 and 80 cm of both parcels**



Sampling and analytical methods

In both parcels, the herbicide glyphosate was applied the same day and only under the rows, leaving a grass band in between them. It is mainly applied in spring time to avoid a nutrient and water competition between grapevines and weeds during the growing season. Application data were obtained from winegrowers and are summarized in Table 8.5-24. In previous years, the same amounts had been applied, but we assumed that all glyphosate and AMPA degrade from year to year according to their properties. Precipitation data were obtained from the closest meteorological station. In order to sample the soil solution, both parcels were equipped at their bottom with porous ceramic suction cups at four different depths: 20, 40, 60 and 80 cm. The herbicide glyphosate and its metabolite AMPA were quantified by LC-MS/MS with a previously developed method, based on their pre-column derivatization with FMOC-Cl and their enrichment by solid phase extraction. The limit of quantification was 10 ng/L and it was tested successfully for the matrix effect that could occur by analyzing soil solution and runoff samples. Dissolved organic and inorganic carbon (DOC/DIC) concentrations were measured with a C-analyzer. A principal component analysis (PCA) was performed on the soil water samples using the R software to help interpreting all the analyses and discriminating the observations made in the two different parcels. In order to determine the surface runoff/throughflows ratio, a mass balance was done for both surface runoff and soil solution samples of parcel 2 (surface = 845 m^2). As glyphosate was applied only under the grapevine rows, the initial quantities correspond to half of the surface. The mass (M) of glyphosate and AMPA were obtained by multiplying the concentrations (C) with cumulative precipitations that fell on the parcel surface between two sampling events (mmINT): M [g] = C [g/L] × mmINT [L].

Table 8.5-24: Quantities of applied product and application dates

Parcel	Product	Quantity (L/ha)	Active Ingredient (A.I)	A.I. applied [g/ha]	Application date
1, 2	Glyfos® [1]	3	Glyphosate, isopropyl amine salt	1080	20 April 2010 15 April 2011

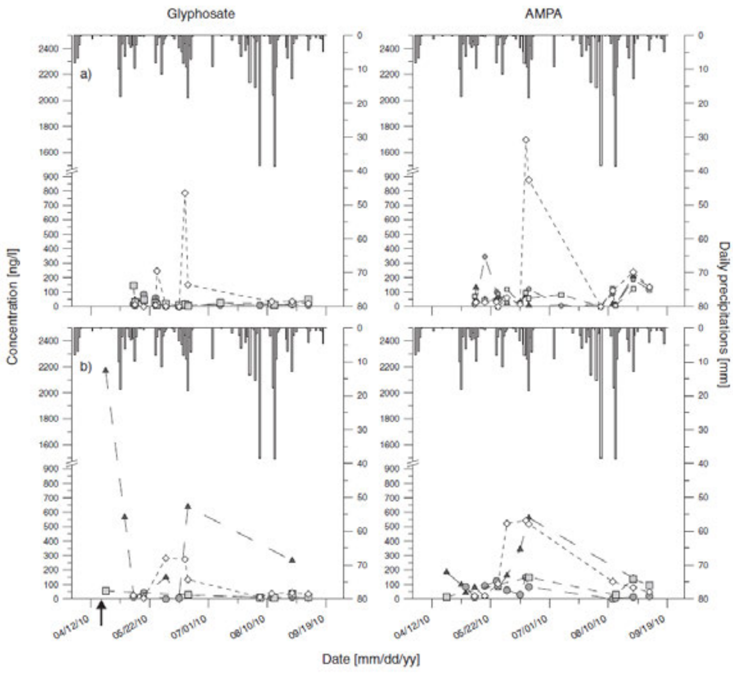
[1]® Cheminova Inc., Lenvig, Denmark

Results and discussion

Soil water samples

Soil water samples had in general pH values between 7.3 and 8.4 and electrical conductivities (EC) between 300 and 550 µS/cm (Figure 8.5-11). Higher range of values was observed at 20 cm in parcel 1 and at 60 and 80 cm in parcel 2, with pH and EC values of 8.4–9 and 450–700 µS/cm, respectively. This certainly reflects the presence of throughflows deep in the profile as previously observed. Dissolved organic carbon (DOC) contents varied in general between 2 and 10 mg/L, except in parcel 2 at 20 cm, where they were between 7 and 24 mg/L. Inorganic carbon (DIC) concentrations were found between 35 and 60 mg/L, with slightly higher values at 80 cm in parcel 2 (between 60 and 75 mg/L). Ion analysis revealed a calcium-dominated composition, with variable magnesium, sodium, nitrate and sulphate contents (data not shown). The variability for the latter was certainly due to the application of sulphur in the two parcels to prevent fungal diseases. A surprising difference in HCO_3^- discriminated samples from the two parcels, with high content for half of the samples from parcel 1 and very low ones for the others. For both parcels, in 2010, glyphosate and AMPA in soil solution were generally found at concentrations higher than 300 ng/L only at 20 and 80 cm (Figure 8.5-12).

Figure 8.5-12: **Growing season 2010. Concentrations of glyphosate and AMPA in soil solution at the bottom of parcel 1 (a) and 2 (b), at 20(♦), 40(□), 60(●) and 80 cm(▲) for the period April–September 2010. The black arrow indicates the date of glyphosate application and the daily precipitations are shown as bars (scale at the right side of the graph).**



In 2011, much higher concentrations were observed, especially in the surface layers: up to 4.7 and 1.75 µg/L at 20 cm in parcel 1 and 12 and 6.5 µg/L at 40 cm in parcel 2, respectively (Figure 8.5-13). Concentration peaks were always related to cumulative rainfall during the previous days, leading to the observed punctual water logging at the surface of this parcel. The succession of important rainfall events in August (>10 mm/day) in the end, induced the presence of AMPA at all depths, revealing a higher mobility than for glyphosate, despite its lower water solubility. In 2011 (Figure 8.5-13a), glyphosate concentrations were in general higher at 20 and 60 cm than at 40 and 80 cm, but only the 20 cm-samples exhibit concentrations at the µg/L level in April-May. Glyphosate concentrations in the 60 cm samples decreased with time, but showed important variations, from 50 to 700 ng/L, linked to important rain events. They first decreased from 700 to 100 ng/L and then re-increased in mid-May to up to 500 ng/L and also in late June up to 400 ng/L. AMPA concentrations in parcel 1 at the same depth showed similar variations, but in contrast, often increased with time (Figure 8.5-13a). Important rain events of more than 20 mm in one day, such as the one of early June, induced also a rise in concentrations at 40 and 80 cm. Furthermore, a much more important increase in concentrations was noticed at 80 cm than with more than 40 mm precipitation in two days, such as on June 17 to 18. Concerning the infiltration processes in parcel 1, the important rainfall events of June 2010 seem to have significantly leached the soil surface layer, desorbing in part glyphosate and AMPA molecules. In parcel 2, in 2010 (Figure 8.5-12b), the highest concentration of glyphosate in soil solution (2170 ng/L) was found at 80 cm depth, two days after its application (22 April 2010).

The gradual rise observed in AMPA concentrations in parcel 2 in June 2010 at 80 cm depth (Figure 8.5-12b) suggests an increasing water saturation of the soil pore space, and certainly the further use of preferential pathways by the soil solution in this parcel. In contrast to parcel 1, the occurrence of these peaks at 80 cm is certainly explained by the steeper hillslope, which represents, with the presence of more impervious reddish marls remnants in the subsoil, favourable conditions for the formation of lateral water circulation within the unsaturated zone. In 2011, still in parcel 2 (Figure 8.5-13b), a surprisingly high concentration peak of glyphosate in late July and a corresponding one of AMPA in early August was noticed at 40 cm. This could reflect either a second application in the neighbourhood parcels or a change in the pore system at this depth, with different inferred water pathways. Figure 8.5-14 shows glyphosate and AMPA concentrations as a function of cumulative rainfall between two sampling periods. In general, with the exception of highly concentrated samples (>2.5 µg/L) and the effect of degradation with time, cumulative rain fall seem to govern glyphosate and AMPA concentration dynamics in the vadose zone in the following way: 1) cumulative rainfalls up to 10 mm decrease herbicide concentrations due to a dilution effect, 2) quantities between 10 and 30 mm lead to a concentration rise, certainly due to an increase in the kinetic energy of the soil solution, with the consequent formation of preferential flow in the parcels with colloid-associated transport, and 3) from 30 mm of cumulative rainfall, the increased surface runoff and dilution are responsible for the decrease in concentration.

Figure 8.5-13: Growing season 2011. Concentrations of glyphosate (left) and AMPA (right) in soil solution at the bottom of parcel 1 (a) and 2 (b), at 20(♦), 40(□), 60(●) and 80 cm(▲) for the period April–September 2011. The black arrow indicates the date of glyphosate application and the daily precipitations are shown as bars (scale at the right side of the graph).

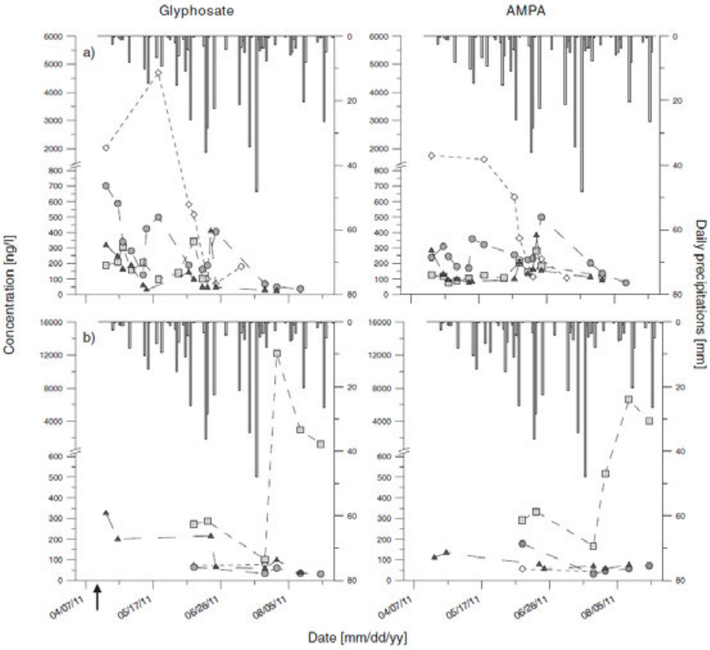


Figure 8.5-14: **Influence of cumulated rainfall between two samples on glyphosate (●) and AMPA (□) concentrations in soil waters of both vineyard parcels. Three phases can be distinguished. 1: An important decrease due to a dilution effect, 2: At medium rainfall, an important increase due to preferential flows and colloid associated transport and 3: At cumulated rain amounts greater than 30 mm, a levelling-off decrease, due to the combined effect of increased surface runoff and dilution.**

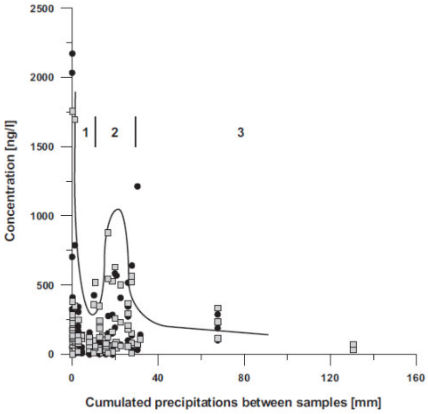
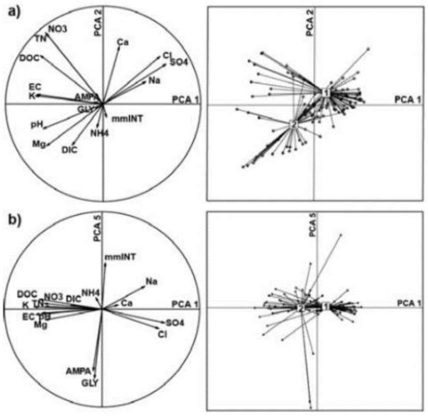


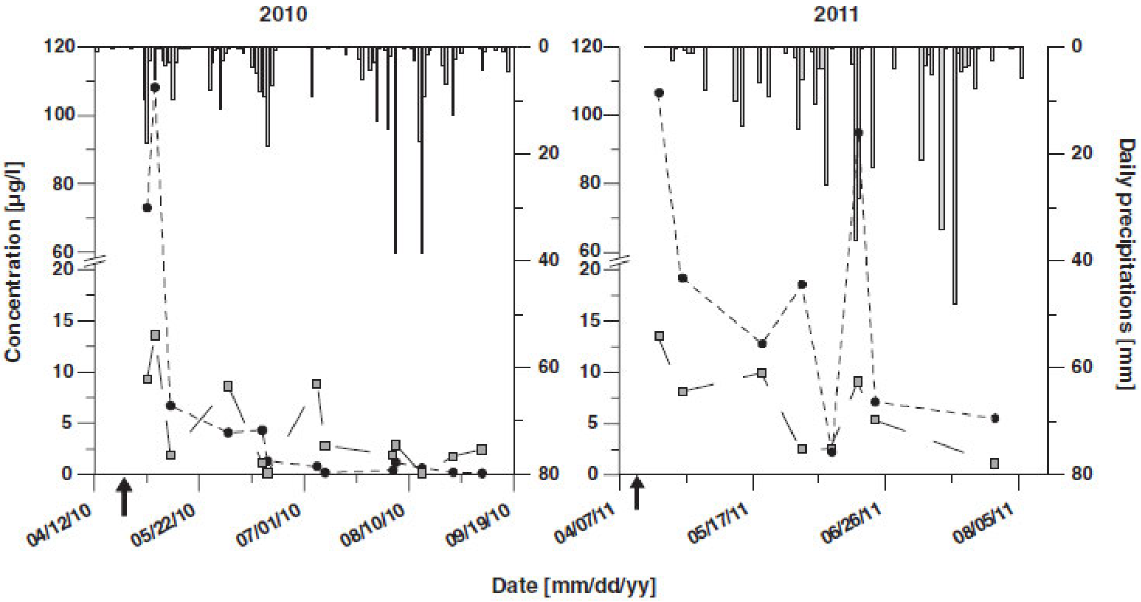
Figure 8.5-15: **Principal Component analysis (PCA) done with R-software on different normalized parameters of the soil water samples: a) correlation circle and projection of the different parameters on the 1st (X) and 2nd (Y) component axis diagram, accounting for 40.8% of the variance, and relative positions of the observations with parcels as gravity centres; b) Idem on the 1st (X) and 5th (Y) component axis diagram, accounting for 32.4% of the variance.**



Surface runoff water

Runoff water samples collected in parcel 2 showed pH between 8.3 and 8.7 and electrical conductivity between 50 and 105 µS/cm. In 2010, high concentrations of glyphosate and AMPA were found in the two first unfiltered (but decanted) runoff samples after the application (Figure 8.5-16): 73 and 110 µg/L, respectively 9 and 14 µg/L. This result is in agreement with the relatively high concentration found (567 ng/L) in the soil solution at 80 cm for the same period (05/05/10). Glyphosate concentrations dropped down to 7 µg/L in May and then to 4 µg/L in early June, before decreasing to 1 µg/L after the succession of rainy days in mid-June.

Figure 8.5-16: **Runoff of parcel 2. Glyphosate (•) and AMPA (□) concentrations in unfiltered, but decanted runoff water samples in 2010 (left) and 2011 (right); the black arrow again indicates the date of glyphosate application and the daily precipitations are shown as bars (scale at the right side of the graph).**



For AMPA, the decrease in concentrations was less drastic, what can be explained by the fact that it is assumed to be constantly produced by glyphosate degradation. The high concentration (~9 µg/L) observed in early July occurred after only one rainy day after a dry period that probably allowed Soil microorganisms to decay glyphosate into AMPA more actively. In 2011, concentrations were in the same range of values and their decrease was also observed, but to a lower extent. In contrast to 2010, AMPA concentrations were never higher than those of glyphosate. At the end of June, high concentrations were observed again with 95 µg/L of glyphosate and 9 µg/L of AMPA. These values are in same range than right after the application in late April, revealing an application on neighbourhood parcels. Indeed, the important rainfall of more than 40 mm in two days induced certainly a huge runoff, possibly passing across the road situated above the parcel, and penetrating it. In order to determine whether glyphosate and AMPA were transported in the dissolved state or bound to soil particles, a syringe filtration (Nylon filters) of runoff samples was made: the fraction <0.45 µm still carried between 70 and 90% of the total concentration, with medians of 78% and 73% for glyphosate and AMPA respectively (n = 10, data not shown). Thus, transport of glyphosate and AMPA associated to coarse particle (>0.45 µm) accounted for 20–30%, which is more than in previous studies despite a smaller cut-off (0.24 µm).

Mass balance

The total amount of glyphosate and AMPA retrieved in both type of samples from parcel 2 (surface = 845 m^2), and likely to be exported from it, was 4.3 g in 2010 and 9.1 g in 2011 (Table 8.5-25). This represents respectively 10 and 20% of the initial amount, which, despite the uncertainty of such kind of calculations, is in agreement with previous studies. The 80–90% remaining were either retained, and possibly as bound residues after some time, or degraded in the soil, as volatilization is not likely to happen due to their properties. The relative contribution of throughflows in the unsaturated zone versus surface runoff in our case was 3–5% versus 95–97%.

Table 8.5-25: Mass balance for glyphosate in parcel 2 for both growing seasons, with amounts retrieved in both types of samples, soil solution and surface runoff, according to cumulated precipitations, as well as percentages of the applied amount and of the relative contribution of throughflows and surface runoff. One g of AMPA was considered arising from 1g of glyphosate.

Year	Applied amount [g]	Soil water [g]	[%]	Runoff [g]	[%]	Throughflows [%]	Runoff [%]
2010	45.6	0.145	0.32	4.179	9.16	3.36	96.64
2011	45.6	0.466	1.02	8.659	18.98	5.10	94.90

Conclusion

This study presents clear evidence for the mobility of the herbicide glyphosate and its metabolite AMPA in the vadose zone despite their high sorption abilities. Though the chemistry of soil solution does not play an important role in their transport, which was mainly governed by the rainfall regime and soil permeability, the presence of copper and the alkaline pH conditions in the studied vineyard soils certainly participate in their mobility by influencing their sorption. Thus, in fine-textured layered soils with significant slope, the increase in moisture content leads to the formation of throughflows just above the more impervious layer, which actively participate in the downhill transport of glyphosate and AMPA. Nevertheless, their transfer from fields to adjacent surface water happens mainly by surface runoff, in a dissolved state or bound to small colloids, representing potential threats for aquatic organisms.

Assessment and conclusion by applicant:

The article reports the mobility of glyphosate and AMPA in soil after application of the parent to a vineyard soil in Switzerland. The maximum reported soil pore water concentrations were <14 µg/L and <8 µg/L (inferred from figure) for glyphosate and AMPA, respectively. The loss to surface waters via surface runoff and throughflows in soils with subsequent exfiltration to surface waters was considered.

The reported parameters are insufficient to allow a complete assessment of the validity of the study.

The article is therefore considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with Applicant conclusions. The results can only be read on the graphs (except from those reported in the text) and are measures through the soil profile (pore water concentration) at 20, 40, 60 and 80 cm depth, which cannot be compared to risk assessment PEC and ecotox RAC.

The study is considered reliable with restrictions.

B.8.5.3. Monitoring data in ground water

New studies/assessments

Data point:	CA 7.5/001
Report author	[redacted]
Report year	2020
Report title	Collection of public monitoring data for European countries for the compartments soil, water, sediment and air for Glyphosate, AMPA and HMPA
Document No	110057-1
Guidelines followed in study	Methodology is based on the Groundwater Monitoring guideline document (Gimsing *et al*., 2019) with respect to chapter 7 (‘Public monitoring data collected by third party organisations’) Minimum quality criteria of monitoring data described by the FOCUS Ground Water Work Group chapter 9.5 (European Commission, 2014)
Deviations from current test guideline	None
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

The report provides information about the outcome of a search for readily accessible and available monitoring data in European countries at a regional/national level for the time period 1995-2019. The main focus was on the time period 2012-2019 while earlier years are already covered by existing data. The search included raw data, requested from regional/national authorities or downloadable from their websites, as well as aggregated data extracted from reports compiled by authorities.

Data from 14 European countries were considered: Austria, Belgium, Denmark, France, Germany, Hungary, Ireland, Italy, The Netherlands, Poland, Romania, Spain, Sweden and the United Kingdom. The countries represent the major markets of products containing glyphosate sold in the EU. The data compilation included the active substance glyphosate and its metabolites AMPA and HMPA, in the soil, groundwater, surface water, tidal water, drinking water, sediment and air environmental compartments.

As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities and other bodies of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were not actually included in any of the monitoring programs.

Groundwater Compartment Conclusion
A large groundwater public monitoring dataset was compiled, comprising raw datasets from 11 countries (AT, BE, DE, DK, ES, FR, IE, IT, NL, SE and UK) and aggregated datasets from published reports for 9 countries (AT, DE, DK, ES, HU, IE, IT, NL, SE). Collectively these cover a wide range of pedoclimatic and hydrogeological settings typically spanning more than a decade.

I. MATERIAL AND METHODS

The general methodology of data collection of public monitoring data and minimum quality criteria is based on existing guideline documents for groundwater monitoring programs. The underlying principles have been applied to all environmental compartments, especially where no specific guidance is at hand. Data search, acquisition and processing approaches are described below. The same approach was applied for each country, compartment and substance. Country specific adaptations to the general procedure were made

in order to generate a harmonized database. The data collected for this report refers to third party organization data regarding all environmental compartments (SOIL, GW, SW, TD, DW, SD, AIR) and was further differentiated into the two different data types, i.e. raw data and aggregated data. Aggregated data refers to information provided in publicly available reports, e.g. from environmental agencies or research institutes. Such reports might hold only summary information on substance findings over space and time and may intersect with the raw data. Raw data refers to mid to long term time series of data that are provided on request by e-mail or by database from governmental authorities and are therefore recognized as official monitoring data. These datasets hold the information of sampling values, quality information (sampling, treatment, limit of detection - LOD, limit of quantification - LOQ) as well as information of location and time of sampling.

The following data source types were investigated in order to collect monitoring data:

- E-mail requests: a general e-mail was sent to the national responsible authorities with regard to the required information.

- Governmental webpages: the official webpages of the national responsible authorities were searched for information regarding available reports and datasets.

- Public online databases: available data from online databases were downloaded as provided by the webpages of governmental authorities and other institutions.

The data search resulted in a very heterogeneous collection of tabular data and reports in different formats and structure. Data were processed into a harmonized tabular format by selecting relevant information and adapting data organisation. In general, the complete datasets were included in the final harmonized database as provided by the authorities, but obvious duplicates were deleted. In general, all entries for the digital database were checked for consistency and plausibility. For the raw data it was assumed that information was already subjected to critical scrutiny by the respective organization. For the aggregated data the same assumption was made with quality assurance of the data (mostly summaries) being the responsibility of the authors of the respective reports.

II. RESULTS AND DISCUSSION

The final data collection of raw data and aggregated data is summarised for each compartment and each country in Table 8.5-26.

Groundwater

- Austria (AT)
    - Raw monitoring data from national authorities for groundwater were downloaded from the H2O-Fachdatenbank.
    - Aggregated monitoring data from reports published by national authorities for groundwater were downloaded from several sources.

- Belgium (BE)
    - Raw monitoring data for groundwater for both Flanders and Wallonia compiled by the Belgian association for the plant protection products industry were received by e-mail.
    - No aggregated monitoring data from reports published by national authorities were considered in case of the compartment groundwater, because of the good data availability *via* raw data.

- Germany (DE)
    - Raw monitoring data from national authorities for groundwater were provided by the German EPA, the regional authorities of Brandenburg, Bavaria, Bremen, Mecklenburg-

    - Vorpommern, North Rhine – Westphalia, Schleswig-Holstein, Saxony, Saarland and Hesse.
    - Aggregated monitoring data from reports published by national authorities were obtained from LAWA, the German parliament, from the German EPA, and the environmental authorities of Mecklenburg-Vorpommern, North Rhine – Westphalia, Rhineland-Palatinate and Schleswig-Holstein.

- Denmark (DK)
    - Raw monitoring data from national authorities for groundwater were provided by GEUS from the GRUMO monitoring programme.
    - Aggregated monitoring data from reports published by national authorities for groundwater were downloaded from GEUS and the National Center for Environment and Energy.

- Spain (ES)
    - Raw monitoring data from national authorities for groundwater were provided from the Ministry of Agriculture, Fisheries and Food after contacting the Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA) per e-mail.
    - Aggregated monitoring data from reports in one scientific paper published by the Spanish Geological and Mining Institute.

- France (FR)
    - In France monitoring data for groundwater are published by the Public Water Information Service (eaufrance). Raw monitoring data from national authorities for groundwater were downloaded from ADES.
    - No aggregated monitoring data from reports published by national authorities were considered, because of the very good data obtained *via* raw monitoring data.

- Hungary (HU)
    - Raw monitoring data from national authorities for groundwater were not available.
    - Aggregated monitoring data from reports published by national authorities for groundwater were obtained in the form of a peer-reviewed paper from the National Agricultural Research and Innovation Centre published in Journal of Chemistry.

- Ireland (IE)
    - Raw monitoring data from national authorities for groundwater were provided by the Irish EPA by e-mail.
    - Aggregated monitoring data from reports published by national authorities for groundwater were downloaded from the Irish EPA and from the governmental page on the Water Framework Directive.

- Italy (IT)
    - Raw monitoring data from national authorities for groundwater were downloaded from the provincial environment agency of Lombardia.
    - Aggregated monitoring data from reports published by national authorities for groundwater were downloaded from ISPRA.

- The Netherlands (NL)
    - Raw monitoring data from national authorities for groundwater were obtained in the form of the stand-alone software tool “Groundwater Atlas for pesticides in The Netherlands”.
    - Aggregated monitoring data from reports published by national authorities for groundwater were downloaded from RIVM and the Dutch Water Quality portal. Further reports were downloaded from Wageningen University & Research.

- Poland (PL)

    - The responsible authorities for monitoring data in Poland are the Polish Geological Institute and the Chief Inspectorate Of Environmental Protection. The latter authority confirmed by e-mail that in Poland there is currently no public monitoring of glyphosate or its metabolites in groundwater.

- Romania (RO)
    - The responsible authority for monitoring data is the Ministry of Water and Forests. The Water Resources Management Directorate confirmed on behalf of the Ministry of Water and Forests that no public monitoring of glyphosate or its metabolites is carried out in any water compartment in Romania.

- Sweden (SE)
    - Raw monitoring data from national authorities in Sweden for groundwater were provided by SLU (Swedish University of Agriculture) via e-mail. Additional raw monitoring data for groundwater were directly downloaded from the SLU homepage. Moreover, SLU provided another database containing raw data for groundwater issued from other sources than national monitoring, e.g. regional monitoring and private wells.
    - Aggregated monitoring refer to a report downloaded with aggregated groundwater monitoring data from the environment department of the municipality of Stockholm and aggregated national monitoring reports in tabular form for groundwater downloaded from the SLU homepage.

- United Kingdom (UK)
    - Raw monitoring data from national authorities for groundwater were downloaded from the Environment Agency for England and Northern Ireland *via* e-mail.
    - No aggregated monitoring data from reports were identified.

Table 8.5-26: **Overview of public monitoring data availability of raw data (R) and aggregated data (A)**

Country	**Soil**	**Water**				**Sediment**	**Air**
		Ground	**Surface**	**Tidal**	**Drinking**		
Austria	-	R, A	R, A	-	A	-	-
Belgium	-	R	R	-	A (Flanders)	-	-
Denmark	-	R, A	A	-	A	-	-
France	-	R	R	-	A	R	-
Germany	R (Brandenburg)	R, A	R, A	R	R (Schleswig-Holstein), A	-	-
Hungary	-	A (one research article)	A (one research article)	-	-	-	-
Ireland	-	R, A	R, A	-	R, A	-	-
Italy	-	R (Lombardia), A	R, A	-	-	-	-
The Netherlands	-	R, A	R, A	-	R	-	-
Poland	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Romania	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Spain	-	R, A	R, A	-	A	-	-
Sweden	-	R, A	R	-	R, A	R	-
UK England	-	R	R	R	A	-	-
UK Northern Ireland	-	R	-	-	-	-	-
UK Scotland	-	-	R	-	-	-	-
UK Wales	-	-	R	-	A	-	-

R raw data available; A aggregated data from reports available; - no raw or aggregated data available

III. CONCLUSIONS

The collection of public monitoring data for glyphosate, AMPA and HMPA in soil, groundwater, surface water, drinking water, tide water, sediment and air resulted in a comprehensive database of 'raw monitoring data from national authorities' and 'aggregated monitoring data from reports published by national authorities'. As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were not actually included in any of the monitoring programs.

A large groundwater public monitoring dataset was compiled, comprising raw datasets from 11 countries (AT, BE, DE, DK, ES, FR, IE, IT, NL, SE and UK) and aggregated datasets from published reports for 9 countries (AT, DE, DK, ES, HU, IE, IT, NL, SE). Collectively these cover a wide range of pedoclimatic and hydrogeological settings typically spanning more than a decade.

Assessment and conclusion by applicant:
The study describes the collection process of public monitoring data for European countries for the compartment soil, water, sediment and air for Glyphosate, AMPA and HMPA.
The study is therefore considered valid.

Assessment and conclusion by RMS:
This report describes the methodology employed for collection of monitoring data for Glyphosate, AMPA and HMPA. The data collection refers to third party organization data regarding all environmental compartments (Soil, GW, SW, TD, DW, SD, AIR), as described for GW in FOCUS 2014 and Gimsing *et al.* 2019. Two different data types were collected, *i.e.* raw data from national authorities and aggregated data from publicly available reports (from environmental agencies or research institute).

The general search strategy was similar for each compartment, country and substance. All details of data acquisition are given in the report, and all data sources are carefully listed and described.
Although the process can clearly not be reproduced, and cannot be checked in details for exhaustiveness, the search strategy is clearly exposed and considered acceptable.

For groundwater compartment, data from 14 countries were considered. Raw data set from 11 countries (AT, BE, DE, DK, ES, FR, IE, IT, NL, SE and UK) and aggregated data from 9 countries were eventually collected AT, DE, DK, ES, HU, IE, IT, NL, SE). Three countries confirmed (PL, HU and RO) that the target substances are not including in national monitoring programs.

Findings from this data collection and corresponding analysis are given in a separate report; see [redacted] [redacted] 2020 below.

The study (groundwater part) is considered acceptable.

Data point:	CA 7.5/002
Report author	[redacted]
Report year	2020
Report title	Glyphosate (GLY) and the primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA): Public monitoring data assessment and interpretation
Report No	EnSa-20-0322
Document No	-
Guidelines followed in study	Groundwater monitoring guideline document (Gimsing *et al.*, 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations'); Article 5 of Directive 2009/90/EC - Technical specifications for chemical analysis and monitoring of water status.
Deviations from current test guideline	Not relevant
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary
The report provides information about the outcome of an analysis of public monitoring data comprising environmental concentrations of glyphosate (GLY) and its primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA) collated from readily available public

monitoring databases held by national/regional environment agencies. This data collection and analysis was designed to expand previous reviews to include other compartments and supplement them for surface water, groundwater and drinking water. Public monitoring data from the following Member States (MS) were assessed for the water, sediment and soil compartments: Austria (AT), Belgium (BE), Denmark (DK), France (FR), Germany (DE), Ireland (IE), Italy (IT), Netherlands (NL), Spain (ES), Sweden (SE) and the United Kingdom (UK). Three MS, namely Poland (PL), Hungary (HU), and Romania (RO) confirmed that they do not conduct analyses for GLY, AMPA and HMPA in any environmental compartment. No data for HMPA was identified for any MS or compartment. Note that at the time the study was started the UK was a Member State and is referred to as a Member State throughout the report.

Analyses of the large spatial and temporal dataset of measured concentrations occurring in several environmental compartments, namely surface water, groundwater, drinking water, tidal water, sediment and soil, were conducted to assess their state. This analysis not only sought to assess the state of the environmental compartment but also to consider the potential impacts this might have on biota, ecosystems and human health by using regulatory endpoints and thresholds from a range of European (EU) Directives. These included the Water Framework Directive (Directive 2000/60/EC) and associated Groundwater (2006/118/EC), Drinking Water (1998/83/EC) and Priority Substances (2008/105/EC28) Directives in addition to the Plant Protection Products Directive (1107/2009/EC).

Groundwater

Groundwater (GW) data from AT, BE, DE, DK, ES, FR, IE, IT, NL, SE and UK were analysed for compliance with a range of regulatory endpoints and thresholds. The data were assessed against the following regulatory endpoints, 0.1 µg/L for GLY and the arbitrarily defined 10 µg/L for AMPA (for which there is no legal limit as AMPA is a non-relevant metabolite). In addition, case study investigations were conducted in ES and UK to investigate atypical elevated frequencies of detection.

Glyphosate

The large GLY public monitoring dataset (>251 000 samples collected from >37 800 sampling sites) was dominated by French data (~79.1%) with smaller contributions from Denmark (~5.8%), Germany (~5.7%) and Austria (~3.8%). Detection of GLY in GW samples was ~2% which compared well with the 1.3% of samples in the previous data collection ([redacted], 2012, CA 7.5/013 and 2016, CA 7.5/010). Compliance with the 0.1 µg/L threshold was very high (99.4% samples from 97% of sites) with very few exceedances (~0.6% of samples from ~3.0% of sites) and compared well with aggregated report values (ranging from 0.0% in DE to ~7.0% in ES) and the 0.6% of samples from the previous data collection. Only 0.089% of samples are consecutively above the threshold indicating the rare exceedances are non-systematic. The assessment of outliers identified 10 outliers in the dataset and if these are excluded the maximum concentration is reduced to 39.2 µg/L which is well below the SW RAC (for groundwater fed ecosystems) and the life time health-based ADI concentration of 1500 µg/L. Case studies exploring elevated rates of groundwater detection in ES and the UK, suggest these findings are most likely a function of direct contamination, like spray drift into open wells.

AMPA

The large AMPA public monitoring dataset (>230 000 samples collected from >34 400 sampling sites) was dominated by the French data (~82.4%) with smaller contributions from Denmark (~6.4%) and Germany (~5.2%). Detection of AMPA in GW samples was ~2.9% which compared well with the ~2.1% of samples in the previous data collection. Compliance with the arbitrarily defined 10 µg/L regulatory threshold for a non-relevant metabolite was very high (99.998% of samples from 99.994% of sites) given exceedances were rare (~0.002% of samples from ~0.006% sites). The maximum concentration of 16 µg/L is well below the SW RAC (for groundwater fed ecosystems) and the lifetime health-based ADI concentration of 3960 µg/L. It should be borne in mind that AMPA may originate from sources other than GLY, for example detergents. In order to compare these AMPA results with previously published and aggregated results, assessment against the threshold of 0.1 µg/L was also undertaken. Compliance with the arbitrarily defined regulatory threshold of 0.1 µg/L was very high (99.3% of samples) with few exceedances (~0.7% of samples) indicated, which compared well with aggregated report exceedance (ranging from 0.0% in SE to ~3% in the IT) of ~0.75% of samples from the previous data collection.

Groundwater Compartment Conclusion

The analysis of the large groundwater dataset for GLY and AMPA indicates they are both occasionally detected above the LOQ in this compartment, however, compliance against regulatory endpoints and thresholds is very high with the frequency of exceedance being very low as would be expected given that the compounds are only slightly mobile in soil. The environmental concentrations typically encountered do not pose a risk for ecosystems or human health from drinking water.

I. MATERIAL AND METHODS

The dataset analysed comprised individual groundwater analysis records as well as existing aggregated analyses extracted from reports sourced from regional/national environment agencies (see [redacted], 2020, CA 7.5/001). The approach taken for the data processing was precautionary in that it preserved samples in the analysis where there was any doubt regarding their reliability. As such the number of records excluded from the analysis was small, especially relative to the total number of samples prior to removal. Similarly, no attempt to remove outliers was undertaken despite the presence of extreme values in the datasets. In order to explore the extreme nature of some of the values included in the groundwater dataset and assess the implications for this analysis, an outlier analysis was performed on the combined EU dataset using the same approach as the European Commission's Joint Research Centre (JRC) in the evaluation of candidate compounds for the priority substance watch list (Carvalho *et al.*, 2016). Analysis and assessment of the data against thresholds was undertaken using the statistical software R (R Core Team, 2019) and graphs produced with the R package ggplot2 (Wickham, 2009). The groundwater public monitoring data was evaluated against the following thresholds:

- Drinking water endpoint: A threshold of 0.1 µg/L for parent compounds and relevant metabolites was used for GLY
- Regulatory threshold: The arbitrarily defined threshold of 10 µg/L for non-relevant metabolites was used for AMPA;
- Drinking water threshold: An additional threshold of 0.75 µg/L for AMPA is also presented. This threshold is based on the tiered testing requirements given in the guidance document on non-relevant metabolites (SANCO 221/2000 rev.10) above which data to set a lifetime safe drinking water limit is required to be obtained. The lifetime safe drinking water limits for glyphosate and AMPA are 1500 µg/L and 3960 µg/L, respectively.

II. RESULTS AND DISCUSSION

The input data collated for analysis of GLY residues in GW were dominated by data sourced from France (~79.1%) with smaller contributions from Denmark (~5.8%), Germany (~5.7%) and Austria (~3.8%). This pattern was also apparent for AMPA residues with French data dominating the combined dataset (~82.4%) with lower, but important contributions from Denmark (~6.4%) and Germany (~5.2%). As such the French dataset is likely to influence statistics and conclusions derived from analysis and consideration of the combined European dataset. The exact nature of a groundwater body and how these are sampled is not generally known from the publicly available data, e.g. how deep the groundwater is or the manner in which it is sampled e.g. piezometer, borehole, well or spring. It is not typically known what the groundwater from these locations is used for or why the water at this location was selected for monitoring. Temporally the GLY (see Figure 8.5-17) and AMPA (see Figure 8.5-18) data indicates some bias at a MS level with fewer samples typically collected in the winter and spring months resulting in a unimodal distribution, e.g. IE, or a bimodal distribution with data collection in spring and autumn during key usage periods being greater than at other times of the year, e.g. FR, DE, NL, SE. The spatial distribution of GLY and AMPA public monitoring locations for MS where data is collected is biased (see Figure 8.5-19 and Figure 8.5-20). For some MS, e.g. DE, IT and ES, this is a function of data only arising from some provincial/regional environment agencies while for others, e.g. the UK, this is likely a function of spatial targeting.

Figure 8.5-17: **Bar chart of monthly groundwater glyphosate (GLY) sampling effort**

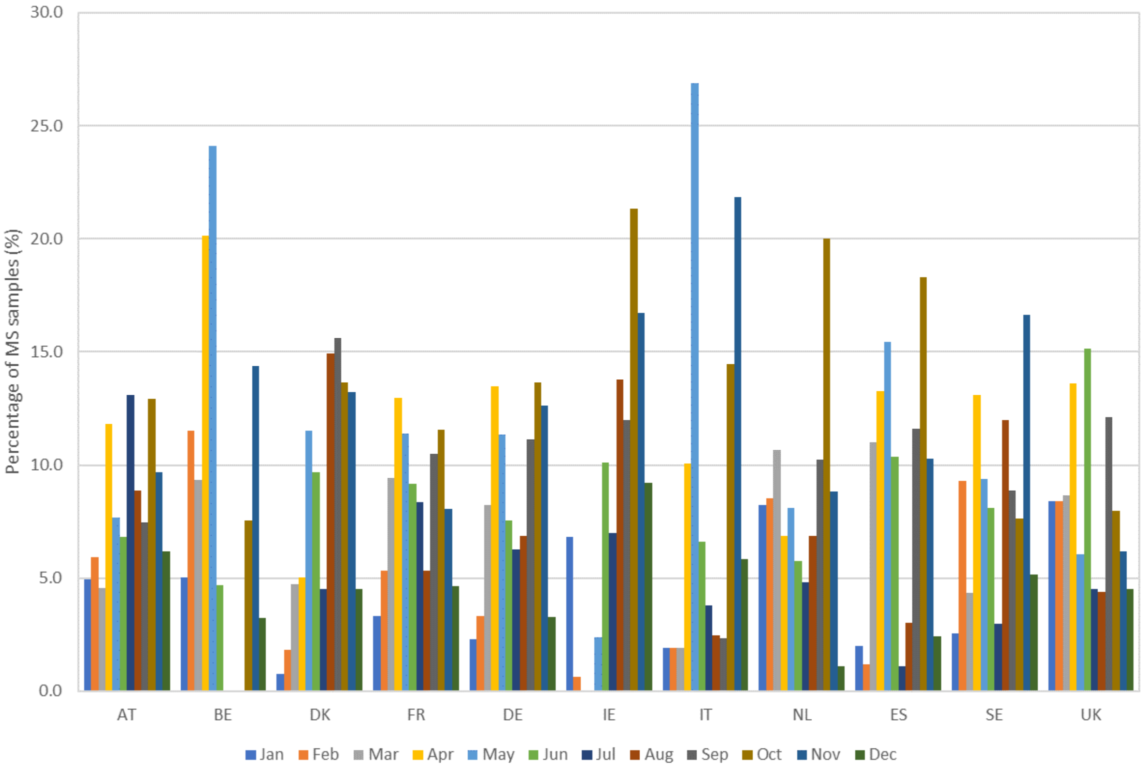


Figure 8.5-18: **Bar chart of monthly groundwater AMPA sampling effort. No data is available for AT, IE and UK.**

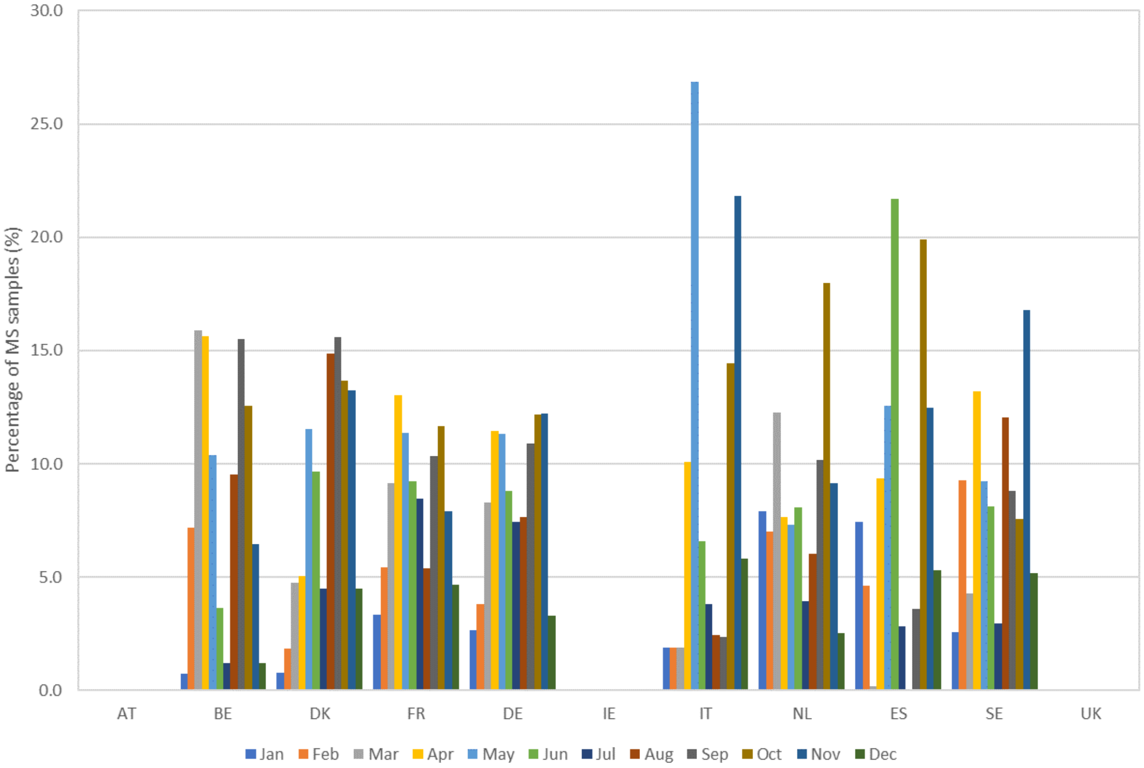


Figure 8.5-19: **Map illustrating the distribution of glyphosate (GLY) groundwater sampling locations. Also illustrated are the number of exceedances of the GW regulatory concentration at each location.**

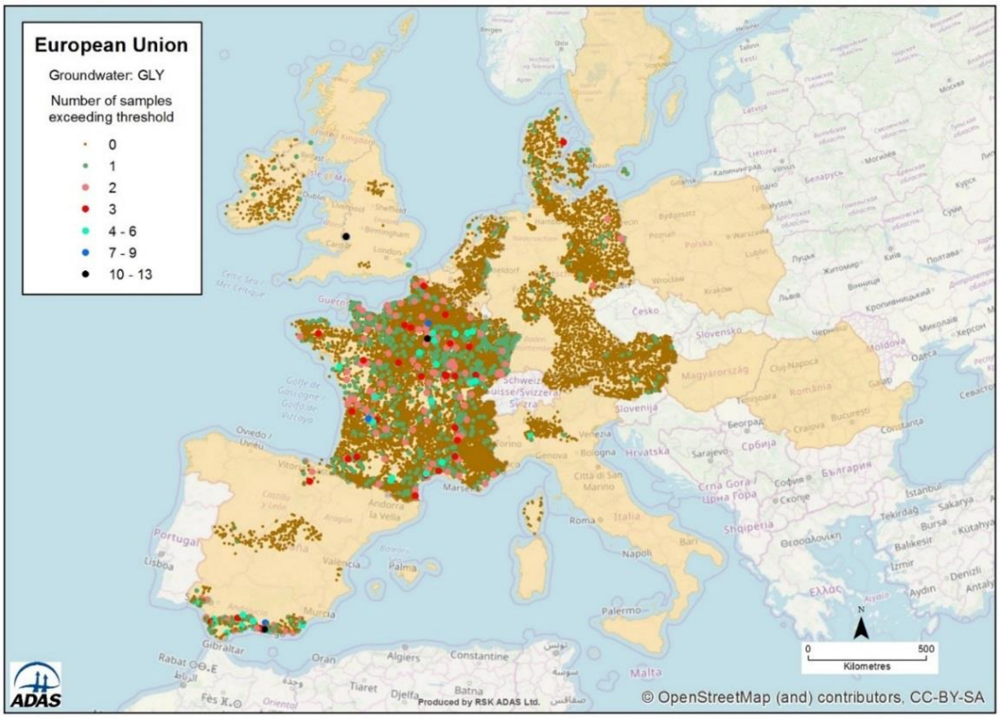
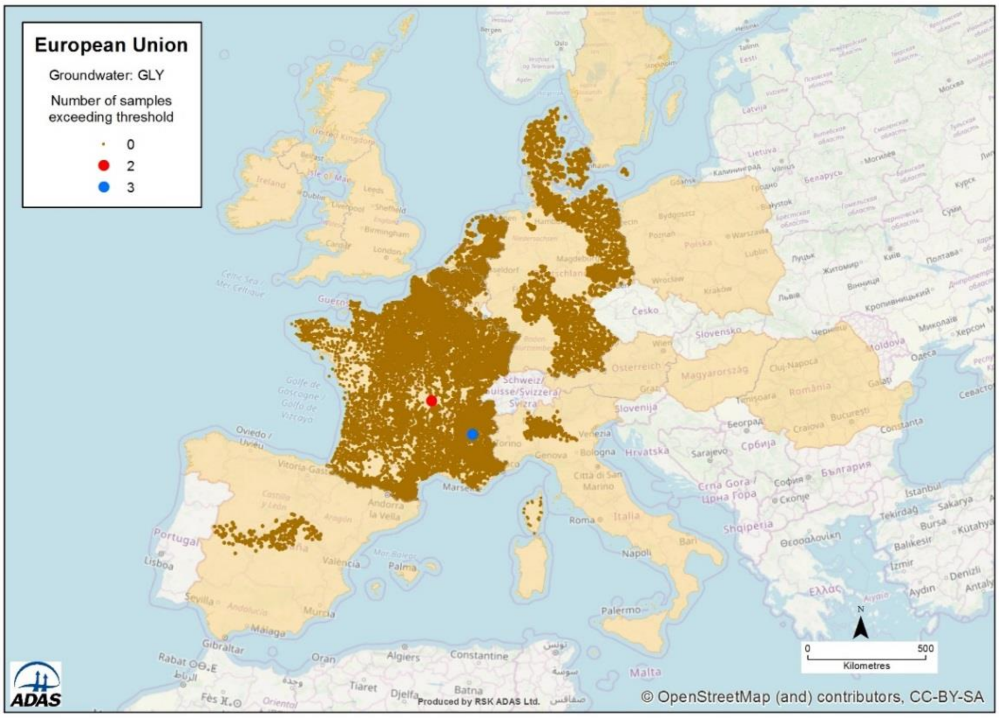


Figure 8.5-20: **Map illustrating the distribution of AMPA groundwater sampling locations. Also illustrated are the number of exceedances of the GW regulatory concentration at each location.**



Glyphosate

Across all MS the GLY public monitoring dataset compiled comprised >251 000 samples collected from >37 800 sampling sites (see Table 8.5-27). Detection of GLY in GW was ~2%, ranging from as low as 0.2% in AT to as high as 10.3% in SE, relative to a varying LOQ with an average of 0.06 µg/L (min: 0.01 – max: 100 µg/L). These compare well with the previous data collection ([redacted], 2012, CA 7.5/013 and 2016, CA 7.5/010) where GLY was detected in 1.3% of samples (see Table 8.5-30).

Compliance with the 0.1 µg/L threshold was very high (99.4% samples from 97% of sites) with very few exceedances (~0.6% of samples from ~3.0% of sites) and compared well with aggregated report values (ranging from 0.0% in DE to ~7% in ES; see Table 8.5-28) and the 0.6% of samples from the previous data collection. Consideration of whether these exceedances were consecutive, an indicator of more systematic groundwater quality issues rather than one off events, indicates that only 0.089% of samples (n = 216) are consecutively above the threshold (see Table 8.5-31). The spatial distribution of the GLY exceedance locations (see Figure 8.5-19) does not indicate any specific patterns or bias.

Maximum measured concentrations up to 1005 µg/L are reported, however, these extreme values are likely anomalous. The 99th percentile concentration, the concentration that 99% of samples is below, is 0.19 µg/L (see Table 8.5-29) while the 0.1 µg/L threshold represents the 98.976th percentile concentration. In line with the precautionary data processing approach adopted in this study possible outliers were not removed from the dataset prior to analysis. However, an additional analysis step was conducted to identify likely outliers in the dataset and the implications of these for the analysis assessed. This identified 10 outliers which if excluded, suggest the maximum concentration would be 39.2 µg/L (see Table 8.5-29) which is well below the SW RAC (for groundwater fed ecosystems) and the lifetime health-based ADI concentration of 1500 µg/L.

AMPA

Across all MS the AMPA public monitoring dataset compiled comprised >230 000 samples collected from >34 400 sampling sites (see Table 8.5-27). Detection of AMPA in GW was ~2.9%, ranging from as low as 0.4% in ES to as high as 19.5% in BE, relative to a varying LOQ with an average of 0.05 µg/L (min: 0.01 – max: 5 µg/L). These compare well with the previous data collection where AMPA was detected in ~2.1% of samples (see Table 8.5-30).

Compliance with the arbitrarily defined regulatory threshold of 10 µg/L for a non-relevant metabolite was very high (99.998% of samples from 99.994% of sites) given exceedances were rare (~0.002% of samples from ~0.006% sites, ranging from 0% in BE to ~0.003% in FR; see Table 8.5-28) and occurred on a single occasion (see Table 8.5-31). Compliance with the testing requirement 0.75 µg/L threshold for a non-relevant metabolite was very high (99.93%) given the small number of exceedances (~0.07%, ranging from 0.0% in ES to ~0.8% in FR).

The maximum concentration is 16 µg/L which is well below the SW RAC (for groundwater fed ecosystems) and the lifetime health-based ADI concentration of 3960 µg/L. The 99th percentile concentration, the concentration that 99% of samples is below, is 0.14 µg/L (see Table 8.5-29) while the arbitrarily defined regulatory threshold of 10 µg/L represents the 99.998th percentile concentration. No outliers were identified in the dataset (see Table 8.5-29). It should be borne in mind that AMPA may originate from sources other than GLY, for example detergents, particularly in GW affected by SW or flooding. In order to compare these AMPA results with previously published and aggregated results, assessment against the arbitrarily defined regulatory threshold of 0.1 µg/L was also undertaken. Detection above the threshold of 0.1 µg/L was ~0.7%, ranging from 0.1% in ES to 2.3% in NL. These compare well with the aggregated values extracted from reports (see Table 8.5-28) ranging from 0.0% in SE to ~3% in IT. Similarly, these are comparable with the previous data collection where ~0.75% of samples were found to exceed 0.1 µg/L.

Annual and monthly investigations of sampling effort and compliance were also documented within the report. These have not been summarised as they do not alter the conclusions of the primary study, but instead provide additional detail.

Table 8.5-27: **Member State and combined European dataset public monitoring summaries for glyphosate (GLY) and AMPA in groundwater**

MS	Substance	Number of Sites	Number of Samples	Years	LOQ (µg/L)	Samples with LOQ≤DrW		Detected >LOQ		Detected >0.1 µg/L		Detected >0.75 µg/L		Detected >10.0 µg/L		Measured Concentration (µg/L)
					Mean (min - max)	Sites	Samples	Samples	%	Samples	%	Samples	%	Number	%	Median (min - max)[1]
AT	AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
AT	GLY	2172	9475	2004 - 2014	0 05 (0 04 - 0 06)	2172	9475	22	0 23	14	0 15	NA	NA	NA	NA	0 03 (0 015 - 2 6)
BE	AMPA	599	5540	2008 - 2018	0 01 (0 01 - 0 50)	599	5539	1078	19 46	98	1 77	10	0 18	0	0 000	0 01 (0 000 - 2 6)
BE	GLY	242	278	2008 - 2017	0 01 (0 01 - 0 01)	242	278	1	0 36	0	0 00	NA	NA	NA	NA	0 00 (0 000 - 0 1)
DE	AMPA	3604	11957	1996 - 2019	0 06 (0 01 - 5 00)	3598	11855	1102	9 30	113	0 95	13	0 11	0	0 000	0 03 (0 000 - 6 0)
DE	GLY	4198	14210	1995 - 2019	0 05 (0 01 - 5 00)	4190	14008	948	6 77	40	0 29	NA	NA	NA	NA	0 04 (0 000 - 7 0)
DK	AMPA	1806	14671	1997 - 2018	0 01 (0 01 - 0 50)	1806	14670	122	0 83	28	0 19	7	0 05	0	0 000	0 01 (0 010 - 9 1)
DK	GLY	1806	14681	1997 - 2018	0 01 (0 01 - 1 00)	1806	14671	145	0 99	25	0 17	NA	NA	NA	NA	0 01 (0 010 - 4 7)
ES	AMPA	241	995	2014 - 2017	0 05 (0 05 - 0 05)	241	995	4	0 40	1	0 10	0	0 00	0	0 000	0 05 (0 050 - 0 4)
ES	GLY	650	3869	2008 - 2017	0 05 (0 01 - 0 30)	650	3855	396	10 27	248	6 43	NA	NA	NA	NA	0 05 (0 010 - 9 6)
EU Trans	AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
EU Trans	GLY	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FR	AMPA	26048	190218	2000 - 2019	0 06 (0 06 - 2 00)	25982	183247	3943	2 15	1218	0 66	118	0 06	5	0 003	0 05 (0 000 - 16 0)
FR	GLY	26219	198622	1999 - 2019	0 06 (0 06 - 100)	26140	191114	3204	1 68	1067	0 56	NA	NA	NA	NA	0 05 (0 000 - 1005)
IE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
IE	GLY	227	1584	2007 - 2014	0 01 (0 01 - 0 02)	227	1584	32	2 02	5	0 32	NA	NA	NA	NA	0 01 (0 005 - 0 5)
IT	AMPA	213	893	2015 - 2017	0 10 (0 05 - 0 10)	213	893	16	1 79	16	1 79	7	0 78	0	0 000	0 10 (0 050 - 5 3)
IT	GLY	213	893	2015 - 2017	0 10 (0 05 - 0 10)	213	893	7	0 78	7	0 78	NA	NA	NA	NA	0 10 (0 050 - 3 4)
NL	AMPA	660	1831	1996 - 2016	0 12 (0 01 - 1 00)	586	1309	95	7 26	30	2 29	1	0 05	0	0 000	0 05 (0 010 - 1 3)
NL	GLY	657	1882	1996 - 2016	0 12 (0 02 - 1 20)	592	1370	74	5 40	32	2 34	NA	NA	NA	NA	0 05 (0 015 - 14 3)
SE	AMPA	1328	4876	1996 - 2017	0 28 (0 05 - 1 00)	1324	4656	25	0 54	7	0 15	2	0 04	0	0 000	0 00 (0 000 - 7 9)
SE	GLY	1334	4898	1996 - 2017	0 27 (0 03 - 1 00)	1329	4817	43	0 89	7	0 15	NA	NA	NA	NA	0 00 (0 000 - 0 2)
UK	AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
UK	GLY	124	866	2000 - 2018	0 21 (0 10 - 1 00)	77	727	51	7 02	51	7 02	NA	NA	NA	NA	0 10 (0 100 - 39 2)
EU All	AMPA	34499	230981	1996 - 2019	0 05 (0 01 - 5 00)	34349	223164	6385	2 86	1511	0 68	158	0 07	5	0 002	0 05 (0 000 - 16 0) 0 05 (0 000 – 16 0)[2]
EU All	GLY	37842	251258	1995 - 2019	0 06 (0 01 - 100)	37638	242792	4923	2 03	1496	0 62	NA	NA	NA	NA	0 05 (0 000 - 1005) 0 05 (0 000 – 39 2)[2]

[1] Values <LOQ and <LOD are treated as equal to LOQ and LOD as a precautionary estimate of the median

[2] Statistics with outliers excluded

ND = Non identified within the timeframe

NA – Not applicable

Table 8.5-28: Summary of monitoring data aggregated in reports for glyphosate (GLY) and AMPA in groundwater

MS	Substance	Number of reports identified	Reports with data relating to threshold						Maximum value (µg/L)
			Number of reports	Date range	Number of samples	Threshold (µg/L)	Samples above threshold	% samples above threshold	
AT	AMPA	4	4	2003 - 2015	18928	3	11	0.06	0.75
	GLY	4	4	2003 - 2016	30495	0.1	53	0.17	NS
BE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
DE	AMPA	5	1	2007-2013	764	10	0	0	NS
	GLY	8	1	2007-2013	643	0.1	0	0	0.43
DK	AMPA	2	2	1990-2017	>34854	0.1	>53	0.15/0.34[1]	9.10
	GLY	2	2	1990-2017	>34901	0.1	>70	0.20/0.46[1]	5.00
ES	AMPA	1	1	2000-2000	55	0.1	1	1.8	0.8
	GLY	1	1	2000-2000	55	0.1	4	7.3	0.6
EU Trans	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
FR	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
IE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	1	1	2005-2006	> 52	0.1	0	0	NS
IT	AMPA	8	8	2007 - 2016	>2475	0.1	>74	2.99/2.82[1]	NS
	GLY	8	8	2007 - 2016	>2412	0.1	95	3.94/5.20[1]	NS
NL	AMPA	3	2	2003-2016	1756	0.1	40	2.3	5.12
	GLY	3	2	2003-2016	1756	0.1	19	1.1	5.5
SE	AMPA	1	1	2011-2012	10	0.1	0	0	0.085
	GLY	1	1	2011-2012	10	0.1	0	0	NS
UK	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND

[1] Report data includes sample counts and % values – The first value is the average using count data only while the second is the average of report averages

ND – No data identified; NS – Not specified; > as missing values to calculate total

Table 8.5-29: Summary statistics for glyphosate (GLY) and AMPA groundwater concentration data considering the influence of outliers

Compound	Outlier Status	Concentration (µg/L)										Percentile of 0.1 µg/L	Percentile of 10.0 µg/L	Number of outliers
		Minimum	Mode	25th Percentile	Median	Mean	75th Percentile	90th Percentile	95th Percentile	99th Percentile	Maximum			
GLY	Included	0	0.05	0.03	0.05	0.070	0.1	0.1	0.1	0.19	1005	98.756	NA	NA
	Excluded	0	0.05	0.03	0.05	0.061	0.1	0.1	0.1	0.19	39.2	98.760	NA	10
AMPA	Included	0	0.05	0.02	0.05	0.058	0.1	0.1	0.1	0.14	16	NA	99.9978	NA
	Excluded	0	0.05	0.02	0.05	0.058	0.1	0.1	0.1	0.14	16	NA	99.9978	0

NA – Not applicable as not considered

Table 8.5-30: **Summary of glyphosate (GLY) and AMPA data in groundwater in Europe (*after* [redacted], 2016, CA 7.5/010)**

Country	**Compound**	**Date**	**Sites**	**Samples**	**Detected (samples)**		**Samples ≥ 0.1 µg/L**		**Max Conc**	**LoQ (LoD)**
		Range	**No.**	**No.**	**No.**	**%**	**No.**	**%**	**µg/L**	**µg/L**
Austria	GLY	2004	~950	3633	7	0.19	2	0.06	>0.1	<0.1
	AMPA	2004	~950	3636	44	1.2	11	0.3	0.75	<0.1
Belgium (Flanders and Wallonia)	GLY F	2006-08	≥448	1488	4	0.03	1	0.01	≤0.5	0.01
	AMPA F	2007-14	≥504	4515	789	17.5	≥8	≥0.18	1.85	0.01
	GLY W	2000-06	450	≥450	0	-	0	-	<0.025	<0.025
	AMPA W	2000-06	450	≥450	13	3	0	-	<0.05	<0.025
Denmark	GLY	1990-13	4941	15552	142	0.9	28	0.2	4.7	(0.01-<0.1)
	AMPA	1990-13	4946	15541	106	0.7	23	0.15	9.1	(0.01-<0.1)
Finland	GLY	2002-08	81	81	0	-	0	-	-	0.1
	AMPA	2002-08	81	81	0	-	0	-	-	0.05
France	GLY	99-2012	≥7028	78431	859	1.1	565	0.7	28	0.01-0.2
	AMPA	2000-12	≥6904	70492	1122	1.6	643	0.9	19	0.01-0.2
Germany	GLY	96-2008	≥430	≥2599	35	1.3	9	0.34	<1.0	<0.1
	AMPA	96-2008	≥387	≥1986	64	3.2	34	1.7	≥1.0	<0.1
Ireland	GLY	2007-09	92	679	6	0.8	1	0.1	0.19	<0.1
Italy (Lombardia Region)	GLY	2005-12	≥359	1497	9	0.6	5	0.2	1.2	0.1
	AMPA	2007-12	≥359	1156	14	1.2	11	0.9	1.3	0.1
Malta	GLY	2009	18	≥18	0	-	0	-	-	0.01
Norway	GLY	99-00	7	8	0	-	0	-	-	0.01
	AMPA	99-00	7	8	1	12.5	0	-	0.02	0.01
Spain	GLY	2009-12	≥461	963	325	34	86	8.9	25	0.03-0.3
Sweden	GLY	2000-14	≥21	5989	26	0.43	10	0.17	0.23	<0.03
	AMPA	2000-14	≥21	5930	31	0.52	≤26	0.43	7.9	<0.05
Switzerland	GLY	2005-06	117	≥234	≥4	1.7	≥3	1.3	0.21	0.05
	AMPA	2005-06	117	≥232	17	7.3	11	4.7	0.46	0.05
Netherlands	GLY	2003-06	<691	691	4	0.58	4	0.58	4.7	(<0.1)
	AMPA	2003-06	<691	691	21	3	21	3	5.1	(<0.1)
UK	GLY	95-2015	≥264	1680	16	0.95	≤6	≤0.35	1.38	(0.01-0.1)
Total	**GLY**	**90-2015**	**≥16160**	**≥113993**	**1437**	**1.3**	**724**	**0.6**	**<0.05-28**	**0.01-0.2**
	AMPA	**90-2013**	**15417**	**≥104718**	**2222**	**2.1**	**788**	**0.75**	**0.02-19**	**0.01-0.2**

Table 8.5-31: Summary of sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA in groundwater

Compound	**GLY**		**AMPA**			
Threshold	**DrW: 0.1 µg/L**	**LTHAC: 1500 µg/L**	**Threshold: 0.1 µg/L**	**Threshold: 0.75 µg/L**	**DrW: 10.0 µg/L**	**LTHAC: 3960 µg/L**
Number of sites	37638	37842	34349	34451	34457	34499
Number of samples	242792	251258	223164	224293	224545	230981
Number of samples > threshold	1496	0	1511	158	5	0
% of samples > threshold	0.6	0.0	0.7	0.1	0.002	0.0
Number of sites > threshold	1128	0	994	112	2	0
% of sites > threshold	3.0	0.0	2.9	0.3	0.006	0.0
Number of consecutive samples > threshold	216	0	359	39	5	0
% of samples that are consecutive samples > threshold	0.089	0.0	0.16	0.017	0.002	0.0
Maximum number of samples > threshold at a single site	13	0	37	13	3	0
Maximum number of consecutive samples > threshold at a single site	8	0	15	13	3	0

LTHAC - lifetime health-based ADI concentration

Case Studies

Case studies were initiated for Spain and the UK to assess why the compliance rates with the 0.1 µg/L threshold are lower in these MS (Spain 93.6% and the UK 93.0%). Several monitoring sites were included in the case studies and were elucidated by a desk-based approach. The aim was to determine whether the findings of glyphosate residues in groundwater relates to urban or agricultural uses and whether the reasons for exceedance are from compliant glyphosate use or could be related to point sources or other contaminations. (The detailed results of the case studies are provided in Appendix 2 of the report).

For Spain it was found that the geographical distribution of monitoring sites exceeding 0.1 µg/L is mainly concentrated in the south of Spain; 128 out of 137 sites showing glyphosate exceedances are situated in the region of Andalucía. Eleven sites which showed the most consecutive exceedances were investigated in more detail. The results showed that all sites are located in rural areas dominated by agricultural use. Most of the monitoring points comprise large diameter wells which are not constructed to a standard of a water quality monitoring well. Almost all wells were used for water abstraction (domestic or irrigation). It was concluded that all 11 monitoring sites that were examined in this case study show deficiencies, mostly due to inappropriate well construction or a location of the well which makes them susceptible to overspray. The sites are therefore not suited for water quality monitoring and for a subsequent assessment of the leaching potential of glyphosate.

In addition, it was noted that in the vicinity of many sites there are orchards (e.g. citrus or olives) where glyphosate may have been used compliantly and repeatedly in high application doses. Glyphosate is reported to strongly sorb, which makes the substance only slightly mobile reducing the leaching risk. However, the soils in southern Spain typically have a low organic content (OC) and it may be possible that the combination of depleted soil OC together with repeated high dosage applications in orchards may cause leaching of glyphosate to shallow groundwater. Further work is ongoing in these localised areas to understand the situation better with a view to adapting local practice through targeted stewardship programs.

For the UK the vast majority of glyphosate exceedances >0.1 µg/L, and all multiple exceedances, relate to a small area near Hereford in west-central England. All detections in this area relate to the time period 2000-2009, as monitoring for glyphosate discontinued in 2010. Most detections, and the highest glyphosate concentrations, relate to the vicinity of a large plant nursery, with some further detections, lower in concentration and less frequent, in the urban area of Hereford. The local focus on glyphosate analyses together with a dense monitoring network and frequency may indicate that a problem with glyphosate occurred in the area and that the contamination spread and temporal course was examined. A possible scenario may have been an accident with glyphosate containing products.

Despite the fact that the glyphosate exceedances in the Hereford area could not be elucidated conclusively, it is evident that the cluster of detections is very local. These contradict the monitoring data from elsewhere in the UK, or indeed in EU member states that were considered as part of the public monitoring data assessment. As such, the glyphosate detections in the Hereford area should be considered as atypical and non-representative.

The UK glyphosate detection rate of 7.0% is strongly driven by the large number of detections in the Hereford area. Excluding the atypical data from this area, the exceedance rate for the UK is 1.1% and therefore much more comparable with that observed for the EU member states that were considered as part of the public monitoring data assessment. Even the 1.1% exceedance may be biased as it relies on a small sample number and is based on only 4 single detections across all of the UK. Further work is ongoing in these localised areas to understand the situation better with a view to adapting local practice through targeted stewardship programs.

III. CONCLUSIONS

The analysis of the large groundwater dataset for GLY and AMPA indicates they are both occasionally detected above the LOQ in this compartment. However, compliance is very high with the frequency of quantification above the regulatory acceptable concentrations very low and non-systematic as would be expected given that the compounds are only slightly mobile in soil. It should be borne in mind that AMPA may originate from sources other than GLY, for example detergents, particularly in GW affected by SW or flooding. The environmental concentrations typically encountered in this environmental compartment do not pose a risk for ecosystem or human health *via* drinking water.

Assessment and conclusion by applicant:
The report describes the analysis of public monitoring data for key European countries for the compartments soil, water and sediment for Glyphosate and AMPA. The maximum GLY concentration in GW of 1005 µg/L is likely anomalous and once outliers are identified and excluded would be 39.2 µg/L which is well below the SW RAC (for groundwater fed ecosystems) of 400 µg/L and the lifetime health-based ADI concentration of 1500 µg/L. The maximum AMPA concentration in GW is 16 µg/L which is well below the SW RAC of 1200 µg/L (for groundwater fed ecosystems) and the lifetime health-based ADI concentration of 3960 µg/L. The available data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in the groundwater compartment.
The study is therefore considered valid.

Assessment and conclusion by RMS:

An extended monitoring data set was collected throughout 14 EU countries and analysis of these data have been proposed by the study authors to assess what they call "the state of all environmental compartments" and "consider the impacts this state might have on biota, ecosystems and human health via drinking water". The present summary focuses on groundwater results, and analysis for other compartments can be found in the relevant corresponding sections.

Results are given for each country, and for the whole combined EU data set (see Table 8.5-27). These include all the samples after removal of unvalidated data (unavailable data, analysis not completed, uncertain data or not validated data), and represents >251 000 samples collected from >37 800 sampling sites.

Analyzing and assessing such public monitoring data is a difficult exercise, as underlined by study authors, since the public monitoring data usually does not meet the kinds of quality criteria defined for higher tier groundwater datasets (GW Tier 4) as laid out in guidance (FOCUS, 2014), or scientific recommendations (Gimsing *et al.*, 2019).

These monitoring programs are indeed not conducted for fulfilling any regulation 1107/2009 requirements and the results cannot be taken as such. However, since the results are analysed in comparison to regulatory triggers, sufficient information shall be available to get a clear picture of what these monitoring data capture.

Study authors included in their analysis a description of some of the biases inherent to public monitoring data that could affect interpretation of the results. However, crucial information are further missing and applicant analysis and conclusions should be regarded with caution, considering the following limitations:

Data handling

A first step of data handling was performed to exclude unusable raw data that often comes with national databases extraction (analysis uncompleted, data not validated, data not attributed to any location, no indication of the LOD/LOQ, no indication of the measurements unit...).The data exluded at this step were excluded in the applicant's analysis reported in Table 8.5-27.

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An additional analysis step was conducted by the study authors to identify likely outliers in the dataset and the implications of these for the analysis assessed. This identified 10 outliers for glyphosate (none identified for AMPA). However, no explanation on this additional step is provided and no details are given on the values excluded (locations, level of concentrations) neither any justification for considering these outliers. Further information are required as data gap on this point. Although the influence of removing the 10 data considered outliers by applicant is of very low impact on the overall conclusions, it has to be ckecked that no reliable higher maximum concentration could be retained from this data set.

Spatial distribution of the data

The whole data set for glyphosate represents >251 000 samples collected from >37 800 sampling sites. However, the spatial distribution of these sampling is heterogeneous throughout EU MS for which data are available (figures 7.5-19 and 7.5-18). Study authors indicated that for some MS (DE, IT and ES) this is due to data only arising from some regional environmental agencies, while in some other case (UK), this is due to specific spatial targeting. Data from FR, which represents about 80% of ground water sample analysis contribution, are homogeneously distributed throughout the territory. However, all sample sites with available results are plotted on the maps while it should be noted that regularity of sampling for each site is not known, and that several sites may provide only very few data over the whole period (see RMS comments hereunder on the sampling effort). Please also note that the sampling points from Sweden are not plotted on the Figure 8.5-19 and Figure 8.5-20 since spatial distribution of the Swedish sampling points is not known.

Temporal distribution of the data - sampling effort

Analysis of the global sampling effort is provided by study authors, indicated an unimodal distribution of data collection (i.e fewer samples in the winter and spring months) for some MS, and a bimodal distribution (data collection in spring and autumn during key use periods being greater than at other times of the year) for other MS (*e.g.* FR, DE, NL, SE);
From the bar chart in figure 7.5-17 and 7.5-18, it can indeed be seen that for the MS with main contribution to the data set (FR, DE, NL, AT), sampling times are sensitively higher during spring and autumn.

However, no detailed information on the sampling frequency and the regularity of sampling per site are available in the report. It is not known whether sampling sites could have been excluded from the data set based on a frequency of sampling criteria. For the whole period 1995-2019 and all EU data set, the mean ratio between the number of sampling results and the sampling sites is 6.5 sampling per sites, which is very low. However, the sampling effort can be very different from a site to another. The study of [redacted] (2016), focusing on the results from the French public monitoring between 1999 and 2013, showed that more than half of stations for which sampling results are available were in fact monitored for one single year other the 15 year period studied (54% and 53% for AMPA and glyphosate, respectively). Stations monitored for 2 years over 15 represents 19 and 18% for AMPA and glyphosate. Eventually, less than 15% of the stations have been monitored for 5 years or more out of 15. This is not only due to the earlier years of monitoring; same trend is reported in [redacted] (2019a) on the 7 years period from 2008 to 2014. With regard to the frequency of sampling within a year in groundwater, [redacted] (2016) reports a frequency varying between once and twice a year, with a majority of measurements being carried out once a year. The exception to this is 2012, where 4 or 5 measurements per year were conducted for more than 40% of stations ([redacted], 2016).

Still, data on annual frequency and regularity of sampling is key information to be provided to allow a multi-year analysis of the data, and to appreciate if a consistent temporal percentile can be covered with the existing data.

Relation to active substance use pattern and false negative issue
One of the main issue while interpreting such monitoring data results is that they cannot be related to any use pattern of the active substance. No sufficient information at each site location is available to evaluate the proportion of sampling sites that are really located down gradient of area where the active substance is used, or even just likely to be used (no data regarding glyphosate containing product use is available at this scale, and neither information on the presence of agriculture). Beyond that, the vulnerability of the sampling site to the substance leaching is not known since cannot be individually evaluated given the high number of sampling sites. However no indication of spatial vulnerability at larger scale is not either given.

While the purpose of the public monitoring programs is indeed to be representative of the diversity of situations throughout a territory, the proportion of false negative linked to a total absence of glyphosate containing product use cannot be evaluated in the whole data set. It is not known on which extent the high percentile of compliance with regulatory triggers indicated by study authors (0.1 µg/L triggers represents the 98.976th percentile concentration for glyphosate) is influenced by a total absence of use of the active substance. However, this influence might be limited in the case of glyphosate, considering the spread and diversity of uses of glyphosate containing products (including agricultural and non-agricultural uses, professional and non professional uses).

False positive issue
On the contrary false positive are also difficult to identify, as underlined by study authors, as "a) the source of the GLY (or AMPA) is unknown, as its knowledge on whether it arises from use in line with the GLY containing product GAP; (b) the quality of the monitoring location or the monitoring sample collection, storage and analysis is unknown owing to limited metadata accompanying datasets".

Aquifers description

Another sensitive issue dealing with these data is that the description of the aquifers from which the samples are taken is not given, so as the sampling depth. Public monitoring programs indeed includes sampling sites of various hydrogeological nature (well or spring, piezometers in the unsaturated zone, saturated zones shallower to 1m, boreholes in deeper saturated zone below 10m, located below treated field, at edge of field, down-gradient, up-gradient….). These are key information lacking, since could highly influence interpretation of the findings. Defining the aquifer type and sampling depth where the active substance is monitored is the key entry for defining a protection goal as exposed in Gimsing *et al.* (2019). While the data presented here are not aimed at being used for risk assessment conclusion purpose, it must be kept in mind that the percentile concentrations calculated on the whole data set cannot be related to a consistent groundwater type.
It is not known here if the 1496 samples with detections above 0.1 µg/L for glyphosate throughout all EU are preferentially found in shallow or very shallow groundwater, or if encountered in any kind of aquifers.

Analytical method
Since the data are collected from multiple sources and throughout a long period, analytical method might be inconsistent between different databases and throughout time. LOD and LOQ from the different databases have been investigated by the study authors and reported. The study investigated the evolution of the mean LOQ, improving from 0.06 µg/L in 2005 to 0.034 µg/L in 2018. In the analyses, only samples coming from analytical method with LOQ<0.1 µg/L were acounted for.

Conclusions from RMS

The study (groundwater part) is considered acceptable.

The following main results arise from this monitoring data collection. RMS however underlines that is should be kept in mind that these statistical results cannot be related to a use pattern of the active substance neither to any "type of concentration" as defined in Gimsing *et al.* (i.e. edge-of-field, below field, unsaturated zone shallower 1m, saturated zone up to 10 m, below 10m…). Also, these results consider samples from all sites where GLY an AMPA were monitored, with no consideration of sampling frequency pattern.

Results - Compliance with thresholds – statistical analysis
Across all MS the GLY public monitoring dataset compiled comprised >251 000 samples collected from >37 800 sampling sites and the AMPA public monitoring dataset compiled comprised >230 000 samples collected from >34 400 sampling sites.

Glyphosate
Detection of GLY in GW across EU was ~2%. These are in line with the previous data collection ([redacted], 2012) where GLY was detected in 1.3% of samples.

Compliance with the 0.1 µg/L threshold was 99.4% samples from 97% of sites, with few exceedances (~0.6% of samples from ~3.0% of sites). The 99th percentile concentration is 0.19 µg/L while the 0.1 µg/L threshold represents the 98.976th percentile concentration.

Once outliers are identified and excluded maximum GLY concentration would be 39.2 µg/L, which is well below the SW RAC (for groundwater fed ecosystems). Futher information on the outlier values excluded are however required to confirm this maximum concentration of 39.2 µg/L.

AMPA
Detection of AMPA in GW across EU was ~2.9%. These are in line with the previous data collection where AMPA was detected in ~2.1% of samples. Compliance with thresholds defined in the SANCO 221/2000 for a non-relevant metabolite was very high (99.93% of samples for the threshold of 0.75 µg/L; 99.998% of samples from 99.994% of sites for the threshold of 10 µg/L).

The 99th percentile concentration is 0.14 µg/L while threshold of 10 µg/L represents the 99.998th percentile concentration. No outliers were identified in the dataset. Detection above the threshold of 0.1 µg/L was ~0.7%, ranging from 0.1% in ES to 2.3% in NL.

The maximum concentration reported from the collection of [redacted], 2020 is 16 µg/L. The data set collected after [redacted], 2016 indicates maximum value of 19 µg/L (see Table 8.5-32). This maximum concentration of 19 µg/L occurred in 2005 and is an isolated peak (next highest concentration is indicated to be 1.5 µg/L in [redacted], 2016). This isolated maximum concentration exceeds the EU trigger of 10 µg/L for non relevant metabolites. However, based on this maximum value, the exposure through drinking water for the most vulnerable consumer is less than 1% of the ADI, see section 2.12 in volume 1 for details. This concentration is also well below the SW RAC (for groundwater fed ecosystems, to be confirmed when final RAC is agreed).

Further Investigation of samples exceeding thresholds

Study authors proposed additional analysis on the samples exceeding the threshold, with notably spatial distribution of the exceedance and consideration of whether these exceedances were consecutive.

They are 1496 samples >0.1 µg/L distributed on 1128 sites, with maximum samples >threshold at single site being 13 for glyphosate.
They are 1511 samples >0.1 µg/L distributed on 994 sites, with maximum samples >threshold at single site being 37 for AMPA.

The maps illustrating the spatial distribution of the wells and exceedance locations of GLY and AMPA (figures 7.5-19 and 7.5-20), do not tend to indicate any specific patterns or bias.

Authors further calculated that the number of consecutive samples with threshold exceedance for GLY (among all sites) was 216. RMS calculated this represented 15% of all samples detected above threshold (note that 0.089% indicated by authors in the Table 8.5-31 is related to the total number of samples, which may not be the most relevant indicator, considering limitations already exposed by RMS above). RMS notes that there is no indication of the total number of sample results available for the sites where the consecutive exceedance are the highest.
It also remains unclear whether the exceedance can be related to specific conditions (vulnerable context, shallow groundwater only, higher pressure of use or misuses of glyphosate containing product….) Additional assessment could be performed on this point to confirm the exceedance are not related to long-term contamination in some locations. This is a data gap identified for applicant.

Data point:	CA 7.5/008
Report author	[redacted]
Report year	2019a
Report title	Phase 1: Traitements et analyses statistiques sur les données SOES UIPP 2008 - 2014 Analyses des données de suivi de glyphosate et de l'AMPA dans les eaux de France Période 2008-2014 (Original in French: Phase 1: Processing and statistical analysis of the 2008-2014 SOES UIPP data. Analysis of the 2008-2014 water monitoring data for glyphosate and AMPA in France)
Document No	REA-DOC-026
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No (but conducted by testing facilities accredited by the Member State)
Acceptability/Reliability:	Acceptable

The study is relevant for multiple subchapters. Only data about ground water monitoring were left in the following summary. Surface water data are summarized in the relvant section.

Executive Summary
This report is an update of a previous report "Analysis of monitoring data for glyphosate and AMPA in French waters in the period 1997-2013" ([redacted], 2016, CA 7.5/009). It includes the 2014 monitoring data for glyphosate and AMPA in ground and surface waters (extracted from the SOES UIPP database in July 2017). The dataset extracted from the SOES UIPP database is analysed in several ways.

Number of measurements and monitoring stations
At the combined national and French overseas level, the entire dataset for surface waters consists of 148561 analyses, of which 74271 are for AMPA and 74290 are for glyphosate. The number of unique stations is 3006 for the whole dataset. The present study only considers data from mainland France. Therefore, the surface water database selected for the study comprises 148295 analyses (74138 for AMPA and 74157 for glyphosate) from 2980 stations (Table 8.5-33).

For groundwater, the database consists of 129364 analyses, of which 64249 are for AMPA and 65115 are for glyphosate. The number of distinct water quality monitoring stations is 14 831 for the whole database (France mainland only).

Both glyphosate and AMPA were monitored every year between 2008 and 2014 in surface waters and groundwater. The majority of stations extracted from the SOES$_{\text{uipp}}$ database have both AMPA and glyphosate monitoring data.

I. MATERIAL AND METHODS

Groundwater
In the SOES$_{\text{uipp}}$ database, the number of analyses for groundwater increased between 2008 and 2011 to a maximum of 13396 analyses. From 2012, this number decreased to roughly the same value as that of 2008 (Figure 8.5-21).

The number of groundwater monitoring stations (Figure 8.5-22) increased between 2008 and 2009, then remained constant until 2011 (approximately 7000 stations monitoring AMPA and glyphosate). After this, the numbers reduced to about 2000 stations monitoring AMPA and glyphosate.

Table 8.5-33: **Number of analyses for glyphosate and AMPA performed during 2008-2014 period**

Year	**Total SOES$_{uipp}$ data points**	**AMPA**	**Glyphosate**	**Year**	**Total SOES$_{uipp}$ data points**	**AMPA**	**Glyphosate**
Groundwater				**Surface water**			
2008	1 421 369	7048	7246	2008	2 074 007	4862	4862
2009	2 446 506	11662	11783	2009	4 000 041	7559	7559
2010	2 833 373	12514	12663	2010	4 428 556	10001	10001
2011	3 136 242	13258	13396	2011	5 100 025	12456	12457
2012	1 887 369	6106	6373	2012	5 123 717	11395	11417
2013	2 122 877	6811	6808	2013	7 039 438	13067	13066
2014	2 431 470	6850	6846	2014	6 944 879	14798	14795
TOTAL	**16 279 206**	**64249**	**65115**	**TOTAL**	**34 710 663**	**74138**	**74157**

Figure 8.5-21: **Evolution of the annual number of groundwater analyses carried out for AMPA and glyphosate.**

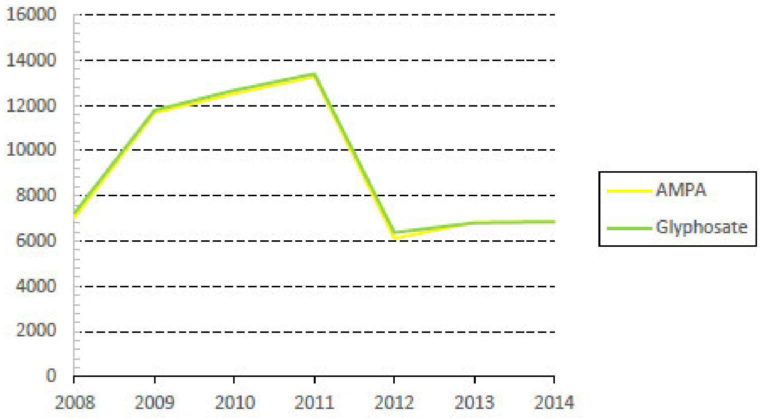
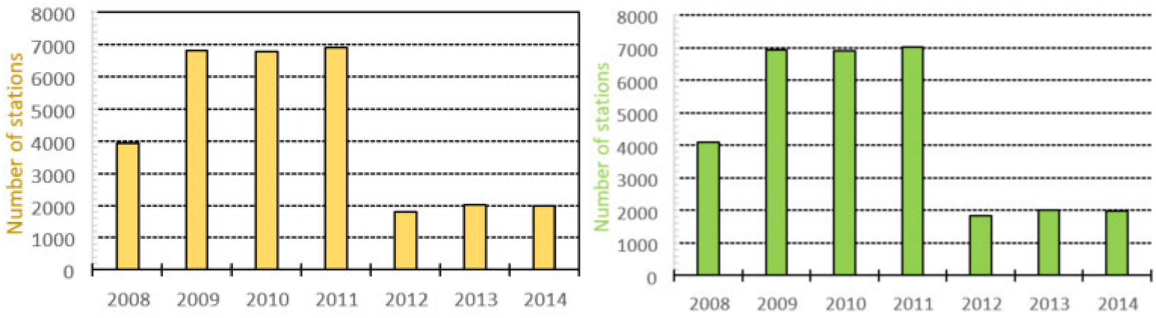
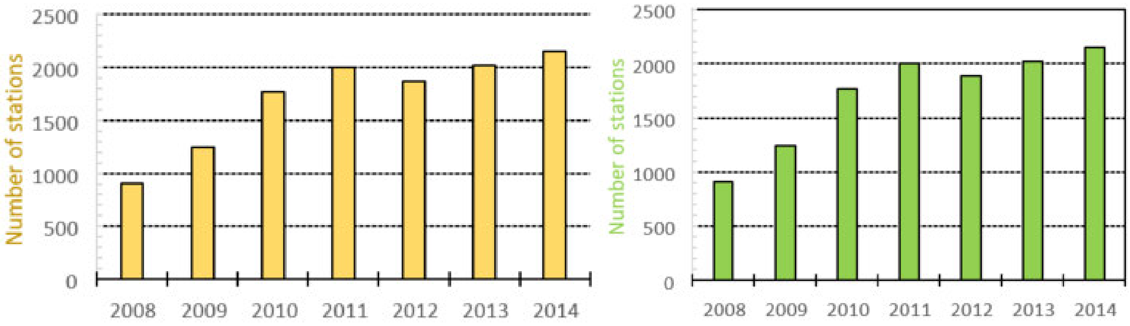


Figure 8.5-22: **Number of stations involved in the groundwater monitoring of (a) AMPA (yellow) and (b) glyphosate (green)**



(a) (b)

Figure 8.5-23: **Number of stations involved in the surface water monitoring of (a) AMPA and (b) glyphosate**



(a) (b)

II. RESULTS AND DISCUSSION

Multi-year continuity analysis

Based on the number of years of monitoring, this section looks at the continuous measurements within the time period and therefore on the ability to draw conclusions in terms of how the multi-annual trends evolved. Taking into account the inter- and intra-annual climatic variability as well as crop rotations, it is necessary to have several years of monitoring data to assess such trends and this does not necessarily require data to be based on consecutive years.

Groundwater

For groundwater (Table 8.5-34), only 8% of stations in the database have monitoring data for AMPA and glyphosate over the seven years studied. More than half of the stations only measured for one year (52% and 54% for AMPA and glyphosate, respectively). This proportion dropped to 23% and 24% of stations over two years, then dropped further to 5% and 6% over 3 years.

Table 8.5-34: **Number of follow-up years of groundwater monitoring from stations between 2008-2014**

	AMPA		**Glyphosate**	
No of follow-up years	**No of stations**	**% of stations**	**No of stations**	**% of stations**
One year	7783	52%	7948	54%
2 years	3411	23%	3520	24%
3 years	812	5%	823	6%
4 years	567	4%	582	4%
5 years	200	1%	199	1%
6 years	351	2%	331	2%
7 years	1127	8%	1154	8%
Total no of stations	14251	-	14557	-

Groundwater

For groundwater monitoring, the greatest majority of stations only had one measurement per year between 2008 and 2011. The number of measurements per station per year increased thereafter. In 2012, 42% of stations had 4-5 measurements per year, and in 2013 and 2014, 41-45% of stations had 2-3 measurements per year. Only 1% of stations recorded more than 10 measurements per year, and this could correspond to a monthly monitoring schedule. No station performed as many as 50 measurements a year. The number of stations sampled per year decreased by about half between 2008 and 2014. Although the number of stations carrying out measurements seems to decrease, the frequencies of measurements increased.

Assessment of the multi-year trend in measurements greater than LOQ (code 1)
In this section, the results of the quantifiable analytical results of glyphosate and AMPA are studied i.e. those results where the concentration of the target molecule is reported as being greater than the limit of quantification (LOQ). The measured concentration values are compared against the regulatory values provided for the provision of drinking water: greater or equal to 0.1 µg/L for drinking water and greater or equal to 2 µg/L for water destined for drinking water.

AMPA
The percent of annual measurements for AMPA > LOQ in groundwater is low (< 5% in all years studied, Table 8.5-35). The lowest such values for AMPA were in 2008-2010 with 0.7-0.9%. From 2013 to 2014, this value for AMPA is *ca.* 2.5% of analyses. In mainland France, fewer than 100 analyses for AMPA exceeded 0.1 µg/L in any one year, except in 2011 where there were 133 exceedances. The concentrations greater than 0.1 µg/L were always <1.1% in groundwater over the seven years of the study. Fewer than five analyses per year exceeded the 2 µg/L limit.

The annual percentage of AMPA measurements >LOQ in surface water were much higher than in groundwater. These vary between 46% and 62.5% with a median quantification rate of 54% (AMPA is detected in more than half of the measurements). Concentrations of AMPA are often > 0.1 µg/L with 33.2% - 53.6% of measurements exceeding this threshold. Concentrations for AMPA >2 µg/L comprise <3% (between 106 and 268 values p.a.) of samples.

Table 8.5-35: Annual measurements above LOQ for AMPA

	2008	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Groundwater							
Number of analyses	7048	11662	12514	13258	6106	6811	6850
Number of analyses with conc. > LOQ	63	101	101	201	254	164	169
% >LOQ (code remarque = 1)	**0.9%**	**0.9%**	**0.8%**	**1.5%**	**4.2%**	**2.4%**	**2.5%**
Number of analyses > LOQ and >= 0.1 µg/L	58	78	85	133	66	47	49
% of analyses > LOQ and >=0.1 µg/L	**0.8%**	**0.7%**	**0.7%**	**1.0%**	**1.1%**	**0.7%**	**0.7%**
Number of analyses > LOQ and >= 2 µg/L	3	2	2	2	2	2	4
% of analyses > LOQ and >=2 µg/L	**<0.1%**	**<0.1%**	**<0.1%**	**<0.1%**	**<0.1%**	**<0.1%**	**0.1%**
Surface water							
Number of analyses	4862	7559	10001	12456	11395	13067	14798
Number of analyses with conc.> LOQ	2557	3887	4597	7789	6148	7307	7983
% >LOQ (code remarque = 1)	**52.6%**	**51.4%**	**46.0%**	**62.5%**	**54.0%**	**55.9%**	**53.9%**
Number of analyses > LOQ and >= 0.1 µg/L	2130	3389	4068	6681	4054	4348	4913
% of analyses > LOQ and >=0.1 µg/l	**43.8%**	**44.8%**	**40.7%**	**53.6%**	**35.6%**	**33.3%**	**33.2%**
Number of analyses > LOQ and >= 2 µg/L	106	190	172	268	176	162	191
% of analyses > LOQ and >=2 µg/L	**2.18%**	**2.51%**	**1.72%**	**2.15%**	**1.54%**	**1.24%**	**1.29%**

Glyphosate

The annual percentage of measurements > LOQ for glyphosate in groundwater is low (<2% in all years studied, Table 8.5-36). The lowest percentages >LOQ in groundwater were 2008-2011 (0.4-1.0% of measurements). From 2012 to 2014, this value is 1.5-1.7%. Fewer than 100 measurements exceeded 0.1 µg/L. Fewer than eight analyses per year exceeded the 2 µg/L limit.

The annual percentage of measurements > LOQ in surface waters are much higher than in groundwater. These vary between 25.3% and 39.1% with a median quantification rate of 32.3% (indicating that glyphosate is detected in one third of analyses). As well as being identified as higher than LOQ, the analyses were often > 0.1 µg/L (14-21.7% of measurements compared to the whole dataset). In addition, <1% (between 25 and 52 values p.a.) of analyses were >2 µg/L.

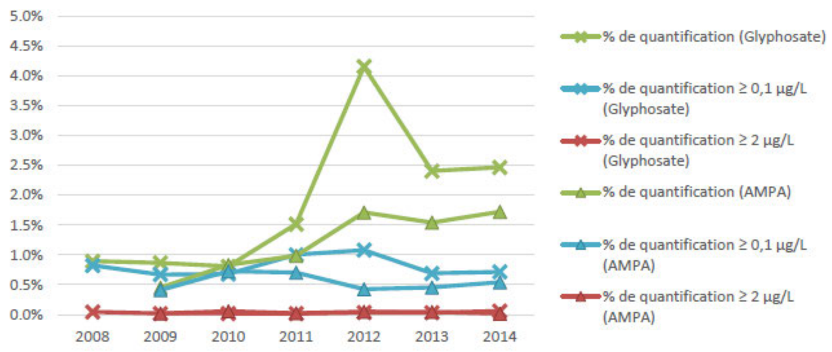
Table 8.5-36: Annual measurements above LOQ for glyphosate

	2008	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Groundwater							
Number of analyses	7246	11783	12663	13396	6373	6808	6846
Number of analyses with conc. > LOQ	NA	53	105	132	109	105	118
% >LOQ (code remarque = 1)		**0.4%**	**0.8%**	**1.0%**	**1.7%**	**1.5%**	**1.7%**
Number of analyses > LOQ and >= 0,1 µg/L	NA	48	92	94	27	31	37
% > LOQ and >=0,1 µg/l		**0.4%**	**0.7%**	**0.7%**	**0.4%**	**0.5%**	**0.5%**
Number of analyses > LOQ and >= 2 µg/L	NA	2	7	3	3	3	1
% of analyses > LOQ and >=2 µg/L		**<0.1%**	**<0.1%**	**<0.1%**	**<0.1%**	**<0.1%**	**<0.1%**
Surface water							
Number of analyses	4862	7559	10001	12457	11417	13066	14795
Number of analyses with conc. > LOQ	1550	1936	2535	4026	4189	5048	5791
% >LOQ (code remarque = 1)	**31.9%**	**25.6%**	**25.3%**	**32.3%**	**36.7%**	**38.6%**	**39.1%**
Number of analyses > LOQ and >= 0,1 µg/L	1051	1404	1757	2697	1937	2004	2072
% of analyses > LOQ and >=0,1 µg/L	**21.6%**	**18.6%**	**17.6%**	**21.7%**	**17.0%**	**15.3%**	**14.0%**
Number of analyses > LOQ and >= 2 µg/L	25	43	36	52	40	41	47
% of analyses > LOQ and >=2 µg/L	**0.5%**	**0.6%**	**0.4%**	**0.4%**	**0.4%**	**0.3%**	**0.3%**

Comparison of concentration levels (greater than LOQ) of AMPA and glyphosate

Groundwater
For groundwater, the annual percentage of measurements with concentrations > 0.1 µg/L were relatively similar for AMPA and glyphosate and were between 0.4% and 1.1% (Figure 8.5-24). Analyses > 2 µg/L were always ≤0.1% for AMPA and glyphosate.

Figure 8.5-24: **Examining the trend in yearly % of measurements in surface water with respect to regulated concentrations.**



Maximum concentrations, 90th, 95th and 99th percentiles
The measured concentrations of AMPA and glyphosate in groundwater and surface waters each year for the period 2008-2014 are described according to their maximum value and their 90th, 95th and 99th percentiles (Table 8.5-37 to Table 8.5-40).

The glyphosate and AMPA maximum concentrations vary between the years, covering a range of ~1 to 3369 µg/L. There is no logical explanation for these maximum concentration values. Hypotheses put forward are:

- The maximum value can be due to pollution events upstream from the monitoring station with minimal dilution.
- This maximum value could simply be erroneous (transcription error, unit error, etc.)

The 99th percentile concentrations range between 1.6 and 26.3 µg/L.
The 95th percentile concentrations range between 0.3 and 2.9 µg/L. While the 90th percentile concentrations range between 0.2 and 1.2 µg/L.

The data shows opposite trends for surface water and groundwater as follows:

- For surface water, glyphosate maximum concentrations during 2008-2014 are less than those measured for AMPA in all percentile assessments.
- On the contrary, groundwater maximum glyphosate concentrations during 2008-2014 are higher than those for AMPA in all percentile assessments.

The surface water concentrations for both AMPA and glyphosate tend to decrease in all percentiles since 2009.

Table 8.5-37: **Annual summary of maximum concentrations (µg/L)**

	Period	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Ground water								
AMPA	9.3	2.36	5.7	9.3	7.78	6.3	5.05	4.07
Glyphosate	1005	0.96	3.91	22	11	1005	140	23.3

Table 8.5-38: **Annual summary of 90th percentile concentrations (µg/L)**

	Period	2008	2009	2010	2011	2012	2013	2014
Ground water								
AMPA	0.32	0.70	0.48	0.78	0.26	0.21	0.18	0.21
Glyphosate	0.47	0.50	0.62	0.86	0.44	0.21	0.25	0.42

Table 8.5-39: Annual summary of 95th percentile concentrations (µg/L)

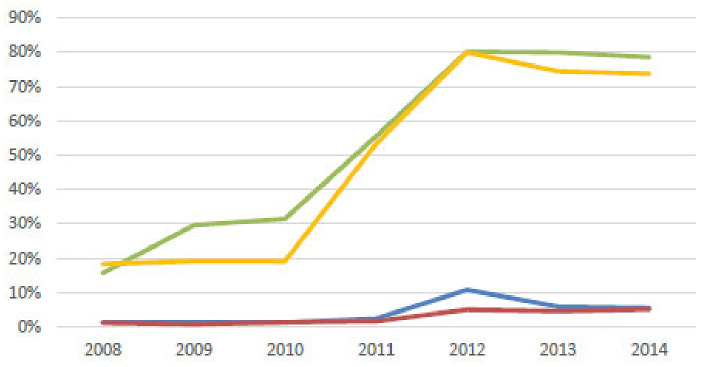
	Period	2008	2009	2010	2011	2012	2013	2014
Ground water								
AMPA	0.68	1.09	0.79	1.10	0.43	0.31	0.31	0.52
Glyphosate	0.91	0.76	1.40	2.86	0.91	0.82	0.46	0.75

Table 8.5-40: Annual summary of 99th percentile concentrations (µg/L)

	Period	2008	2009	2010	2011	2012	2013	2014
Ground water								
AMPA	2.52	2.26	3.80	2.00	1.77	1.55	2.24	3.35
Glyphosate	10.67	0.92	3.02	9.74	7.92	26.25	11.41	1.77

Assessment of quantification (concentrations greater than LOQ) with respect to monitoring stations
These results mirror those from the preceding section in that both target molecules are not frequently measured and quantified during groundwater monitoring (Figure 8.5-25). For surface water, AMPA is measured and quantified in ~80% of monitoring stations quoted compared to ~70% for glyphosate.

Figure 8.5-25: Groundwater Red- % of stations with glyphosate concentrations measured/quantified; Blue- % of stations with AMPA concentrations measured/quantified; Yellow: % of stations with glyphosate concentrations measured/quantified less than/equal to 0.1 µg/L; Green- % of stations with AMPA concentrations measured/quantified less than/equal to 0.1 µg/L



Seasonal assessment of quantifications (concentrations greater than LOQ)
Glyphosate is mainly applied between March and June. Analytical measurements of glyphosate occurred mainly in the Spring. For AMPA, higher concentrations were mostly seen in the summer and “rest of the year”. The lowest concentrations of both glyphosate and AMPA were in winter.

For groundwater, on average half of concentrations above LOQ for AMPA and glyphosate are between July and October (Figure 8.5-26 and Figure 8.5-27).

Figure 8.5-26: Groundwater distribution of glyphosate from the dataset

	2008	2009	2010	2011	2012	2013	2014	2008-
Jan to Mar	33%	0%	22%	0%	0%	0%	10%	9%
Apr to Jun	11%	13%	44%	11%	0%	0%	20%	16%
Jul to Sep	22%	60%	22%	56%	80%	71%	40%	48%
Oct to Dec	33%	27%	11%	33%	20%	29%	30%	27%
No of quantifications	9	15	9	9	5	7	10	64

Figure 8.5-27: Groundwater distribution of AMPA from the dataset

	2008	2009	2010	2011	2012	2013	2014	2008-14
Jan to Mar	100%	0%	0%	0%		0%	33%	16%
Apr to Jun	0%	0%	0%	0%		40%	0%	11%
Jul to Sep	0%	100%	67%	100%		40%	0%	53%
Oct to Dec	0%	0%	33%	0%		20%	67%	21%
No of quantifications	2	4	3	2	0	5	3	19

III. CONCLUSIONS

The present study only considers data from mainland France.

For groundwater, the database consists of 129364 analyses, of which 64249 are for AMPA and 65115 are for glyphosate. The number of distinct water quality monitoring stations is 14831 for the whole database (France mainland only).

Both glyphosate and AMPA were monitored every year between 2008 and 2014 in groundwater. The majority of stations extracted from the $\text{SOES}_{\text{uipp}}$ database have both AMPA and glyphosate monitoring data. The analysis focusses on those concentrations measured/detected which are above the LOQ, then assesses from those measurements which are ≤ 0.1 µg/L and greater than 2.0 µg/L.

For groundwater maximum glyphosate concentrations during 2008-2014 are higher than those for AMPA in all percentile assessments.

Assessment and conclusion by applicant:

The report describes the analyses for both surface water and groundwater for glyphosate and AMPA across mainland France during the monitoring period of 2008-2014. The analysis focusses on those concentrations measured/detected which are above the LOQ, then assesses from those measurements which are ≤ 0.1 µg/L and greater than 2.0 µg/L.

The study is therefore considered valid.

Assessment and conclusion by RMS:

Please note that the original report is written in French and that only the present summary is available in English.

This report focuses on data from the French public monitoring data during the period 2008-2014.
It is an update of the report [redacted], 2016, which was focusing on time period 1999-2013.

Pease refer to [redacted], 2016 for more detailed analysis from RMS.

Data point:	CA 7.5/009
Report author	[redacted]
Report date	2016
Report title	Analyse des données de suivi du glyphosate et de l'AMPA dans les eaux de France - Période 1997-2013 (Original in French: Analysis of monitoring data for glyphosate and AMPA in French waters – Time period 1997-2013)
Document No	Rapport_AMPA_Glyphosate_1997-2013(V3)
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No (but conducted by testing facilities accredited by the Member State)
Acceptability/Reliability:	Acceptable

Executive Summary

This report is an update of a previous report « analyse des données de suivi du glyphosate et de l'AMPA dans les eaux de France, période 1999-2012 » of July 2015 (Analysis of monitoring data for glyphosate and AMPA in French waters, time period 1999-2012). It includes the 2013 monitoring data for glyphosate and AMPA in ground and surface waters (extracted from the IFEN$_{uipp}$ database in 2015).

Glyphosate was monitored in surface waters since 1997 and in groundwaters since 1999. AMPA was monitored in surface waters since 1998 and in groundwaters since 2000. Both substances are followed simultaneously in groundwaters and surface waters between 2000 and 2013.

The dataset extracted from the IFEN$_{uipp}$ database was analysed, for each substance, in terms of 1) the volume of individual measurements and 2) the number of stations contributing to the measurements, on an annual basis. The dataset for surface waters consists of 93302 and 103583 analyses, for AMPA and glyphosate, respectively. There were 4392 and 4632 stations associated with the monitoring, for AMPA and glyphosate, respectively. The dataset for groundwater consists of 76951 and 85067 analyses, for AMPA and glyphosate, respectively. There were 17130 and 18216 stations associated with the monitoring, for AMPA and glyphosate, respectively.

I. MATERIAL AND METHODS

Groundwater

There is a general move over the years for stations to more routinely monitor AMPA and glyphosate in groundwater (Figure 8.5-28, Figure 8.5-29, Figure 8.5-30).

Figure 8.5-28: **Annual progression in the number of analyses for glyphosate and AMPA in groundwater**

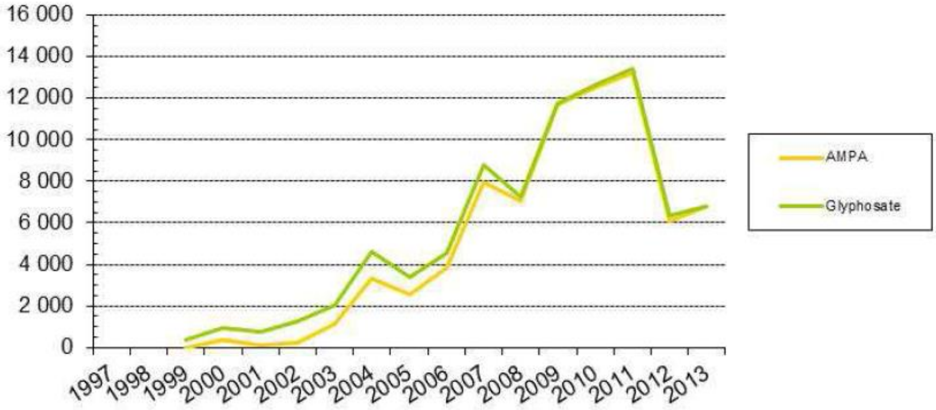


Figure 8.5-29: **Evolution of the number of stations monitoring for AMPA in groundwater (left axis: Number of stations as bar chart; right axis: Share of stations of the IFFEN database as a line chart)**

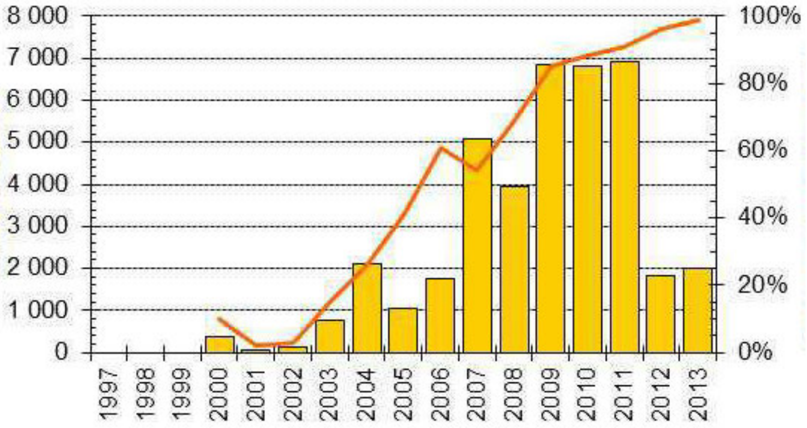
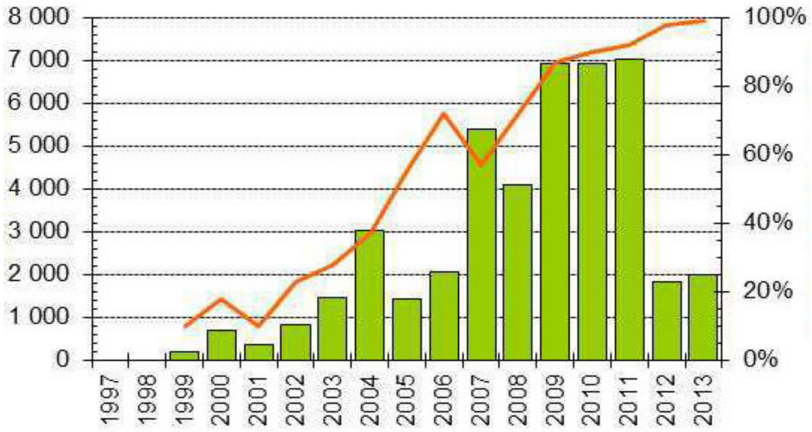


Figure 8.5-30: **Evolution of the number of stations monitoring for glyphosate in groundwater (left axis: Number of stations as bar; right axis: Percent of stations of the IFFEN database as a line chart)**

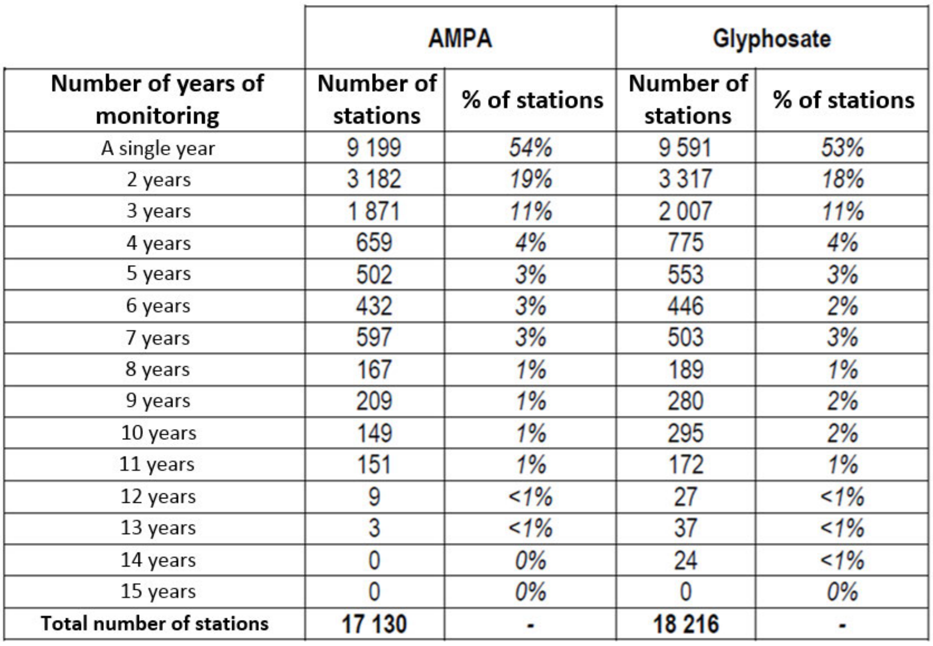


Multi-year continuity analysis of measurements

Based on the number of years of monitoring, an assessment was conducted to look at the continuous measurements within the time period and therefore on the ability to draw conclusions in terms of how the multi-annual trends evolve. It is worth noting that the stations are ordered by years of monitoring without the monitoring being necessarily in consecutive years (e.g. a station may be included in 5 years, corresponding to 1999, 2005, 2010, 2011, 2012).

Though the dataset corresponds to 15 years of AMPA and glyphosate monitoring (1999-2013), no station is monitored on an annual basis within the 15-year period. At best, some stations are monitored for 14 years (for glyphosate).

Table 8.5-41: **Number of years of monitoring of 'groundwater' stations on the 1999-2013 period**



	AMPA		Glyphosate	
Number of years of monitoring	Number of stations	% of stations	Number of stations	% of stations
A single year	9 199	*54%*	9 591	*53%*
2 years	3 182	*19%*	3 317	*18%*
3 years	1 871	*11%*	2 007	*11%*
4 years	659	*4%*	775	*4%*
5 years	502	*3%*	553	*3%*
6 years	432	*3%*	446	*2%*
7 years	597	*3%*	503	*3%*
8 years	167	*1%*	189	*1%*
9 years	209	*1%*	280	*2%*
10 years	149	*1%*	295	*2%*
11 years	151	*1%*	172	*1%*
12 years	9	*<1%*	27	*<1%*
13 years	3	*<1%*	37	*<1%*
14 years	0	*0%*	24	*<1%*
15 years	0	*0%*	0	*0%*
Total number of stations	**17 130**	**-**	**18 216**	**-**

Analysis of the frequency of measurements within a monitoring year
The multi-year continuity analysis comprises an analysis of the frequency of measurements within a year of monitoring. For groundwater, the frequency varies between once and twice a year, with a majority of measurements being carried out once a year. The exception to this is 2012, where 4 or 5 measurements per year were conducted for more than 40% of stations.

II. RESULTS AND DISCUSSION

Assessment of the multi-year trend in measurements higher than LOQ
Quantification rates of AMPA in groundwater (Table 8.5-42) are typically below 2.5% (except 2002, 2003 and 2012). The period between 2008 and 2010 has the lowest levels of quantification (0.8 to 0.9% of measurements). Quantification rates ≥2 µg/L are typically <0.1%.

Quantification rates of glyphosate in groundwater (Table 8.5-43) are low and vary, depending on the years, around 1.5%. Quantification rates ≥2 µg/L are typically <0.1%.

Comparison of concentration level (above LOQ) of AMPA and glyphosate
The annual quantification rates above 0.1 µg/L were compared on the 2000-2013 time period. Quantification rates above 0.1 µg/L vary between 40 and 60% for AMPA and 20 and 40% for glyphosate. There is no apparent correlation in terms of quantification rate value and consecutive annual variations.

Analysis of measurements depending on their detection/quantification status ("Code Remarque")
This assessment considered measurement results associated with each analysis status ("code remarque") that may have one of 4 values:

- 1: concentration is above the limit of quantification
- 2: concentration is below limit of detection
- 7: concentration is above the limit of detection and below the limit of quantification
- 10: concentration is below the limit of quantification (no indication given as to whether the substance was detected)

Table 8.5-42: Quantification rates of AMPA in groundwater

Year/Statistics	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Groundwater																	
Number of analyses				380	107	272	1124	3347	2527	3840	7955	7048	11672	12514	13258	6106	6811
Number >LOQ				0	1	59	41	69	48	54	115	63	101	101	201	254	164
% >LOQ				0%	0.9%	21.7%	3.6%	2.1%	1.9%	1.4%	1.4%	0.9%	0.9%	0.8%	1.5%	4.2%	2.4%
Number ≥0.1 µg/L				0	1	31	39	64	44	49	98	58	78	85	133	66	43
% ≥0.1 µg/L				0%	0.9%	11.4%	3.5%	1.9%	1.7%	1.3%	1.2%	0.8%	0.7%	0.7%	1.0%	1.1%	0.6%
Number ≥2 µg/L				0	0	0	0	1	1	0	1	3	2	2	2	2	2
% ≥2 µg/L				0%	0%	0%	0%	<0.1%	<0.1%	0%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%

Table 8.5-43: Quantification rates of glyphosate in groundwater

Year/Statistics	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Groundwater																	
Number of analyses			370	948	735	1290	2064	4639	3404	4553	8795	7246	11793	12663	13396	6373	6808
Number >LOQ			5	6	29	37	23	94	57	96	59	50	53	105	132	109	105
% >LOQ			1.4%	0.6%	3.9%	2.9%	1.1%	2.0%	1.7%	2.1%	0.7%	0.7%	0.4%	0.8%	1.0%	1.7%	1.5%
Number ≥0.1 µg/L			5	6	22	25	23	84	57	90	53	46	48	92	94	27	30
% ≥0.1 µg/L			1.4%	0.6%	3.0%	1.9%	1.1%	1.8%	1.7%	2.0%	0.6%	0.6%	0.4%	0.7%	0.7%	0.4%	0.4%
Number ≥2 µg/L			0	0	0	2	2	2	1	3	4	0	2	7	3	3	3
% ≥2 µg/L			0%	0%	0%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	0%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%

Table 8.5-44: Maximum concentrations recorded per year (in µg/L)

	Period	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Groundwater																		
AMPA	19				1	0.9	0.59	1.65	8	19	0.97	3.4	2.36	5.7	9.3	7.78	6.3	5.05
Glyphosate	1005			0.4	0.4	0.54	2.17	6.78	4.95	24	4.87	12.9	0.96	3.91	22	11	1005	140

Table 8.5-45: 90th percentile concentrations recorded per year (in µg/L)

	Period	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Groundwater																		
AMPA	0.4					0.9	0.21	0.72	0.43	0.55	0.41	0.47	0.7	0.48	0.78	0.26	0.21	0.18
Glyphosate	0.54			0.36	0.26	0.4	0.79	1.4	0.47	0.44	0.72	0.7	0.5	0.62	0.85	0.44	0.21	0.25

Table 8.5-46: 95th percentile concentrations recorded per year (in µg/L)

	Period	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Groundwater																		
AMPA	0.7					0.9	0.24	0.8	0.53	0.84	0.55	1	1.09	0.79	1.1	0.43	0.31	0.31
Glyphosate	1.1			0.38	0.33	0.4	1.36	2.3	1.1	0.55	1.32	2.12	0.76	1.4	2.85	0.91	0.82	0.46

Table 8.5-47: 99th percentile concentrations recorded per year (in µg/L)

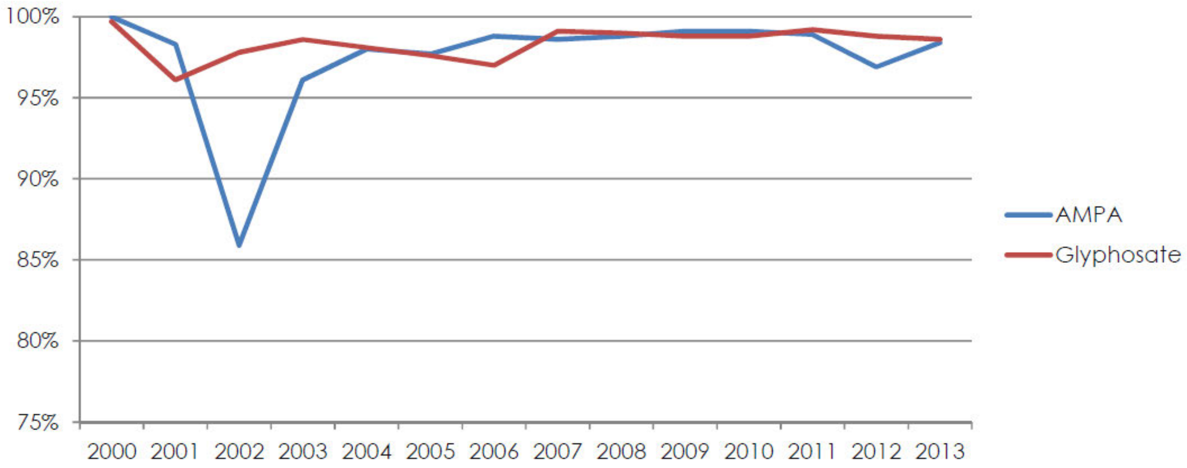
	Period	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Groundwater																		
AMPA	2.21					0.9	0.51	1.64	3.58	10.8	0.91	1.4	2.26	3.8	2	1.77	1.55	2.24
Glyphosate	8.94			0.4	0.39	0.5	2.14	5.81	2.95	11	4.71	7.91	0.92	3.02	9.73	7.92	26.25	11.41

Assessment of quantification (concentrations above LOQ) with respect to stations

To avoid an assessment limited by its focus on the number of measurements, the number of stations without quantification >0.1 µg/L is considered. For the vast majority of stations looking at groundwater, measurements do not show the presence of AMPA and glyphosate (Figure 8.5-31):

- In 1999-2013, 96.6% and 96.1% of stations do not show a quantification greater than 0.1 µg/L for AMPA and glyphosate.
- From 2006 for AMPA and 2007 for glyphosate, every year more than 98% of stations did not quantify the substances above 0.1 µg/L, with the exception of 2012 (although 2012 is characterized by a drop in the number of stations recorded)

Figure 8.5-31: Annual evolution of the percent of stations without measurements quantified at >0.1 µg/L in groundwater



Analysis of measurement results by Department

An analysis of the geographical breakdown of the preceding results is also presented. This does not alter the primary observations.

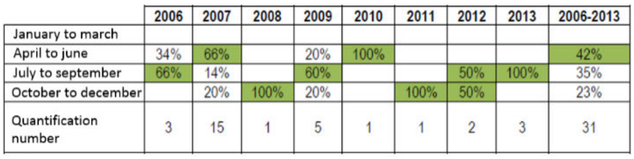
Analysis of a smaller dataset composed of higher-frequency measurements

Complementary investigations were carried out by limiting the type of data used to only the higher-frequency monitoring programmes. Observations that complement preceding sections are presented.

Analysis of the seasonality of the quantifications, based on a subset composed of higher-frequency measurements

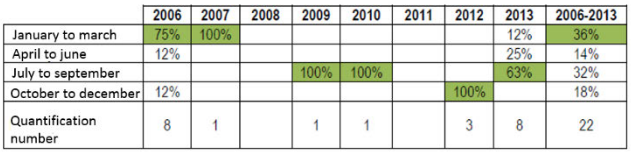
For groundwater (Figure 8.5-32 and Figure 8.5-33), there is no apparent relationship between quantifications and time of year. This may demonstrate the randomness of groundwater quantifications, linked to temporary pollution. The lack of correlation may also be due to the travel time to groundwater.

Figure 8.5-32: Seasonal distribution of AMPA quantification in groundwater - smaller dataset

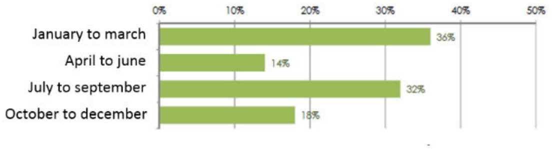


	2006	2007	2008	2009	2010	2011	2012	2013	2006-2013
January to march									
April to june	34%	66%		20%	100%				42%
July to september	66%	14%		60%			50%	100%	35%
October to december		20%	100%	20%		100%	50%		23%
Quantification number	3	15	1	5	1	1	2	3	31

Figure 8.5-33: **Seasonal distribution of Glyphosate quantification in groundwater - smaller dataset**



	2006	2007	2008	2009	2010	2011	2012	2013	2006-2013
January to march	75%	100%						12%	36%
April to june	12%							25%	14%
July to september				100%	100%			63%	32%
October to december	12%						100%		18%
Quantification number	8	1		1	1		3	8	22



III. CONCLUSIONS

Glyphosate was monitored in surface waters since 1997 and in groundwaters since 1999. AMPA was monitored in surface waters since 1998 and in groundwaters since 2000. Both substances are followed simultaneously in groundwaters and surface waters between 2000 and 2013. The dataset extracted from the IFEN$_{uipp}$ database was analysed, for each substance, in terms of 1) the volume of individual measurements and 2) the number of stations contributing to the measurements, on an annual basis.

The dataset for groundwater consists of 76951 and 85067 analyses, for AMPA and glyphosate, respectively. There were 17130 and 18216 stations associated with the monitoring, for AMPA and glyphosate, respectively.

For the vast majority of stations looking at groundwater, measurements do not show the presence of AMPA and glyphosate:

- In 1999-2013, 96.6% and 96.1% of ESO stations do not show a quantification greater than 0.1 µg/L for AMPA and glyphosate, respectively.
- From 2006 for AMPA and 2007 for glyphosate, every year more than 98% of stations did not quantify the substances above 0.1 µg/L, with the exception of 2012 (although 2012 is characterized by a drop in the number of stations recorded).

Assessment and conclusion by applicant:
The report describes the analyses of both surface water and groundwater for glyphosate and AMPA across France during the monitoring period of 1997-2013. The data analysis focusses on those concentrations measured/detected which are quantified above 0.1 µg/L.
The study is therefore considered valid.

Assessment and conclusion by RMS:

Please note that the original report is written in French and that only the present summary is available in English. Only data from groundwater results were left here. Data from the surface water monitoring are summarized in the relevant section.

This report focuses on data from the French public monitoring data during the period 1999-2013.

Therefore the raw data used in this study are *de facto* included in the data collection and analysis conducted in [redacted] (2020).

This study however gives additional relevant information on the sampling sites for FR groundwater monitoring and notably on the sampling regularity (multi year continuity analysis and annual number of sampling) and its effect on interpretation of the results.

Indeed, though the dataset corresponds to 15 years of AMPA and glyphosate monitoring (1999-2013), no station is monitored on an annual basis within the 15-year period. At best, some stations are monitored for 14 years for glyphosate (less than 1%). For groundwater, most stations cannot contribute to a multi-year analysis, with 54% and 53% of stations monitored for only a single year for AMPA and glyphosate, respectively. Less than 15% of the stations have been monitored for 5 years or more out of 15.

With regard to the frequency of sampling within a year in groundwater, the frequency varies between once and twice a year, with a majority of measurements being carried out once a year. The exception to this is 2012, where 4 or 5 measurements per year were conducted for more than 40% of stations.

Analysis on smaller data set, with high-frequency measurements
Study authors proposed an analysis on restricted data set, which excluded some of the monitoring sites that provided only isolated and irregular analyses. Criteria set to retain the sampling sites in the smaller data set were:

- Period 2006-2013
- At least 4 annual GLY or AMPA measurement including the 4 seasons (January-March, April-June, July-September, October-december)

The resulting set is drastically reduced (for AMPA and GLY, respectively 2 and 4% of the samples, and 0.2 and 0.4% of sites from the original set corresponds to the criteria).

In term of seasonality of quantification of the smaller data set, author indicated there was no apparent relationship between quantifications and time of year (figure 7.5-41 to 44)

Also comparison of the % of quantification >0.1µg/L for "higher-frequency measurements" data set and original whole data set indicates only punctual difference for AMPA detection in 2007 and 2009. For glyphosate, the evolution of the % of exceedance through the period follow the same trend in the 2 sets, with sensibly lower proportion of exceedance in the reduced data set.

However, although analysing a reduced data set provides robustness on the temporal issue (since based on continuous and regular sampling period), it does not provide further confidence on the relation between results and pressure of use. Relevant sites (i.e. that could be related to glyphosate containing products) might have been excluded while false negative might still be included in the set. Since no further information on the pressure of use is available for the reduced data set, no straightforward conclusions can be drawn from this analysis.

The study (groundwater part) is considered acceptable.

Data point:	CA 7.5/010
Report author	[redacted]
Report year	2016
Report title	Survey of glyphosate and AMPA in groundwaters and surface waters in Europe - 2015/16 update review – final report
Report No	MSL0027535
Document No	-
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

The study is relevant for multiple subchapters. The summary provided here includes only data from ground water monitoring. Data from surface water monitoring are summarized in the relevant section.

Executive Summary

The report represents a review of glyphosate and AMPA monitoring results for surface (fresh) waters and groundwater across Europe, i.e. all 28 Member States of the European Union, as well as Norway and Switzerland, where information was available. The review is based on an earlier review carried out in 2012, which has been updated to include the latest available information.

Information has been obtained from professional contacts across Europe (government departments and research organisations). In addition, some data provided by Monsanto Europe, as well as from web and literature searches, and on-line databases are included. Some data from the previous review has been omitted where more up-to-date information has become available.

Additional data were collected for 13 countries, i.e. Belgium, the Czech Republic, Denmark, Finland, France, Germany, Italy, Norway, the Slovak Republic, Spain, Sweden, the Netherlands and the UK, as well as the Danube River Basin. In total, there is data for 17 countries, 16 countries plus the Danube River Basin for surface water, and 15 countries for groundwater, with most countries including both.

Groundwater

Glyphosate and AMPA have been increasingly analysed and occasionally detected in groundwater. Glyphosate has been analysed in about 114,000 samples from over 16,000 sites (1990-2015) and detected in 1.3% of samples, with 0.6% above 0.1 µg/L. AMPA has been analysed in almost 105,000 samples from over 15,000 sites (1990-2013) and detected in 2.2% of samples, with 0.8% above 0.1 µg/L. The highest numbers of detections have been reported from Denmark, France and Spain. These seem to occur in shallow water or spring water, which is often included in groundwater surveys, sometimes associated with contamination incidents, and even unsuitable sampling sites and analytical techniques.

From a current perspective, there seems to be no evidence of any persistent and confirmed groundwater contamination with glyphosate or AMPA. In many cases, detections occur in isolated samples rather than consistently at the same sampling site. Where the necessary information is available, it is frequently shown that glyphosate detections are only observed in shallow groundwater (e.g. Denmark and the Netherlands) or wells with direct surface water influence.

The majority of detections occurred only once, which is a clear indication that there is no real groundwater contamination. The small number of multiple detections occurred in shallow groundwater (spring water) or wells unsuitable for groundwater monitoring, suggesting superficial short-term contamination.

I. MATERIAL AND METHODS

The report represents a review of glyphosate and AMPA monitoring results for surface (fresh) waters and groundwater across Europe, i.e. all 28 Member states of the European Union, as well as Norway and Switzerland, where information was available. The review is based on an earlier review carried out in 2012, which has been updated to include the latest available information.

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Additional data were collected for 13 countries, i.e. Belgium, the Czech Republic, Denmark, Finland, France, Germany, Italy, Norway, the Slovak Republic, Spain, Sweden, the Netherlands and the UK, as well as the Danube River Basin.

In total, there is data for 17 countries, 16 countries plus the Danube River Basin for surface water, and 15 countries for groundwater, with most countries including both. However, the Czech and Slovak Republics monitor only surface water, whereas for Malta only groundwater was monitored in a special investigation. Data was mainly collated at national level, but in some cases at regional level, e.g. for Belgium (two regions) and Germany (surface water data Rhine and some individual Länder). 11 countries have confirmed that there is no monitoring of glyphosate and AMPA (Bulgaria, Croatia, Cyprus, Greece, Hungary, Latvia, Lithuania, Luxembourg, Poland, Portugal and Romania).Although it has been confirmed that glyphosate and AMPA are monitored in Slovenia, it has not been possible to obtain any data to date, nor has any information been received from Estonia. Although overall most data are considered reasonably reliable, it was not possible to fully assess their reliability, notably the French database which provides a comprehensive source of data for surface water and groundwater, includes several extremely high values, which were considered ‘outliers’ and excluded from this analysis.

II. RESULTS AND DISCUSSION

Table 8.5-48 provide an overview of the main data for surface water and groundwater, respectively. The summarised data is not precise but presents a best estimate, mainly because of the various forms in which the data was obtained, e.g. some results in terms of samples, others in terms of sites, and other information gaps.

Groundwater

Table 8.5-48: Summary of glyphosate and AMPA data in groundwater in Europe

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples ≥ 0.1 µg l^{-1}		Max. Conc.	LoQ (LoD)
				No.	%	No.	%	µg/L	µg/L
Austria									
Glyphosate	2004	~950	3633	7	0.19	2	0.06	>0.1	<0.1
AMPA	2004	~950	3636	44	1.2	11	0.3	0.75	<0.1
Belgium (Flanders & Wallonia)									
Glyphosate (Flanders)	2006-2008	≥448	1488	4	0.03	1	0.01	≤0.5	0.01
AMPA (Flanders)	2007-2014	≥504	4515	789	17.5	≥8	≥0.18	1.85	0.01
Glyphosate (Wallonia)	2000-2006	450	≥450	0	-	0	-	<0.025	<0.025

Table 8.5-48: Summary of glyphosate and AMPA data in groundwater in Europe

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples ≥ 0.1 µg l^{-1}		Max. Conc.	LoQ (LoD)
				No.	%	No.	%	µg/L	µg/L
AMPA (Wallonia)	2000-2006	450	≥450	13 (s)	3 (s)	0	-	< 0.05	<0.025
Denmark									
Glyphosate	1990-2013	4941	15552	142	0.9	28	0.2	4.7	(0.01-<0.1)
AMPA	1990-2013	4946	15541	106	0.7	23	0.15	9.1	(0.01-<0.1)
Finland									
Glyphosate	2002-2008	81	81	0	-	0	-	-	0.1
AMPA	2002-2008	81	81	0	-	0	-	-	0.05
France									
Glyphosate	1999-2012	≥7028	78431	859	1.1	565	0.7	28	0.01-0.2
AMPA	2000-2012	≥6904	70492	1122	1.6	643	0.9	19	0.01-0.2
Germany									
Glyphosate	1996-2008	≥430	≥2599	35	1.3	9	0.34	<1.0	<0.1
AMPA	1996-2008	≥387	≥1986	64	3.2	34	1.7	≥1.0	<0.1
Ireland									
Glyphosate	2007-2009	92	679	6	0.8	1	0.1	0.19	<0.1
Italy (Lombardia Region)									
Glyphosate	2005-2012	≥359	1497	9	0.6	5	0.2	1.2	0.1
AMPA	2007-2012	≥359	1156	14	1.2	11	0.9	1.3	0.1
Malta									
Glyphosate	2009	18	≥ 18	0	-	0	-	-	(0.01)
Norway									
Glyphosate	1999-2000	7	8	0	-	0	-	-	(0.01)
AMPA	1999-2000	7	8	1	12.5	0	-	0.02	(0.01)
Spain									
Glyphosate	2009-2012	≥461	963	325	34	86	8.9	25	0.03-0.3
Sweden									
Glyphosate	2000-2014	≥ 21	5989	26	0.43	10	0.17	0.23	<0.03
AMPA	2000-2014	≥ 21	5930	31	0.52	≤26	0.43	7.9	<0.05
Switzerland									
Glyphosate	2005-2006	117	≥ 234	≥4	1.7	≥3	1.3	0.21	(0.05)
AMPA	2005-2006	117	≥ 232	17	7.3	11	4.7	0.46	(0.05)
The Netherlands									
Glyphosate	2003-2006	<691	691	4	0.58	4	0.58	4.7	(<0.1)
AMPA	2003-2006	<691	691	21	3.0	21	3.0	5.1	(<0.1)
UK									
Glyphosate	1995-2015	≥264	1680	16	0.95	≤6	≤0.35	1.38	(0.01-0.1)
Total									
Glyphosate	1990-2015	≥16160	≥113993	1437	1.3	724	0.6	<0.05-28	0.01-0.2
AMPA	1990-2013	15417	≥104718	2222	2.1	788	0.75	0.02-19	0.01-0.2

LoQ = limit of quantification (LoD = limit of detection)
(s) sites (number of samples not known)
- not relevant

Glyphosate and AMPA have been increasingly analysed and occasionally detected in groundwater. Glyphosate has been analysed in about 114 000 samples from 16 000 sites (1990-2015) and detected in 1.3% of samples, with 0.6% above 0.1 µg/L; AMPA has been analysed in 105 000 samples from over 15 000 sites (1990-2013) and detected in 2.2% of samples, with 0.8% above 0.1 µg/L. The highest numbers of detections have been reported from Denmark, France and Spain. These seem to occur in shallow water or spring water, which is often included in groundwater surveys, sometimes associated with contamination incidents (where the information is available), and even unsuitable sampling sites and analytical techniques (investigations in Denmark, France, Germany and the Netherlands-although no details are available for the detection in Spain).

From a current perspective, there seems to be no evidence of any persistent and confirmed groundwater contamination with glyphosate or AMPA. In many cases, detections occur in isolated samples rather than consistently at the same sampling site. Where the necessary information is available, it is frequently shown that glyphosate detections are only observed in shallow groundwater (e.g. Denmark and the Netherlands) or wells with direct surface water influence, where the surface water contaminated groundwater.

Reports from some countries stated that groundwater contamination with glyphosate and AMPA was not of concern, e.g. Belgium-Wallonia, Finland, Norway, the Czech and Slovak Republics, nor does it seem to be an important issue in the Netherlands. Some countries have reduced or discontinued glyphosate monitoring in groundwater as a result of special investigations or routine monitoring, where it was rarely found, e.g. Austria, Belgium-Flanders, Baden-Württemberg (Germany), Finland, Ireland, Malta, Norway, Sweden and the UK. Portugal decided on the basis of risk assessments that it was not necessary to monitor glyphosate and AMPA.

III. CONCLUSION

Ground and surface water monitoring data were gathered from 17 European countries, 16 countries plus the Danube River Basin for surface water, and 15 countries for groundwater, with most countries including both.

In groundwater, glyphosate and AMPA have been increasingly monitored and occasionally detected above the 0.1 µg/L limit (0.6% of the analysed samples for glyphosate and 0.8% for AMPA). From a current perspective, there seems to be no evidence of any persistent and confirmed groundwater contamination with glyphosate or AMPA.

Assessment and conclusion by applicant:
The study provides an overview on monitoring data (up to 2015) for groundwater and surface water from 15 and 17 European countries, respectively. No specific guideline is applicable to this data point.
The study is therefore considered valid.

Assessment and conclusion by RMS:

This study is an update of the study of [redacted], 2012 assessed in the RAR, 2015. It includes data from 1997-2015. Only data from groundwater results were left here. Data from the surface water monitoring are summarized in the relevant section.

Data collected from groundwater survey in this study overlaps the one collected in [redacted] 2020. Results are included in the summary of the study of [redacted], 2020.

However, the present report may give further information and clarification on findings above 0.1 µg/L. Some of the comments are taken from the evaluation of [redacted], 2012 in the RAR 2015, if no further data from previous review is available.

In AT, no further data compared to the previous review of [redacted] 2012. Glyphosate was detected in isolated cases. AMPA was detected somewhat more frequently and at higher concentrations. There is no information about the type of groundwater, although the results, as presented, related to pore groundwater only, not the springs from fractured aquifers. Traces of AMPA were also found in two spring water samples and it was considered unclear at the time whether these findings were related to glyphosate or to aminophosphonates from detergents.

In Denmark, there is no further analysis of data above 0.1 µg/L, other than the depth being less than 15 metres in all samples analysed since 2004. Study author however indicate that "a recent study ([redacted], 2011) reported the investigation of four of the wells where glyphosate and AMPA had been detected in the GEUS groundwater survey. It was concluded that the occurrence of glyphosate and AMPA was unlikely to be caused by agricultural and other approved usages."

In FR, investigations (ISL, 2007; [redacted] 2015) relating to a small number of detections of glyphosate in drinking waters, most of which were derived from groundwater, revealed that the detections were most likely due to sample contamination, analytical problems or short-term contamination of small private or community wells. From the findings of a recent study (Anonymous, 2012 CA 7.5/011), which analysed the potential contamination of groundwater with glyphosate (and AMPA) at 27 sites from 2007-2010, it is clear that none of the glyphosate detections could be attributed to long-term contamination of typical groundwater. The majority of detections occurred once only, which is anindication that there is no real groundwater contamination, and the small number of multiple detections occurred in shallow groundwater (spring water) or wells unsuitable for groundwater monitoring, suggesting superficial short-term contamination

In DE, Groundwater data is collated at Federal level and glyphosate and AMPA data has been obtained for the years 1996-2008 (though 2008 data was incomplete, and no more recent data has become available). Glyphosate and AMPA have been reported for a small number of sites, with AMPA at higher frequency and concentrations. However, an investigation (up to 2004) of sites with glyphosate detections showed all these to have been due to invalid analyses or contaminated observation wells.

In the Netherlands, no more data available compared to [redacted], 2012. Both glyphosate and AMPA have been detected in a small number of groundwater samples (once each in 10 different wells). These were investigated in detail and it was concluded that 5 of the results (all at levels below 0.15 µg/L were uncertain (high margins of error) whilst overall, all sampling points with positive detections were in cultivation areas with sandy or highly sandy soils, and samples were taken mainly from shallow groundwater.

In Spain, Glyphosate monitoring data for groundwater have become available for 2009-12.Glyphosate was frequently detected (34% of samples) in groundwater, and above 0.1 µg l-1 in 8.9% of samples, with a maximum concentration of 25 µg/L in 2012. There was no information on the type or depth of groundwater, or whether the focus was on particularly vulnerable sites as in an earlier study (2007-10), where glyphosate was detected in a number of groundwater samples taken during glyphosate application periods. No further investigations of these detection is given in the report.

The study is considered acceptable.

Existing studies/assessments

Data point:	CA 7.5/011 CA 7.5/012 (Translation)
Report author	Anonymous
Report year	2012
Report title	Analysis of groundwater contamination with glyphosate/AMPA
Report No	GDY/MGI/10332_Rapport_final_V5
Document No	
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	Yes, accepted in RAR (2015)
GLP/Officially recognised testing facilities	No (no experimental work performed)
Acceptability/Reliability:	Supportive

Executive Summary

The annual reports of the French Environmental Institute (Institut Français de l'Environnement, Ifen) monitoring the plant protection products in the French waters mentioned the detection of glyphosate and its degradation product, AMPA, above 0.1 µg/L in several groundwater sampling sites. A selection of 27 sites for further investigation was performed based on the information available in the ADES database (Accès au Données sur les Eaux Souterraines – access to groundwater data) at the start of the project (April 2010). The sites were selected based on the following criteria:

- Sites with multiple glyphosate detections
- Sites with glyphosate and AMPA detection,
- Priority wells as defined by the WFD (Water Framework Directive) with at least one glyphosate detection
- Detection of glyphosate without subsequent confirmatory analysis after the detection.

Two sites were rejected early in the study, due to their low vulnerability (confined water body) suggesting that the reported detects were not reliable. An in-depth investigation was conducted on the remaining 25 wells to verify the analytical data and the site vulnerability. Based on the information gathered during the investigation, a confidence (reliability) index related to the glyphosate/AMPA detect was estimated for each site.

Eight different labs were involved in the analysis of the samples and in most cases the analytical method included a direct FMOC-Cl derivatization (no or limited sample clean-up) followed by HPLC quantification with either fluorescence or MS detection. Of the 25 sites, 19 reported a single detect of glyphosate and out of those, 16 had follow-up analyses <0.1 µg/L reported in the ADES database since the start of the project, whilst no analysis were available after the detection for three sites. Six sites reported multiple detects: two sites (used for drinking water supply) showed two detects the same year, but samplings the years after showed glyphosate results <0.1 µg/L. The four other sites with multiple detects had no well protection, and were not suited for groundwater monitoring (fire well, piezometer, spring, private well).

The geological investigation showed that the groundwater vulnerability of 21 out of the 25 sites was high to very high and the detection of numerous other plant protection products were observed in several wells. Overall, the detects from seven wells have been given an estimated confidence index ≥8 (very high confidence that the detect is real): five of these are sites with multiple detects, one is a private well with no well protection and one is a WFD priority site (spring in karstic soil, shallow water which showed many detects of plant protection products including one isolated glyphosate detect >0.1 µg/L).

None of the detects could be attributed to long-term contamination of typical groundwater. The majority of detections occurred once only, which is a clear indication that there is no real groundwater contamination, and the small number of multiple detections occurred in shallow groundwater (spring water) or wells unsuitable for groundwater monitoring, suggesting superficial short-term contamination.

I. MATERIAL AND METHODS

The investigation of the groundwater contamination with glyphosate/AMPA included three phases:

- Phase 1: Survey on the sampling and analysis conditions: first, the parties organizing the analyses were contacted with a view of identifying the laboratories that performed the analyses with glyphosate/AMPA detections. After identification, those laboratories were contacted in order to identify the various elements of the sampling and analysis process.
- Phase 2: Investigation of the wells and their environment:
  - The hydrogeological characteristics of each well is described mainly on the basis of available information from existing databases. The collected elements were later corroborated during site visits. The various researched data included the use of the well, the existence of a well protection (water supply well), water yield, depth of the works and, if possible, groundwater level, the geology at the well and in its proximity. The analysis of these elements enabled the assessment of the "hydrogeological vulnerability of the well".
  - The analysis of the soil characteristics was performed based on soil cores taken within 1 km around the well within the boundaries of the catchment area. Therefore, three soil cores were taken at each site. When the topographic features allowed it (slopes, break of slope, deep ditch), a soil profile study was performed, in order to describe the existing soils in a more detailed manner. The collected soil information included the soil texture, colour of the different horizons, soil depth, depth of rock weathering layer occurrence and depth of occurrence for the parent rock itself, load of coarse elements, hydromorphy, organic matter content, and characteristics of the underlying geological layer.
  - Within 1 km around the well and depending on the well catchment area, the land use was surveyed for the following elements:
    - agricultural area: crop type for each plot (when the plot is ploughed and where possible, the previous crop was identified on the basis of crop residues);
    - non-agricultural area: residential areas, industrial and commercial areas, road infrastructure. Any development likely to contribute to groundwater contamination through glyphosate use.

For each well, a cartographic representation on an orthophoto base was prepared, comprising the above elements.

- Phase 3: Summary of data and definition of a confidence (or reliability) index related to groundwater glyphosate/AMPA contamination. This index is a crossing between the risk of groundwater contamination by glyphosate (based on land (glyphosate potential) use and site/aquifer vulnerability) and the characteristics of the analyses performed (laboratory, method, detection frequency, presence of other plant protection products, nitrates, coliforms). It does not take into account the inherent physico-chememical properties of glyphosate and its metabolite AMPA. A reliability index from 1 to 10 (low to high confidence) has been estimated for each site.

II. RESULTS AND DISCUSSION

The table below provides information on the method used by laboratories that performed the glyphosate and AMPA analyses, as well as the number of sites covered by the lab.

Table 8.5-49: Methods of analyses

Laboratory	Clean-up step	Derivatization	Detection	Quantification	Number of sites
IPL (Maxeville)	Concentration and clean-up on FPC cartridge	FMOC-Cl	LC/MS/MS	Internal standard (cysteic acid)	13
SGS laboratory	Acidification and sample concentration	O-Phthalaldehyde	HPLC - Fluorescence	External standard	1
CAR (Illkirch)	Sample concentration and acidification	O-Phthalaldehyde	HPLC - Fluorescence	External standard	1
IPL (Lille)	No	FMOC-Cl	LC/MS/MS	Internal standard ($^{13}C^{15}N$ glyphosate)	2
LASAT (La Rochelle)	No	FMOC-Cl	HPLC - Fluorescence	External standard	1
ASPOSAN (Montbonnot)	No	FMOC-Cl	HPLC - Fluorescence	External standard	2
LD26 (Valence)	No	FMOC-Cl	HPLC - Fluorescence	External standard	4
Labo des Pyrénées (Lagor)	Concentration after derivatization	FMOC-Cl	HPLC - Fluorescence	External standard	1

The most reliable methods are the ones involving LC/MS/MS with an internal standard, which is the case for the IPL laboratories (Lille and Maxeville). However, the laboratory from Maxeville has only been acquired by IPL in 2008, and the analytical method previously used may not have been the one described in the table above.

The quantification limit of most of the analytical methods was at 0.1 µg/L; suggesting that a relatively high margin of error will be associated to detects close to this value (below 0.15 µg/L).
The table below summarizes the results of the investigation for the 27 wells.

Table 8.5-50: Investigation results

Site (use of the well)	Well water table (m)	Well depth (m)	Findings	Results investigation	Confidence index[1]
Sites rejected (not investigated)					
Lureuil	81	-	0.14 µg/L glyphosate (04/2008)	Confined aquifer- low vulnerability	low
Sarreinseming	256	-	0.23 µg/L glyphosate/2 µg/L AMPA (04/2008)	Low vulnerability	low
Sites with single glyphosate detects (no AMPA) (2007-2008)					
Nort sur Erdre (DW supply)	63	up to 8 m	0.17 µg/L glyphosate (06/2007) 15 subsequent analyses <0.1 µg/L(2007-2010)	Highly vulnerable water body – permeable soils - Numerous pesticides>0.1 µg/L + nitrates >50 mg/L Glyphosate use likely	high
Avant-les-Ramerupt (DW supply)	50	Up to 10.7 m	0.15 µg/L glyphosate (10/2007) 2 subsequent analyses <0.1 µg/L (2010)	Highly vulnerable water body – permeable soils Some pesticides >0.1 µg/L Glyphosate use likely	high
Boissy le Repos (Petroleum research)	64	-	0.3 µg/L glyphosate (04/2007) Single analysis	Water body of medium vulnerability - No well protection Glyphosate use unlikely	low
Bouy (DW supply)	28	up to 8.3 m	0.13 µg/L glyphosate (10/2007) 4 subsequent analyses <0.1 µg/L (2009-2010)	Water body of medium to high vulnerability – permeable soils Glyphosate use likely	medium
Vernoy (DW supply)	6.6	up to 0.9 m	0.27 µg/L glyphosate (10/2007) Analysis 2 days later : <0.1 µg/L 21 subsequent analyses <0.1 µg/L (2008-2010)	Highly vulnerable water body Numerous pesticides>0.1 µg/L – regular detection of coliforms Glyphosate use likely	high
Tonnay Charente (DW supply)	9	up to 6.2 m	0.19 µg/L glyphosate (11/2007) No subsequent analysis	Highly vulnerable water body and permeable soils – nitrates > 50 mg/L Glyphosate use likely	high
Castagnède (DW supply)	-	-	1.19 µg/L glyphosate (06/2007) One subsequent analysis <0.1 µg/L (2008)	Highly vulnerable water body (possible contact with surface water) – no other pesticide detects. – permeable soils Glyphosate use unlikely	low
Sites with single glyphosate detects(no AMPA) (2007-2008)					
La Chapelle Agnon (DW supply)	-	-	0.21 µg/L glyphosate (10/2008) Four subsequent analyses <0.1 µg/L (2009-2010)	Water body of average to high vulnerability – permeable soils -no other pesticides detected Glyphosate use unlikely	low
La Roche Noire (DW supply)	-	-	0.12 µg/L glyphosate (10/2008) Three subsequent analyses <0.1 µg/L	Highly vulnerable water body (possible contact with surface water) – permeable soils - one other pesticide detect Glyphosate use possible	low

Table 8.5-50: Investigation results

Site (use of the well)	**Well water table (m)**	**Well depth (m)**	**Findings**	**Results investigation**	**Confidence index[1]**
Saint Cyr sous Dourdan (DW supply)	88	up to 3 m	2.06 µg/L glyphosate (09/2007) One subsequent analysis (2009) <0.1 µg/L	Highly vulnerable water body – no other pesticide detected >0.1 µg/L Glyphosate use possible	medium
Houvin-Houvigneul (DW supply)	54.5	up to 35.1 m	0.3 µg/L glyphosate (11/2007) One subsequent analysis (2010) <0.1 µg/L	Highly vulnerable water body – no other pesticide detected >0.1 µg/L Glyphosate use likely	high
Aubignan (Private well - Qualitometer)	7	-	0.2 µg/L glyphosate (10/2007) No subsequent analysis	Highly vulnerable water body – permeable soils - few other pesticide detected >0.1 µg/L Glyphosate use likely No well protection	high
Grosne (DW supply)	5.5	-	0.12 µg/L glyphosate (12/2007) One subsequent analysis <0.1 µg/L (2009)	Water body of medium vulnerability – no other pesticide detected Glyphosate use possible	low
Issans (DW supply)	5.2 m (spring)		0.2 µg/l glyphosate (08/2007) 3 subsequent analyses <0.1 µg/L	Highly vulnerable water body – many other pesticides detected – permeable soils Glyphosate use likely	very high
Villers-Farlay (DW supply)	-	-	0.31 µg/L glyphosate (07/2007) Four subsequent analyses <0.1 µg/L (2010)	Highly vulnerable water body – many other pesticides detected – permeable soils Glyphosate use likely	high
Machecoul (DW supply)	-	-	0.13 µg/L glyphosate (06/2007) 20 subsequent analyses <0.1 µg/L	Highly vulnerable water body – many other pesticides detected – very permeable soils Glyphosate use likely	high
Sites with simultaneous glyphosate and AMPA single detects (2007-2008)					
Saint Georges d’Esperanche (DW supply)	56	up to 34.7 m	0.22 µg/L glyphosate (01/2008) 0.22 µg/L AMPA (01/2008) 14 subsequent analyses <0.1 µg/L (2008-2010)	Water body of medium to high vulnerability – few other pesticides detected – very permeable soils Glyphosate use likely	high
Monteynard (DW supply)	-	-	0.3 µg/L glyphosate (01/2008) 0.14 µg/L AMPA (01/2008) Two subsequent analyses <0.1 µg/L (2009-2010)	Highly vulnerable water body – no other pesticide detected >0.1 µg/L Glyphosate use unlikely	low
La Flotte (private well)	20	up to 8m	0.21 µg/L glyphosate (09/2008) 0.19 µg/L AMPA (09/2008) Four subsequent analyses <0.1 µg/L (2009-2010)	Water body of medium to high vulnerability – very permeable soils Glyphosate use very likely No well protection area	very high

Table 8.5-50: Investigation results

Site (use of the well)	Well water table (m)	Well depth (m)	Findings	Results investigation	Confidence index[1]
Sites with multiple detects					
Chepy (fire well)	4	-	0.56 µg/L glyphosate (09/2007) 3.4 µg/L AMPA (09/2007) 2.36 µg/L AMPA (10/2008) 0.63 µg/L glyphosate (04/2009) 0.21 µg/l AMPA (0.4/2009) 0.63 µg/L glyphosate (10/2010) 1.04 µg/L AMPA (10/2010)	Very highly vulnerable water body – many other pesticides detected – nitrates >50 mg/L Glyphosate use very likely No well protection area	very high
Corbeilles (piezometer)	19	up to 9 m	0.254 µg/L glyphosate (05/2007) 0.14 µg/L glyphosate (10/2010) 0.19 µg/L glyphosate (12/2010) Regular AMPA detects 2007-2010 (average 0.2 µg/L)	Very highly vulnerable water body – many other pesticides detected – nitrates >50 mg/L Glyphosate use	very high
Blanzay (DW supply)	60	up to 9.5 m	0.2 µg/L glyphosate (10/2008) 0.5 µg/L glyphosate (12/2008) Nine subsequent analysis <0.1 µg/L (2009-2010)	Highly vulnerable water body – few other pesticides detected – nitrates >50 mg/L Glyphosate use likely	very high
Fontenay le Pesnel (DW supply)	3.8	up to 2 m	0.137 µg/L glyphosate 04/2007) 12.9 µg/L glyphosate (10/2007) 0.92 µg/L AMPA (10/2007) Six subsequent analyses <0.1 µg/L (2008-2010)	Highly vulnerable water body – few other pesticides detected Glyphosate use likely	high
Evans (Qualitometer)	spring	-	0.16 µg/L glyphosate (07/2008) 0.95 µg/L AMPA (07/2008) 0.1 µg/L glyphsoate (07/2010) 1.1 µg/L AMPA (07/2010) 0.24 µg/L glyphosate (05/2010) 0.73 µg/L AMPA (05/2010)	Highly vulnerable water body – many other pesticides detected Glyphosate use likely	very high
Avrille (private use)	6.5	up to 1.65 m	0.68 µg/L glyphosate (05/2007) 0.3 µg/L glyphosate (03/2008) AMPA regularly detected – average 0.41 µg/L (1007-2010)	Highly vulnerable water body – many other pesticides detected – nitrates >50 mg/L permeable soils Glyphosate use very likely	very high

[1] This index provides the level of confidence in the reported detects, based on the vulnerability of the aquifer, soil permeability, land (glyphosate) use in the area, analytical method and detection frequency. It does not take into account the inherent phys-chem properties (and thus the low leaching potential) of glyphosate and AMPA.

Two sites were rejected early in the process due to their low vulnerability and no further investigation was performed. Out of the 25 remaining sites, 16 showed a single detect of glyphosate (without AMPA) and three showed a single detect for both glyphosate and AMPA. With the exception of three sites at which no subsequent glyphosate analysis were performed after the detect, all other sites had samples analyzed within the months/years after the detect showing glyphosate/AMPA results <0.1 µg/L, demonstrating that the contamination was not widespread in the aquifer and not long-term.

Multiple detects were observed in six sites, two of which were used for drinking water supply. At those sites, the detects occurred the same year, and the analyses performed the following years showed no further contamination by glyphosate and AMPA. The four other sites with multiple detects had no well protection area, and were not suited for drinking water supply (private or fire well, piezometer, qualitometer, spring).

The estimated confidence index was very high for seven of the 25: five of those are sites with multiple detects, one is a private well with no well protection area, and one is a site used for DW supply (spring in a karstic soil, shallow water which showed many detects of plant protection products including one isolated detects of glyphosate).

The estimated confidence index was low for six of the 25 sites: in those areas the use of glyphosate was questionable.

III. CONCLUSION

In an attempt to investigate the presence of glyphosate/AMPA in groundwater, a selection of 27 groundwater abstraction sites was evaluated. Two sites were rejected early in the process due to their low vulnerability, suggesting that the reported detect was not accurate.

An in-depth investigation was performed on the 25 remaining sites. The results show that in 76% of the cases, the detections were sporadic (one sample of several analysis), demonstrating that the contamination was not widespread in the aquifer. Four sites showed a more serious contamination, with multiple detects over the years, but none of these are used for drinking water supply and none had a well protection area.
In summary, none of the glyphosate detects could be attributed to long-term contamination of typical groundwater.

Assessment and conclusion by applicant:
The study elucidates findings of glyphosate and AMPA in groundwater in France. The methods and results are sufficiently described.
The study is therefore considered valid.

Assessment and conclusion by RMS:
This report has already been provided and evaluated in the previous RAR in 2015 by RMS DE.
The following assessment from RMS DE is reported :

The annual reports of the French Environmental Institute (Institut Français de l'Environne-ment, Ifen) monitoring the plant protection products in the French waters mentioned the detection of glyphosate and its degradation product, AMPA, above 0.1 µg/L in several groundwater sampling sites. A selection of 27 sites for further investigation was performed.

Thereby, two sites were rejected early in the process due to their low vulnerability and no further investigation was performed. Out of the 25 remaining sites, 16 showed a single detect of glyphosate (without AMPA) and three showed a single detect for glyphosate and AMPA. With the exception of three sites, all other sites had samples analysed within the months/years after the detection showing glyphosate/AMPA results <0.1 µg/L, demonstrating that the contamination was not widespread in the aquifer and not long-term. Multiple detects were observed in six sites, two of which were used for drinking water supply. At those sites, the detections occurred the same year, and the analyses performed the following years showed no further contamination by glyphosate and AMPA. The four other sites with multiple detects had no well protection area, and were not suited for drinking water supply (private or fire well, piezometer, qualitometer, spring).

It has to be noted that this groundwater glyphosate/AMPA contamination constitutes a limited approach for the following reasons:

- Heterogeneity of analytical data and sometimes absence of data
- Only one site visit focused on the analysis of the physical setting within a 1 km range
- Difficulty concerning the confidence index related to glyphosate/AMPA groundwater detection
- Absence of information on glyphosate use (agricultural and non-agricultural uses).

The study is therefore considered supportive.

Data point:	CA 7.5/013
Report author	[redacted]
Report year	2012
Report title	Survey of glyphosate and AMPA in groundwaters and surface waters in Europe
Report No	-
Document No	BVL No. 2310291
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	Yes, accepted in RAR (2015)
GLP/Officially recognised testing facilities	No (no experimental work performed)
Acceptability/Reliability:	Acceptable

The study is relevant for multiple subchapters. Only results related to surface water have been left in the following summary.

Executive Summary
This review is based on an earlier review carried out in 2009, which has been updated to include the latest available information. The review covers glyphosate and AMPA monitoring results for surface (fresh) waters and groundwater across Europe, *i.e.* all 27 Member States of the European Union, as well as Norway and Switzerland, where available.

Information has been obtained from professional contacts across Europe (government departments and research organisations), and including some data provided by Monsanto Europe, as well as from web and literature searches, and by querying on line databases. Some data from the previous review has been omitted where more up to date information has become available.

Groundwater

Glyphosate and AMPA have been increasingly analysed and occasionally detected in groundwater**.** Glyphosate has been analysed in almost 67 000 samples from about 675 sites (1993-2010) and detected in 1% of samples, with 0.6% above 0.1 µg/L; AMPA has been analysed in 52 000 samples from 1 345 sites (1993-2011) and detected in 2.6% of samples, with 0.8% above 0.1 µg/L. These seem to occur in shallow water or spring water, which is often included in groundwater surveys, sometimes associated with contamination incidents (where the information is available), and even unsuitable sampling sites and analytical techniques (investigations in France and Germany).

To date, there seems to be no evidence of any persistent and confirmed groundwater contamination with glyphosate or AMPA. In many cases detections occur in isolated samples rather than consistently at the same sampling site. Where the necessary information is available, it is frequently shown that glyphosate detections are only observed in shallow groundwater (e.g. Denmark and the Netherlands) or wells with surface water influence, for example contamination.

I. MATERIAL AND METHODS

This investigation is a desk study, and the information was obtained from professional contacts across Europe (government departments and research organisations in each of the countries), and including some data provided by Monsanto Europe, as well as from web and literature searches, and by querying on line databases.

II. RESULTS AND DISCUSSION

Table 8.5-51 provide an overview of the main data for groundwater. The summarised data is not precise but presents a best estimate, mainly because of the various forms in which the data were obtained, *e.g.* some results in terms of samples, others in terms of sites, and other gaps in information.

In total, there is data for 17 countries, 14 each for surface water and groundwater, with most countries including both. However, the Czech and Slovak Republics monitor only surface water, and data for Spain was available for surface water only; for Malta and Switzerland only groundwater data was obtained. Data were mainly collated at national level, but in some cases regional, as for Belgium (two regions), Italy (one region), and Germany (surface water data for several Länder). Seven countries have confirmed that there is no monitoring of glyphosate and AMPA (Bulgaria, Cyprus, Hungary, Latvia, Lithuania, Luxembourg, Romania), no information was obtained from the remaining five countries (Estonia, Greece, Poland, Portugal and Slovenia).

Groundwater

Table 8.5-51: Summary of glyphosate and AMPA data in groundwater in Europe

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples ≥ 0.1 µg l^{-1}		Max. Conc.	LoQ (LoD)
				No.	%	No.	%	µg/L	µg/L
Austria									
Glyphosate	2004	~950	3633	7	0.19	2	0.06	>0.1	<0.1
AMPA	2004	~950	3636	44	1.2	11	0.3	0.75	<0.1
Belgium (Flanders & Wallonia)									
Glyphosate (Flanders)	2007-08	450	1088	1	0.1	0	nr	0.011	0.01
AMPA (Flanders)	2007-11	504	3933	707	18	-[1]	nr	1.85	0.01
Glyphosate (Wallonia)	2000-06	450	≥450	0	nr	0	nr	<0.025	<0.025
AMPA (Wallonia)	2000-06	450	≥450	13 (s)	3 (s)	0	nr	< 0.05	<0.025
Denmark									
Glyphosate	1993-10	1825	9908	117	1.2	21	0.21	4.7	(0.01-<0.1)
AMPA	1993-10	1840	9906	84	0.84	18	0.18	4.2	(0.01-<0.1)
Finland									
Glyphosate	2002-08	80	80	0	nr	0	nr	nr	0.1
AMPA	2002-08	80	80	0	nr	0	nr	nr	0.05
France									
Glyphosate	99-09	≥7403	45960	515	1.1	390	0.8	24	0.01-0.1
AMPA	99-09	≥7184	30529	442	1.4	321	1.1	19	0.01-0.1
Germany									
Glyphosate	2007	196	≥ 196	7 (s)	3.6 (s)	0	nr	≤ 0.1	<0.1
AMPA	2007	326	≥ 326	10 (s)	3.1 (s)	5	1.5	≥ 1	-[1]
Ireland									
Glyphosate	2007-09	92	679	6	0.8	1	0.1	0.19	<0.1
Italy (Lombardia Region)									
Glyphosate	2005-08	359	961	0	nr	0	nr	<0.1	0.1
AMPA	2007-08	359	≥619	3	≤0.5	3	≤0.5	0.9	0.1
Malta									
Glyphosate	2009	18	≥ 18	0	nr	0	nr	nr	(0.01)
Norway									
Glyphosate	99-00	7	8	0	nr	0	nr	nr	(0.01)
AMPA	99-00	7	8	1	12.5	0	nr	0.02	(0.01)
Sweden									
Glyphosate	2009-10	≥ 21	1247	1	0.08	0	nr	0.04	(<0.03)
AMPA	2009-10	≥ 21	1242	3	0.24	1	0.08	0.72	(<0.03)
Switzerland									
Glyphosate	2005-06	117	≥ 234	4 (s)	3.4	3 (s)	2.6 (s)	0.21	(0.05)
AMPA	2005-06	117	≥ 232	≥ 10 ≤ 17 (s)	≥ 9 ≤ 14 (s)	≥ 6 ≤ 11 (s)	≥ 5 ≤ 9 (s)	0.46	(0.05)
The Netherlands									
Glyphosate	2003-06	<691	691	4	0.58	4	0.58	4.7	(<0.1)
AMPA	2003-06	<691	691	21	3.0	21	3.0	5.1	(<0.1)
UK									
Glyphosate	95-07	≥ 217	1509	13	0.9	≤ 3	≤ 0.2	0.47	(0.014-0.4)
Total									
Glyphosate	93-2010	12876	≥66662	675	1.0	424	0.64	0.01-24	0.01-0.4
AMPA	93-2011	12525	≥51652	1345	2.6	398	0.77	0.02-19	0.01-0.1

LoQ = Limit of Quantification, LoD = Limit of Detection

[1] No information

(s) sites (number of samples not known)

nr = not relevant

Glyphosate and AMPA have been increasingly analysed and occasionally detected in groundwater**.** Glyphosate has been analysed in almost 67 000 samples from about 675 sites (1993-2010) and detected in 1% of samples, with 0.6% above 0.1 µg/L; AMPA has been analysed in 52 000 samples from 1 345 sites (1993-2011) and detected in 2.6% of samples, with 0.8% above 0.1 µg/L. These seem to occur in shallow water or spring water, which is often included in groundwater surveys, sometimes associated with contamination incidents (where the information is available), and even unsuitable sampling sites and analytical techniques (investigations in France and Germany).

To date, there seems to be no evidence of any persistent and confirmed groundwater contamination with glyphosate or AMPA. In many cases detections occur in isolated samples rather than consistently at the same sampling site. Where the necessary information is available, it is frequently shown that glyphosate detections are only observed in shallow groundwater (e.g. Denmark and the Netherlands) or wells with surface water influence, for example contamination.

Reports from some countries stated that groundwater contamination with glyphosate and AMPA was not of concern, e.g. Belgium – Wallonia, Finland, Norway, the Czech and Slovak Republics. Some countries have reduced or abandoned glyphosate monitoring in groundwater as a result of special investigations or routine monitoring, where it was rarely found, e.g. Austria, Belgium - Flanders, Baden-Württemberg (Germany), Italy, Sweden and the UK.

Whereas an increase in glyphosate detection and/or concentrations before 2009 in Denmark was indicated, a decrease was reported in 2010. It would need further data and statistical analyses before any conclusions can be drawn.

III. CONCLUSION

Ground and surface water monitoring data were gathered from 17 European countries, 14 each for surface and groundwater, with most countries including both. In groundwater, glyphosate and AMPA have been increasingly monitored and occasionally detected above the 0.1 µg/L limit (0.6% of the analyzed samples for glyphosate and 0.8% for AMPA). To date, there seems to be no evidence of any persistent and confirmed groundwater contamination with glyphosate or AMPA.

Assessment and conclusion by applicant:
The study compiles drinking water quality data (up to 2012) for glyphosate and AMPA from national authorities in Europe. The methods and results are sufficiently described.
The study is considered valid.

Assessment and conclusion by RMS:

This study has already been peer-reviewed in the RAR 2015. An updated review for the current renewal dossier is available in [redacted] 2016. RMS DE assessment from the RAR 2015 is reported below for the groundwater part of the study:

[redacted] (2012) provided a review that covers glyphosate and AMPA monitoring results for surface (fresh) waters and groundwater across Europe, i.e. all 27 Member States of the EU.

Glyphosate and AMPA have been increasingly analysed and occasionally detected in groundwater. Glyphosate has been analysed in 66662 samples from about 675 sites (1993-2010) and detected in 1 % of samples, with 0.64 % above 0.1 µg/L; AMPA has been analysed in 51652 samples from 1345 sites (1993-2011) and detected in 2.6 % of samples, with 0.77 % above 0.1 µg/L. The highest numbers of glyphosate detections have been reported from Denmark (4.7 µg/L) and France (24 µg/L). Findings exceeding the limit concentration 0.1 µg/L have also been measured in groundwater aquifers in Austria, Ireland, the Netherlands and the UK.

Clarification of glyphosate groundwater findings > 0.1 µg/L is presented and discussed partly. The following main causes have been identified in the study:

- In Austria, Glyphosate was detected in isolated cases. AMPA was detected somewhat more frequently and at higher concentrations. There is no information about the type of groundwater, although the results, as presented, related to pore groundwater only, not the springs from fractured aquifers. Traces of AMPA were also found in two spring water samples and it was considered unclear at the time whether these findings were related to glyphosate or to aminophosphonates from detergents.
- Recent reported findings in Denmark all relate to groundwater at less than 15 meter depth. Investigations into earlier detections have shown that these occurred in shallow groundwater wells only
- Earlier investigations in France relating to a small number of detections of glyphosate in drinking waters, most of which were derived from groundwater, revealed that the detections were most likely due to sample contamination or analytical problems. However, these related to 2001-2003 and more recent findings in groundwater may warrant further investigation. From the findings of a recent study to analyse the potential contamination of groundwater with glyphosate (and AMPA) at 27 sites from 2007-2010, it is clear that none of the glyphosate detections could be attributed to long-term contamination of typical groundwater. The majority of detections occurred once only, which is a clear indication that there is no real groundwater contamination, and the small number of multiple detections occurred in shallow groundwater (spring water) or wells unsuitable for groundwater monitoring, suggesting superficial short-term contamination.
- For the glyphosate groundwater findings > 0.1 µg/L in Ireland no clarification is given in the study.
- According to the present study the detection of glyphosate in groundwater in Switzerland may be attributable to short-term contamination of shallow groundwater or spring water.
- In The Netherlands, both glyphosate and AMPA have been detected in a small number of groundwater samples (once each in 10 different wells). These were investigated in detail and it was concluded that 5 of the results (all at levels below 0.15 µg/L were uncertain (high margins of error) whilst overall, all sampling points with positive detections were in cultivation areas with sandy or highly sandy soils, and samples were taken mainly from shallow groundwater.
- In the UK a number of positive samples and high maximum concentrations were found in Wales in the investigations of pollution incidents. There seems to be a particular problem in Wales, which may warrant further investigation.

The study is considered acceptable.

Data point:	CA 7.5/014
Report author	[redacted]
Report year	2006
Report title	Clarification of well-related findings of glyphosate and AMPA in groundwater
Report No	IF-06/00603024
Document No	BVL No. 2310282
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	Yes, accepted in RAR (2015)
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary

The Federal Office of Consumer Protection and Food Safety (BVL) requested registration owners of glyphosate containing plant protection products to investigate the causes of findings ≥0.1 µg/L of glyphosate and its metabolite AMPA in the groundwater, which were reported from monitoring points in Bavaria, Baden-Wuerttemberg and Hessen since 2003. Glyphosate was found only at 5 wells, while the metabolite AMPA appeared at 21 locations. A detailed investigation was conducted, during which available information about the wells and findings were gathered and evaluated, eventually followed by a site or laboratory visit. This study has furnished a plausible explanation of the origin of glyphosate or AMPA findings for all 24 reported locations. The findings can be classified in groups of causes:

Five wells showed inflow of surface water or bank filtrate and one well was affected by a waste deposit. In one case the well was located inside a sewage plant and showed the influence of the waste water .In another site the sample was contaminated at the well which serves as a processing water well for a tank filling place. The 16 findings reported from Hessen were due to an analysis which was obviously deficient.

I. MATERIAL AND METHODS

The clarification of the reported glyphosate and AMPA findings was done in stepwise procedure. In a first step all easily accessible information was requested from the responsible authorities. Then it was checked within a pre-evaluation, if on this basis definite conclusions regarding the validity and origin of the finding are possible. Provided other causes than the normal and proper use of the active ingredient or the origin of the findings were obvious, the investigations were terminated. For findings, where this was not the case, a detailed investigation was conducted. For this purpose relevant data with regard to technical, hydrogeological information were gathered and local authorities or the owners of the wells were contacted. Then a site inspection was conducted and if possible an interview with persons who are able to contribute to the clarification, as farmers, well operators etc. was performed. In an additional step information on the analytical details were queried from the laboratories.

II. RESULTS AND DISCUSSION

The table below provides an overview of the findings and the result of the assessment

Table 8.5-52: Overview on findings of glyphosate/AMPA and results of the assessments

Well	Finding glyphosate [µg/L] (year)	Finding AMPA [µg/L] (year)	Cause of the finding
Bavaria			
Sulzbach	0.25 (2003) 0.25 (2004)	–	well contamination by surface water
Woelsbach	B18: 0.16 (2004) B26: 0.12 (2004)	–	influence from a waste deposit
Escherndorf	0.06 (2003)	0.20 (2003)	sample contamination
Bamberg (Luisenhain FB1 / FB2 and Gereuth FB9)	FB1: 0.16, FB2 0.12 FB9 0.32 (2001)	–	bank filtrate
Hessen			
Meineringhausen	–	0.11 (2004)	analysis not valid
Muehlenberg	–	0.16 (2004)	analysis not valid
Battenberg B2	–	0.11 (2004)	analysis not valid
Ronshausen	–	0.11 (2004)	analysis not valid
Schoenberg	–	0.14 (2004) 0.16 (2005)	analysis not valid
Bicken	–	0.10 (2004)	analysis not valid
Kleinlueder	–	0.18 (2005)	analysis not valid
Spring Weiher (Ober-Hoegern)	–	0.16 (2004)	analysis not valid
B5 (Ober-Hoegern)	–	0.13 (2004)	analysis not valid
BUGA (Praunheim III)	–	0.18 (2004)	analysis not valid
Geisenheim	–	0.14 (2004)	analysis not valid
Niederrad I	–	0.40 (2004)	analysis not valid
Walldorf	–	0.12 (2004)	analysis not valid
Messenhausen	–	0.11 (2004)	analysis not valid
Seeheim-Jugenheim	–	0.10 (2004	analysis not valid
Viernheim	–	0.10 (2004)	analysis not valid
Baden-Wuerttemberg			
Riesbuerg-Pflaumloch	0.17 (2002) 0.08 (2003)	0.5 (2002) 0.27 (2003)	wastewater influence from a sewage plant
Laufenburg	–	0.15 (2002) 0.12 (2003)	bank filtrate
Laudenbach	–	0.18 (2002) 0.06 (2003)	surface water inflow
Weinheim	–	0.11 (2002) 0.15 (2003)	deficient monitoring well quality / contamination by surface or sewage water

III. CONCLUSION

The detailed investigation has resulted in plausible explanations of the origin of the glyphosate and AMPA findings at the 24 locations. In all cases, if the analysis was not a false positive, the origin of the glyphosate and/or AMPA concentrations could be allocated to surface or waste water influences. There was not a single case for which the findings could be correlated with the normal and proper use of the active ingredient in the field.

Assessment and conclusion by applicant:
The study elucidates findings of glyphosate and AMPA in German groundwater wells. The methods and results are sufficiently described.
The study was seen as valid.

Assessment and conclusion by RMS:
This study has already been peer-reviewed in the RAR 2015. RMS DE assessment from the RAR 2015 is reported below.

The Federal Office of Consumer Protection and Food Safety (BVL) has requested registration owners of glyphosate containing plant protection products to investigate the causes of findings ≥ 0.1 µg/L of glyphosate and its metabolite AMPA in the groundwater, which were reported from monitoring points in Germany, more specifically in Bavaria, Baden-Wuerttem-berg and Hessen since 2003. Thereby, glyphosate was found at 5 wells, while the metabolite AMPA appeared at 21 locations.

The further detailed investigation during this study has furnished a plausible explanation of the origin of glyphosate or AMPA findings for all 24 locations of finding. The findings can be classified in groups of causes: Five wells showed inflow of surface water or bank filtrate (Sulzbach, Bamberg, Laufenburg, Laudenbach and Weinheim) and one well was affected by a waste deposit (Woelsau). In one case the well was located inside a sewage plant and showed the influence of the waste water (Riesburg-Pflaumloch). In Escherndorf the sample was contaminated at the well which serves as a processing water well for a tank filling place. 16 findings reported from Hessen were due to an analysis which was obviously deficient.

Furthermore, it was shown that there is not a single case in which there is a direct connection with the normal and proper use of the active ingredient in the field and the findings of glyphosate and AMPA in groundwater.

The study is considered acceptable.

Data point:	CA 7.5/015
Report author	[redacted]
Report year	2005
Report title	An investigation of reported borehole contamination in the Vemmenhög Catchment, Sweden
Report No	-
Document No	BVL No. 2310285
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	Yes, accepted in RAR (2015)
GLP/Officially recognised testing facilities	No (no experimental work performed)
Acceptability/Reliability:	Supportive

Executive Summary

Glyphosate was detected in 2 experimental boreholes between August 2004 and February 2005 in the Vemmenhög catchment in Southern Sweden. In the first well, to the North East of the catchment, the concentration reached 0.045 µg/L whilst in the second well located in the Center/West of the catchment, glyphosate was detected at 0.18 and 0.035 µg/L. A review of the regional characteristics showed that extensive drainage systems are in place in the catchment. The tile drains were placed at 1 m depth, although due to the undulated topography they end up in much deeper depth in some places. About 23% of the catchment was treated with glyphosate and this included application to the immediate or near vicinity of the boreholes. The historical data review and observations at the site demonstrate that there can be potential for direct hydrological connectivity between surface water and shallow groundwater at about 0.7-4 m depth via artificial drainage systems.

I. MATERIAL AND METHODS

The clarification of the reported glyphosate and AMPA findings was done in stepwise procedure. In a first step all information on the characteristics of the watershed, water management, land and glyphosate use were gathered and evaluated. The second step involved an on-site investigation of the watershed, including inspection of the boreholes and evaluation of the farm management practices.

II. RESULTS AND DISCUSSION

The table below shows the glyphosate concentrations in water samples taken from 4 boreholes of the Vemmeshög catchment.

Table 8.5-53: Overview on findings of glyphosate in the Vemmeshög catchment

Sample date/location	Glyphosate residue in µg/L (LOD)	GW depth (m)	Date of adjacent glyphosate application
19/08/2004			
North/East 1	0.045 (0.03)	-3.27	29/10/2003
North/East 2	ND (0.03)	-3.03	
Center West 1	ND (0.03)	-2.14	05/07/2003
Center West 2	ND (0.03)	-2.12	
16/11/2004			
North/East 1	ND (0.02)	-3.24	No
North/East 2	ND (0.02)	-3.13	
Center West 1	0.18 (0.02)	-1.42	20/10/2004
Center West 2	ND (0.02)	-1.13	
09/02/2005			
North/East 1	ND (0.02)	-3.24	No
North/East 2	ND (0.02)	-2.89	
Center West 1	0.035 (0.02)	-1.51	20/10/2004
Center West 2	ND (0.02)	-1.23	

The investigation showed that groundwater often remains close or above field drain depth over the winter period, responding to recharge from excess rainfall. The field drainage in the catchment has been designed to rapidly remove excess water from the surface and also from rooting layers. Although the drains are generally installed at approximately 1-1.5 m depth, they may be as deep as 4 m to accommodate the undulated topography and maintain gradient requirements. There is thus a potential for direct hydrological connectivity between surface water and shallow groundwater.

III. CONCLUSION

The detailed investigation has evidenced a potential contact between ground and surface water through the drainage system in place at this watershed.

Assessment and conclusion by applicant:
The study elucidates findings of glyphosate in two experimental groundwater boreholes in Sweden. The methods and results are sufficiently described.
The study is considered valid.

Assessment and conclusion by RMS:
This study has already been peer-reviewed in the RAR 2015. RMS DE assessment from the RAR 2015 is reported below

Glyphosate was detected in two pairs of boreholes between August 2004 and February 2005 in the Vemmenhög catchment in Southern Sweden. In the first well the concentration reached 0.045 µg/L whilst in the second well located glyphosate was detected at 0.18 and 0.035 µg/L. A review of the regional characteristics showed that extensive drainage systems are in place in the catchment. About 23 % of the catchment was treated with glyphosate and this included application to the immediate or near vicinity of the boreholes. Historical data reviews as well as observations at the site demonstrate that there can be potential for direct hydrological connectivity between surface water and shallow groundwater via artificial drainage systems.

For these reason, the study is considered supportive

Relevant literature articles

Articles from the literature have been provided by applicant, considered relevant or partially relevant for the groundwater compartment, and are summarized below. Please note that some are newly submitted for AIR V renewal whereas some of them have already been reviewed in the RAR 2015. The following table lists all the references provided and indicate whether they had already been reviewed in the RAR 2015.

Data point	Study (author, year)	Study type	Substance(s)	Status
CA 7.5/016	Rosenbom, A. *et al*., 2019	The Danish Pesticide Leaching Assessment Programme	Glyphosate AMPA	Reliable
CA 7.5/099	Rosenbom, A. *et al*., 2020			
CA.7.5/101	De Polo, A. et al.	Samplings in 12 wells of the water network intended for domestic consumption	Glyphosate AMPA	Reliable with restrictions
CA 7.5/017	Poiger, T. *et al*., 2017	Simplified procedure for determination in water samples	Glyphosate AMPA	Reliable
CA 7.5/018	Di Guardo, A., Finizio, A., 2016	A moni-modelling approach to manage groundwater risk	Glyphosate	Reliable with restrictions
CA 7.5/019	Rosenbom, A. *et al*., 2015	The Danish Pesticide Leaching Assessment Programme	Glyphosate AMPA	Reliable
CA 7.5/048	Székács, A. *et al*., 2015	Monitoring results for pesticide residues in surface and groundwater in Hungary	Glyphosate	Reliable with restrictions
CA 7.5/020	McManus, S. *et al*., 2014	Groundwater monitoring study in Ireland	Glyphosate	Reliable with restrictions
CA 7.5/021	Norgaard, T. *et al*., 2014	Leaching from an agricultural field	Glyphosate AMPA	Reliable with restrictions
CA 7.5/022	Martin, J. *et al*., 2013	Review of 10 year monitoring of herbicides and water pollution in Reunion Island	Glyphosate AMPA	Reliable with restrictions
CA 7.5/023	Martin, J. *et al*., 2013	Translation of CA 7.5/022	See above	See above

CA 7.5/024	Mörtl, M. *et al*., 2013	A monitoring study with an immunoassay analytical method	Glyphosate	Reliable with restrictions
CA 7.5/025	Sanchís, J. *et al*., 2012a	Analysis of groundwater samples by immunoassay and mass spectrometry	Glyphosate	Reliable
CA 7.5/026	Sanchís, J. *et al*., 2012b	Erratum to Sanchís, J. *et al*., 2012a	Glyphosate	Reliable
CA 7.5/027	Bruchet, A. *et al*., 2011	Monitoring experiment in France	Glyphosate AMPA	Reliable with restrictions
CA 7.5/028	[redacted], 2011	Investigation of potential groundwater contamination in Lombardia region (North Italy)	Glyphosate	Reliable
CA 7.5/029	[redacted] 2010	Groundwater monitoring in The Netherlands	Glyphosate AMPA	Reliable
CA 7.5/030	[redacted] 2010	Translation of CA 7.5/029	See above	See above

Data point:	CA 7.5/016
Report author	Rosenbom, A. *et al.*
Report year	2019
Report title	The Danish Pesticide Leaching Assessment Programme
Report No	-
Document No	-
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

Data point:	CA 7.5/099
Report author	Rosenbom, A. *et al.*
Report year	2020
Report title	The Danish Pesticide Leaching Assessment Programme
Report No	-
Document No	-
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

Full summary

In 1998, the Danish Parliament initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides and/or their degradation products (metabolites) under field conditions. The specific aim is to analyse whether pesticides applied in accordance with current regulations will result in leaching of the pesticide and/or its degradation products to groundwater in unacceptable concentrations.

The two updates on the previous PLAP monitoring cover glyphosate and AMPA monitoring results besides leaching data on other pesticides of five or six selected representative fields in Denmark. In the monitoring periods July 2015-June 2017 and July 2016 – June 2018, the maximum allowed dose of glyphosate containing products was applied). Data collected in these periods were summarised and incorporated in the results of the complete monitoring campaign. Additionally, data on bromide leaching, soil water dynamics and water balance were analysed within the report.

During the monitoring period July 2015-June 2017, glyphosate was applied at the fields of Silstrup, Estrup and Faardrup. Glyphosate and AMPA were analysed in 65 and 116 water samples collected from the variably-saturated Zone (VZ; drains and suction cups) and saturated Zone (SZ; groundwater screens), respectively. Glyphosate was detected in 12 samples from the VZ with no detection ≥0.1 µg/L and a maximum concentration of 0.05 µg/L. In samples collected from the SZ, glyphosate was detected three times with one detection ≥0.1 µg/L and a maximum concentration of 0.13 µg/L. AMPA was detected in 51 samples from the VZ with two detections ≥0.1 µg/L and a maximum concentration of 0.14 µg/L. In samples collected from the SZ, AMPA was detected two times with no detection ≥0.1 µg/L and a maximum concentration of 0.02 µg/L.

During the monitoring period of July 2016-June 2018, glyphosate and AMPA were analysed in 26 and 111 water samples collected from the Variably-saturated Zone (VZ; drains and suction cups) and Saturated Zone (SZ; groundwater screens), respectively. Glyphosate was detected in 21 samples from the VZ with eight detections ≥0.1 µg/L and a maximum concentration of 8.60 µg/L. In samples collected from the SZ, glyphosate was not detected. AMPA was detected in 23 samples from the VZ with five detections ≥0.1 µg/L and a maximum concentration of 1.30 µg/L. In samples collected from the SZ, AMPA was detected on two occasions with a maximum concentration of 0.01 µg/L, with no detection ≥0.1 µg/L overall.

Data on the complete PLAP-monitoring period (when glyphosate was also applied at the two sandy soil sites before 2015) revealed a negligible leaching risk on the coarse sandy soil of Jyndevad, whereas evidence of glyphosate leaching was seen on clayey till soils. Glyphosate and AMPA leached at 1 m depth in average concentrations exceeding 0.1 µg/L within the first season after application at Silstrup and Estrup. They were detected in more than three consecutive samples or in a single sample in concentrations exceeding 0.1 µg/L and an average concentration (1 m depth) below 0.1 µg/L within the first season after application at Faardrup and Lund. The aim of including the new clayey till field overlaying chalk (Lund) in PLAP was to contribute to an improved understanding of the vulnerability of clayey tills, and hereby improve the early warning in relation to leaching through such fields.

The numbers of detections exceeding 0.1 µg/L in groundwater monitoring wells is very limited. In groundwater, glyphosate and AMPA leached in a concentration exceeding 0.1 µg/L within the first season after application at Estrup. At Jyndevad, Silstrup and Faardrup, glyphosate and AMPA were detected in more than three consecutive samples or in a single sample in concentration exceeding 0.1 µg/L and concentrations below 0.1 µg/L within the first season after application. At Lund, glyphosate and AMPA were either not detected or only detected in very few samples in concentrations below 0.1 µg/L.

Materials and methods

Until the monitoring period July 2015-June 2017, the PLAP encompassed five fields that are representative for the dominant soil types and the climatic conditions in Denmark with shallow groundwater tables, which enable pesticide leaching to groundwater to be rapidly detected. For the monitoring period July 2016-June 2018 the Lund-field was newly established. Cultivation of the PLAP fields is done in accordance with conventional agricultural practice in the area and the maximum permitted dose of the pesticides are applied in the manner specified in the regulations. Characteristics of the six fields included in the monitoring for the period 1999-2018 are shown in the table below.

Table 8.5-54: Characteristics of the six PLAP fields included in the PLAP–monitoring for the period 1999–2018 (field Lund newly established for the period July 2016 – June 2018)

Parameter	**Tylstrup**	**Jyndevad**	**Silstrup**	**Estrup**	**Faardrup**	**Lund**
Location	Brønderslev	Tinglev	Thisted	Askov	Slagelse	Lund
Precipitation[1] (mm y^{-1})	668	858	866	862	558	-
Pot. evapotransp.[1] (mm y^{-1})	552	555	564	543	585	-
Classification of top soil texture	Loamy sand	Sand	Sandy clay loam / sandy loam	Sandy loam	Sandy loam	Sandy loam
Clay content (%)	6	5	18–26	10–20	14–15	10-25
Silt content (%)	13	4	27	20–27	25	30-35
Sand content (%)	78	88	8	50–65	57	30-50
pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6	7.4-9.1
TOC (%)	2.0	1.8	2.2	1.7 – 7.3	1.4	0-1.3

[1] Yearly normal based on a time series for the period 1961–90. The data refer to precipitation measured 1.5 m above ground surface.

The reports present the results of the monitoring periods July 2015 to June 2017 and July 2016 to June 2018, comprising analyses conducted on water samples collected at the five and since July 2017 six PLAP-fields. During these periods, PLAP has evaluated the leaching risk of glyphosate and AMPA (amongst other pesticides) after applying the maximum allowed dose. Glyphosate products applied were listed in the table below.

Table 8.5-55: Agricultural management of glyphosate containing products at the six sites - relevant for July 2015 to June 2018

Year	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Lund
2012	Aug 2012 2.4 L/ha Glyfonova 450 Plus (not analysed)		Sept 2012 4.8 L/ha Glyfonova 450 Plus			
2013			Aug 2013 2.4 L/ha Glyfonova 450 Plus	Aug 2013 2.4 L/ha Glyphonova 450 Plus		
2014		April 2014 1.5 L/ha Glyphogan	July 2014 2.4 L/ha Glyfonova 450 Plus	Jul 2014 2.4 L/ha Glyphonova 450 Plus	Aug 2014 4.0 L/ha Glyfonova Plus	
2015	Aug 2015 2.7 L/ha Glyphogan (i.e. 972 g a.s./ha)					
2016					Aug 2016 2.0 kg/ha Roundup PowerMax (i.e. 1440 g a.s./ha)	
2017				Aug 2017 2.5 L/ha Glyphomax HL (i.e. 1152 g a.s../ha)	Oct 2017 2.5 L Glyphomax (i.e. 900 g a.s./ha)	Oct 2017 3.2 L/ha Glyphomax HL (i.e. 1536 g a.s../ha)

Glyphosate and its degradation product AMPA were evaluated within this study. Besides pesticide leaching, the leaching of bromide as well as soil water dynamics and water balance were analysed. This data is not covered within this summary.

From each of the PLAP fields, samples were collected of groundwater, drainage water and soil water in the variably-saturated zone. Throughout the years, the sample collection interval of the monitoring study changed. Until March 2002, pesticide analysis was performed monthly on water samples from the suction cups, two screens of the horizontal monitoring wells and two of the downstream vertical monitoring wells. Every four month, all sample points were monitored. Pesticide analysis was also performed on drainage water samples.

Until 2012, the number of pesticide analyses was reduced. Monthly monitoring was restricted to one monitoring well. All samples points were monitored every six month (except for Tylstrup).

The drainage system was sampled time proportionally weekly until July 2004. Additional samples were analysed during storm events. From July 2004 and onwards pesticide analysis were done weekly on water sampled flow-proportionally from the drainage water system.

In 2011, new horizontal wells with three new horizontal screens were established. A horizontal well with three PE-screens (3 m long, separated by 1 m packer-section attached 0.8 m bentonite, slits of 0.1 mm) was installed September 2011 at all five PLAP-fields to optimize monitoring of the fields both in time and space. From these wells, water samples were collected monthly at the sandy fields (Tylstrup and Jyndevad). 3 L were sampled from each filter via applying suction onto the two tubes. A half-litre of the 3 L was passed through cells in a flow box measuring pH, temperature and conductivity. The remaining 2.5 L was pooled with equal volumes from the two other filters. Subsamples for analysis were then taken from the 7.5 L pooled sample. At clayey till fields (Silstrup, Estrup and Faardrup), water samples were collected monthly if the groundwater table nearest vertical monitoring well was situated more than 20 cm above the screen. Having saturated conditions, one litre of water sample was collected from each screen via the two tubes during approximately 10 minutes. The litre sample was passes through cells in a flow box measuring pH, temperature and conductivity. The samples from each screens are then pooled and send for analysis.

LOD and LOQ of the detection of glyphosate and AMPA were not reported. Detailed analysis methods are described in Kjær *et al*. (2002).

Results and discussion

Glyphosate was not analysed at Tylstrup or Jyndevad for the period of 2011-2018. The application of Glyphosate for Silstrup, Estrup, Faardrup and Lund as well as the weighted average concentration 1 m below ground surface (C_{mean}) is shown in the tables below, and provides an overview of the detection of glyphosate and AMPA in the variably-saturated zone and the saturated zone.

Table 8.5-56: Glyphosate and AMPA application and analysis at the PLAP–fields. Application date (Appl. date), end of monitoring period (End. mon.) are listed. C_{mean} refers to average leachate concentration [µg/L] at 1 m below ground surface the first year after application.

Crop	Applied product	Analysed Pesticide	Appl. date	End mon.	C_{mean}
Silstrup					
Red fescue 2012	Glyfonova 450 Plus	Glyphosate	Sep 12	Jun 15[1]	0.15
		AMPA	Sep 12	Jun 15[1]	0.067
Spring barley 2013	Glyfonova 450 Plus	Glyphosate	Aug 13	Apr 16	0.01
		AMPA	Aug 13	Apr 16	0.01
Winter wheat 2014	Glyfonova 450 Plus	Glyphosate	Jul 14	Apr 16	<0.01
		AMPA	Jul 14	Apr 16	<0.01
Estrup					
Winter wheat 2011	Roundup Max	Glyphosate	Oct 11	Jun 15	0.88
		AMPA	Oct 11	Jun 15	0.26
Pea 2013	Glyfonova 450 Plus	Glyphosate	Aug 13	Apr 16	0.10
		AMPA	Aug 13	Apr 16	0.07
Winter wheat 2013	Glyfonova 450 Plus	Glyphosate	Jul 14	May 16	0.06
		AMPA	Jul 14	May 16	0.1
Faardrup					
Spring barley and White clover 2012	Glyphogan	Glyphosate	Oct 11	Aug 12	<0.01
		AMPA	Oct 11	Aug 12	<0.01
Lund					
Spring barley 2017	Glyfonova 450 Plus	Glyphosate	Oct 17	Jun 18	n.d.
		AMPA	Oct 17	Jun 18	n.d.

[1] Monitoring continues the following year
n.d. no estimates are available

Table 8.5-57: The number of water samples analysed collected from the variably–saturated Zone (VZ; drains and suction cups), saturated Zone (SZ; groundwater screens) are presented together with the results of analysis on samples from VZ and SZ given as number of detections (Det.), detections >0.1 µg/L and maximum concentration (Max conc.)

Pesticide	Analyte	Number of samples		Results of analysis					
		VZ	SZ	VZ			SZ		
				Det.	>0.1 µg/L	Max conc. [µg/L]	Det.	>0.1 µg/L	Max conc. [µg/L]
June 2015 – July 2018									
Glyphosate	Glyphosate	65	116	12	0	0.05	3	1	0.13
	AMPA	65	116	51	2	0.14	2	0	0.02
June 2016– July 2019									
Glyphosate	Glyphosate	26	111	21	8	8.60	0	0	-
	AMPA	26	111	23	5	1.30	2	0	0.01

During the monitoring period of July 2015-June 2017, glyphosate and AMPA were analysed in 65 and 116 water samples collected from the Variably-saturated Zone (VZ; drains and suction cups) and Saturated Zone (SZ; groundwater screens), respectively. Glyphosate was detected in 12 samples from the VZ with no detection ≥0.1 µg/L and a maximum concentration of 0.05 µg/L. In samples collected from the SZ, glyphosate was detected three times with one detection ≥0.1 µg/L and a maximum concentration of 0.13 µg/L. AMPA was detected in 51 samples from the VZ with two detections ≥0.1 µg/L and a maximum concentration of 0.14 µg/L. In samples collected from the SZ, AMPA was detected two times with no detection ≥0.1 µg/L and a maximum concentration of 0.02 µg/L.

During the monitoring period of July 2016-June 2018, glyphosate and AMPA were analysed in 26 and 111 water samples collected from the Variably-saturated Zone (VZ; drains and suction cups) and Saturated Zone (SZ; groundwater screens), respectively. Glyphosate was detected in 21 samples from the VZ with eight detections ≥0.1 µg/L and a maximum concentration of 8.60 µg/L. In samples collected from the SZ, glyphosate was not detected. AMPA was detected in 23 samples from the VZ with five detections ≥0.1 µg/L and a maximum concentration of 1.30 µg/L. In samples collected from the SZ, AMPA was detected two times with no detection ≥0.1 µg/L and a maximum concentration of 0.01 µg/L.

The following results encompass the complete monitoring period of the PLAP study (data from 2015-2018 and data from previous years). Glyphosate (and AMPA; not distinguished in this result) revealed a leaching risk through fractured clayey tills. The frequency of glyphosate detection as well as the monitoring output of glyphosate and AMPA from all sample points is given in the tables below.

Table 8.5-58: Frequency of glyphosate detections in water collected from drainage and suction cups at 1 m depth and from groundwater monitoring screens

Frequency	Pesticide	Sand		Clayey till			
		Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Lund
Drainage and suction cups a 1 m depths							
High	Glyphosate		o	X	X	•	•
Groundwater monitoring screens							
High	Glyphosate		•	•	X	•	o

X: The pesticide (or its degradation products) leached at 1 m depth in average concentrations exceeding 0.1 µg/L within the first season after application.

•: The pesticide (or its degradation products) was detected in more than three consecutive samples or in a single sample in concentrations exceeding 0.1 µg/L; average concentration (1 m depth) below 0.1 µg/L within the first season after application.

o: The pesticide either not detected or only detected in very few samples in concentrations below 0.1 µg/L.

Table 8.5-59: Monitoring output of glyphosate and AMPA from drainage at 1 m depth, suction cups at 1 m depths and from the groundwater monitoring screens given for each of the five fields. Output given as the total number (T) of samples analysed, number of detections (D), number of detections exceeding 0.1 µg/L (X) and the max conc. M (µg/L).

Substance		**Jyndevad**				**Silstrup**			
		T	**D**	**X**	**M**	**T**	**D**	**X**	**M**
Glyphosate	Drainage/ Suction cups	72	0	0	–	257	108	22	4.7
	Groundwater	223	0	0	–	646	40	0	0.05
AMPA	Drainage/ Suction cups	72	1	0	0.01	258	203	18	0.35
	Groundwater	223	2	0	0.02	646	40	0	0.08
Substance		**Estrup**				**Faardrup**			
		T	**D**	**X**	**M**	**T**	**D**	**X**	**M**
Glyphosate	Drainage/ Suction cups	601	343	109	31	236	5	0	0.09
	Groundwater	1017	53	6	0.67	451	5	0	0.03
AMPA	Drainage/ Suction cups	601	499	120	1.6	236	15	1	0.11
	Groundwater	1018	8	0	0.07	451	2	0	0.03
Substance		**Lund**							
		T	**D**	**X**	**M**				
Glyphosate	Drainage/ Suction cups	26	21	8	8.6				
	Groundwater	112	2	0	0.01				
AMPA	Drainage/ Suction cups	26	23	5	1.3				
	Groundwater	112	0	0	-				

Glyphosate and AMPA were found to leach through the variably saturated zone to the tile drains in high concentrations at the clayey till fields Silstrup, Estrup, Faardrup and Lund. At the clayey till fields glyphosate has been applied eleven times at Silstrup, ten times at Estrup, three times at Faardrup and one time at Lund within the total monitoring period (2000 - 2018). All applications have resulted in detectable leaching of glyphosate and AMPA into the drainage, often at concentrations exceeding 0.1 µg/L several months after application. Higher leaching levels of glyphosate and AMPA have mainly been confined to the depth of the drainage system and were rarely detected in monitoring screens located below the depth of the drainage systems, although it should be noted that detections of particularly glyphosate in groundwater monitoring wells at Estrup seem to increase over the years. For Lund, it is too early to evaluate on the leaching of glyphosate and monitoring continues.

QA of the analytical methods indicates that the true concentration of glyphosate may have been underestimated from June 2007 to July 2010.

On two occasions, heavy rain events and snowmelt triggered leaching to the groundwater monitoring wells in concentrations exceeding 0.1 µg/L, more than two years after application.

However, the numbers of detections exceeding 0.1 µg/L in groundwater monitoring wells is very limited. Glyphosate and AMPA were detected in drainage water at the clayey till field of Faardrup, but in low concentrations. Leaching risk was negligible on the coarse sandy soil of Jyndevad, whereas evidence of glyphosate leaching was seen on clayey till soils.

At the Silstrup field, glyphosate and AMPA have been detected in concentrations up to 0.66 µg/L in drainage after application in September 2012. After application in August 2013, glyphosate was detected in drainage in low concentrations up to 0.036 µg/L and AMPA in concentrations up to 0.054 µg/L. In nine groundwater samples, glyphosate and AMPA were detected in low concentrations up to 0.052 µg/L.

In drainage from Estrup, glyphosate and AMPA were detected frequently in high concentrations ≥0.1 µg/L after application in October 2011 and in August 2013. Glyphosate was detected in one groundwater sample in concentration ≥0.1 µg/L (0.13 µg/L) after the 2012 application. After the application of August 2013, glyphosate and AMPA were not detected in groundwater from Estrup. The leaching of glyphosate and

AMPA were highly climate driven, controlled by the timing and intensity of the first rainfall event after glyphosate application.

The Silstrup and Estrup fields were sprayed in July 2014, 23 and 10 days, respectively, before the harvest of winter wheat. In the first sampling of drainage at Silstrup on 27 August 2014, the concentration of glyphosate was 0.27 µg/L and the concentration of AMPA was 0.089 µg/L. An additional 21 samples contained glyphosate (0.01 to 0.14 µg/L). AMPA was detected in 53 of a total 65 samples (0.012 to 0.14 µg/L). Glyphosate and AMPA were only detected in 15 and 16 groundwater samples, respectively, all having concentrations below 0.1 µg/L. For glyphosate, all samples were collected before April 2015.

Following the latter application at Estrup in July 2014, glyphosate was detected in 26 drainage samples out of 68 with two samples having concentrations of 0.13 and 0.32 µg/L. Only six detections of glyphosate were obtained on groundwater samples with the two highest concentrations being 0.09 µg/L in September 2015 and 0.13 µg/L in March 2016. These detections seem to be weather driven, in this case by heavy rain and snowmelt events, respectively. Following the July 2014 application, AMPA was not detected in the groundwater samples but in 60 samples out of 68 samples from drainage with nine exceeding 0.1 µg/L (max. conc. 0.21 µg/L). Monitoring at Silstrup and Estrup ended May 2016, but continues at Lund.

Conclusion

The leaching of glyphosate and AMPA was reported within a monitoring program that covers the leaching risk of all together 50 pesticides and 65 degradation products in Denmark between 1998 and 2021 (so called PLAP-pesticide leaching assessment program). During the monitoring period 2015-2017, glyphosate and AMPA (among further 5 pesticides and 17 degradation products) were analysed in 65 and 116 water samples collected from the variably-saturated zone and saturated zone, respectively. Glyphosate was detected in 12 samples from the VZ with a maximum concentration of 0.05 µg/L and in three samples collected from the SZ with a maximum concentration of 0.13 µg/L. AMPA was detected in 51 samples from the VZ with a maximum concentration of 0.14 µg/L. In samples collected from the SZ, AMPA was detected two times with a maximum concentration of 0.02 µg/L.

During the monitoring period of July 2016-June 2018, glyphosate and AMPA were analysed in 26 and 111 water samples collected from the variably-saturated zone and saturated zone, respectively. Glyphosate was detected in 21 samples from the VZ with a maximum concentration of 8.60 µg/L. In samples collected from the SZ, glyphosate was not detected. AMPA was detected in 23 samples from the VZ with a maximum concentration of 1.30 µg/L. In samples collected from the SZ, AMPA was detected two times with a maximum concentration of 0.01 µg/L.

Data on the complete PLAP-monitoring period revealed a leaching risk for glyphosate and AMPA through fractured clayey tills.

Data on the complete PLAP-monitoring period revealed a negligible leaching risk on the coarse sandy soil, whereas evidence of glyphosate leaching was seen on clayey till soils. Glyphosate and AMPA leached at 1 m depth in average concentrations exceeding 0.1 µg/L within the first season after application at Silstrup and Estrup. The numbers of detections exceeding 0.1 µg/L in groundwater monitoring wells is very limited.

Assessment and conclusion by applicant:
The article is issued by the Danish Ministry of Energy, Utilities and Climate. The research program PLAP has high quality assurance measures.
The article is considered reliable.

Assessment and conclusion by RMS:
The article is considered reliable.

During the monitoring period 2015 2017, glyphosate and AMPA (among further 5 pesticides and 17 degradation products) were analysed in 65 and 116 water samples collected from the variably saturated zone (VZ) and saturated zone (SZ), respectively. Glyphosate was detected in 12 samples from the VZ with a maximum concentration of 0.05 µg/L and in three samples collected from the SZ with a maximum concentration of 0.13 µg/L. AMPA was detected in 51 samples from the VZ with a maximum concentration of 0.14 µg/L.
In samples collected from the SZ, AMPA was detected two times with a maximum concentration of 0.02 µg/L.

Data on the complete PLAP monitoring period revealed a negligible leaching risk on the coarse sandy soil, whereas evidence of glyphosate leaching was seen on clayey till soil, with Glyphosate and AMPA leached at 1 m depth in average concentrations exceeding 0.1 µg/L within the first season after application.

During the monitoring period of July 2016-June 2018, glyphosate and AMPA were analysed in 26 and 111 water samples collected from the variably-saturated zone and saturated zone, respectively. Glyphosate was detected in 21 samples from the VZ with a maximum concentration of 8.60 µg/L. In samples collected from the SZ, glyphosate was not detected. AMPA was detected in 23 samples from the VZ with a maximum concentration of 1.30 µg/L. In samples collected from the SZ, AMPA was detected two times with a maximum concentration of 0.01 µg/L.

Data point:	CA 7.5/101
Report author	De Polo, A. *et al.*
Report year	2019
Report title	From the traces in the wells of the urban aqueduct network to the subsequent prohibition of the use of glyphosate: the case of an area of high-intensity wine production in the province of Treviso, Veneto. Original Title: Dai residui nei pozzi della rete acquedottistica urbana al successivo divieto di utilizzo del glifosate: il caso di un'area ad alta intensità vitivinicola in provincia di Treviso, Veneto.
Document No	Igiene e sanità pubblica, (2019) Vol. 75, No. 6, pp. 451-460
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Reliable with restrictions

In 2016, extraordinary samplings of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) were carried out in 12 wells of the water network intended for domestic consumption in the territory of the Ulss2 (*Unità Locale Socio-Sanitaria*, Local Health Unit) 2 - District of Pieve di Soligo, Province of Treviso, Veneto region, Italy. The area includes 13 municipalities at high-intensity "Prosecco d.o.c.g." wine production. Traces of glyphosate (maximum reached 0.08 µg/L) and AMPA (maximum reached 0.25 µg/L) were detected in 2 wells supplying an urban area. Following these findings, an inter-municipal order to suspend the use of glyphosate was introduced and then entered definitively in the rural police regulation concerning all the municipalities in the Prosecco d.o.c.g. area, which led to the elimination of glyphosate and AMPA also in the initially contaminated wells. The case shows that high-consumption herbicides can reach the drinking water network of a city surrounded by territories with high agricultural activity. Moreover, the combined intervention of the institutions was fundamental to eliminate a “probable carcinogen” from the urban drinking water and to promote the abandonment of potentially harmful agricultural practices in favour of solutions with reduced environmental and health impact.

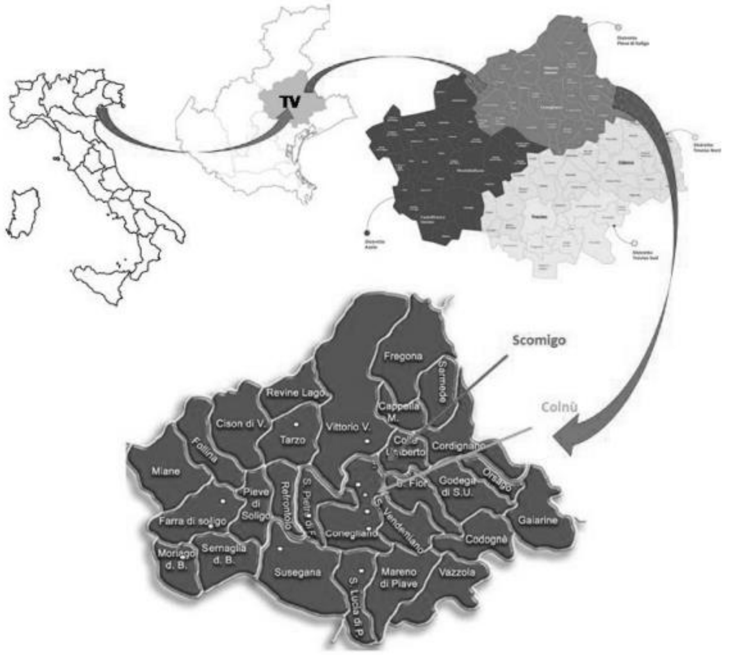
Materials and methods

The monitoring plan was developed in accordance with the 2014-2018 Regional Prevention Plan of Veneto "Plant protection products and health protection: raising awareness of compliance with correct sales conditions and the adoption of good usage practices". In 2016, the Prevention Department of the Ulss2 - *Marca Trevigiana* of Veneto prepared a monitoring plan for glyphosate and AMPA. This involved twelve drinking water sampling works in the territory (ex Ulss7) of the district of *Pieve di Soligo* (Treviso), a territory (of about 215,000 inhabitants) including 13 of the 15 municipalities forming the area of high wine business intensity for the production of Prosecco d.o.c.g. (Figure 1).

It should be pointed out that the two molecules, sampled by USGS Techniques and Methods 5-A10:2009, are subject to the same limits:

- The lower detection rate, intrinsic to the precision of the instrument, which at the beginning of the monitoring period was 0.05 µg/L, then lowered to 0.02 µg/L from 01/05/2017 thanks to technical improvements.
- The higher limit, defined by law as 0.1 µg/L (as per Legislative Decree 31/01).

Figure 1: **Location of the geographical area of interest. Province of Treviso, Ulss2 *Marca Trevigiana*, District of *Pieve di Soligo*.**



Results

As reported in the Table 8.5-60, ten of the twelve sampled sites showed no traceable glyphosate or AMPA residues. The other two, belonging to the water network of the city of *Conegliano* (Treviso), reported significant traces of glyphosate while the AMPA level reached the limit value imposed by law.

Table 8.5-60: List of 12 drinking water collection works sampled in the *Pieve di Soligo* district by the Ulss2 Prevention Department - *Marca Trevigiana del Veneto* (Food Hygiene and Nutrition Service), in the period March-July 2016

ID	Aqueduct	Sample date	Glyphosate [µg/L]	AMPA [µg/L]
1	*Conegliano* (*Scomigo*)	30/03/2016	0.05	0.10
2	*Vittorio Veneto*	27/04/2016	<0.05	<0.05
3	*Moriago della Battaglia*	11/05/2016	<0.05	<0.05
4	*Conegliano* (*Colnù*)	25/05/2016	0.08	<0.05
5	*Susegana*	11/07/2016	<0.05	<0.05
6	*San Pietro di Feletto*	15/06/2016	<0.05	<0.05
7	*Santa Lucia di Piave*	22/06/2016	<0.05	<0.05
8	*Tarzo*	29/09/2016	<0.05	<0.05
9	*Conegliano*	06/07/2016	<0.05	<0.05
10	*Farra di Soligo*	13/07/2016	<0.05	<0.05
11	*Farra di Soligo*	20/07/2016	<0.05	<0.05
12	*Conegliano*	27/07/2016	<0.05	<0.05

The two wells that tested positive at the first sampling have a depth of 22 m (*Scomigo*) and 30 m (*Colnù*) respectively. Both were then monitored approximately every month from March 2016 to February 2017. Traces of glyphosate and AMPA were detected in numerous subsequent samplings, exceeding the legal limit in three of them (Figures 2 and 3).

Following these findings, the municipality of *Conegliano* and four of its neighbouring municipalities (*Colle Umberto, San Pietro di Feletto*, *Tarzo* and *Vittorio Veneto*) have adopted, starting from 2 March 2017, a mayoral decree to suspend the use of glyphosate-based herbicides on the respective municipal soils, in compliance with the measures proposed by the Ulss2 Public Health and Hygiene Service. Following this ordinance, the monthly checks on the two wells in the city of *Conegliano,* which were positive at the first sampling, gave a stable negative result for all the following 12 months (Figures 4 and 5). It should be noted that, also as a result of other problems, the *Scomigo - Cal dell'Ebreo* well was excluded from the *Conegliano* drinking water network following the first evidence of contamination. However, a further check carried out on a public fountain in the urban centre of *Conegliano* (sampled monthly starting from 2017) reported traces of glyphosate (0.04 µg/L) on 14/06/2017 (Figure 6). Although this value is well below the legal limit and even lower than the traceability limit of the previously used instrument (until 01/05/2017), it confirmed the persistence of sporadic residual uses of glyphosate, as well as the ease with which the groundwater is subject to contamination.

Based on these considerations, the mayoral decree prohibiting the use of glyphosate was initially reiterated in all five municipalities also for the year 2018; it was then included in the inter-municipal regulation of the rural police, effective from the 1 January 2019 and concerning all 15 municipalities of the Prosecco d.o.c.g wine production area. This legislation banned the use of herbicides containing glyphosate, as well as all other herbicides, with the exception of those of natural and/or organic origin, on all crops, herbaceous, arboreal, arable land and orchards. An exception is made for orchards and vineyards that are young within three years of life or located on slopes where mechanical weeding is not feasible, for which the use of herbicides is allowed as long as they do not contain glyphosate, hazard warnings or risk phrases for human health.

Figure 8.5-34: **Levels of glyphosate and AMPA in sequential sampling at the well located in the hamlet of *Scomigo* in the municipality of *Conegliano* in the period March 2016 to February 2017**

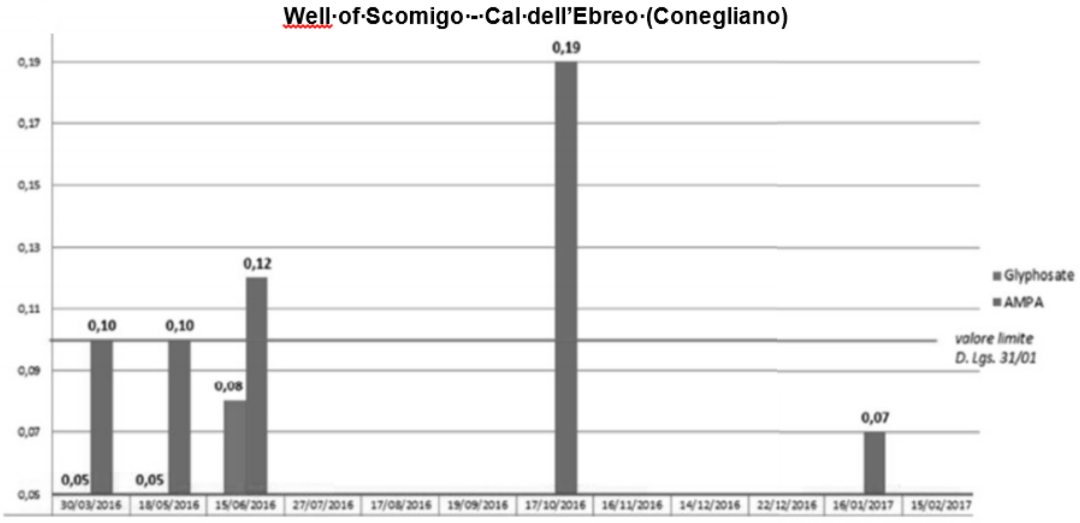


Figure 8.5-35: **Levels of glyphosate and AMPA in sequential sampling at the well located in *Colnù* in the municipality of *Conegliano* in the period May 2016 to February 2017**

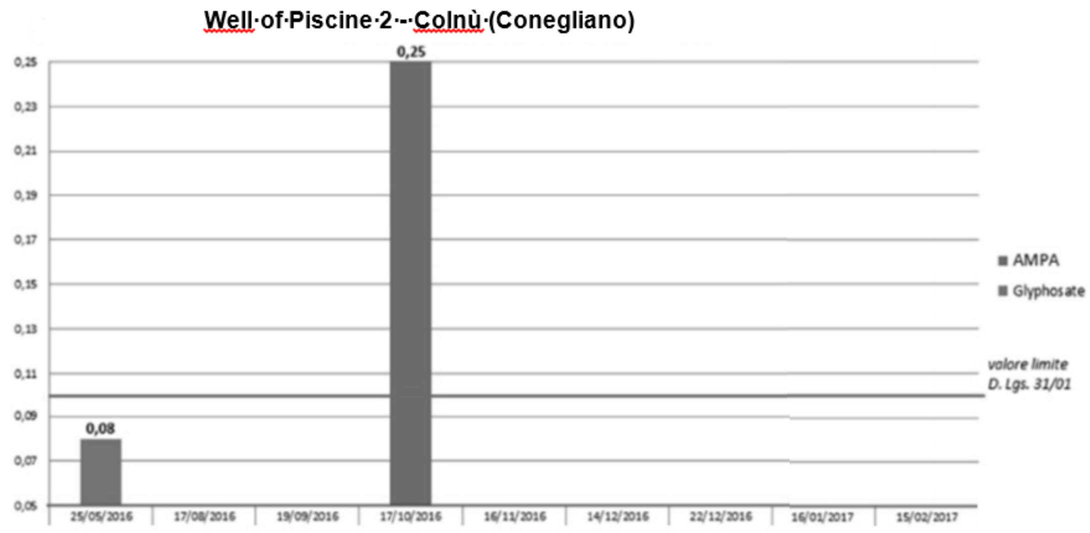


Figure 8.5-36: **Levels of glyphosate and AMPA in sequential sampling at the well located in the hamlet of *Scomigo* in the municipality of *Conegliano* in the period March 2017 to February 2018**

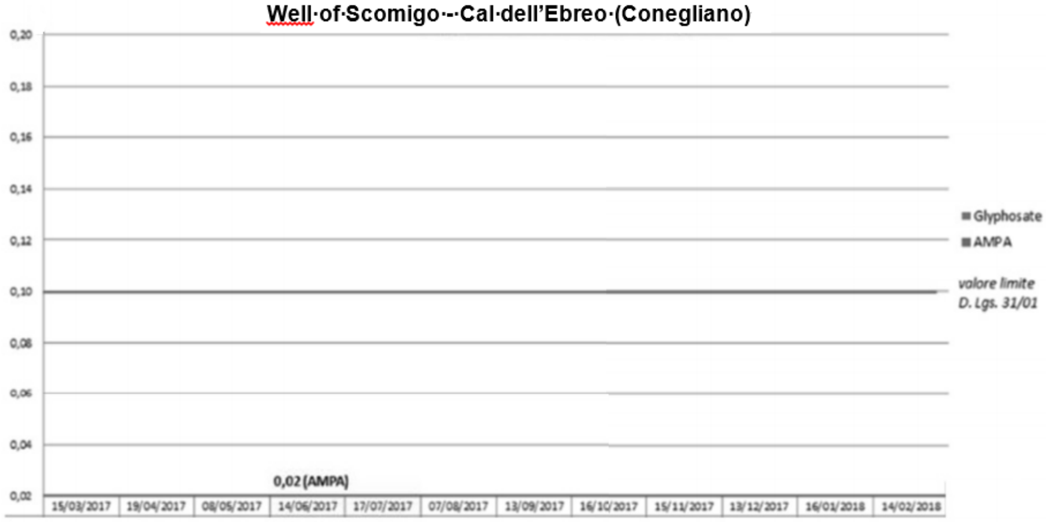


Figure 8.5-37: **Levels of glyphosate and AMPA in sequential sampling at the well located in the *Colnù* locality of the municipality of *Conegliano* in the period March 2017 to February 2018**

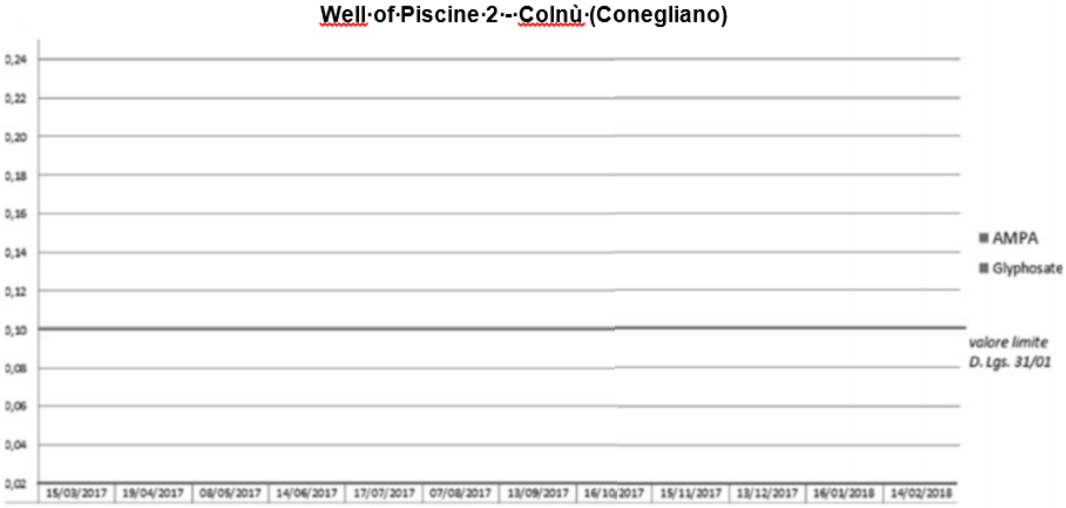
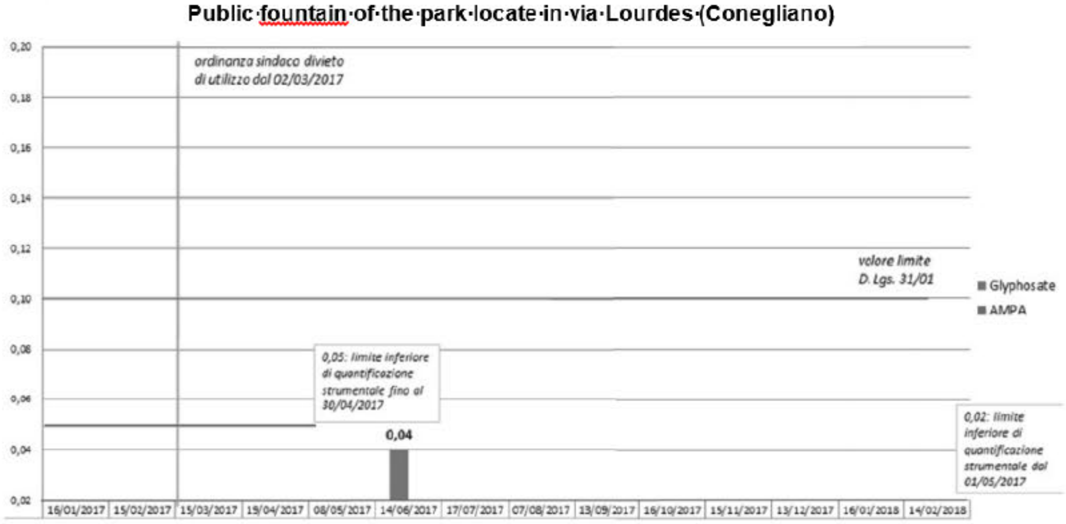


Figure 8.5-38: **Levels of glyphosate and AMPA in sequential sampling at the fountain of the public garden in *via Lourdes*, *Conegliano* in the period January 2017 to February 2018**



Conclusions

High-consumption herbicidal products such as glyphosate, and consequently its metabolite AMPA, can reach the drinking water network of an urban settlement surrounded by areas with high agricultural and wine-growing activity. Although the issue about the toxicity of glyphosate for humans is still widely debated, the experience of the Venetian Ulss2 demonstrates how the joint intervention of the institutions (in this case, the local Hygiene and Public Health Service and the municipal administrations) can contribute to eliminating the presence of a "probable carcinogen" in the city's drinking water. Furthermore, such interventions can make it mandatory to abandon potentially harmful agricultural practices, in favour of alternative solutions characterized by reduced impact on the environment and the health of local populations.

Assessment and conclusion by applicant:

The article reports concentrations of glyphosate and AMPA found in 12 wells used for drinking water consumption in Northern Italy, situated within a wine growing area. Traces of glyphosate (maximum reached 0.08 µg/L) and AMPA (maximum reached 0.25 µg/L) were detected in 2 wells supplying an urban area. The article is therefore considered as reliable with restrictions. Sampling and analytical methods are not described. Nature of groundwater wells not described, point sources could be possible. No information on precipitation is reported. No description of monitoring sites other than very rough map of area and aqueduct names.

Assessment and conclusion by RMS:

Agrees with applicant conclusions. This study is considered reliable with restrictions.

It provides monitoring results from 12 wells used for drinking consumption in Northern Italy, within a wine growing area. Results are however not clearly exposed. Authors report "traces of glyphosate (maximum reached 0.08 µg/L) and AMPA (maximum reached 0.25 µg/L) were detected in 2 wells supplying an urban area."

However no further detailed are given.

Data point:	CA 7.5/017
Report author	Poiger, T. *et al.*
Report year	2017
Report title	Occurrence of the herbicide glyphosate and its metabolite AMPA in surface waters in Switzerland determined with on-line solid phase extraction LC-MS/MS
Document No	Environmental Science and Pollution Research (2017) 24:1588-1596
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (Agroscope)
Acceptability/Reliability:	Reliable

Glyphosate is currently one of the most important herbicides worldwide. Its unique properties provide for a wide range of uses in agriculture, but also in non-agricultural areas. At the same time, its zwitterionic nature prevents the inclusion in multi-residue analytical methods for environmental monitoring. Consequently, despite its extensive use, data on occurrence of glyphosate in the aquatic environment is still scarce. Based on existing methods, we developed a simplified procedure for the determination of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) in water samples using derivatization with fluorenylmethyl chloroformate FMOC-Cl, combined with on-line solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS) detection. This method was extensively tested on over 1000 samples of surface water, groundwater, and treated wastewater and proved to be simple, sensitive, and reliable. Limits of quantification of 0.005 µg/L were routinely achieved. Glyphosate and AMPA were detected in the vast majority of stream water samples in the area of Zurich, Switzerland, with median concentrations of 0.11 and 0.20 µg/L and 95th percentile concentrations of 2.1 and 2.6 µg/L, respectively. Stream water data and data from treated wastewater indicated that non-agricultural uses may significantly contribute to the overall loads of glyphosate and AMPA in surface waters. In the investigated groundwater samples, selected specifically because they had shown presence of other herbicides in previous monitoring programs, glyphosate and AMPA were generally not detected, except for two monitoring sites in Karst aquifers, indicating that these compounds show much less tendency for leaching.

Materials and Methods

Chemicals

Glyphosate (purity 98 %), glyphosate-FMOC (99.5 %), AMPA-FMOC (97 %), $^{13}C_2$ ^{15}N-glyphosate (internal standard, 98 %), AMPA (99 %) $^{13}C_2$ $^{15}ND_2$-AMPA (100 mg/L in water) were obtained commercially. Stock solutions of the unlabeled compounds were prepared at concentrations of 500 mg/L in acetonitrile/water (7:3). To aid dissolution of glyphosate and AMPA, 100 µL 1 M aqueous NaOH solution was added to 20 mL of stock solution. All solvents were of HPLC grade.

Water samples

Grab samples from various streams in the area of Zurich, Switzerland, were collected during routine samplings by the Office for Waste, Water, Energy, and Air of the Canton of Zurich (AWEL) from 2006 to 2013. Further grab samples from a small stream in the Canton of Vaud were provided by the water protection laboratory of the canton from 2011 to 2014. Groundwater samples were collected by the Federal Office for the Environment (FOEN) at selected monitoring sites of the NAQUA National Groundwater Monitoring Program during a pilot study in 2010 and 2011, and by the official food control authority of the Canton of Zurich in 2006, 2007, and 2012. Grab samples and 24-h flow proportional composite samples of treated wastewater from various WWTPs in Switzerland were obtained from the personnel of these plants. All samples were collected in 125-mL high-density polyethylene (HDPE) flasks, shipped in ice-cooled containers (not frozen), and stored at 4°C after addition of internal standard (see below). Storage time was usually less than 2 weeks.

Derivatization with FMOC-Cl

Upon arrival at the laboratory, exactly 100 mL of each water sample was retained in the HDPE container while the rest was discarded. Samples were fortified with 100 µL of a solution of $^{13}C_2$ ^{15}N-glyphosate and $^{13}C_2$ $^{15}ND_2$-AMPA (0.1 ng/µL each) in acetonitrile/water (7:3) to yield concentrations of 100 ng/L in the samples. Spiked samples were kept for at least 24 h at 4°C to allow for equilibration between dissolved and particulate phase. To an aliquot of water sample, 0.1 M borate buffer solution and 2 mM FMOC-Cl solution were added, shaken, and left at room temperature overnight. To remove excess reagent and side products, as well as a substantial fraction of the acetonitrile, dichloromethane was then added to the derivatized samples. The samples were shaken and left undisturbed until the phases were completely separated. Specific details of the derivatization are provided in the article. 'Matrix matched' standards were prepared in 'fossil' groundwater, which was also used for blank determination. Concentrations ranged from 10 to 2000 ng/L glyphosate and AMPA (depending on the concentrations present in the samples). The internal standards were added at the same concentration as in the water samples, and derivatization was done together with the real samples.

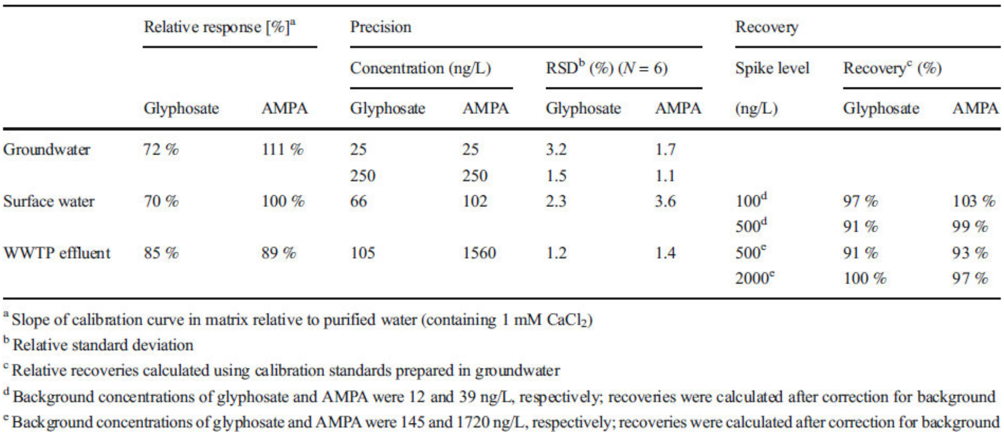
On-line SPE and liquid chromatography-tandem mass spectrometry

The instrumental setup was similar to the one reported earlier (Gulkowska *et al*. 2014) and consisted of an auto-sampler equipped with two six-port valves for column switching, a sample loop, and an on-line extraction cartridge. Pre-concentration of the derivatized analytes was achieved using a column switching technique. A PEEK loop was loaded with the derivatized sample solely from the upper, aqueous layer via the auto-sampler syringe. The sample was then transferred from the loop to the SPE cartridge with purified water. After valve switching, the enriched analytes were eluted backward directly on to a C-18 column equipped with a guard column followed by separation using the mobile phase program. The HPLC column was connected to an API 4000 triple quadrupole mass spectrometer equipped with a turbo ion spray (TIS) source operated in negative mode and multiple reaction monitoring (MRM). The characteristic fragmentation reaction for the primary transition was the cleavage of the FMOC moiety from the derivatized molecule. Specific HPLC and mass spectrometer conditions, and ion transitions monitored are reported in the paper. Quantification was based on peak area ratios of analyte versus internal standard in reference to standards in spiked fossil groundwater. Concentrations were determined separately using the primary (Q) and secondary ion transitions (q), and measurements were flagged when the concentration ratio Q/q was not within 0.8-1.2.

Relative response, method precision, and recovery in different matrices

The influence of the sample matrix on the intensity of MRM transitions for glyphosate and AMPA was studied in groundwater, surface water (Sagentobelbach, sampled on August 18, 2015), WWTP effluent (Dübendorf, August 18, 2015), and purified water containing calcium chloride. Standards were prepared in these matrices by appropriate dilution of a stock solution of the isotopically labeled surrogate compounds (concentrations, 62.5, 125, 250, 500, 1000, and 2000 ng/L), followed by derivatization. By using the isotopically labeled surrogate compounds, a possible influence of background levels could be excluded. The slopes of the respective calibration curves were used to calculate responses in matrix relative to purified water (Table 8.5-61). Method precision was determined by replicate analysis (N = 6) of WWTP effluent (Villars-sous-Yens, August 11, 2015), surface water (Boiron, July 17, 2015), and groundwater (Aqui, spiked with glyphosate and AMPA at concentrations of 25 and 250 ng/L, respectively). Recoveries were determined in surface water (Sagentobelbach, August 18, 2015) and WWTP effluent (Villars-sous-Yens, August 11, 2015) relative to calibration standards in groundwater (Aqui) at two spike levels each.

Table 8.5-61: Influence of sample matrix on responses of glyphosate and AMPA in groundwater, river water, and WWTP effluent; method precision; and recovery



	Relative response [%][a]		Precision				Recovery		
			Concentration (ng/L)		RSD[b] (%) ($N = 6$)		Spike level	Recovery[c] (%)	
	Glyphosate	AMPA	Glyphosate	AMPA	Glyphosate	AMPA	(ng/L)	Glyphosate	AMPA
Groundwater	72 %	111 %	25	25	3.2	1.7			
			250	250	1.5	1.1			
Surface water	70 %	100 %	66	102	2.3	3.6	100[d]	97 %	103 %
							500[d]	91 %	99 %
WWTP effluent	85 %	89 %	105	1560	1.2	1.4	500[e]	91 %	93 %
							2000[e]	100 %	97 %

[a] Slope of calibration curve in matrix relative to purified water (containing 1 mM $CaCl_2$)

[b] Relative standard deviation

[c] Relative recoveries calculated using calibration standards prepared in groundwater

[d] Background concentrations of glyphosate and AMPA were 12 and 39 ng/L, respectively; recoveries were calculated after correction for background

[e] Background concentrations of glyphosate and AMPA were 145 and 1720 ng/L, respectively; recoveries were calculated after correction for background

Quality assurance in routine monitoring

Several measures were used to assure accurate determination of glyphosate and AMPA during monitoring campaigns. Blank samples (fossil groundwater) and a control standard of spiked groundwater were analyzed with each batch of samples. Selected samples were analyzed in triplicate to determine precision (RSD values were in the range of those reported in Table 8.5-61). In longer campaigns, selected samples from previous sampling events were reanalyzed to determine intermediate precision (measured concentrations, usually within ±10%) and storage stability (peak area of internal standards over time, usually within ±10%). Storage stability varied between 1 and 2 months (groundwater) and 2 weeks (WWTP effluent). During storage, concentrations of the analytes and internal standards did not decrease continuously but rather dropped rapidly after a certain 'lag phase.' However, peak area ratios (analyte vs. internal standard) remained constant.

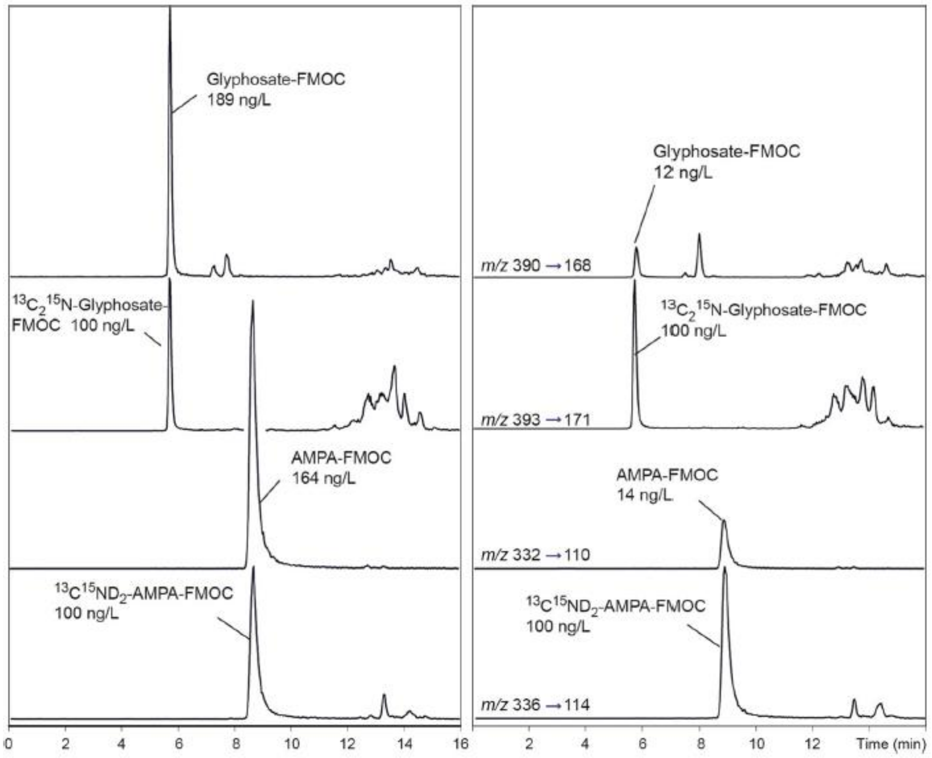
Results and Discussion

Optimization of the analytical procedure

Derivatization of glyphosate and related compounds with FMOC-Cl offers several advantages. First, the reaction proceeds directly in aqueous samples (with a certain amount of acetonitrile as co-solvent) so that there is no need for pre-concentration or solvent exchange prior to derivatization. Second, the derivative is significantly more lipophilic than the underivatized test substances and thus more easily concentrated from water and more suited for reversed-phase HPLC. Third, the main by-product of the derivatization, the FMOC alcohol, can easily be removed as it is far more lipophilic than the derivatives. The procedure requires only 5 mL of sample and no transfer steps prior to derivatization. On-line preconcentration requires no dedicated equipment except a dual injection valve and an auxiliary HPLC pump for transfer of sample from sample loop to cartridge precolumn used for preconcentration.

In chromatograms from natural water samples, some of the mass traces also contain substantial signals other than those of the target compounds (Figure 8.5-39). This is due to the fact that the major transitions observed in negative ion tandem mass spectrometry result from loss of the FMOC moiety. Therefore, we optimized the chromatographic separation between target compounds and possible interferences by using a rather high pH eluent (≈ 9.15) in combination with an HPLC column that is sufficiently stable at this high pH. As can be seen in the figure, glyphosate and AMPA elute earlier than any of the interferences.

Figure 8.5-39: Typical chromatograms of glyphosate and AMPA in samples from the river Aabach at Mönchaltorf (weekly composite sample, September 30 to October 6, 2013, left) and from Lake Greifensee (1 m depth, October 7, 2013, right)



Signal responses in different matrices, detection limits, precision, and recoveries

Relative responses (expressed in % of the response in purified water) showed fairly narrow variation between different matrices (Table 8.5-61). Limits of quantification (LOQs) for glyphosate and AMPA of 5 ng/L (signal/noise ratio of >10 for the ion trace used for quantification and S/*N* >3 for the ion trace used for confirmation) were achieved under most circumstances, except for surface water samples with high particle loads and groundwater samples with low pHs (see below). Method precision was excellent with relative standard deviations for replicate analyses ranging from 1.1 to 3.6% with no clear trend with regard to matrix or substance. Recoveries in spiked surface water and WWTP effluent ranged from 91 to 103%.

Field testing of the analytical procedure

The optimized procedure was extensively tested on a total number of more than 1000 samples of groundwater, surface water from different streams and lakes, and effluents from WWTPs and proved to be robust and sensitive. Some of the experiences during application of the method are discussed hereafter. In some groundwater samples, fairly low signals were obtained for internal standards as well as the test substances. This phenomenon was reported by other researchers and attributed to possible complexation of the test substances with metals (Ibanez *et al*. 2006). In our experience, low signals were limited to groundwater samples with low pHs (<6.5) and low calcium content. In these cases, adjusting the pH to ≥7 and addition of 1 mM $CaCl_2$ prior to derivatization resulted in a substantial improvement in signal intensity.

Samples were normally analyzed without prior filtration. After addition of the internal standard, the particles were allowed to settle and a subsample from the supernatant was subjected to derivatization and analysis. Assuming that the time between addition of internal standard and derivatization (24 h) was long enough to allow for an equilibration between aqueous and particulate phases, the measured concentration thus reflects the total amount in the sample, including the fraction which is adsorbed to particles. Surface water samples from storm events with very high content of organic matter (particulate and/or dissolved) sometimes also yielded low signal intensities. Regardless of whether this was due to signal suppression, low derivatization yield, or both, dilution with blank (fossil) groundwater improved the situation.

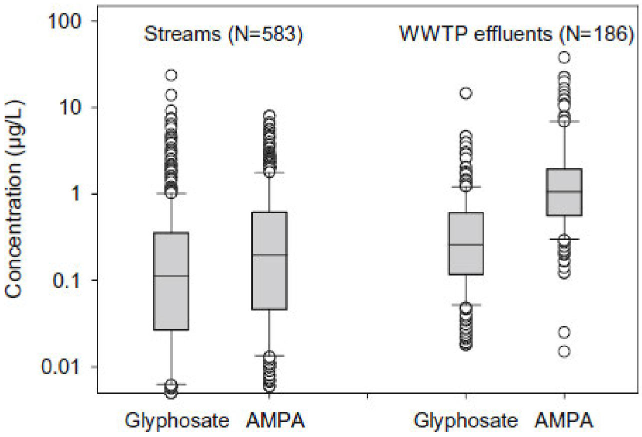
Glyphosate in groundwater samples

A total of 141 groundwater samples from 14 monitoring sites in Switzerland in 2010 and 2011 were analyzed as part of an intensive campaign conducted by the FOEN to determine the concentration dynamics of pesticides at these stations. Concentration dynamics were expected to be high at these locations due to high vulnerability. Glyphosate was detected twice above the LOQ of 0.005 µg/L at one location (0.009 and 0.025 µg/L, respectively). AMPA was regularly detected at two locations above the LOQ of 0.005 µg/L in concentrations of 0.08-0.65 and 0.017-0.070 µg/L, respectively. Both monitoring sites are located in vulnerable Karst aquifers with a shallow soil cover. During 2006, 2007, and 2012, further single groundwater samples from eight locations were analyzed with no detections above the LOQ of 0.005 µg/L. Some of these locations are known to receive substantial amounts of river bank infiltration (Buerge *et al*. 2009). Overall, these results confirm the low potential of glyphosate and AMPA for leaching to groundwater which is due to strong sorption to soil particles combined with fairly rapid dissipation (European Food Safety Authority (EFSA) 2015).

Occurrence of glyphosate and AMPA in rivers and streams

From 2006 to 2013, glyphosate and AMPA were analyzed in numerous water samples from various locations in Switzerland, particularly in the canton of Zurich. In the following, we present results from monitoring campaigns where monthly grab samples were taken between March and November (no sampling during winter and early spring) as part of the pesticide monitoring program of the canton of Zurich (AWEL 2016). Both compounds were regularly detected in the investigated streams with median concentrations of 0.11 and 0.20 µg/L and 95th percentile concentrations of 2.1 and 2.6 µg/L, respectively (Figure 8.5-40).

Figure 8.5-40: **Distribution of glyphosate and AMPA concentrations in rivers and streams (*N* = 583) and WWTP effluents (*N* = 186), analyzed from 2006 to 2013. The boxes indicate median and 25th and 75th percentiles, the whiskers the 5th and 95th percentiles. Values outside this range are plotted individually.**



Only 40 out of 583 samples showed glyphosate concentrations below the LOQ of 0.005 µg/L (27 for AMPA). On average, concentrations of AMPA were higher than those of glyphosate. On a sample-by-sample basis, in only 28% of samples, concentrations of AMPA were lower than those of glyphosate. Nevertheless, the highest overall concentrations were found for glyphosate. Widespread occurrence in streams as well as the detected concentrations compare well to findings in other studies (Battaglin *et al*. 2014; Daouk *et al*. 2013; European Glyphosate Environmental Information Sources (EGEIS) 2009; Hanke *et al*. 2008; Hanke *et al*. 2010; Kolpin *et al*. 2006). The seasonal variation of glyphosate and AMPA concentrations in weekly, flow-proportional composite samples was monitored in various streams in the canton of Zurich from spring to fall. For example, in the Furtbach, a small stream in the north of Zurich (long-term mean discharge, 655 L/s; Q347 = 208 L/s), receiving inputs from agricultural land as well as from three municipal WWTPs serving a total population of approximately 32,000, glyphosate was already present in the water samples in April and increased to a maximum of 1.9 µg/L at the end of May (Figure 8.5-41 (top)). Thereafter, the concentrations remained relatively high until mid-September, consistent with its main application window in August, and then dropped to below 0.1 µg/L at the beginning of November. The minima in June, August, and end of September correspond to weeks with no precipitation. Glyphosate was detected at elevated concentrations for a much longer part of the year than other herbicides that are applied in large quantities such as isoproturon or metolachlor and which are typically found primarily during a narrow time window during and immediately following the application period. Concentrations of AMPA in the same samples varied much less. While, overall, higher concentrations were observed in summer, the differences between summer and spring/fall were smaller than for glyphosate. Particularly, the minima in June and August were not observed for AMPA. Concentration ratios AMPA/glyphosate were calculated for all weekly composite river water samples analyzed from 2006 to 2013. To eliminate some of the variability due to different meteorological conditions, the calculated values were grouped monthly. Concentration ratios varied greatly as indicated by the wide range that is spanned by the 5th and 95th percentile whiskers in Figure 8.5-41 (bottom). Nevertheless, there is a trend toward lower ratios in summer, when glyphosate concentrations are at their maximum.

Wastewater treatment plants as a source of glyphosate and AMPA in surface waters
Glyphosate and AMPA were regularly present in treated wastewater. Concentrations tended to be higher than in rivers and streams with median concentrations of 0.38 and 1.3 µg/L, respectively (Figure 8.5-42). Comparison of glyphosate and AMPA concentrations in WWTP effluents (data not shown) do not indicate that occurrence of these two compounds is linked. Concentration ratios (AMPA/glyphosate) ranged from 1.2 to 38 and seemed to be related to the particular WWTP rather than to any other parameter (such as time of year, high or low concentrations, etc.). All these observations indicate that AMPA, although a major metabolite of glyphosate, must have other sources as well. Indeed, AMPA is also a major degradation product of a number of phosphonates used, e.g., in detergents as chelating agents (Nowack 2003). Comparison of in-stream concentrations of glyphosate and AMPA upstream and downstream of WWTPs indicated that treated wastewater indeed is a source of these compounds in surface waters (Figure 8.5-42). For glyphosate, contribution of WWTP effluent to downstream concentrations was predominant (>90%) in 6 out of 47 cases, significant (20 to 90%) in another 21, and negligible (<20%) in 20 cases.

Figure 8.5-41: **Example of the seasonal variation of glyphosate and AMPA concentrations in flow-proportional weekly composite samples from a small river (Furtbach 2008, top) and of the AMPA/glyphosate concentration ratios in various small rivers in the Canton of Zurich, Switzerland (2008-2013, bottom).**

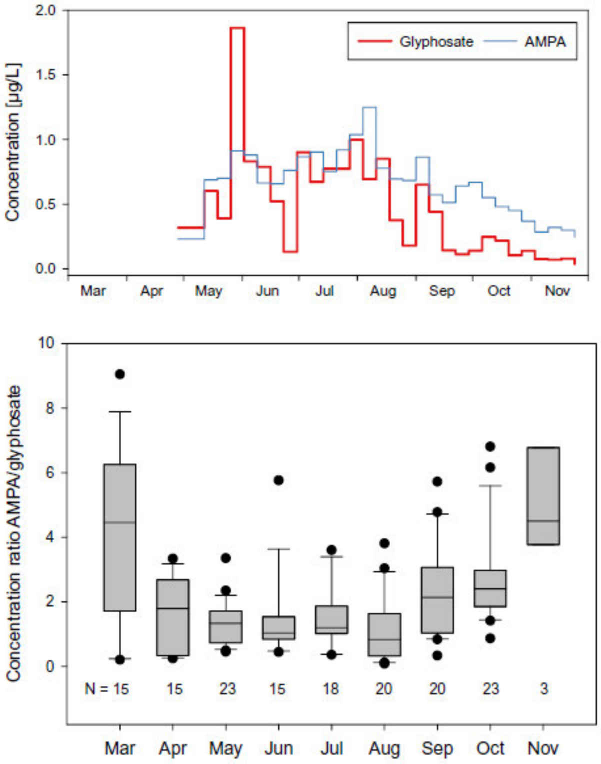
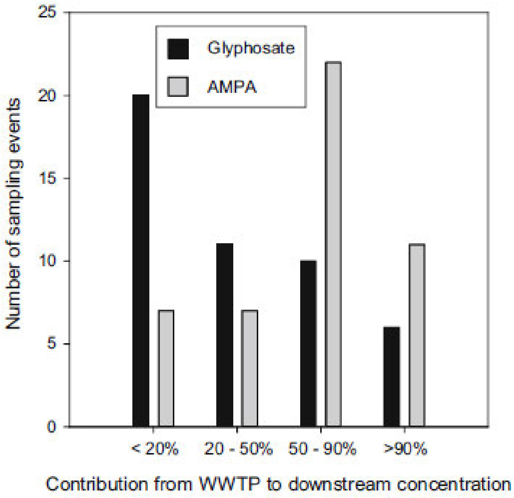


Figure 8.5-42: **Evidence of contribution of treated wastewater to total loads of glyphosate and AMPA in surface waters from a comparison of in-stream concentrations, upstream and downstream of municipal WWTPs (*N* = 47)**



Urban contribution to total load of glyphosate in surface waters
Ubiquitous occurrence of glyphosate in wastewater indicates that non-agricultural uses of glyphosate may substantially contribute to the total burden to surface waters. Potential candidates are uses for weed control along highways and railroads as well as private and semi-private application such as in gardening and weed

control in residential areas, parks, golf courses, etc. Our data from streams and WWTP effluents clearly support this finding. Due to its unique combination of properties, glyphosate has found many applications in areas where other herbicides would be expected to pose significant risk for contamination of surface and/or groundwater. Despite its favorable properties, glyphosate losses from urban uses can be quite significant (Ramwell *et al.* 2014) and may contribute substantially to the elevated concentrations in surface waters over extensive periods of time. Even though these concentrations are still well below the currently proposed environmental quality standards for surface waters in Switzerland and some EU Member States (Johnson 2012; Maycock *et al.* 2010; Oekotoxzentrum2016), it appears to be warranted to reduce the use of glyphosate particularly in those areas (e.g., application on or along sealed surfaces) where the potential losses are high.

Assessment and conclusion by applicant:
The article describes the derivation of a simplified procedure for the determination of glyphosate and AMPA in water samples. More than 1000 samples from ground and surface waters, and from treated wastewaters in Switzerland were tested with this method and the results are reported.
The article is considered reliable.

Assessment and conclusion by RMS:
The article is considered reliable.

It describes the derivation of a simplified procedure for the determination of glyphosate and AMPA in water samples.
More than 1000 samples from ground and surface waters, and from treated wastewaters in Switzerland were tested with this method and the results are reported.

For groundwater:
A total of 141 groundwater samples from 14 monitoring sites in Switzerland in 2010 and 2011 were analyzed as part of an intensive campaign to determine the concentration dynamics of pesticides at these stations.

Concentration dynamics were expected to be high at these locations due to high vulnerability. Glyphosate was detected twice above the LOQ of 0.005 µg/L at one location (0.009 and 0.025 µg/L, respectively). AMPA was regularly detected at two locations above the LOQ of 0.005 µg/L in concentrations of 0.08 0.65 and 0.017 0.070 µg/L, respectively.
Both monitoring sites are located in vulnerable Karst aquifers with a shallow soil cover. During 2006, 2007, and 2012, further single groundwater samples from eight locations were analyzed with no detections above the LOQ of 0.005 µg/L. Some of these locations are known to receive substantial amounts of river bank infiltration (Buerge *et al.* 2009).

Study authors concluded that these results confirm the low potential of glyphosate and AMPA for leaching to groundwater which is due to strong sorption to soil particles combined with fairly rapid dissipation

Data point:	CA 7.5/018
Report author	Di Guardo, A., Finizio, A.
Report year	2016
Report title	A moni-modelling approach to manage groundwater risk to pesticide leaching at regional scale
Document No	Science of the Total Environment 545–546 (2016) 200–209
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Historically, the approach used to manage risk of chemical contamination of water bodies is based on the use of monitoring programs, which provide a snapshot of the presence/absence of chemicals in water bodies. Monitoring is required in the current EU regulations, such as the Water Framework Directive (WFD), as a tool to record temporal variation in the chemical status of water bodies. More recently, a number of models have been developed and used to forecast chemical contamination of water bodies. These models combine information of chemical properties, their use, and environmental scenarios. Both approaches are useful for risk assessors in decision processes. However, in our opinion, both show flaws and strengths when taken alone. This paper proposes an integrated approach (moni-modelling approach) where monitoring data and modelling simulations work together in order to provide a common decision framework for the risk assessor. This approach would be very useful, particularly for the risk management of pesticides at a territorial level. It fulfils the requirement of the recent Sustainable Use of Pesticides Directive. In fact, the moni-modelling approach could be used to identify sensible areas where implement mitigation measures or limitation of use of pesticides, but even to effectively re-design future monitoring networks or to better calibrate the pedo-climatic input data for the environmental fate models.

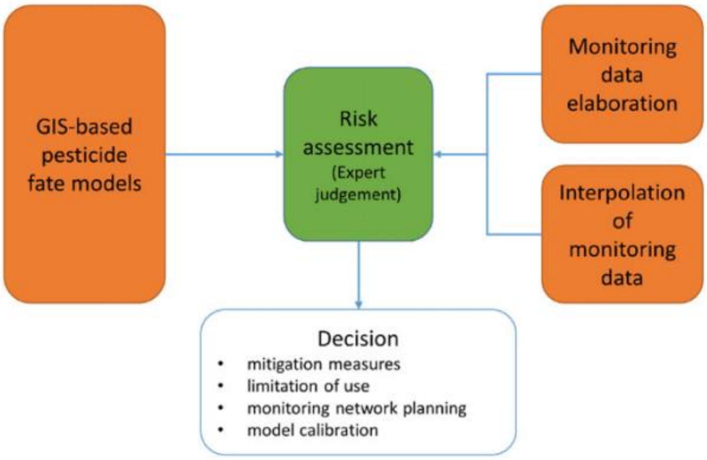
A case study is presented, where the moni-modelling approach is applied in Lombardy region (North of Italy) to identify groundwater vulnerable areas to pesticides. The approach has been applied to six active substances with different leaching behaviour, in order to highlight the advantages in using the proposed methodology.

Materials and Methods

Overview of the methodology

The moni-modelling approach, here briefly described (Figure 8.5-43), is based on coupling spatial modelling of environmental fate and long term monitoring data of Plant Protection Products (PPPs) occurrence in wells. A methodology of comparison between the results of the two types of information permits to take valuable conclusions on the effective vulnerability of the area. In the first instance, it foresees the definition of vulnerability maps at regional scale using GIS-coupled models for predicting the potential pesticide concentrations in groundwater at regional scale. On the other side, another brick of information for decision making is given by the availability of long term monitoring data of PPPs residues in groundwater. Generally, monitoring points (wells) can be easily georeferenced in a GIS map by using geographical coordinates. Considering the availability of long term data on PPPs residues in groundwater it is possible to create a map of 95th percentile of each PPP monitored observed in each monitoring site. This map can be used as input for a geostatistical analysis (i.e. using an ordinary block kriging interpolation method) to produce a new map highlighting the influence areas of different wells in the territory.

Figure 8.5-43: Flux diagram of the proposed methodology. Colours represent different spatial levels of each action (in orange at regional level, in green at local level)



By evaluating both monitoring and modelling results, decision makers will have a powerful tool to identify specific areas at risk where implement risk mitigation measures. In addition, decision maker will have useful information to plan better monitoring networks and/or better calibrations of predictive models.

Case study: Lombardy region (North Italy)

Description of the area

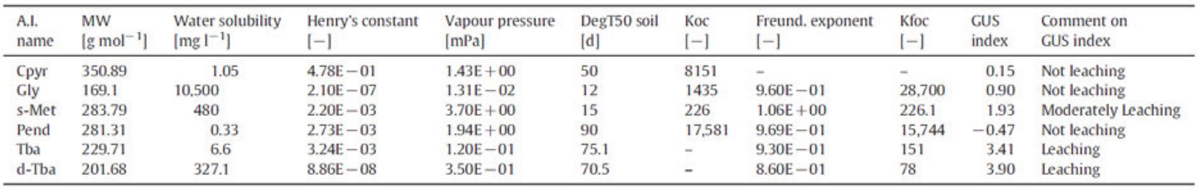
Lombardy region has an extension of about 23.844 km^2 which almost a half of it is plain (47%) and the rest consists of hills (12%) and mountains (41%). Flat areas extend from West to East, while mountains are located at North (Alps) and in the South-West (Apennine). The last agriculture census reports that arable crops are cultivated in the 92.1% of the available crop area of the Lombardy plain, while the remaining part is dedicated to woody crops and grasslands; maize is the main crop of the Lombardy region, where it covers almost a half of the total arable area.

Plant Protection Products under evaluation

In order to set up the methodology and to give some examples of how the outcomes could be very useful for risk managers, we considered five PPPs and a metabolite. Particularly, terbuthylazine (Tba), glyphosate (Gly), pendimethalin (Pend) and s-metolachlor (s-Met) herbicides, the insecticide chlorpyriphos (Cpyr) and the terbuthylazine metabolite desethyl-terbuthylazine (d-Tba) were considered.

Table 8.5-62, reports a summary representation of the main physical–chemical properties and persistence (degradation time in soil: $DegT_{50}$) of the selected substances; data are from the online PPDB database maintained by the Agriculture & Environment Research Unit (AERU) at the University of Hertfordshire.

Table 8.5-62: Main physical-chemical properties of selected active ingredients from PPBD database (Pesticide Properties Database)



A.I. name	MW [g mol^{-1}]	Water solubility [mg l^{-1}]	Henry's constant [−]	Vapour pressure [mPa]	DegT50 soil [d]	Koc [−]	Freund. exponent [−]	Kfoc [−]	GUS index	Comment on GUS index
Cpyr	350.89	1.05	4.78E−01	1.43E+00	50	8151	–	–	0.15	Not leaching
Gly	169.1	10,500	2.10E−07	1.31E−02	12	1435	9.60E−01	28,700	0.90	Not leaching
s-Met	283.79	480	2.20E−03	3.70E+00	15	226	1.06E+00	226.1	1.93	Moderately Leaching
Pend	281.31	0.33	2.73E−03	1.94E+00	90	17,581	9.69E−01	15,744	−0.47	Not leaching
Tba	229.71	6.6	3.24E−03	1.20E−01	75.1	–	9.30E−01	151	3.41	Leaching
d-Tba	201.68	327.1	8.86E−08	3.50E−01	70.5	–	8.60E−01	78	3.90	Leaching

The modelling system

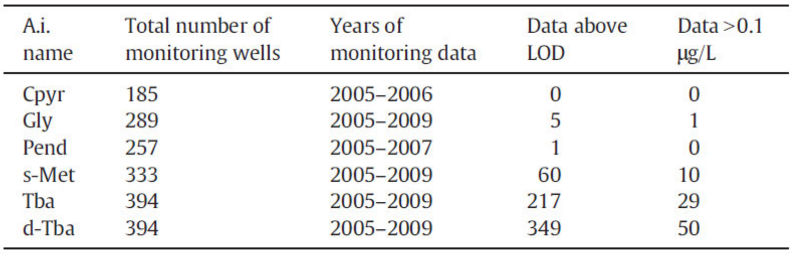
VULPES is an exposure assessment tool to identify groundwater vulnerable areas to PPPs at regional level. It focuses the attention to the interaction of active ingredients with the agricultural and environmental characteristics of the area. It uses the PELMO v.3.2 model to evaluate the pesticide fate in groundwater.

For s-Met, Pend, Cpyr, Gly simulations were made by considering the maximum allowed application rates for each active ingredient, as reported in the commercial formulation labels.

Monitoring data
The presence of the six substances in Lombardy groundwater is actually monitored by ARPA Lombardia, the environmental protection agency of the Lombardy region. We analysed five years data from 2005 to 2009 from 320 monitoring stations evenly distributed in the Po plain part of the Lombardy region.

Table 8.5-63, reports a brief summary of the main characteristics of the monitoring data provided, For each well and substance we then calculated the 95th percentile of observed values. Values below the level of detection (LOD) was taken into account into the next elaborations, assuming an observed value equal to a half of LOD (in agreement with the 2009/90/CE Directive).

Table 8.5-63: Statistical summary of monitoring data for the six substances



A.i. name	Total number of monitoring wells	Years of monitoring data	Data above LOD	Data >0.1 μg/L
Cpyr	185	2005–2006	0	0
Gly	289	2005–2009	5	1
Pend	257	2005–2007	1	0
s-Met	333	2005–2009	60	10
Tba	394	2005–2009	217	29
d-Tba	394	2005–2009	349	50

Geostatistical elaborations
Monitoring data provide information on the local contamination and they are related to a single point in space. In order to compare monitoring data with modelling output expressed as areas of vulnerability, we adopted the ordinary block kriging (an optimal interpolation technique based on regression against observed values of surrounding data points, weighted according to spatial covariance values). For each active substance, we elaborated the available monitoring data in order to obtain the 95th percentile for each well and we used the kriging tool implemented in the SAGA-GIS software to elaborate maps of interpolated observation values of substance concentrations in the water table.

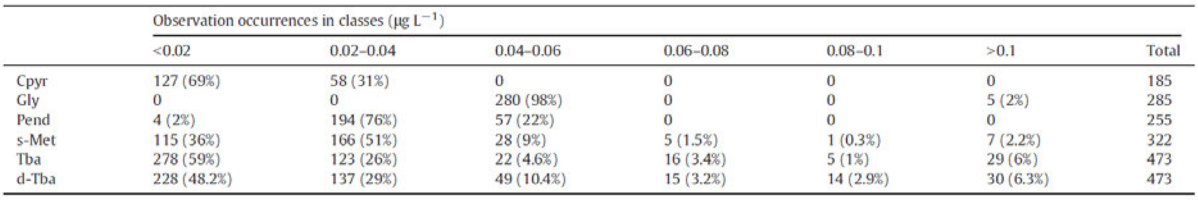
Results

Maps of predicted concentration of PPPs residues in groundwater of Lombardy region (vulnerability maps)
VULPES produced six vulnerability maps, which highlight the 80th percentile of the investigated active ingredient concentration at 1 m below the soil surface taking into account all the years of meteorological data available. Results are grouped into six categories; hence, values can be directly compared with the legal limit for active ingredient concentration in the groundwater, actually set to 0.1 μg/L. No map has been reported for Cpyr, Gly and Pend because VULPES system did not identify any vulnerability related problem with these substances. Resulting maps demonstrate two different behaviours. In agreement with GUS index the simulations for Pend, Gly and Cpyr indicated a non-leaching behaviour (each polygon falls into the class below 0.02 μg/L). On the contrary, s-Met demonstrated leachability in some areas (particularly those characterised by highly permeable soils), while Tba and d-Tba are likely to leach in several parts of the region well beyond the trigger value of 0.1 μg/L.

Maps of measured concentration of PPPs residues in groundwater of Lombardy region
In Table 8.5-64, we report a general picture of the 95th percentiles values of monitoring data for each of the considered active ingredient. In order to have a direct comparison with the vulnerability maps produced by VULPES we used the same division in classes. For non-leaching substances (Cpyr, Gly and Pend) values fall into the first three classes except for a consistent presence of Gly in 5 wells. Browsing raw data, almost all are below the LOD, hence values in the three classes testify the different LOD used in several part of the region. Among leaching substances, the 96% of s-Met data falls into the first three classes, while only

the remaining 4% lies within the higher ones. The same general trend applies for Tba and d-Tba (89% and 87% values falls into the first three classes respectively). However, noticeably, 6% of values are above the trigger limit for both substances.

Table 8.5-64: Classification of 95th percentile monitoring values of each well for the six active ingredients



	Observation occurrences in classes (μg L^{-1})						
	<0.02	0.02–0.04	0.04–0.06	0.06–0.08	0.08–0.1	>0.1	Total
Cpyr	127 (69%)	58 (31%)	0	0	0	0	185
Gly	0	0	280 (98%)	0	0	5 (2%)	285
Pend	4 (2%)	194 (76%)	57 (22%)	0	0	0	255
s-Met	115 (36%)	166 (51%)	28 (9%)	5 (1.5%)	1 (0.3%)	7 (2.2%)	322
Tba	278 (59%)	123 (26%)	22 (4.6%)	16 (3.4%)	5 (1%)	29 (6%)	473
d-Tba	228 (48.2%)	137 (29%)	49 (10.4%)	15 (3.2%)	14 (2.9%)	30 (6.3%)	473

In order to get a spatial distribution of the yearly-observed monitoring data we apply the ordinary block kriging as a geostatistical interpolation method. Cpyr, Gly and Pend do not have evidences in wells; hence, no meaningful maps could be obtained by kriging interpolation.

Discussion

VULPES allows identifying potentially vulnerable areas to pesticides on a territorial scale, while monitoring data gives information on single points where contamination occurred. Analysis of map of interpolated monitoring data and vulnerability map could be done at two different spatial levels, following a top down approach. In case of leaching active ingredients (such as Tba, d-Tba and s-Met), when leachability strongly depends to environmental characteristics of the area, analysis should be focused at a local level. Particularly, both vulnerability map produced by VULPES and map of interpolated monitoring data should be analysed in deep details in order to highlight whether information are concordant or discordant. At this scale, 3 different situations could occur a) predicted and observed data are consistent (no risk or a certain level of potential pollution in the area), b) models forecast a feasible level of vulnerability, but no observations support it, c) observations denote a pollution in the area, but models indicates no vulnerability.

***Case a**. Agreement between predicted and observed data.*

When there is agreement on the lack of pollution in a particular area, then the risk assessor could reasonably judge that no mitigation measures or limitation of use are necessary in that area, even if occasional controls through monitoring should be considered. On the contrary, when the agreement is on the presence of the substance in the water table, then, depending on the extension of the area or the level of pollution, the risk assessor could be confident on adopting mitigation measures or limitation of use of the active ingredient.

***Case b** Vulnerability detected by model and no observed values in monitoring data*

In this case, the leaching model forecasts a high vulnerability to the active ingredient, while the surrounding wells does not provide values of it above the LOD. Analysing details of the location of wells, we could distinguish two case. If they belong to non-agricultural areas or to agricultural areas not cultivated at maize then probably their position in the area should be improved to evaluate if the vulnerability forecasted by the model could be definitively confirmed or not. The risk assessor could operate in that direction and re-evaluate the area with new data. If monitoring wells are correctly placed in areas cultivated with the studied crop and assuming the representativeness of the observed data, then there should be some weaknesses on input parameters of model simulations. They could belong to a wrong representation of the soil permeability of the area or to a lesser use of the active ingredient in the area. The risk assessor could evaluate the realisation of an in-depth analysis of the soil characteristics or take in consideration the effective average use of the active ingredient in the area and re-run the model simulation with the real amounts.

***Case b** No vulnerability detected by model and positive values in monitoring data*

The opposite occurs when the map elaborated by the leaching model does not forecast vulnerability, but the monitoring wells provide values of detection near or above the legal limit for groundwater (0.1 μg/L).

Several considerations could be done. In case of just one exceeding in a well while the others in proximity have values below the LOD, then the area could be interested by a point source contamination due for example to an unsustainable use of the active ingredient. However, if the vulnerability map with the map of 95th percentiles of the monitoring values is overlapped, then it can be observed that in the area there is only one point well beyond the threshold of 0.1 µg/L (exactly 0.199 µg/L), while the others are below the LOD. In case of several exceeding in nearby wells, probably the input data (such as pedology, meteorology, irrigation amounts) used as input for the model in the area do not represent its environmental characteristics. Input data should be checked with ad hoc measurement campaigns to verify their representativeness. Another important factor to be taken into account is the real pesticide usage in the area: the gap between observed and predicted could be explained if, for some reasons, commercial formulations containing the active ingredient have been used at higher rates than allowed.

Conclusion

The moni-modelling approach here presented provides risk assessors with a complete methodology to investigate the groundwater vulnerability to pesticide, raising the knowledge of the active substance presence and movement in the considered territory. It combines vulnerability maps obtained with pesticide fate models and monitoring data analysis in order to identify areas where mitigation measure or limitation of use of the investigated active ingredient should apply. Moreover, it could be useful to verify the appropriateness of the current monitoring network or to suggest its repositioning. At last, it could identify areas where simulation models could not represent the correct substance transport in the groundwater, probably due to an incorrect parameterisation of the pedo-climatic characteristic of the area.

Assessment and conclusion by applicant:

The article presents an approach for combining long-term groundwater monitoring data from the Lombardy Region, Northern Italy with regional scale vulnerability modelling. No experimental or monitoring data were generated.

The 95th percentile monitoring values indicate that the groundwater concentrations of glyphosate ranged between 0.04 – 0.06 µg/L in 280 wells (98%) and greater than the parametric drinking water limit of 0.1 µg/L in 5 wells (2%).

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

This article describes a "moni-modelling approach" based on coupling spatial modelling of environmental fate and long term monitoring data of Plant Protection Products (PPPs) occurrence in wells.

As indicated in applicant conclusions, the study does not generate any monitoring data, but results from long-term monitoring data are taken from the environmental protection agency of the Lombardy region (ARPA Lombardia). The results from the monitoring are reported as a brief summary of the the total number of monitoring wells, the number of data above the limit of detection (LOD) and above the trigger value of 0.1 µg/L. No further information are given. It also noted that the results for glyphosate are reported in 2 different tables in the article, but there are small unconsistencies on the total number of wells and number of detection above 0.1 µg/L (285 vs 289 wells, number of detection above the 0.1 µg/L trigger of 5 vs 1).

The following results may however be be retained:

From 2005 to 2009, results from 285 monitoring stations evenly distributed in the Po plain part of the Lombardy region are available. The overall number of samples per year is reported to be 65 to 228, the 95th percentile monitoring values indicate that the groundwater concentrations of glyphosate ranged between 0.04 – 0.06 µg/L in 280 wells (98%) and greater than the parametric drinking water limit of 0.1 µg/L in 5 wells (2%).

The article is considered reliable with restrictions, since only overall statistical summary of the results is avaialable, and the data can be considered little outdated.

Data point:	CA 7.5/019
Report author	Rosenbom, A. *et al*.
Report year	2015
Report title	Pesticide leaching through sandy and loamy fields – Long-term lessons learnt from the Danish Pesticide Leaching Assessment Programme
Document No	Environmental Pollution 201 (2015) 75-90
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (div. not named commercial laboratories)
Acceptability/Reliability:	Reliable

The European Union authorization procedure for pesticides includes an assessment of the leaching risk posed by pesticides and their degradation products (DP) with the aim of avoiding any unacceptable influence on groundwater. Twelve-year's results of the Danish Pesticide Leaching Assessment Programme reveal shortcomings to the procedure by having assessed leaching into groundwater of 43 pesticides applied in accordance with current regulations on agricultural fields, and 47 of their DP. Three types of leaching scenario were not fully captured by the procedure: long-term leaching of DP of pesticides applied on potato crops cultivated in sand, leaching of strongly sorbing pesticides after autumn application on loam, and leaching of various pesticides and their DP following early summer application on loam. Rapid preferential transport that bypasses the retardation of the plow layer primarily in autumn, but also during early summer, seems to dominate leaching in a number of those scenarios.

Materials and Methods

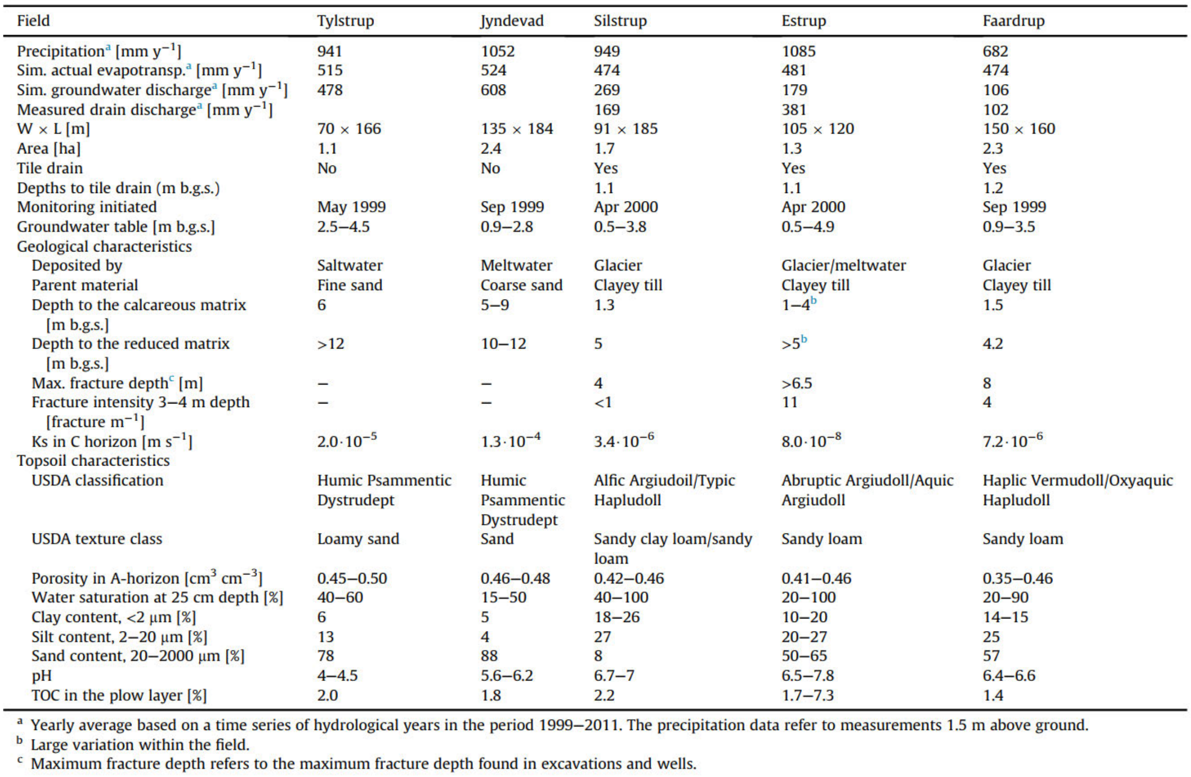
Selection of the five fields

Five agricultural fields were selected for Pesticide Leaching Assessment Programme (PLAP) - two sandy soil fields (at Tylstrup and Jyndevad) and three loamy soil fields (at Silstrup, Estrup and Faardrup). Instrumentation was installed during 1999. Monitoring began at the Tylstrup, Jyndevad and Faardrup fields in 1999 and at the Silstrup and Estrup fields in 2000 (Table 8.5-65). The three loamy fields are characterized by preferential transport through macropores (biopores, fractures) in a low permeable soil matrix (Rosenbom et al., 2009b), while other forms of preferential transport in the soil matrix may be found in the sandy fields (Rosenbom et al., 2009a).

Monitoring design of the PLAP fields

In order to determine whether or not the yearly flux-averaged concentration 1 m b.g.s. and the groundwater concentration of a single pesticide and/or its degradation product exceeds MAC (European-Commission, 1994) the following studies were undertaken: (i) a detailed geological, pedological and hydrogeological characterization of the field; (ii) long-term detailed monitoring of the water balance of the field (Table 8.5-65), e.g. climate, soil water content, groundwater table, drainage flow); (iii) numerical modeling of the field using MACRO version 5.2 (Larsbo *et al.*, 2005) to estimate the water balance, including percolation 1 m b.g.s.; and finally (iv) long-term detailed monitoring of the single pesticides and/or their degradation product/products at 1 m b.g.s. and deeper. To avoid any artificial leaching of pesticides, all installations and soil sampling deeper than 20 – 30 cm b.g.s. (plow depth) were restricted to the buffer zones surrounding the fields.

Table 8.5-65: Characteristics of the five PLAP fields



Field	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Precipitation[a] [mm y^{-1}]	941	1052	949	1085	682
Sim. actual evapotransp.[a] [mm y^{-1}]	515	524	474	481	474
Sim. groundwater discharge[a] [mm y^{-1}]	478	608	269	179	106
Measured drain discharge[a] [mm y^{-1}]			169	381	102
W × L [m]	70 × 166	135 × 184	91 × 185	105 × 120	150 × 160
Area [ha]	1.1	2.4	1.7	1.3	2.3
Tile drain	No	No	Yes	Yes	Yes
Depths to tile drain (m b.g.s.)			1.1	1.1	1.2
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999
Groundwater table [m b.g.s.]	2.5–4.5	0.9–2.8	0.5–3.8	0.5–4.9	0.9–3.5
Geological characteristics					
Deposited by	Saltwater	Meltwater	Glacier	Glacier/meltwater	Glacier
Parent material	Fine sand	Coarse sand	Clayey till	Clayey till	Clayey till
Depth to the calcareous matrix [m b.g.s.]	6	5–9	1.3	1–4[b]	1.5
Depth to the reduced matrix [m b.g.s.]	>12	10–12	5	>5[b]	4.2
Max. fracture depth[c] [m]	–	–	4	>6.5	8
Fracture intensity 3–4 m depth [fracture m^{-1}]	–	–	<1	11	4
Ks in C horizon [m s^{-1}]	$2.0\cdot10^{-5}$	$1.3\cdot10^{-4}$	$3.4\cdot10^{-6}$	$8.0\cdot10^{-8}$	$7.2\cdot10^{-6}$
Topsoil characteristics					
USDA classification	Humic Psammentic Dystrudept	Humic Psammentic Dystrudept	Alfic Argiudoll/Typic Hapludoll	Abruptic Argiudoll/Aquic Argiudoll	Haplic Vermudoll/Oxyaquic Hapludoll
USDA texture class	Loamy sand	Sand	Sandy clay loam/sandy loam	Sandy loam	Sandy loam
Porosity in A-horizon [cm^3 cm^{-3}]	0.45–0.50	0.46–0.48	0.42–0.46	0.41–0.46	0.35–0.46
Water saturation at 25 cm depth [%]	40–60	15–50	40–100	20–100	20–90
Clay content, <2 μm [%]	6	5	18–26	10–20	14–15
Silt content, 2–20 μm [%]	13	4	27	20–27	25
Sand content, 20–2000 μm [%]	78	88	8	50–65	57
pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6
TOC in the plow layer [%]	2.0	1.8	2.2	1.7–7.3	1.4

[a] Yearly average based on a time series of hydrological years in the period 1999–2011. The precipitation data refer to measurements 1.5 m above ground.
[b] Large variation within the field.
[c] Maximum fracture depth refers to the maximum fracture depth found in excavations and wells.

The monitoring equipment used and the aspects monitored include: a) piezometers - potentiometric pressure of the groundwater; b) vertical and horizontal monitoring wells - sampling of groundwater and measurement of groundwater level; c) suction cups - water samples from the variably saturated soil; d) automatic ISCO samplers - sampling of drainage water; e) weather stations - precipitation, air temperature, solar radiation and wind speed; f) TDR probes - soil water content; g) Pt100 sensors - soil temperature; and h) pressure sensors - barometric pressure. The location of the two nests of suction cups S1 and S2, the drainwater monitoring well and the vertical wells at all the PLAP fields was determined by the direction of the shallow groundwater flow. All suction cups and horizontal wells and all but one of the vertical wells are installed down-gradient to capture leaching from the field. The one remaining vertical well enables solute mass contributions from neighboring up-gradient fields to be accounted for. In the sandy fields, water samples from the variably saturated zone are collected using suction cups. In the loamy fields, the water samples for pesticide and/or degradation product analysis are collected from the drains (see Table 8.5-65 for drain depth) and, until March 2002, also from suction cups installed 1 m b.g.s. The latter sampling ceased due to cuts to PLAP funding when this type of sampling was found given the loamy soil texture to be less representative of the conditions in the variably saturated.

Selection of pesticide products and crops

The selection of pesticides and/or their degradation products for evaluation in PLAP for a period of at least two years focuses on compounds in the following three categories: (i) newly authorized pesticide products that are expected to be used either in large amounts and/or to be applied over a large area; (ii) pesticide products that have already been applied for several years either in large amounts and/or over a large area; (iii) authorized pesticides where there are indications of a potential risk of leaching either from the authorization procedure or from new information about them and or/their degradation products. In the latter group, not all the degradation products included in PLAP are found to be relevant metabolites according to the EU guidelines. Once the pesticide products have been selected, appropriate crops are chosen for the fields so that the pesticides can be applied to the crops for which their use is authorized and the best possible crop rotation can be maintained. Cultivation of the PLAP fields is in line with conventional agricultural practice in the locality except that the pesticides are always applied at the maximum permitted dosage. The monitoring studies thus represent the worst-case scenario since farmers often apply the pesticides in lower doses. During the 12 years of monitoring with a minimum of two years in between, a few of the pesticides included in PLAP were applied up to four times on some of the fields (e.g. glyphosate on Estrup). These pesticides and/or their degradation products are often not detectable after two years of monitoring and can therefore be applied to a different crop, if found to be appropriate. In contrast, if pesticides and/or their degradation products are found to leach in high concentrations two years after application, monitoring is often continued (up to nine years after application).

Water sampling and data processing

The concentration of the selected pesticides and/or their degradation product(s) is obtained via analysis of water samples collected from 1 m b.g.s (collected via suction cups and drains) and groundwater monitoring screens (installed 1.5 - 4.5 m b.g.s.). Soil water samples are collected monthly using 16 Teflon suction cups, each connected via a single length of PTFE tubing to a sampling bottle placed in a refrigerator in the instrument shed. The soil water is extracted by applying a continuous vacuum (approx. 80 kPa) to each of the suction cups one week before sampling. The 16 suction cups are clustered in four groups. Each group of four suction cups covers a horizontal distance of 2 m. Chemical analysis is performed on a single, pooled water sample from each of the four groups. Drainage water samples were collected using time-proportional (up to July 2004) and flow-proportional sampling (July 2004 onwards) in the loamy fields as described by Plauborg *et al*. (2003). Time-proportional sampling refers to sampling at regular intervals throughout the whole drainage season. During the period of continuous drainage, a 70-mL subsample is collected every hour regardless of the flow rate. Twenty-four samples are collected per bottle, giving 1680 mL/d. Chemical analysis is then performed on a weekly basis on a pooled sample, derived from the seven bottles. Flow-proportional sampling refers to sampling drainwater induced by sudden precipitation events. Here the flow-proportional sampler collects a 200 ml subsample for every 3000 L of drainage flow during the winter season (September-May) and for every 1500 L of drainage flow during the summer season (June-August). Every week, all the subsamples collected are pooled and a sample of these analyzed at the laboratory. Samples are refrigerated (at around 5ºC) and stored in darkness at all times. As the samples are pooled, they do not represent peak concentrations that may occur during the week. The weighted average concentration of pesticides in the tile-drainage water is subsequently calculated according to the equation described in Kjaer *et al*. (2005b). Groundwater samples are collected monthly from selected vertical and horizontal well screens. The results of the analysis of water samples collected from the groundwater screens for each pesticide and/or degradation product are presented as the number of detections, since it is not yet possible to estimate the flux at the sampling point.

Analysis and quality assurance

All pesticide analyses are carried out at commercial laboratories selected on the basis of a competitive tender. In order to ensure the quality of the analyses, the call for tenders included a requirement that the laboratory's quality assurance (QA) system comprised both an internal and an external control procedure. In addition to specific quality control under PLAP, the laboratories are accredited by the Danish Accreditation and Metrology Fund (DANAK), based on the international standard DS/EN ISO/IEC 17025. Two types of sample are used in the quality control - samples with known pesticide composition and concentration are used for internal monitoring of the laboratory method, while externally spiked samples collected every four months are used to incorporate additional procedures, such as sample handling, transport and storage. Blank samples consisting of HPLC water are included in the external QA procedure every month to address possible blank positives and contamination risk (such as input from the atmosphere). All samples included in the control and blank sample are labeled with coded reference numbers and shipped together with conventional samples so that the analyzing laboratory is unaware of the samples used for quality control and the origin of the sample.

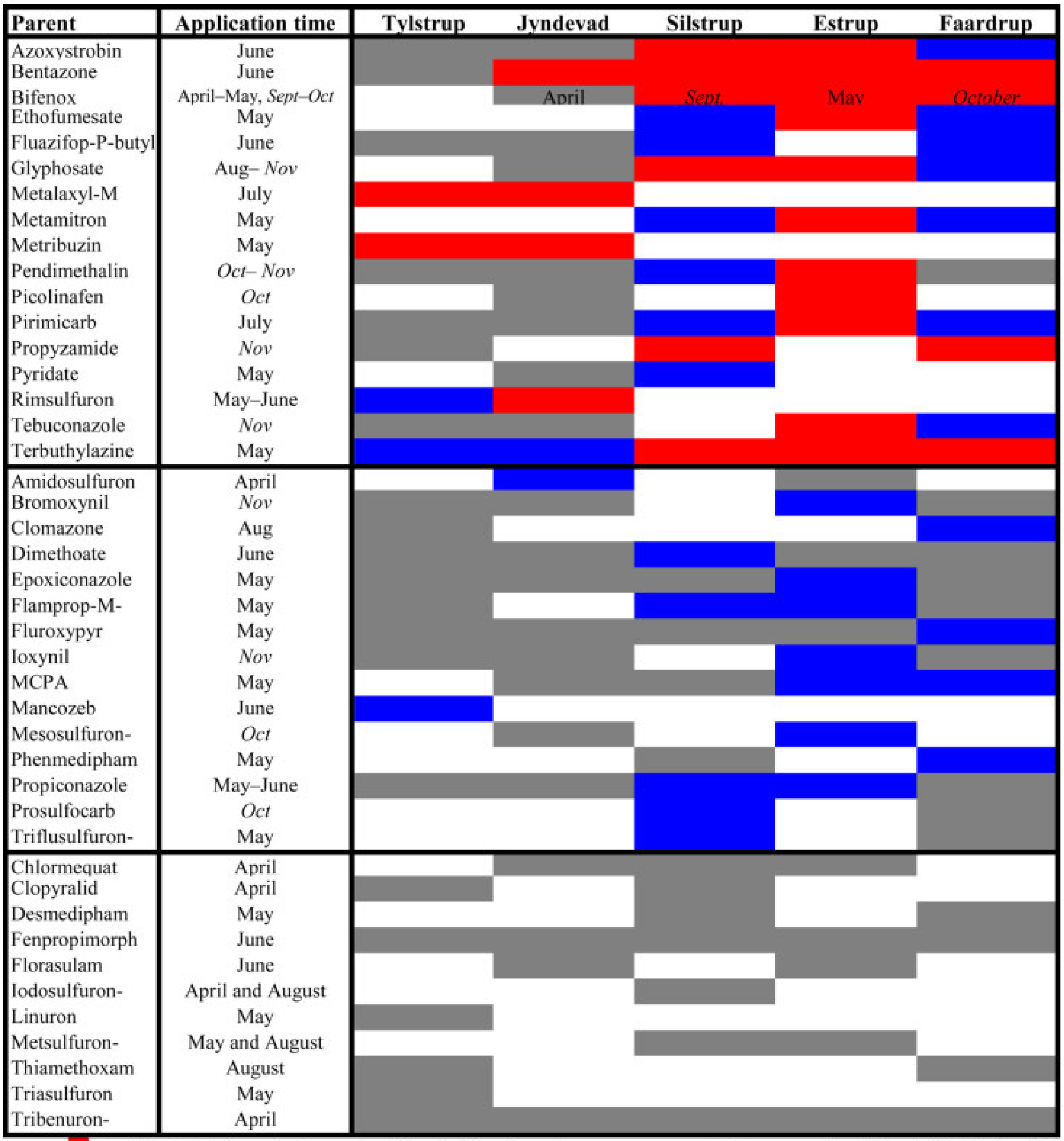
Results and discussion

PLAP's monitoring results for the period from May 1999 - June 2011 reveal differences in pesticide detection between the sandy and loamy fields. To describe the compounds' environmental fate properties with respect to soil degradation and sorption, the data were categorized following Hertfordshire (2013).

Pesticide detections in sandy and loamy fields

In general, the applied pesticides resulted in less frequent detections at both 1 m b.g.s. (Table 8.5-66 and Table 8.5-67) and in the groundwater (Table 8.5-68 and Table 8.5-69) in the sandy fields than in the loamy fields. This also applies in cases where the concentration exceeds 0.1 µg/L. In the sandy fields, it is primarily degradation products that are detected in high frequency, even though only a few compounds are involved. In the loamy fields, in contrast, pesticides are also detected in high frequency (Table 8.5-67 and Table 8.5-69). The degradation products diketo-metribuzin (metribuzin) and CGA108906 (metalaxyl-M) are detected in more than 60% of the samples analyzed in both the variably saturated zone and the saturated zone in the sandy fields (Figure 8.5-44). The detection frequency is much lower in the saturated zone in the loamy fields. Here the highest detection frequency recorded is 42% for the degradation product desethylterbuthylazine, which is frequently detected in water samples from drains approximately 1 m b.g.s. (Figure 8.5-45). Overall, the PLAP results therefore indicate that the highest risk of leaching is posed by degradation products in the sandy fields, and by a mixture of pesticides and/or their degradation products in the loamy fields.

Table 8.5-66: **Leaching 1 m b.g.s. of pesticides and/or their degradation products in the five PLAP fields after application of the pesticide (analysis of water collected via suction cups and, if present, drainage)**



Parent	Application time	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin	June	▨	▨	🟥	🟥	🟦
Bentazone	June	▨	🟥	🟥	🟥	🟥
Bifenox	April–May, *Sept–Oct*		▨ April	🟥 *Sept.*	🟥 May	🟥 *October*
Ethofumesate	May			🟦	🟥	🟦
Fluazifop-P-butyl	June	▨	▨	🟦		🟦
Glyphosate	Aug– *Nov*		▨	🟥	🟥	🟦
Metalaxyl-M	July	🟥	🟥			
Metamitron	May			🟦	🟥	🟦
Metribuzin	May	🟥	🟥			
Pendimethalin	*Oct– Nov*	▨	▨	🟦	🟥	▨
Picolinafen	*Oct*		▨		🟥	
Pirimicarb	July	▨	▨	🟦	🟥	🟦
Propyzamide	*Nov*	▨		🟥		🟥
Pyridate	May		▨	🟦		
Rimsulfuron	May–June	🟦	🟥			
Tebuconazole	*Nov*	▨	▨		🟥	🟦
Terbuthylazine	May	🟦	🟦	🟥	🟥	🟥
Amidosulfuron	April		🟦		▨	
Bromoxynil	*Nov*	▨	▨		🟦	▨
Clomazone	Aug	▨				🟦
Dimethoate	June	▨	▨	🟦	▨	▨
Epoxiconazole	May	▨	▨	▨	🟦	▨
Flamprop-M-	May	▨		🟦	🟦	▨
Fluroxypyr	May	▨	▨	▨	▨	🟦
Ioxynil	*Nov*	▨	▨		🟦	▨
MCPA	May		▨	▨	🟦	🟦
Mancozeb	June	🟦				
Mesosulfuron-	*Oct*		▨		🟦	
Phenmedipham	May			▨		🟦
Propiconazole	May–June	▨	▨	🟦	🟦	▨
Prosulfocarb	*Oct*			🟦		▨
Triflusulfuron-	May			🟦		▨
Chlormequat	April		▨	▨	▨	
Clopyralid	April	▨		▨		
Desmedipham	May			▨		▨
Fenpropimorph	June	▨	▨	▨	▨	▨
Florasulam	June		▨		▨	
Iodosulfuron-	April and August			▨		
Linuron	May	▨				
Metsulfuron-	May and August			▨	▨	
Thiamethoxam	August	▨				▨
Triasulfuron	May	▨				
Tribenuron-	April	▨	▨	▨	▨	▨

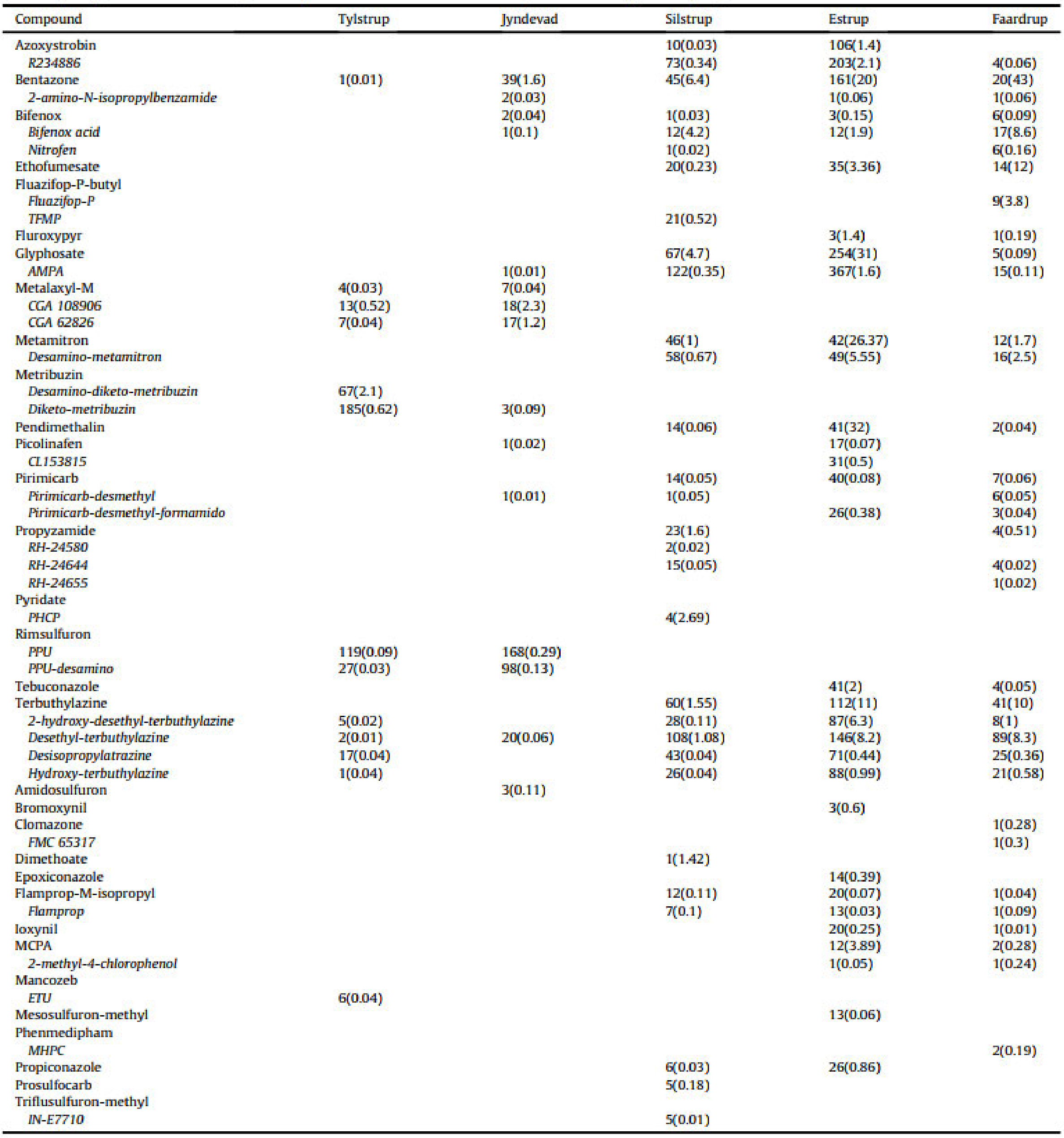
🟥 Pesticide (or its degradation products) leached 1 m b.g.s. in average concentrations exceeding 0.1 µg L^{-1} (MAC) within the first season after application.

🟦 Pesticide (or its degradation products) detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding MAC; average concentration (1 m b.g.s.) below MAC within the first season after application.

▨ Pesticide either not detected or only detected in a very few samples in concentrations below 0.1 µg L^{-1}.

White cells indicate that the pesticide has not been included in PLAP for this field. For at least one field application, leaching to 1 m b.g.s. and/or groundwater is high for 17 pesticides (average concentration above 0.1 µg/L), medium for 15 pesticides and low for 11 pesticides. The month in which the pesticide is applied is shown. Autumn applications are indicated by italic text. Pesticides applied in spring 2011 are not included in the table.

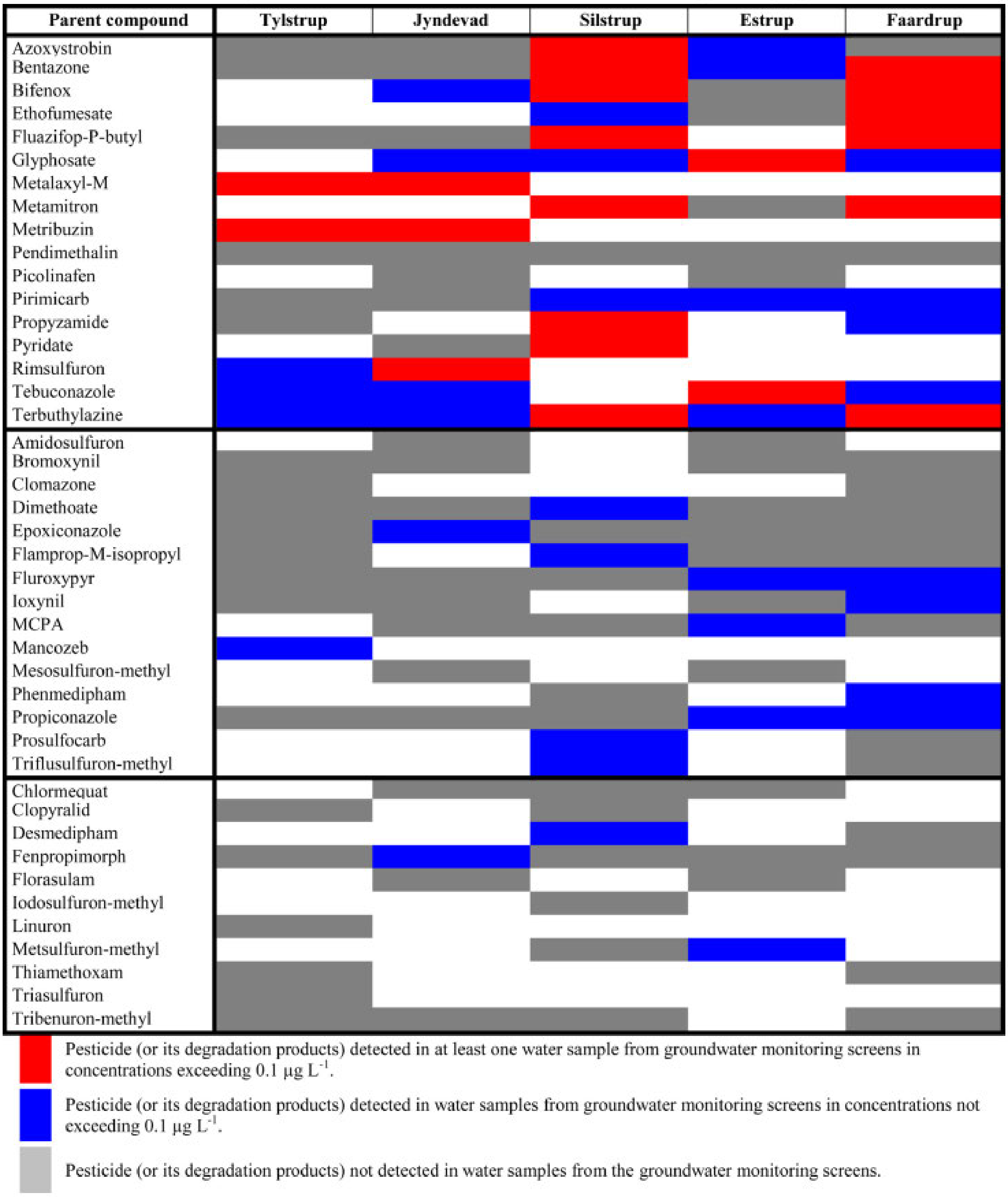
Table 8.5-67: Number of samples from 1 m b.g.s. in which the various pesticides and/or their degradation products were detected in each field with maximum concentration (µg/L) in parentheses



Compound	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin			10(0.03)	106(1.4)	
R234886			73(0.34)	203(2.1)	4(0.06)
Bentazone	1(0.01)	39(1.6)	45(6.4)	161(20)	20(43)
2-amino-N-isopropylbenzamide		2(0.03)		1(0.06)	1(0.06)
Bifenox		2(0.04)	1(0.03)	3(0.15)	6(0.09)
Bifenox acid		1(0.1)	12(4.2)	12(1.9)	17(8.6)
Nitrofen			1(0.02)		6(0.16)
Ethofumesate			20(0.23)	35(3.36)	14(12)
Fluazifop-P-butyl					
Fluazifop-P					9(3.8)
TFMP			21(0.52)		
Fluroxypyr				3(1.4)	1(0.19)
Glyphosate			67(4.7)	254(31)	5(0.09)
AMPA		1(0.01)	122(0.35)	367(1.6)	15(0.11)
Metalaxyl-M	4(0.03)	7(0.04)			
CGA 108906	13(0.52)	18(2.3)			
CGA 62826	7(0.04)	17(1.2)			
Metamitron			46(1)	42(26.37)	12(1.7)
Desamino-metamitron			58(0.67)	49(5.55)	16(2.5)
Metribuzin					
Desamino-diketo-metribuzin	67(2.1)				
Diketo-metribuzin	185(0.62)	3(0.09)			
Pendimethalin			14(0.06)	41(32)	2(0.04)
Picolinafen		1(0.02)		17(0.07)	
CL153815				31(0.5)	
Pirimicarb			14(0.05)	40(0.08)	7(0.06)
Pirimicarb-desmethyl		1(0.01)	1(0.05)		6(0.05)
Pirimicarb-desmethyl-formamido				26(0.38)	3(0.04)
Propyzamide			23(1.6)		4(0.51)
RH-24580			2(0.02)		
RH-24644			15(0.05)		4(0.02)
RH-24655					1(0.02)
Pyridate					
PHCP			4(2.69)		
Rimsulfuron					
PPU	119(0.09)	168(0.29)			
PPU-desamino	27(0.03)	98(0.13)			
Tebuconazole				41(2)	4(0.05)
Terbuthylazine			60(1.55)	112(11)	41(10)
2-hydroxy-desethyl-terbuthylazine	5(0.02)		28(0.11)	87(6.3)	8(1)
Desethyl-terbuthylazine	2(0.01)	20(0.06)	108(1.08)	146(8.2)	89(8.3)
Desisopropylatrazine	17(0.04)		43(0.04)	71(0.44)	25(0.36)
Hydroxy-terbuthylazine	1(0.04)		26(0.04)	88(0.99)	21(0.58)
Amidosulfuron		3(0.11)			
Bromoxynil				3(0.6)	
Clomazone					1(0.28)
FMC 65317					1(0.3)
Dimethoate			1(1.42)		
Epoxiconazole				14(0.39)	
Flamprop-M-isopropyl			12(0.11)	20(0.07)	1(0.04)
Flamprop			7(0.1)	13(0.03)	1(0.09)
Ioxynil				20(0.25)	1(0.01)
MCPA				12(3.89)	2(0.28)
2-methyl-4-chlorophenol				1(0.05)	1(0.24)
Mancozeb					
ETU	6(0.04)				
Mesosulfuron-methyl				13(0.06)	
Phenmedipham					
MHPC					2(0.19)
Propiconazole			6(0.03)	26(0.86)	
Prosulfocarb			5(0.18)		
Triflusulfuron-methyl					
IN-E7710			5(0.01)		

The table encompasses pesticides/degradation products detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/L. Pesticides and degradation products are mentioned when analyzed. Pesticides applied in spring 2011 are not included**.**

Table 8.5-68: **Pesticides and/or their degradation products detected in water samples from the groundwater monitoring screens in the five PLAP fields after pesticide application**



Parent compound	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin	▒	▒	🟥	🟦	▒
Bentazone	▒	▒	🟥	🟦	🟥
Bifenox		🟦	🟥	▒	🟥
Ethofumesate			🟦	▒	🟥
Fluazifop-P-butyl	▒	▒	🟥		🟥
Glyphosate		🟦	🟦	🟥	🟦
Metalaxyl-M	🟥	🟥			
Metamitron			🟥	▒	🟥
Metribuzin	🟥	🟥			
Pendimethalin	▒	▒	▒	▒	▒
Picolinafen		▒		▒	
Pirimicarb	▒	▒	🟦	🟦	🟦
Propyzamide	▒		🟥		🟦
Pyridate		▒	🟥		
Rimsulfuron	🟦	🟥			
Tebuconazole	🟦	🟦		🟥	🟦
Terbuthylazine	🟦	🟦	🟥	🟦	🟥
Amidosulfuron		▒		▒	
Bromoxynil	▒	▒		▒	▒
Clomazone	▒				▒
Dimethoate	▒	▒	🟦	▒	▒
Epoxiconazole	▒	🟦	▒	▒	▒
Flamprop-M-isopropyl	▒		🟦	▒	▒
Fluroxypyr	▒	▒	▒	🟦	🟦
Ioxynil	▒	▒		▒	🟦
MCPA		▒	▒	🟦	▒
Mancozeb	🟦				
Mesosulfuron-methyl		▒		▒	
Phenmedipham			▒		🟦
Propiconazole	▒	▒	▒	🟦	🟦
Prosulfocarb			🟦		▒
Triflusulfuron-methyl			🟦		▒
Chlormequat		▒	▒	▒	
Clopyralid	▒		▒		
Desmedipham			🟦		▒
Fenpropimorph	▒	🟦	▒	▒	▒
Florasulam		▒		▒	
Iodosulfuron-methyl			▒		
Linuron	▒				
Metsulfuron-methyl			▒	🟦	
Thiamethoxam	▒				▒
Triasulfuron	▒				
Tribenuron-methyl	▒	▒	▒		▒

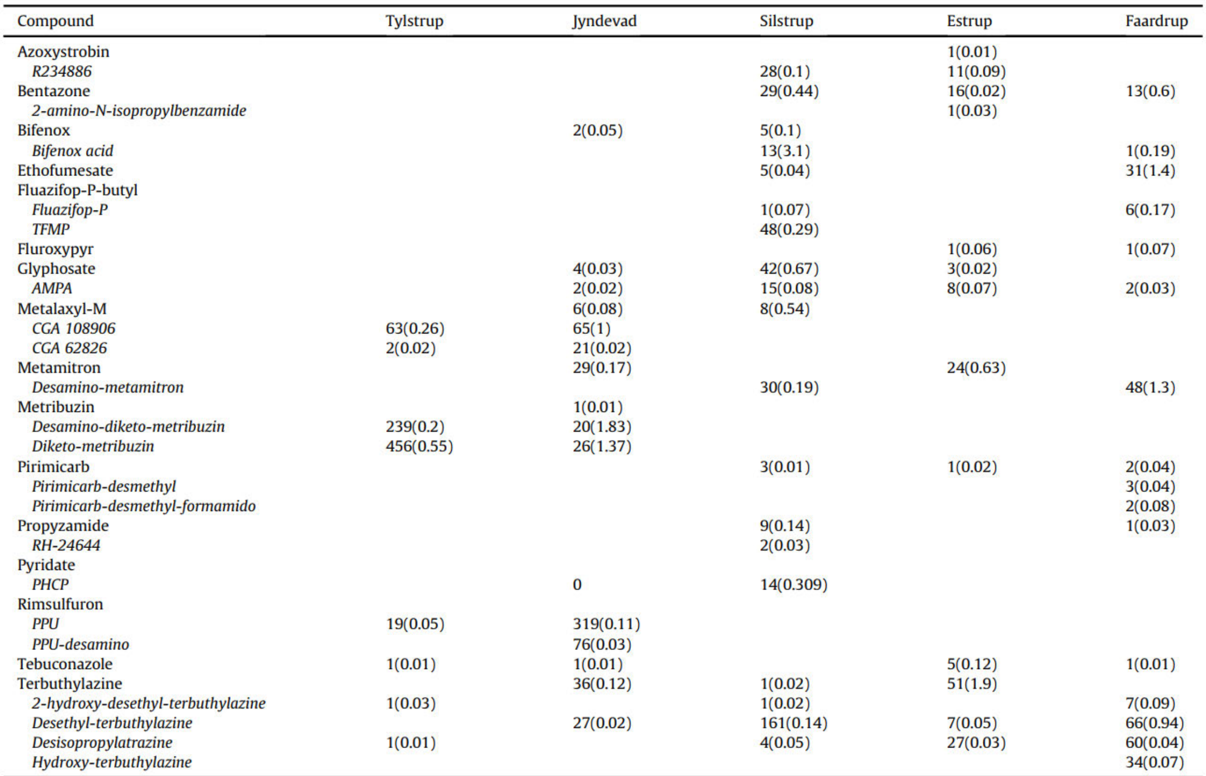
🟥 Pesticide (or its degradation products) detected in at least one water sample from groundwater monitoring screens in concentrations exceeding 0.1 µg L^{-1}.

🟦 Pesticide (or its degradation products) detected in water samples from groundwater monitoring screens in concentrations not exceeding 0.1 µg L^{-1}.

▒ Pesticide (or its degradation products) not detected in water samples from the groundwater monitoring screens.

White cells indicate that the pesticide has not been included in PLAP for this field. Pesticides applied in spring 2011 are not included in this table.

Table 8.5-69: The number of samples from the groundwater monitoring screens in which the various pesticides and/or their degradation products were detected at each field



Compound	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin				1(0.01)	
R234886			28(0.1)	11(0.09)	
Bentazone			29(0.44)	16(0.02)	13(0.6)
2-amino-N-isopropylbenzamide				1(0.03)	
Bifenox		2(0.05)	5(0.1)		
Bifenox acid			13(3.1)		1(0.19)
Ethofumesate			5(0.04)		31(1.4)
Fluazifop-P-butyl					
Fluazifop-P			1(0.07)		6(0.17)
TFMP			48(0.29)		
Fluroxypyr				1(0.06)	1(0.07)
Glyphosate		4(0.03)	42(0.67)	3(0.02)	
AMPA		2(0.02)	15(0.08)	8(0.07)	2(0.03)
Metalaxyl-M		6(0.08)	8(0.54)		
CGA 108906	63(0.26)	65(1)			
CGA 62826	2(0.02)	21(0.02)			
Metamitron		29(0.17)		24(0.63)	
Desamino-metamitron			30(0.19)		48(1.3)
Metribuzin		1(0.01)			
Desamino-diketo-metribuzin	239(0.2)	20(1.83)			
Diketo-metribuzin	456(0.55)	26(1.37)			
Pirimicarb			3(0.01)	1(0.02)	2(0.04)
Pirimicarb-desmethyl					3(0.04)
Pirimicarb-desmethyl-formamido					2(0.08)
Propyzamide			9(0.14)		1(0.03)
RH-24644			2(0.03)		
Pyridate					
PHCP		0	14(0.309)		
Rimsulfuron					
PPU	19(0.05)	319(0.11)			
PPU-desamino		76(0.03)			
Tebuconazole	1(0.01)	1(0.01)		5(0.12)	1(0.01)
Terbuthylazine		36(0.12)	1(0.02)	51(1.9)	
2-hydroxy-desethyl-terbuthylazine	1(0.03)		1(0.02)		7(0.09)
Desethyl-terbuthylazine		27(0.02)	161(0.14)	7(0.05)	66(0.94)
Desisopropylatrazine	1(0.01)		4(0.05)	27(0.03)	60(0.04)
Hydroxy-terbuthylazine					34(0.07)

The maximum concentration (µg/L) is shown in parentheses. Only pesticides and or their degradation products where at least one of the compounds is detected in more than three samples from one field are included. Pesticides applied in spring 2011 are not included.

Types of leaching scenario

More detailed studies of leaching scenarios in the sandy fields reveal long-term leaching of degradation products in concentrations continuously exceeding 0.1 µg/L (Table 8.5-66 and Table 8.5-68) up to six years after application of the pesticides metribuzin in May and rimsulfuron in June to potato crops Recent PLAP results show that the slightly mobile and moderately persistent fungicide metalaxyl-M, applied in July on potatoes, exhibits the same long term leaching of its degradation products (CGA62826 and CGA108906). However, this parent compound was also detected in water samples from 1 m b.g.s in groundwater in both the sandy fields. The concentration exceeded 0.1 µg/L in 5 % of the ground water samples collected from the Jyndevad field (Figure 8.5-44).

In the loamy fields, dominant preferential flow results in leaching scenarios that differ from those seen in the sandy fields. Leaching occurred following both the early summer and autumn application of pesticides. Early summer application resulted in considerable leaching of pesticides and/or their degradation products, grouped below according to their fate properties (See paper for discussion of detection of terbuthylazine, fluazifop-P-butyl, azoxystrobin, and bentzon and/or their metabolites).

Autumn application of pesticides resulted in leaching of several strongly-sorbing pesticides. Glyphosate (sorbs to the mineral soil fraction, hydrophilic, non-persistent, application period 11 August- 9 November) and pendimethalin (sorbs to the organic soil fraction, moderately persistent, applied in May as well as October - November) were found to leach to a 1 m depth and below in the loamy fields, primarily in dissolved form. Neither of the two compounds leached in the sandy fields. In contrast, bifenox, a strongly sorbing, non-persistent herbicide (sorbs to organic sorption sites, application date: 27 April at Jyndevad, 1 May at Estrup, 9 September at Silstrup and 25 October at Faardrup), was detected 1 m b.g.s. in all three loamy fields as well as in the sandy Jyndevad field (Table 8.5-67). Furthermore, it was detected in groundwater in both the Jyndevad and Silstrup fields (Figure 8.5-44, Figure 8.5-45, Table 8.5-69). Degradation products of bifenox were detected at some sites as well.

Figure 8.5-44: **Frequency of detection in water samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) in the sandy soil fields: Tylstrup (A, B) and Jyndevad (C, D).**

Frequency is estimated for the entire monitoring period during which the different pesticides and/or degradation products have been included in PLAP. When pesticides are applied several times or result in long-term leaching, the entire monitoring period can consist of multiple monitoring periods of at least two years or long-term monitoring of up to nine years. The number of analyzed samples therefore varies considerably among the different pesticides and/or degradation products. Compounds monitored for less than one year are not included. The crop on which the pesticide is applied is indicated.

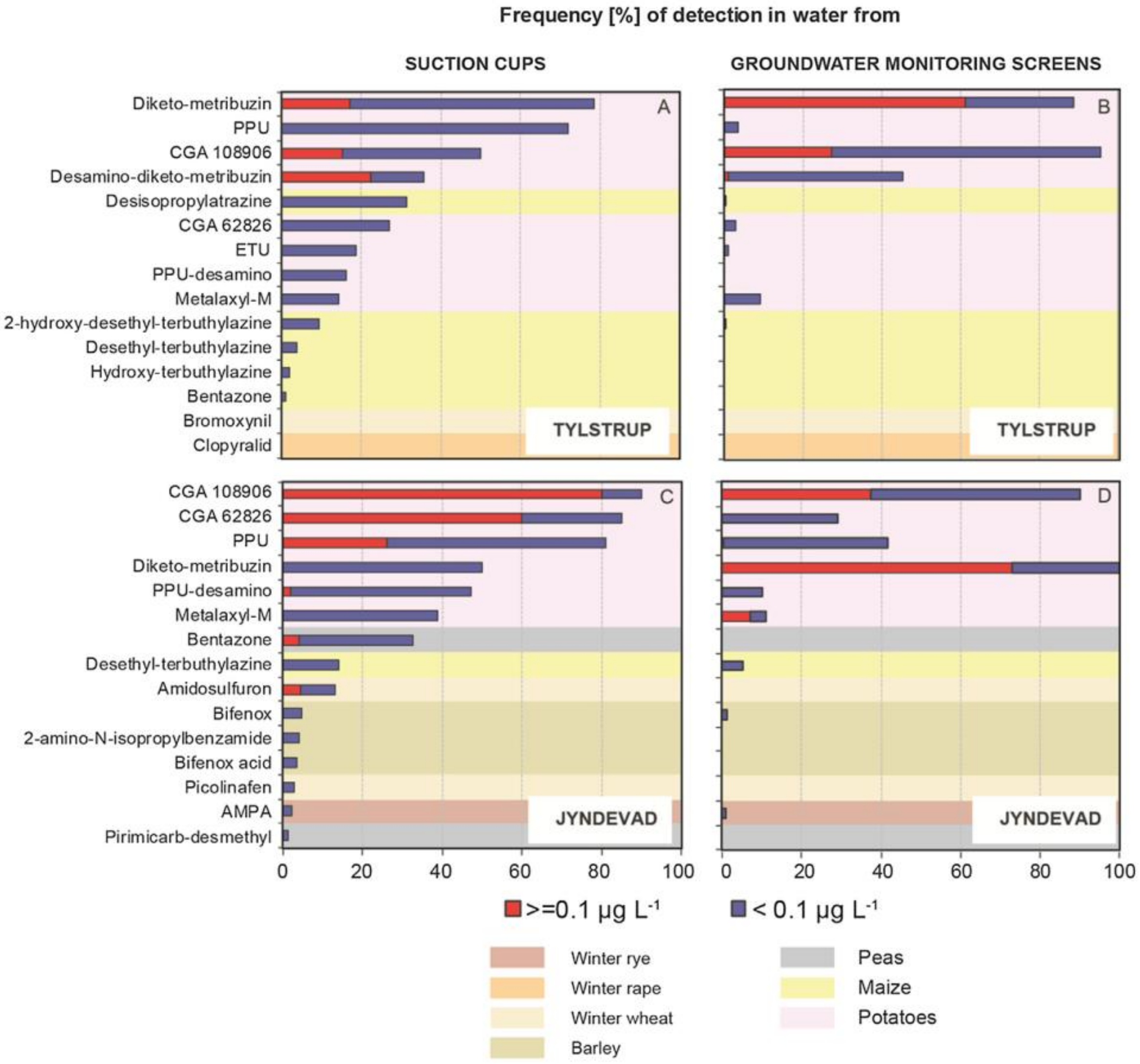
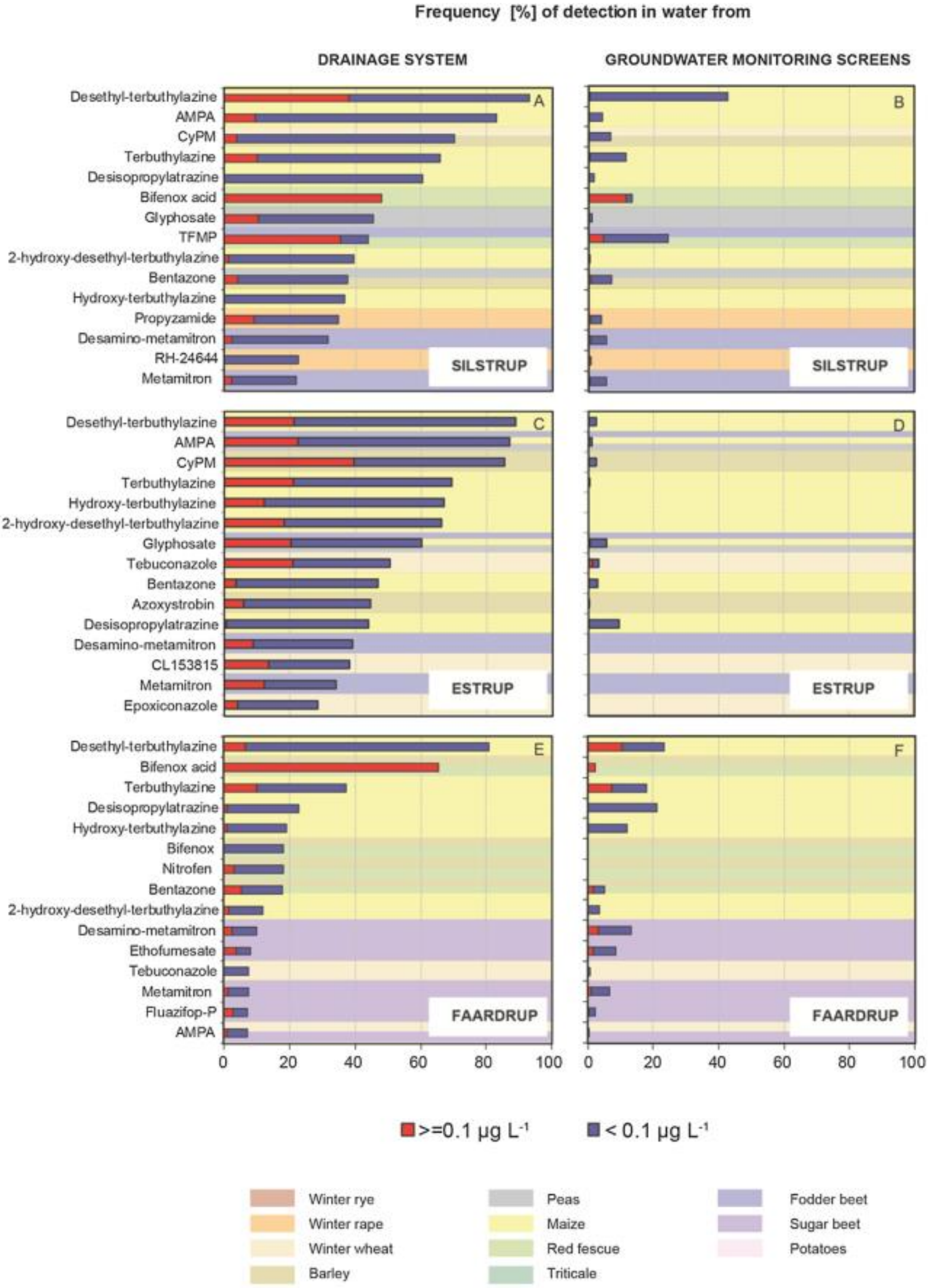


Figure 8.5-45: Frequency of detection in water samples from the drainage system (left) and groundwater monitoring screens (both vertical and horizontal) located deeper than the drainage system (right) in the loamy soil fields: Silstrup (A, B), Estrup (C, D), and Faardrup (E, F).

Frequency is estimated for the entire monitoring period that the different pesticides and/or degradation products have been included in the PLAP program. When pesticides are applied several times or result in long-term leaching, the entire monitoring period can consist of multiple monitoring periods of at least two years or long-term monitoring of up to nine years. The number of analyzed samples therefore varies considerably among the different pesticides and/or degradation products. The figure includes only the 15 most frequently detected pesticides and degradation products. Compounds monitored for less than one year are not included. The crop on which the pesticide is applied is indicated.



Impact of fate processes and hydrogeological setting on leaching
In the sandy fields, the long-term leaching of degradation products following pesticide application in the early summer or summer months seems to be the primary leaching scenario of concern. The high frequency of leaching in the loamy fields demonstrates the dominance of effective transport processes in these soils. It is well documented that the effective porosity in loamy soil corresponding to connected discontinuities, such as wormholes and fractures, is low compared to that of sandy soil, with the result that climatic conditions have a greater impact on the pore system. The consequences are: (i) immediate response to a precipitation or snowmelt event causing rapid flow and transport through discontinuities, which may sometimes be directly connected to drains; and (ii) seasonal fluctuations of up to 4 m in the groundwater table with resultant drainage, primarily in periods when the groundwater table is located above the drains (above 1.1 - 1.2 m b.g.s.). This very dynamic hydrogeological setting enables a larger variety of pesticides and their degradation products to reach groundwater in intense pulses, before being diluted or retarded to varying degrees. Glyphosate is an example of a pesticide suddenly appearing in intense pulses of high concentrations more than two years after application and following several pronounced rain events (more than 50 mm/day) during the late summer. Such leaching scenarios can only be a result of very slow degradation and strong adsorption in the topsoil, which is supported by, who found half-life DT_{50}-values greater than 100 days for soils with strong adsorption and as short as 10 days for soils with weak adsorption. The PLAP results demonstrate that pesticide leaching occurs after both early summer and autumn application. Analysis of the data in Table 8.5-66 for the three loamy fields reveals notable leaching of 23% of the pesticides applied in early summer, and 60% of the pesticides applied in the autumn. Pesticides applied in summer (April - August) accounted for 7 of the 13 pesticides having a high degree of leaching, 11 of the 15 pesticides having a medium degree of leaching, and all nine of the pesticides having in a low degree of leaching. Based on fate studies, the first seven pesticides can be grouped as follows:

- slightly mobile hydrophobic + persistent (azoxystrobin) or non-persistent (fluazifop-P-butyl). Even though the persistent pesticide azoxystrobin was detected in water from the drainage system, it was primarily the long-term leaching of R234886 (degradation product of azoxystrobin) in the Silstrup and Estrup fields and TFMP (degradation product of fluazifop-P-butyl) in the Silstrup field that was of concern.

- moderately mobile + persistent and hydrophobic (ethofumesate and terbuthylazine) or non-persistent (metamitron (log P = 0.85) and pirimicarb (log P = 1.7)). Notable leaching of these pesticides was unexpected due to their fate properties. All four of the pesticides were detected in water from the saturated zone, especially at the Silstrup and Faardrup fields (Table 8.5-68 and Table 8.5-69), and leached to 1 m b.g.s. in average concentrations exceeding 0.1 µg/L within the first season following application, primarily at the Estrup field (Table 8.5-66 and Table 8.5-67).

- mobile hydrophilic + non-persistent (bentazone). The fact that bentazone is found to be non-persistent (DT_{50} <30 days) in the plow layer apparently does not play a role in its retardation in the topsoil. Bentazone was detected in water from the saturated zone in the three loamy fields, especially the Silstrup field (Table 8.5-68 and Table 8.5-69), and leached to 1 m b.g.s. in average concentrations exceeding 0.1 µg/L within the first season after application, primarily in the Estrup field (Table 8.5-66 and Table 8.5-67).

In Denmark, most pesticides authorized for autumn application are strongly adsorbing due to the increased leaching risk caused by periods of intense precipitation. Hence, the pesticides applied in the autumn and causing unpredicted leaching scenarios were in fate studies found to be:

- non-mobile hydrophobic + non-persistent (bifenox) or moderately persistent (pendimethalin and picolinafen) and

- slightly mobile + non-persistent (glyphosate) or moderately persistent and hydrophobic (propyzamide and tebuconazole).

Pesticides that strongly sorb to minerals and organic sorption sites were nevertheless detected in water samples, primarily from the drains and occasionally from the saturated zone. The more frequent detection in water from drains is attributable to the groundwater table often being above drain depth during the autumn and winter periods. Applying pesticides under these conditions allows their drain-facilitated direct transfer from the uppermost groundwater to the surface water. The difference in the hydrogeological setting in early summer and autumn is evident in relation to the risk of leaching. During early summer, the drier soil profile leaves the plow layer and dead-end discontinuities more open to entry by the applied pesticides and retardation compared to autumn when the pore space will be close to full saturation, allowing rapid preferential transport through the well-connected discontinuities. The leaching scenarios in the three loamy fields indicate hydrogeological settings dominated by rapid, preferential transport and low retardation capacity of the plow layer.

Crop related effects on leaching
Of the eleven crops included in PLAP, leaching seems to be greatest with potatoes, maize and beet crops (Figure 8.5-45). One common attribute of these crops is that they are all cultivated in systems with wide row spacing (maize 0.5 - 0.75 m; beet 0.5 - 0.63 m; potato 0.75 m).

Pesticide detection in the different types of installation
A comparison of the monthly sum of samples containing pesticide/degradation products in concentrations either below, equal to or exceeding MAC in water from installations approximately 1 m b.g.s. (cups or drains) and in the saturated zone (vertical or horizontal wells) reveals that (Figure 8.5-46):

- The percentage of water samples containing pesticide/degradation products is higher in water from the suction cups than from the vertical wells in the sandy fields, which can be explained by the dilution or retardation of solute mass on its way through the soil profile.

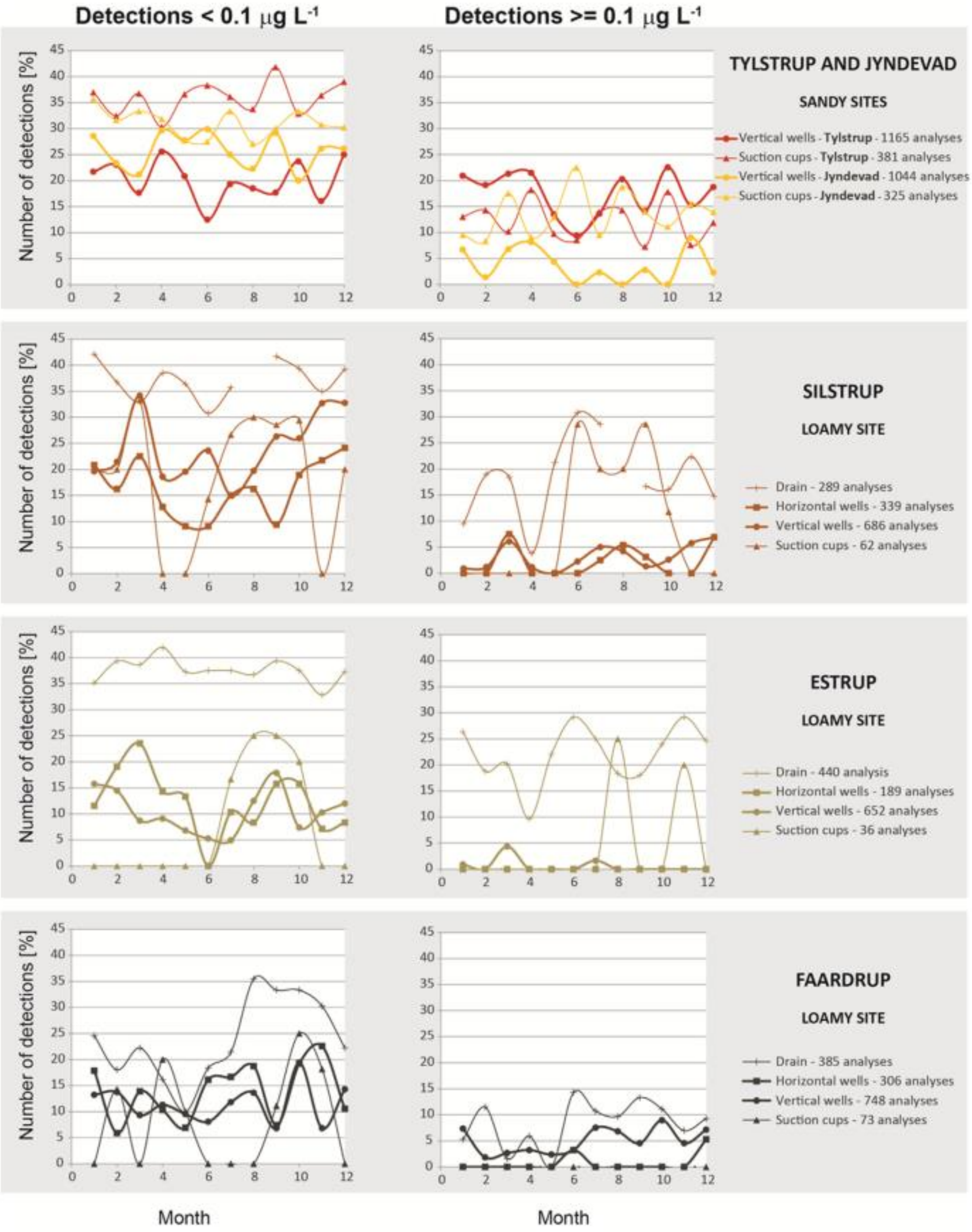
- The percentage of pesticide-containing samples from the vertical and horizontal wells each month during the 12-year period at each of the loamy fields is more or less identical for both <MAC and ≥MAC. A small difference between detections ≥MAC in vertical and horizontal detections is, however, to be found in Faardrup.

- The percentage of pesticide-containing water samples from the drainage system was fairly similar at the Silstrup and Estrup fields, but much lower at the Faardrup field for concentrations both <MAC and ≥MAC.

- The percentage of water samples with detections from the variably saturated zone (drainage system and suction cups) and saturated zone (vertical and horizontal wells) respectively was very similar at Faardrup, but less similar at Silstrup and Estrup.

- There does not seem to be any relationship between the percentage of samples that contain pesticides and the month of the year, i.e. the percentage is not significantly higher in any particular month or months.

Figure 8.5-46: **Percentage of samples containing pesticides for each month of the year subdivided into samples with concentrations either below (left) or equal/exceeding 0.1 mg/L (right) shown for each field (sandy fields: Tylstrup and Jyndevad; loamy fields: Silstrup, Estrup, and Faardrup) and installation type (suction cups, drain, vertical and horizontal wells). The total number of analyses is shown for each installation type and field.**



Conclusions

The PLAP monitoring results show that fewer pesticides and/or their degradation products are detected in water samples collected both 1 m b.g.s. (Table 8.5-66 and Table 8.5-67) and from groundwater (Table 8.5-68 and Table 8.5-69) in the sandy fields than in the loamy fields. A number of groundwater leaching scenarios do not seem to be adequately described by the European Union pesticide authorization procedure, including long-term leaching of degradation products of pesticides applied to potato crops on sandy fields and leaching of a variety of pesticides and degradation products following pesticide application to loamy fields. Leaching exceeding MAC in yearly averages at 1 m depth and/or in detections in the groundwater was seen with 32% of the pesticides applied to the loamy fields in early summer and with 60% of those applied in the autumn. Based on the insight into the fields' hydrogeological setting, the compound properties and crop development, these findings indicate that rapid preferential transport through well-connected discontinuities such as wormholes and fractures enable the pesticides to bypass the otherwise retarding plow layer. This seems to be triggered by the soil profile being close to saturation following autumn application and by possible sealing of the soil surface following the early summer application of pesticides. The physics behind this rapid preferential transport is not fully understood and hence not fully accounted for in the EU pesticide authorization procedure. Furthermore, agricultural practice seems to enhance leaching in the case of pesticides applied to crops with widely-spaced rows, such as potatoes, maize, and beet. Comparison of pesticide detection frequency in water from the installations in the variably saturated and saturated zones provides a good indication of the hydraulic contact between the zones and whether the quality of the water in the variably saturated zone can serve as an early warning of the trend in water quality in the saturated zone or surface waters. Pesticide detection frequency does not appear to depend on the month of the year, but monthly variation in detection frequency is higher in the loamy fields than in the sandy fields, primarily due to the dominant effect of spatial and temporal variation in preferential transport in the variably saturated zone of the loamy soils.

Assessment and conclusion by applicant:

The article describes results from the Danish pesticide leaching program. Analytics are not well described, but there is a statement of careful selection and strong quality control of the laboratories.

The article is considered reliable.

Assessment and conclusion by RMS:
These are results from the Danish Pesticide Leaching Programs. Five agricultural fields were selected - two sandy soil fields (at Tylstrup and Jyndevad) and three loamy soil fields (at Silstrup, Estrup and Faardrup).

It is noted that the results in Glyphosate measurements from the Estrup site are also described in the study of Norgaard, T., et al., 2014, CA 7.5/021, in which analytical issues are reported. However, the maximum concentration reported for this site dates from before the analytical issue reported. Also in Norgaard, 2014, on the site of Estrup is it clearly indicated that "our results also highlight complications in relating the flux of pesticides to the groundwater based on measurements made in drain systems […] When the water table is above the drains, there is no guarantee that the drain flow is solely related to infiltration because it also captures groundwater, and the concentration in the drains may be a mixture of groundwater and infiltration. When the water table is below the drains, we may expect bypass flow of the drain system because preferential flow has also been associated with biopores other than in the drain system" The results from this site should therefore be considered carefully to evaluate potential leaching to groundwater.

Glyphosate and AMPA were monitored among 43 active substances and 47 degradation products. Maximum concentration report for GLY in soil pore water at 1 m bgs is 31.0 µg/L for glyphosate and 1.6 µg/L for AMPA.

It should be noted that, as for many other compounds, leaching potential of glyphosate and is metabolite AMPA appeared higher in the Loamy sites than in the sandy sites (not detected in the sandy sites). This is expected to be due to preferential flow in the loamy soils.

The article is considered reliable.

Data point:	CA 7.5/048
Report author	Székács, A., *et al.*
Report year	2015
Report title	Monitoring Pesticide Residues in Surface and Ground Water in Hungary: Surveys in 1990–2015
Document No	Journal of Chemistry, Vol. 2015, 717948, 01.01.2015
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted under GLP/Officially recognised testing facilities (Agro-Environmental Research Institute, National Agricultural Research and Innovation Centre)
Acceptability/Reliability:	Reliable with restrictions

This study was only listed in the surface water compartment literature review by applicant. However it concerns both ground water and surface water monitoring results. However only limited information on glyphosate concentration are reported in the article and it is not summarized here. See summary under B8.5.4.

Assessment and conclusion by applicant:
The article reports monitoring results for pesticide residues in surface and groundwater in Hungary. For Glyphosate a specific analytical method was used as with the methods used for other substances, no

reliable LOD's were achieved. Only limited information on the results for glyphosate were reported. A maximum glyphosate concentration of 1 µg/L was reported.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions. The article is considered reliable with restrictions.

Only limited information on the results for glyphosate were reported. No detailed measured concentration are reported. Only the following can be extracted from the full text article:

The main information available in the paper are the following:
"The concentration of glyphosate was […] determined by ELISA method in 42 surface and ground water samples collected from Bekes county in Hungary. Half of the 42 surface and ground water samples collected in September 2010 were contaminated by glyphosate at concentrations of 540–980 ng/L. Exceedingly high glyphosate levels (nearly 1000 ng/L) were measured in five ground water samples and significant concentrations (540–760 ng/L) were determined in 16 cases (3 surface and 13 ground water samples)."

Data point:	CA 7.5/020
Report author	McManus, S. *et al*.
Report year	2014
Report title	Pesticide occurrence in groundwater and the physical characteristics in association with these detections in Ireland
Document No	Environmental Monit Assess (2014) 186:7819–7836
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities (EPA Ireland)
Acceptability/Reliability:	Reliable with restrictions

This study explores the associations of pesticide occurrence in groundwater to geological characteristics of the monitoring points (MPs) contributing area. Pesticide analyses were undertaken during a 2-year groundwater monitoring campaign, which generated 845 samples. MCPA and mecoprop were the most frequently detected pesticides in groundwater. Each MP (n = 158) had a specifically delineated zone of contribution (ZOC) and the dominant physical characteristics present from nine national datasets were recorded for each ZOC. Associations between detections in groundwater and the dominant physical characteristic in each MPs ZOC tested were then statistically analyzed using Fisher's exact test, logistic regression, and multiple logistic regression. The original physical characteristic datasets used that were associated with detections in groundwater were the type of MP, aquifer type, and Quaternary deposit type. Logistic regression revealed that springs, regionally important aquifer types, aquifers with a karstic flow regime, and alkaline Quaternary deposits in existence above karst aquifers in a MP's ZOC were more likely to have a pesticide detection in groundwater. Multiple regression from this exploratory work showed some mutual dependency between soil association, aquifer type, and the Geological Survey of Ireland groundwater vulnerability map. The combination of national monitoring data and physical attribute datasets can be used to explore key areas where groundwater is more vulnerable to pesticide contamination.

Materials and Methods

Groundwater monitoring network summary and analytical methods

Many of the monitoring points (MPs) in the monitoring network are public or private drinking water supplies with relatively large abstraction rates (7,000 m^3/day) or springs with relatively large discharges (12,000 m^3/day). These MPs were targeted because the water quality from their relatively large ZOC is less likely to be impacted by localized pressures (Craig *et al*. 2005). This study focuses on a period between

2007 and 2008. During this period, 158 MPs were sampled between one and nine times (average 5; median 6). Representative samples were collected using standard methods (ISO 5667).

For solid phase extraction (SPE), groundwater was loaded through a Biotage C18 (Uppsala, Sweden) SPE cartridge conditioned using liquid chromatography (LC)-grade dichloromethane, left to dry, then further conditioned using LC-grade methanol. Compounds were eluted from the cartridge using dichloromethane and blown down under argon gas. Quantification was carried out using an Agilent gas chromatogram mass spectrometer (GC-MS) in electron ionization (EI) mode. The method was validated in accordance with criteria provided in SANCO guidelines (SANCO/825/00 and SANCO/10232/2006). The 13 pesticides analyzed are detailed in Table 8.5-70 along with their current registration status in Ireland.

Zones of contribution

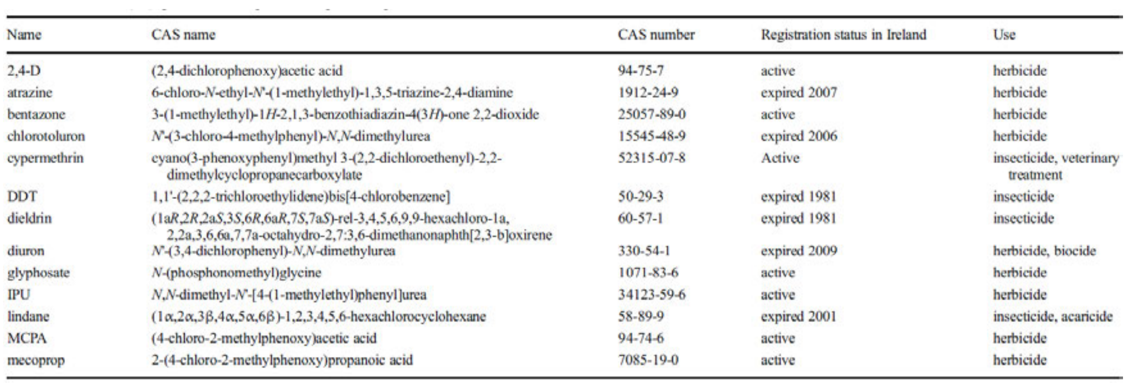
A ZOC is defined as the catchment area that contributes water to an abstraction or a spring (Misstear *et al*. 2006) which supports the abstraction point, monitoring point, or spring discharge (hereafter referred to as MPs) from long-term groundwater recharge. Hydrogeologically mapped ZOCs are preferred over arbitrary radii around a MP, since the latter generally do not adequately characterize the pressures and pathways contributing to any concentrations measured at a MP (Franzetti and Guadagnini 1996; Lim *et al*. 2010), especially in heterogeneous environments. The ZOC polygons were manually aligned to honor hydrogeological controls on the orientation, with scaling to match abstraction with recharge. As such, the ZOCs represent a relatively robust, but rapidly derived, spatial estimate of the region contributing groundwater flow to a MP (Kelly 2010).

Dataset assembly for statistical analysis with corresponding ZOCs

The dataset was categorized into three levels based on the detected pesticide concentration found at each MP. This approach was required because of the extremely high level of censoring in the dataset due to analytical limits of detection. In our study, non-detects did not have values substituted by another numerical value as it may lead to abnormalities in the statistical conclusions, and because of this, standard methods for continuous data could not be applied. For every compound, the limit of detection was 0.01 µg/L and this was unadjusted for all data analysis.

The concentration category levels that MPs were grouped into were as follows: 1. MPs which never had a detection greater than or equal to the analytical detection limit of 0.01 µg/L during the 2-year monitoring period. 2. MPs with at least one detection greater than the analytical limit of detection but less than the DWS 3. MPs with at least one detection greater than or equal to the DWS. The concentration level detected at each MP explained above and the most widespread category for each physical characteristic in the MP's ZOC (explained below) were then collated to produce a combined dataset. This was used to generate count tables for statistical analysis in SAS (2004).

Table 8.5-70: Pesticides (a.i) quantified during monitoring, their registration status in Ireland 2017 and use



Name	CAS name	CAS number	Registration status in Ireland	Use
2,4-D	(2,4-dichlorophenoxy)acetic acid	94-75-7	active	herbicide
atrazine	6-chloro-*N*-ethyl-*N*'-(1-methylethyl)-1,3,5-triazine-2,4-diamine	1912-24-9	expired 2007	herbicide
bentazone	3-(1-methylethyl)-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide	25057-89-0	active	herbicide
chlorotoluron	*N*'-(3-chloro-4-methylphenyl)-*N*,*N*-dimethylurea	15545-48-9	expired 2006	herbicide
cypermethrin	cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	52315-07-8	Active	insecticide, veterinary treatment
DDT	1,1'-(2,2,2-trichloroethylidene)bis[4-chlorobenzene]	50-29-3	expired 1981	insecticide
dieldrin	(1a*R*,2*R*,2a*S*,3*S*,6*R*,6a*R*,7*S*,7a*S*)-rel-3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphth[2,3-b]oxirene	60-57-1	expired 1981	insecticide
diuron	*N*'-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea	330-54-1	expired 2009	herbicide, biocide
glyphosate	*N*-(phosphonomethyl)glycine	1071-83-6	active	herbicide
IPU	*N*,*N*-dimethyl-*N*'-[4-(1-methylethyl)phenyl]urea	34123-59-6	active	herbicide
lindane	(1α,2α,3β,4α,5α,6β)-1,2,3,4,5,6-hexachlorocyclohexane	58-89-9	expired 2001	insecticide, acaricide
MCPA	(4-chloro-2-methylphenoxy)acetic acid	94-74-6	active	herbicide
mecoprop	2-(4-chloro-2-methylphenoxy)propanoic acid	7085-19-0	active	herbicide

CAS = Chemical Abstracts Service

Physical characteristic national dataset summary

The most prevalent ZOC physical characteristics for each MP were assigned from national datasets in Table 8.5-71. MP type was classified by the Irish EPA as springs, drilled boreholes, and wells. (Wells include sites known to be dug wells and sites where the well construction method is unknown). ZOC size corresponding to each MP was placed into one of the following seven categories: 0-4.9, 5-9.9, 10-19.9, 20-199, 200-399, 400-699, 700-799 km^2.

Land use was taken from the Corine land cover dataset in 2006 (European Environment Agency 2011) and categories within the entire Corine land cover dataset were amalgamated into a fewer number of categories (Table 8.5-71) so (1) there were enough observations for statistical analysis and (2) there were fewer categories to assist logistic regression.

Two national soil datasets are currently available, and both were examined. Nine amalgamated categories were created from each of the two datasets. These are listed in Table 8.5-71. Quaternary deposit (subsoil) type was subdivided using two methods: the first according to the type of Quaternary deposit (genesis) and the second (Quaternary deposit acid/base) based on its reaction with 10% v/v hydrochloric acid to determine the calcium carbonate ($CaCO_3$) content. Subsoil permeability was determined by the GSI using the British Standards Institution BS 5930 system (1981) (Swartz *et al*. 2003). Textural descriptions were made of each subsoil (Quaternary deposit) using plasticity, dilatency, density, compactness, and the presence of discontinuities (Misstear and Daly 2008). Bedrock geology was obtained from the GSI (1999) and contains 27 bedrock units created by grouping over 1,200 bedrock Formations and Members based on their hydrogeological properties and other factors from the original bedrock geology file. Some of the most commonly occurring bedrock geologies are listed. The bedrock geology map was also the foundation for the national aquifer type map which produced 11 aquifer types across Ireland of which two groupings were used for statistical analysis.

Groundwater vulnerability in Ireland is determined primarily according to the thickness and permeability of the Quaternary deposits. Categories listed in Table 8.5-71 are in order of decreasing vulnerability. Subsoil deposits 0-3 m thick are classified as extreme (E) with a subset of the “extreme” category termed the “X-extreme” category, relating to areas of bedrock outcrop or subcrop, or within 30 m of a location of point recharge (Daly 2004). Areas with deposits greater than 3 m thick are classified as high, moderate, or low vulnerability based on subsoil thickness and permeability after (Daly 2004).

Table 8.5-71: National datasets for physical characteristics selected for the prediction of groundwater pesticide occurrence and categories for each characteristics subsequent association within each category

MP type	Corine Land Cover 2006[1]		Soil Type		Quaternary deposits (subsoil)			Bedrock geology[6]	Aquifer type[5]		Gro vul
	Land use II	Land use III	Soil association[2†]	IFS soil type II[3‡]	Quaternary deposit genesis[4]	Quaternary deposit acid/base[4]	Subsoil permeability[5]		GSI aquifer importance	WFD flow regime	
Spring	Agriculture (non-irrigated arable land and pasture)	Arable (non-irrigated arable land)	Acid brown earth	Deep well drained mineral	Alluvium	Acidic	High	Granites and other Igneous intrusive rocks	Poor aquifers	Poorly productive fissured bedrock	Exp
Drilled borehole	Forestry[§]	Non-arable (pasture land)	Blanket peat	Shallow well drained mineral	Peat	Alkaline	Low	Dinantian pure bedded limestones	Locally important aquifers	Karstic	Ext
Well	Other land use[††]	Forestry[§]	Brown podzolic	Deep poorly drained mineral	Gravels		Low-high	Dinantian lower impure limestones	Regionally important aquifers	Productive fissured bedrock	Hig
		Other land use[††]	Degraded brown podzolic	Shallow poorly drained mineral	Irish sea tills		Low-low	Dinantian pure unbedded limestones		Intergranular	Hig
			Gley	Poorly drained mineral soils with peaty topsoil	Karstified rock		Medium	Dinantian upper impure limestones			Mo
			Grey brown podzolic	Shallow, lithosolic or podzolic type soils potentially with peaty topsoil	Tills		Medium-high	Dinantian (early) sandstones, shales, and limestones			Lo
			Minimal grey brown podzolic	Alluvium			Medium-low	Ordovician metasediments			
			Rendzina and outcropping rock	Peats			M/L*	Devonian old red sandstones			
			Shallow brown earth	Miscellaneous				Ordovician volcanics			

[1] European Environment Agency (2011)

[2] Gardiner and Radford (1980)

[3] Bulfin et al. (2002)

[4] Fealy et al. (2009); GSI (2011)

[5] GSI (2011)

[6] GSI (1999)

[†] Dominant soil type for each association in each ZOC

[‡] Amalgamation of categories listed by Bulfin et al. (2002) into a fewer number for input into statistical analyses

[*] Where incomplete vulnerability or permeability was assigned an 'interim' classification

[§] Forestry includes broad leaved forest, coniferous forest, mixed forest, and transitional woodland scrub

[††] Other land use includes natural vegetation, urban land use, bare rocks, mineral extraction sites, and peat bogs

Statistical methods

For each MP, the most prevalent category for each physical characteristic within its ZOC was recorded to generate count tables for input into SAS (2004). These tables of observational data were analyzed using the categorical data analysis procedures of SAS (2004). As the analysis is exploratory in spirit, both marginal tests of one factor at a time and multiple regression were used to assess the association of ZOC characteristics with pesticide detections.

For the marginal tests, tables were generated using the three concentration level categories listed above with an emphasis on answering a priori questions. All statistical results have been given with 95 % confidence intervals ($p \leq 0.05$).

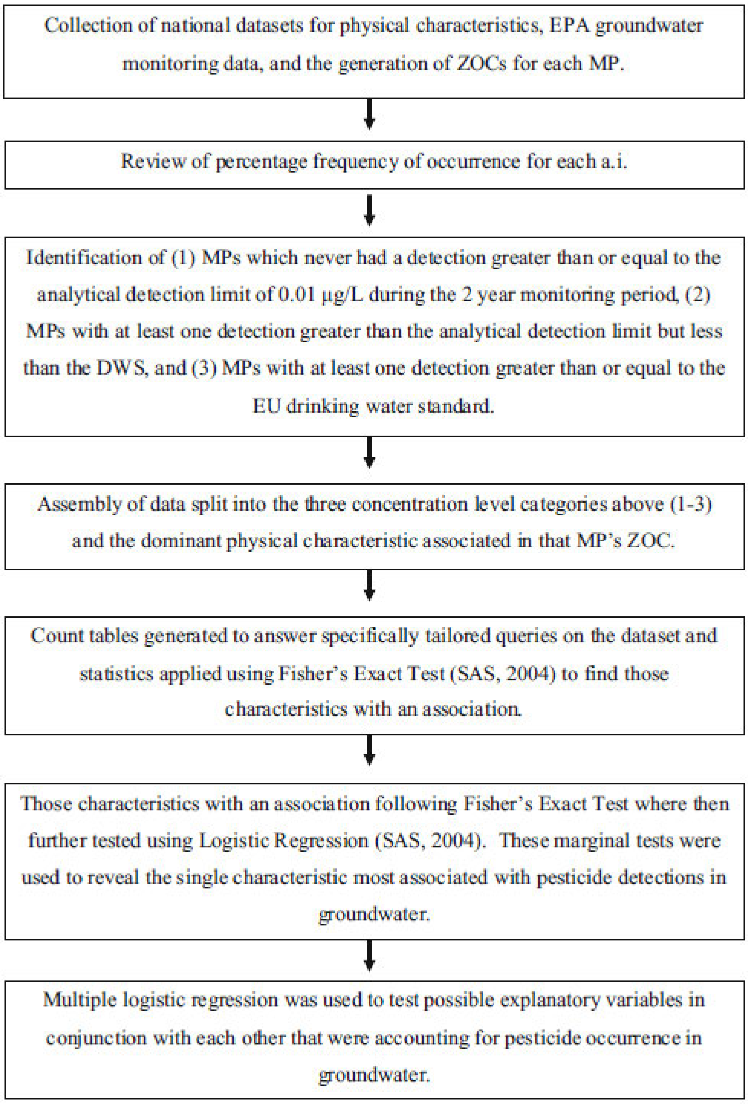
Fisher's exact test (Agresti 2002), a non-parametric test, was used for the analysis of the summary data tables as the low counts caused by non-detects in a large proportion of the cells made a chi-square test unreliable. The analysis was carried out using the Proc Freq procedure in SAS (2004) using the Monte-Carlo approximation for larger tables. Physical characteristics were deemed to be significantly associated with pesticide occurrence if the Fisher's exact test p value was <0.05. Any significant associations were then further examined using logistic regression (Agresti 2002) to determine which categories within the physical characteristic differed and which had the greatest likelihood of a pesticide detection. Odds ratios from logistic regression were the main tool for assessing this detail. Statistical tests of various sub-groupings of the data set are intended to be interpreted in an exploratory sense and are not adjusted for the multiplicity of tests carried out. The sequence of method steps for identification of physical characteristics most associated with pesticide detections in groundwater is summarized in Figure 8.5-47. A second analysis approach used multiple logistic regression and automatic variable selection procedures (SAS 2004) to determine which factors from the marginal tests were jointly associated with pesticide detections.

Results

National pesticide occurrence

Of the 845 samples analyzed, 73% had no detection of any pesticide, 24% had detections greater than the analytical limit of detection but less than the DWS of 0.1 µg/L, and 3% of samples had at least one detection greater than or equal to the DWS. The percentage frequency of occurrence from the national groundwater pesticide dataset (Figure 8.5-48) shows pesticide occurrence during monitoring on one sampling occasion, with the number of detections for each pesticide expressed as a percentage of the total number of samples analyzed for that particular pesticide. Nationally, MCPA and mecoprop were the most frequently observed pesticides in groundwater, being found in 8.7 and 8% of samples, respectively.

Figure 8.5-47: Sequence of work undertaken to allow for the assessment of ZOC physical characteristics and pesticide detections in groundwater



Collection of national datasets for physical characteristics, EPA groundwater monitoring data, and the generation of ZOCs for each MP.

Review of percentage frequency of occurrence for each a.i.

Identification of (1) MPs which never had a detection greater than or equal to the analytical detection limit of 0.01 µg/L during the 2 year monitoring period, (2) MPs with at least one detection greater than the analytical detection limit but less than the DWS, and (3) MPs with at least one detection greater than or equal to the EU drinking water standard.

Assembly of data split into the three concentration level categories above (1-3) and the dominant physical characteristic associated in that MP's ZOC.

Count tables generated to answer specifically tailored queries on the dataset and statistics applied using Fisher's Exact Test (SAS, 2004) to find those characteristics with an association.

Those characteristics with an association following Fisher's Exact Test where then further tested using Logistic Regression (SAS, 2004). These marginal tests were used to reveal the single characteristic most associated with pesticide detections in groundwater.

Multiple logistic regression was used to test possible explanatory variables in conjunction with each other that were accounting for pesticide occurrence in groundwater.

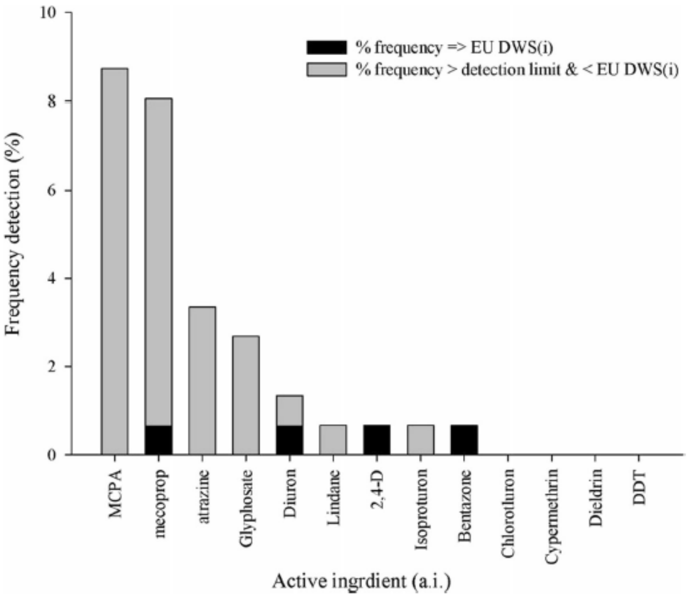
The DWS was exceeded for mecoprop in one sample. Five priority substances: atrazine, isoproturon (IPU), DDT, dieldrin, and diuron, were tested during monitoring. Atrazine was detected in five samples and IPU was detected in one sample, but none were observed greater than or equal to the DWS. Diuron was detected in two samples, with one having a detection greater than the DWS. Lindane, glyphosate, bentazone, and 2,4-D were also included for analysis and found in detectable concentrations with only bentazone and 2,4-D exceeding the DWS. Samples were analyzed for chlorotoluron, dieldrin, DDT, and cypermethrin but no detections greater than the analytical detection limit were observed for these four compounds.

When positive detections were expressed as a function of the total number of MPs sampled during the campaign, 47.5 % of MPs had no detection, 40.5 % of MPs had one or more detections greater than the analytical detection limit but less than the DWS, and 12 % of MPs had a detection greater than or equal to the DWS on at least one sampling occasion. No samples processed during the monitoring campaign exceeded the 0.5 µg/L DWS limit set for total pesticides in any one sample. Figure 8.5-49 indicates the spatial distribution of MPs and the concentration category level throughout the course of monitoring. Figure 8.5-50 shows the geographic distribution of the four most commonly detected pesticides, with a cluster of MPs in the West of Ireland with frequent detections. Mecoprop and MCPA were the most commonly encountered pesticides at MPs with 36 and 39 % of MPs having at least one detection of these compounds, respectively. Lindane was detected in at least at 17 % of MPs and glyphosate at 8 %. The percentage of MPs with detections for each of the other individual compounds not shown in Figure 8.5-50 was 6 % for atrazine, 4 % for 2,4-D, 3 % for bentazone and diuron, and 0.6 % for IPU.

Statistical analysis of occurrence with ZOC properties

This dataset is a sample of convenience since samples were not collected in a truly random fashion. Thus, there may be some unquantifiable bias associated with it. However, given the large size and wide coverage of the dataset, it is the authors' opinion that it is informative and can be used effectively to examine relationships in a purely exploratory manner.

Figure 8.5-48: Frequency of pesticide detections as a % of the total number of samples analyzed for a particular pesticide compound in 1 month during the sampling campaign in 2007-2008. Values are adjusted to each compound's analytical detection threshold of 0.01 µg/L. The Council Directive 98/83/EC drinking water standard (DWS) is 0.1 µg/L



Fisher's exact test

Pesticide detections in groundwater were found to be significantly related to seven of the physical characteristics present in each MPs ZOC (Table 8.5-72). Some of the original physical characteristic national datasets were further amalgamated into a smaller number of categories (Table 8.5-71).

Logistic regression

Following Fisher's exact test, the five physical characteristics with a significant degree of association were tested using logistic regression. The results indicate that springs are more likely to have a pesticide detection followed by wells, and then closely followed by boreholes ($p = 0.0028$) (Figure 8.5-51a).

With aquifer types split according to their GSI classification based on aquifer importance, the output revealed (Figure 8.5-51b) that there is a greater likelihood of a detection in a regionally important aquifer compared to a locally important aquifer or a poor aquifer (*p* = 0.0007).

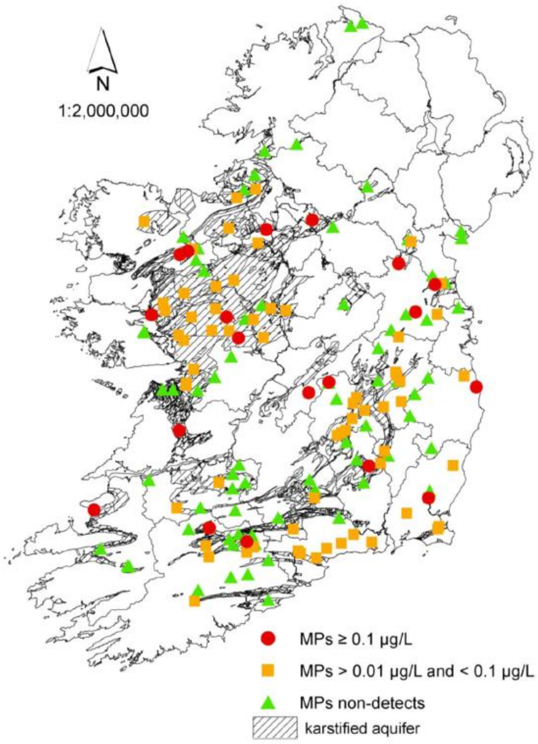
The 11 aquifer types were also classified using the Irish system of flow regime used for the WFD (Table 8.5-71; Figure 8.5-51c). In descending order of probability of a pesticide detection in groundwater were karstic aquifers >intergranular >productive fissured bedrock >poorly productive fissured bedrock aquifer types (*p* = 0.0002).

Pesticide detections at MPs were tested in relation to aquifer transmissivity, using aquifer importance as a surrogate (GSI aquifer importance, Table 8.5-71). Higher yielding regionally productive and potentially higher transmissivity aquifers were more likely to have a pesticide detection in groundwater than poor - or locally important - aquifer types (*p* = 0.0007, Figure 8.5-51b). Karstic aquifer types (Rkc and Rkd) were removed from the dataset so they did not influence the outcome. The count tables were reanalyzed and Fisher's exact test revealed there was still an association between pesticide detections in groundwater and regionally important aquifer types (*p* = 0.0013) (Table 8.5-72). Figure 8.5-51 shows the SAS output for logistic regression.

An association was found between Quaternary deposits and groundwater pesticide detections using Fisher's exact test (*p* = 0.0260). Splitting Quaternary deposit types into six categories (Quaternary deposit genesis; Table 8.5-71) revealed no association (*p* = 0.1820) using Fisher's exact test; thus, no further logistic regression was performed.

Logistic regression on Quaternary deposit chemistry classification revealed that there was a significantly (*p* = 0.0048) greater chance of a pesticide detection in an alkaline Quaternary deposit compared to an acidic Quaternary deposit (Figure 8.5-51d). Although Fisher's exact test indicated an association between pesticide detections in groundwater and IFS soil type II using Fisher's exact test (*p* = 0.0095), logistic regression on this classification indicated that there was no further statistically significant relationship within the nine categories listed in Table 8.5-71 (*p* = 0.1069) due to sparseness in the table (detections vs. non-detections among the categories listed in Table 8.5-71 for IFS soil type).

Figure 8.5-49: Spatial distribution of MPs with detections exceeding the EU DWS, MPS with detectable detections of pesticides, and MPs which never had a pesticide detection throughout the 2-year monitoring campaign



Multiple logistic regression

Severe numerical problems during multiple logistic regression prevented satisfactory modeling of the three-level multinomial response for detection but it was possible to fit a binary response for detect/non-detect using the logistic procedure in SAS with penalized likelihood using the Firth option. There were difficulties in this process too because of multicollinearity but Table 8.5-74 contains the outcome for this dataset. It is of interest to contrast the factors found to be useful in the multiple regression model with those in the marginal tests. Only GSI aquifer type and Quaternary deposit acid/base were significant in marginal tests.

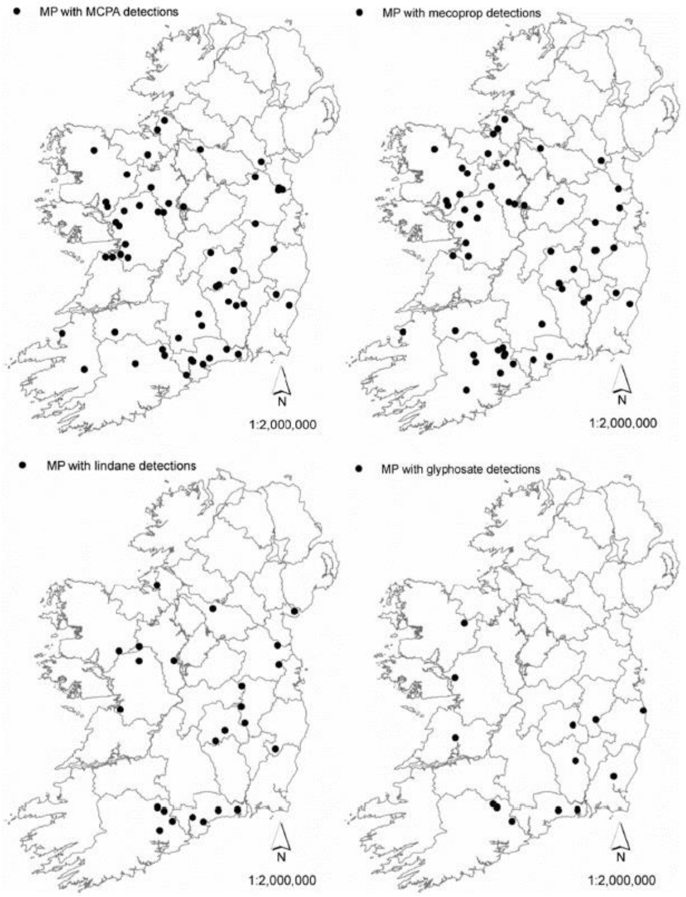
While it is difficult to interpret all of these changes in detail because of sparseness in the tables results in some extreme odd ratios, it appears from simple effect testing within the interactions that there was an impact of GSI aquifer type at the extremes of groundwater vulnerability, i.e., high or greater (p <0.0001) and moderate or lower (p = 0.0007) but not for H-L (p = 0.45). For the soil association × groundwater vulnerability interaction, there was an impact of groundwater vulnerability for shallow soils (p = 0.0002) and acid brown earth soils (p = 0.0013).

Discussion

Frequency of pesticides

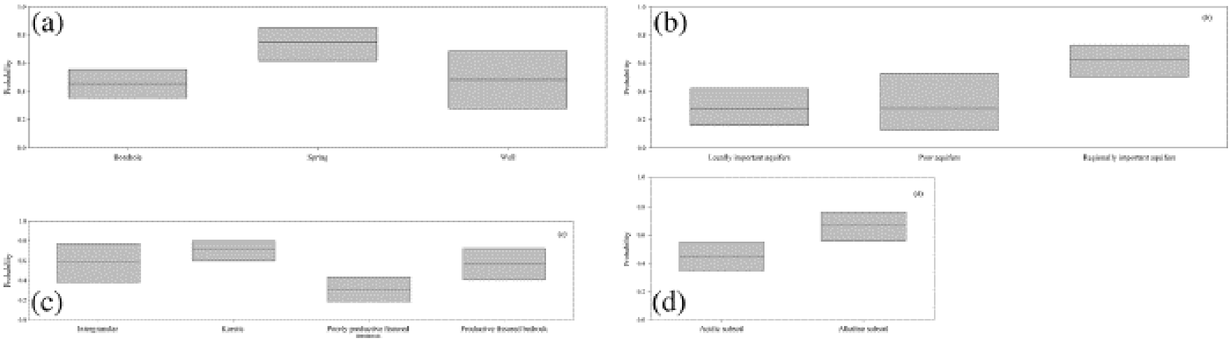
From the whole monitoring campaign, MCPA and mecoprop were the most frequently detected pesticides to exceed the DWS with detections in less than 1 % of samples collected between 2007 and 2008 (Figure 8.5-48). MCPA and mecoprop are extensively used in varying land uses across Ireland. IPU never exceeded the DWS during monitoring while bentazone was detected in samples at concentrations equal to the DWS. From Table 8.5-73, less bentazone was applied in comparison to IPU, yet all four detections of bentazone exceeded the DWS. IPU had approximately 191 times the amount applied in Ireland in comparison to bentazone (Table 8.5-73) yet IPU was rarely detected. Three compounds (atrazine, lindane, and diuron), banned between 2000 and 2008 (Table 8.5-70), were detected in groundwater. Neither chlorotoluron, cypermethrin, dieldrin nor DDT were detected in groundwater between 2007 and 2008. Transformation products should be considered for future monitoring campaigns not just in Ireland but across the world, to help further understand their fate, transport, persistence, and ecological significance in the environment.

Figure 8.5-50: Spatial distribution of MPs with detections of each individual pesticide:MCPA, mecoprop, lindane and glyphosate on at least one occasion



Frequency of detections at monitoring points
The cluster of detections in the West of Ireland corresponds to an area dominated by karst geology, alkaline Quaternary deposits, and where many of the MPs are springs - also highlighted during statistical analysis (Figure 8.5-51). Detections for individual compounds (Figure 8.5-50) are not located in any one particular County of Ireland although no glyphosate was detected in the North East. For the four most frequently detected compounds, their detections, as with Figure 8.5-49, center in karst areas in the west and south.

Figure 8.5-51: **Results from logistic regression based on (a) The type of monitoring point (*p*=0.0028); (b) Aquifer type classified using the GSI classification system based on aquifer importance (*p*=0.0007); (c) Aquifer type classified using the Irish system of flow regime adopted for the WFD (*p*=0.0002); and (d) Acid versus Quaternary deposits as identified by their reaction (RxN) with 10 *v/v* hydrochloric acid (*p*=0.0048)**



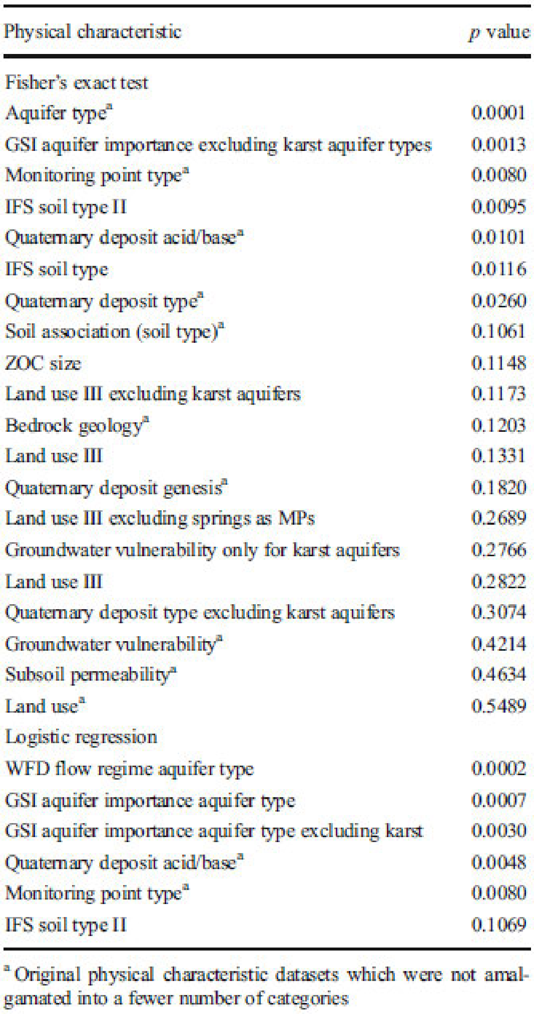
Physical characteristics associated with pesticide detections

Aquifer type

Regionally important aquifers are capable of yielding water on a regional scale owing to a greater number, size, and connectivity of fractures and fissures within their lithology compared to locally important - and poor aquifers. Even with regionally important karst aquifers removed from the dataset, the statistical outcome remained that regionally important aquifer types were more associated with pesticide detections. Within the WFD aquifer flow regime classification, karstic aquifers had the highest probability of having a pesticide detection ($p = 0.0002$). Karst systems are very heterogeneous with many having solution features that can act as easy access points for water containing pesticides to enter the groundwater below. Karst aquifers are mainly found in the west and north west of Ireland (Figure 8.5-49 and Figure 8.5-50).

Karstic, intergranular, and productive fissured flow regime aquifers all had a greater association with pesticide detection in groundwater compared to poorly productive bedrock flow regime aquifers (Figure 8.5-51c) since regionally important aquifers with flow through fissures can act as fluid pathways. The fractures are larger and more connected than those present in poorly productive fissured aquifers potentially allowing more movement of pesticides within aquifers. Inter-granular flow aquifers, which in Ireland are generally composed of fluvioglacial sands and gravels, ranked second in their association with pesticide occurrence in groundwater (Figure 8.5-51c). Multiple logistic regression revealed that groundwater vulnerability in conjunction with GSI aquifer type can be used to indicate which areas are more associated with pesticide occurrence (Table 8.5-74). The groundwater vulnerability map assesses areas based on the depth of overburden material (soil and subsoil above bedrock). The shallower this protective layer above bedrock, in conjunction with a regionally productive aquifer was an area identified to be more associated with pesticide detections in groundwater across Ireland.

Table 8.5-72: **Statistical analysis *p* values for Fisher's exact test and logistic regression, $p<0.05$ infers an association between pesticide occurrence in groundwater and the physical characteristic or amalgamated category tested**



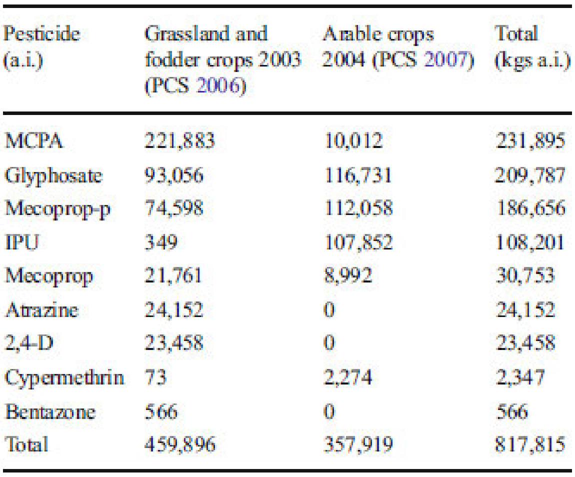
Physical characteristic	*p* value
Fisher's exact test	
Aquifer type[a]	0.0001
GSI aquifer importance excluding karst aquifer types	0.0013
Monitoring point type[a]	0.0080
IFS soil type II	0.0095
Quaternary deposit acid/base[a]	0.0101
IFS soil type	0.0116
Quaternary deposit type[a]	0.0260
Soil association (soil type)[a]	0.1061
ZOC size	0.1148
Land use III excluding karst aquifers	0.1173
Bedrock geology[a]	0.1203
Land use III	0.1331
Quaternary deposit genesis[a]	0.1820
Land use III excluding springs as MPs	0.2689
Groundwater vulnerability only for karst aquifers	0.2766
Land use III	0.2822
Quaternary deposit type excluding karst aquifers	0.3074
Groundwater vulnerability[a]	0.4214
Subsoil permeability[a]	0.4634
Land use[a]	0.5489
Logistic regression	
WFD flow regime aquifer type	0.0002
GSI aquifer importance aquifer type	0.0007
GSI aquifer importance aquifer type excluding karst	0.0030
Quaternary deposit acid/base[a]	0.0048
Monitoring point type[a]	0.0080
IFS soil type II	0.1069

[a] Original physical characteristic datasets which were not amalgamated into a fewer number of categories

Soil type

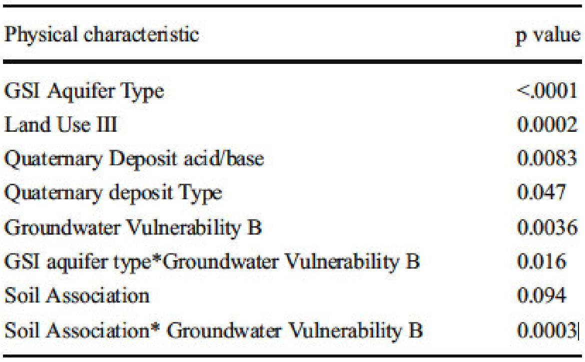
The majority of MPs were located on well-drained soils with 32.3% of these MPs having a detection less than the DWS and 12% of MPs on well-drained soils had a detection greater than the DWS. Well-drained soils appear more likely to have a detection but this finding cannot be confirmed statistically. Our marginal test results indicate that the IFS soil type classification is more influential than soil association (Table 8.5-71) when using large robust datasets in an exploratory manner to predict the physical characteristics which affect pesticide leaching to groundwater in a MP's particular ZOC. The lack of a statistically significant marginal relationship between soil type derived from soil associations and groundwater pesticide occurrence may be due to the contrasting properties of the 13 pesticide compounds tested, with differences in their solubility and adsorption properties. The multiple regression results (Table 8.5-74) revealed some of the interactions with soil association that may be important to examine in future surveys. Multiple logistic regression revealed that soil association in conjunction with groundwater vulnerability had explanatory power to pesticide occurrence in groundwater.

Table 8.5-73: **Total amount of a.i. applied to arable, and grassland and fodder crops in Ireland**



Pesticide (a.i.)	Grassland and fodder crops 2003 (PCS 2006)	Arable crops 2004 (PCS 2007)	Total (kgs a.i.)
MCPA	221,883	10,012	231,895
Glyphosate	93,056	116,731	209,787
Mecoprop-p	74,598	112,058	186,656
IPU	349	107,852	108,201
Mecoprop	21,761	8,992	30,753
Atrazine	24,152	0	24,152
2,4-D	23,458	0	23,458
Cypermethrin	73	2,274	2,347
Bentazone	566	0	566
Total	459,896	357,919	817,815

Table 8.5-74: **Statistical analysis p values for Multiple Logistic Regression.** ***p*****<0.05 infers an association between pesticide occurrence in groundwater and the physical characteristic or amalgamated category tested**



Physical characteristic	p value
GSI Aquifer Type	<.0001
Land Use III	0.0002
Quaternary Deposit acid/base	0.0083
Quaternary deposit Type	0.047
Groundwater Vulnerability B	0.0036
GSI aquifer type*Groundwater Vulnerability B	0.016
Soil Association	0.094
Soil Association* Groundwater Vulnerability B	0.0003

Conclusion

Using simple logistic regression on a 2-year national groundwater monitoring campaign revealed several physical characteristics were more associated with pesticide detections in groundwater. These were springs, karstic flow regime aquifer types, regionally important aquifers, and alkaline Quaternary deposits in existence with karst aquifers. There was some evidence from multiple regression that there was mutual dependency between some of these factors and that they interacted with soil association and the GSI groundwater vulnerability dataset. The geographic distribution of monitoring points with exceedances coincides with mapped karst areas, which was also confirmed statistically. Of monitoring points, 47.5% never had a pesticide detection greater than the limit of detection, while 12% of monitoring points had a detection greater than the European Union Drinking Water Standard of 0.1 µg/L on at least one occasion.

Of the 13 pesticides monitored, MCPA and mecoprop were the most frequently detected, although banned compounds such as lindane and atrazine were still detected but not exceeding the EU drinking water standard. Provided a large sample size is available, the methods used here can highlight geographical areas more susceptible to groundwater contamination. Future monitoring programs should analyze for each parent active ingredient along with any relevant transformation products to assess their depletion in the environment. It is hoped this study will improve conceptual understanding and assist in the assessment of groundwater chemistry through the interpretation of groundwater quality data: a fundamental requirement of the WFD.

Assessment and conclusion by applicant:
The article reports the evaluation of a two-years national groundwater monitoring campaign in Ireland. Methods and results are sufficiently described.
The article is considered reliable.

Assessment and conclusion by RMS:
This study explores the associations of pesticide occurrence in groundwater in Ireland to geological characteristics of the monitoring points (MPs) contributing area. Pesticide analyses were undertaken during a 2-year groundwater monitoring campaign, which generated 845 samples.

Is is noticeable, that among the 13 pesticides of interest in this article, Glyphosate was the 2nd most applied pesticide and the 4th most frequently detected. Article report that Glyphosate is encountered in 8% of the samples.

However, the physical characteristics of the monitoring points are tested with regard to the overall pesticide detection and therefore no conclusions are specific to glyphosate.
It seem that glyphosate is not detected at level above 0.1 µg/L, however no further quantitative conclusions on glyphosate use and its presence in GW can be made.

The article is considered reliable with restrictions.

Data point:	CA 7.5/021
Report author	Norgaard, T. *et al*.
Report year	2014
Report title	Leaching of Glyphosate and Aminomethylphosphonic Acid from an Agricultural Field over a Twelve-Year Period
Document No	Vadose Zone J. doi:10.2136/vzj2014.05.0054
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The globally used herbicide glyphosate [*N*-(phosphonomethyl)glycine] and its most frequently detected metabolite, aminomethylphosphonic acid (AMPA), were studied in a unique 12-yr field-scale monitoring program. The leaching of glyphosate, AMPA, and soil particles was studied in a shallow drainage system beneath a 1.26-ha field. Five annual glyphosate applications were applied with different autumn application dates. Solute mass flux from the drain system following the five glyphosate applications were compared to determine how different factors affect the leaching of glyphosate, AMPA, and particles. Glyphosate and AMPA leaching were highly event driven, controlled by the time and intensity of the first rainfall event after glyphosate application. A high similarity in cumulative drainage and leached pesticide masses with time suggests near-constant drainage and leaching rates. There was no clear relationship between particle-facilitated transport and the transport of glyphosate or AMPA. However, soil particles, glyphosate, and AMPA all showed distinct, simultaneous concentration curves, indicating common dominant transport mechanisms. Also, soil-water content at the time of application and the level of the groundwater table relative to the drain depth exerted clear controls on detection of solutes in the drainage water. To summarize our findings, we present a leaching risk chart to illustrate the dependence of glyphosate, AMPA, and soil particle leaching based on rainfall intensity and the timing of rainfall events after glyphosate application.

Materials and methods

This study analyzed the results from a unique 12-yr field-scale monitoring program measuring the leaching of glyphosate and AMPA. Measurements were made in a shallow drainage system beneath a 1.26-ha field. The study compared five glyphosate applications with different autumn application dates. The overall objective was to determine which climatic conditions and soil properties affected the leaching of glyphosate, AMPA, and soil particles. Based on previous studies, we hypothesized that the timing of rainfall events in relation to glyphosate application, the applied glyphosate dose, and location-specific conditions promoting particle-facilitated transport would be important factors controlling the leaching of glyphosate and AMPA. Based on this high-resolution, long-term monitoring data set, we developed a risk chart and propose directions for further development in research on glyphosate and AMPA leaching.

Leaching of glyphosate and its degradation product AMPA was studied at a Danish experimental field site in Estrup, southern Jutland.

The field site in Estrup is a loamy, highly heterogeneous soil with considerable variations in both topsoil and aquifer characteristics. The field is located on glacial till and covers an area of 1.8 ha, where 1.26 ha is cultivated. The field is virtually flat, with a slope of 0 to 1° toward the northeast. The soil is heavily fractured and bioturbated to the 1-m depth, with a plow layer containing 100 to 1000 biopores m^{-2}. The Estrup field site has a relatively shallow water table located approximately 1 to 3 m below ground surface (bgs), and the field site is systematically tile drained at an average depth of about 1.1 m.

Tile-drainage water from the cultivated area is directed to a monitoring well with a Thomson weir (30° V-notch) at the outlet of the drainage system in the northeastern corner of the field. The water height behind the Thomson weir is measured automatically using a pressure transducer (PDCR1830, Druck) coupled to a CR10X datalogger (Campbell Scientific), and the drainage is sampled using flow-proportional sampling. A sample of 200 mL is taken for every 3000 L (0.24 mm) of drainage flow from September to April and 1500 L (0.12 mm) from May to August; therefore, the sampling rate depends on the intensity of drainage flow. Analyses of pesticides and inorganic chemicals were performed weekly on the pooled 200-mL subsamples, such that the reported concentrations represent the weekly average concentrations in the drainage water collected. Because the samples were pooled, they do not represent peak concentrations that may occur during the week. Before July 2004, drainage was sampled both time proportionally and flow proportionally.

However, this study used only the flow-proportional sampling, which was collected consistently throughout the 12-yr monitoring period. Glyphosate has been applied to the agricultural field site in Estrup five times, including the first application on 10 Oct. 2000. Table 8.5-75 shows the glyphosate application dates and the amount of active ingredient applied.

Table 8.5-75: Glyphosate application dates and conditions during application

Date	Type of glyphosate [1]	Application rate	Amount of active ingredient (g/ha)	Cover before application	Air temperature at application (°C)
13 Oct. 2000	Roundup Bio	4.0 L/ha	1440	Stubble, 10 cm	9.5
2 Sept. 2002	Roundup Bio	4.0 L/ha	1440	Stubble, 14 cm	20.1
9 Nov. 2005	Roundup Bio	4.0 L/ha	1440	Stubble, 20 cm	10.0
24 Sept. 2007	Roundup Max	1.5 L/ha	1020	Stubble, 12 cm, and shredded straw	15.2
3 Oct. 2011	Roundup Max	2.0 L/ha	1360	Stubble, 12 cm, and shredded straw	17.5

[1] The active glyphosate ingredient in Roundup Bio is the isopropylamine salt of glyphosate in a liquid form, whereas the active ingredient in Roundup Max is an ammonium salt of glyphosate in a granular form

From 31 Oct. 2000 to 17 Mar. 2011, the particle concentrations were measured as the amount of suspended matter determined by filtration through a 1.6-mm Whatman glass fiber filter (DS/EN 872:2005). From 22 Sept. 2010 and onward, the particle concentrations were also determined from the turbidity of the sample using a Hach 2100AN turbidimeter. These results were converted to a particle concentration (mg L^{-1})

according to the procedure of Schelde *et al*. (2002). For a period of 2 yr, whenever enough water could be sampled, both methods were used simultaneously. From this period, a regression was obtained between the particle concentrations determined from the suspended matter method and the turbidity method (suspended matter concentration [mg L^{-1}] = 0.51 × turbidity concentration [mg L^{-1}] + 1.51, *R*2 = 0.7987) to allow for consistent analyses throughout the monitoring period.

Until July 2007, glyphosate and AMPA were analyzed according to Method 2275 (Eurofins Environment Denmark, Internal Method 76 542275, Glyphosate and AMPA in water by GC/MS). After July 2007, this method was replaced by Method 8270 (Eurofins Environment Denmark, Internal Method 76 548270, Glyphosate and AMPA in water by LC/MS/MS). Unfortunately, field-site control samples showed an underestimation of glyphosate using the newer method. This underestimation was assumed to be caused by a complex formed between glyphosate and potential multivalent cations (like Ca, Zn, Cu, Fe, Ni, and Cd) in the samples. This was discovered in 2010, and from 1 July 2010, an extended version of Method 8270 with acid-shock treatment was applied. Glyphosate concentrations analyzed in the period from 1 July 2007 to 1 July 2010 have been corrected to allow for the underestimation by multiplying by a factor of two following the procedure of Kjær *et al*. (2011b).

Results

For Applications 1, 2, and 3, the active glyphosate ingredient in Roundup Bio was the isopropylamine salt of glyphosate in a liquid form, whereas for Applications 4 and 5, the active glyphosate ingredient in Roundup Max was an ammonium salt of glyphosate in a granular form. It is unclear whether this difference in formulation would affect the fate properties of glyphosate and hence leaching, but the concentrations of AMPA were slightly lower after Applications 4 and 5.

Application 4 stands out from the remaining applications because the concentrations of glyphosate and AMPA were considerably smaller after Application 4 and, in contrast to the pesticide concentrations after Applications 1, 2, and 3, these concentrations with time curves were bell shaped. The smaller concentrations could be due to the smaller dose in Application 4 (1020 g ha^{-1}) compared with Applications 1, 2, and 3 (1440 g ha^{-1}, Table 8.5-75) or attributed to the shredded straw left on the field before glyphosate application. The straw might have retained some of the applied glyphosate, providing a slower release to the soil. This, however, contradicts the findings of Gjettermann *et al*. (2009), where the adsorption coefficient for glyphosate to straw (*K*d <1 L kg^{-1}) was smaller than to soil (*K*d = 503 L kg^{-1}). Similar to Application 4, straw was shredded on the field before Application 5. However, this did not result in the same low concentrations as after Application 4. The applied dose in Application 5 was almost the same as in Applications 1, 2, and 3, and therefore we assume that the low glyphosate concentrations detected after Application 4 were the result of a lower applied dose rather than the shredded straw.

It is difficult to generalize about the direct effects of tillage operations on glyphosate and AMPA leaching due to differences in weather conditions among the five glyphosate applications. In some cases, the potential direct effects of tillage operations are easily confounded by the effects of high-intensity rain events. Although similarities in the responses of particle, glyphosate, and AMPA leaching suggest common underlying dominant transport processes, there were no direct correlations between glyphosate, AMPA, and particle concentrations (data not shown), probably due to the complex interactions of flow processes, transport, degradation, climate conditions, and GWT fluctuations. The particle concentration curve has the same shape as the glyphosate and AMPA concentration curves, suggesting that the dominant processes controlling particle leaching are the same as those for glyphosate and AMPA. In summary, although we hypothesized that particle-facilitated transport would be an essential driver for glyphosate and AMPA leaching, this was not evident from our long-term field results.

The largest amounts of precipitation and drainage within the first 150 d after application occurred after Applications 1 and 5, whereas the largest amount of glyphosate (11.26 g) was leached after Application 3. The main contributor to this high glyphosate mass was the concentration detected on 17 Nov. 2005 of 31 µg L^{-1}, which contributed 53 % (5.95 g) to the total leached glyphosate mass. Glyphosate was applied on 9 Nov. 2005, and on 15 November there was a rainfall of 21 mm. The second-largest amount of glyphosate (3.16 g) was leached within the first 150 d after Application 5. This glyphosate mass mainly originated from the glyphosate leached on 19 Oct. 2011, which contributed 51 % (1.62 g) to the total glyphosate mass leached-most likely as a consequence of the high-intensity rain event on 18 October (36 mm). In our study, for Applications 3 and 5, the main contributing rain events fell within the first 6 and 15 d following glyphosate application.

Although the amount of AMPA leached within the first 150 d is larger after Application 3, the ratio between leached glyphosate and AMPA is also considerably higher after Application 3 than after the other applications. The high glyphosate/AMPA ratio probably reflects rapid glyphosate transport shortly after glyphosate application with insufficient time for degradation. Rain events and SWC definitely had an influence on the glyphosate/AMPA ratio. The daily SWC in the first month after Application 3 was the second highest of the five applications. Application 3 also had the latest application time in the year and a low outside air temperature at application (10°C, Table 8.5-75), which possibly led to less microbial activity and hence limited glyphosate degradation. Applications 1 and 3 had the same low air temperatures at application of 9.5 and 10.0°C, respectively. Nevertheless, the leached concentrations of glyphosate and AMPA for the two applications were of completely different magnitudes and thus it is reasonable to assume that the outside air temperature at the time of application was less essential for the leached concentrations than the application timing.

Application 3 had the smallest amount of precipitation within the first 150 d and the cumulative drainage was not considerably different from the other applications. Rather, the highest loss of glyphosate took place in the period after Application 3, suggesting that more likely the timing of the application in relation to the next high-intensity rain event is crucial.

This event-driven transport mechanism explains the first detected concentrations of glyphosate, AMPA, and soil particles on 31 Oct. 2000 (Application 1, 13 October) after a long-duration rain event where the rain intensity peaked on 30 October. Also, it is more likely that the occasional glyphosate, AMPA, and particle concentrations detected between 12 Sept. 2001 and March 2002, after Application 1, was a consequence of event-driven leaching rather than glyphosate, AMPA, and particle mobilization due to harvest.

After Application 2, we measured increased particle, glyphosate, and AMPA concentrations in the drainage water collected from the end of November 2003 to April 2004, which was probably also the effect of increased rain frequency and intensities. It is possible that harvest on 29 Aug. 2004 mobilized soil particles and AMPA, but the continuous detections for almost 1 yr could only have originated from event-driven leaching because there were no other influencing processes in this time period. The high concentrations of glyphosate and AMPA on 17 Nov. 2005 (8 d after Application 3 on 9 November) following a rain event on 15 November emphasizes the event-driven leaching mechanism. Similarly, multiple periods of continuous concentration detections after Application 4 indicate event-driven leaching, possibly also a result of more intensified tillage procedures. Finally, the concentrations of glyphosate and AMPA detected on 19 Oct. 2011, 16 d after Application 5 (3 October) were also possibly the effect of a high-intensity rain event of 35 mm on 18 October.

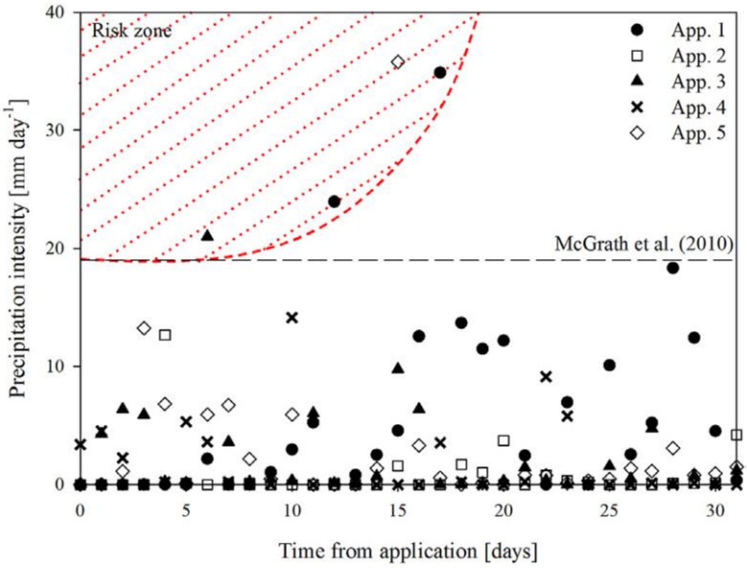
The results of our long-term observations, over five applications, strongly suggest that precipitation intensity following application represents a major control on particle and pesticide leaching. To summarize this finding, Figure 8.5-52 presents a risk chart of the daily precipitation intensity within the first 31 d after each of the five glyphosate applications. McGrath *et al*. (2010) identified a minimum threshold for a single rainfall event of 19 mm as an indicator for a high likelihood of rapid herbicide transport. We suspect that the 19-mm threshold arises from interplay of evaporation, rainfall timing and intensities, and soil hydraulic properties valid for a specific soil type, different climate conditions, and the experimental fieldscale setup. Therefore, this threshold might not necessarily be universally applicable. Rainfall depths <19 mm might also trigger preferential flow events if the water content of the soil is already near the critical infiltration capacity. Thus, more frequent but less intense rainfall events might also contribute to preferential flow (McGrath *et al*., 2010).

All of the rain events observed in the first month after the five applications in our study were below the 19-mm threshold except for four events. The first event was on Day 6 after Application 3, another event was from Day 15 after Application 5, and the last two events were from Days 12 and 17 after Application

1.We have added an approximate potential elevated-risk zone to build on the threshold concept of McGrath *et al*. (2010). This zone includes the 19-mm threshold of McGrath *et al*. (2010) and captures the four mentioned events. Strikingly, the four events within the elevated-risk zone are from the three applications that led to the highest leached masses of glyphosate and AMPA.

As noted above, the event on Day 6 after Application 3 contributed 5.95 g (53%) to the total glyphosate leaching loss within the first 150 d after application. The event after Application 5 contributed 1.62 g (51%) to the total leached glyphosate within the first 150 d. The two events after Application 1 contributed 0.48 g (23%) of the total leached glyphosate mass within the first 150 d after application.

Figure 8.5-52: **Risk chart showing rain intensity each day within the first 31 d after each of the five glyphosate applications. The dashed horizontal line is the 19-mm threshold for rapid herbicide transport events (McGrath *et al*., 2010). This study suggests an elevated-risk zone for rapid glyphosate and aminomethylphosphonic acid (AMPA) leaching as emphasized by the red area.**



The smaller contribution of the two events after Application 1 to the total leached glyphosate within the first 150 d is probably due to the delay in precipitation after glyphosate application compared with Applications 3 and 5. Thus, there was no precipitation until Day 6 and the SWC on the day of Application 1 was the lowest of the three applications. These results indicate that precipitation intensity and timing of rain events after glyphosate application are decisive for glyphosate leaching.

Assuming that particle leaching is controlled by the same factors as the leaching of glyphosate and AMPA, namely the timing of high-intensity rain events after soil disturbance could equally well cover particle leaching dynamics. The boundaries of the elevated-risk zone are only approximately defined by this study. The non-constant risk zone is defined based on the assumption that higher intensities are required to trigger enhanced glyphosate leaching with longer times between glyphosate application and the next intense rainfall event. Still, the boundaries of the risk zone will depend on, e.g., soil type, drain depth, and climate conditions. We would suggest that future work should be focused on identifying the soil properties and field conditions that define the limits of the risk zone with the hope of developing a universally applicable guideline for leaching risk assessment.

Conclusion

We have presented an extensive data series of glyphosate, AMPA, and particle leaching collected over 12 yr, including five glyphosate applications. In this initial examination of the data, we have examined previous hypotheses about particle and pesticide transport in light of this new data set. Our ultimate objectives are to examine these hypotheses with an eye toward guiding the responsible use of glyphosate. We have also made efforts to identify the remaining questions that are not resolved by this data set, thereby suggesting possible future research priorities. We specifically examined two hypotheses. First, that the timing of precipitation in relation to glyphosate application is a controlling factor for glyphosate and AMPA leaching. This hypothesis was supported by our field observations, which showed that the leaching of these two compounds was highly event driven. Taken together, these findings suggest that care should be taken to avoid the application of glyphosate in periods when the leaching potential is relatively high. Particle leaching was also seen to be event driven; however, it was controlled by the timing and intensity of the precipitation event in relation to the most recent soil disturbance, not to the timing of glyphosate application. Our second hypothesis was that particle-facilitated leaching controls the leaching of glyphosate and AMPA. This hypothesis is not supported by our observations.

Specifically, while there were clear similarities in the concentration vs. time curves for the particles and pesticides, there was no direct correlation between their leached concentrations. In addition, to decrease the likelihood of particle-facilitated transport, management procedures that cause intensified soil disturbance should be separated in time from glyphosate application.

Our results also highlight complications in relating the flux of pesticides to the groundwater based on measurements made in drain systems. The soil-water content at the time of application and the elevation of the water table in relation to the drain depth are critical factors for determining whether solutes are captured by the drains or bypass the drain system. This has clear implications for the representativeness of drainage water for recharge water. We suggest a risk concept that relates precipitation intensity and timing in relation to glyphosate application to the likelihood of glyphosate and AMPA leaching into drains. A risk chart that is suggested to illustrate the risk and results of this monitoring series was compared with the results of previous work in this context.

Despite the extensive data set presented here, there are still significant uncertainties regarding pesticide transport. Factors such as soil tillage should be considered further to see if intensified soil disturbance creates a higher risk for particle-facilitated leaching of glyphosate. More studies should be conducted in areas that experience high-intensity precipitation during pesticide application periods to define the suggested elevated-risk zone more clearly. It is our hope that this new data set will lead to improved understanding of pesticide leaching, leading to improved guidance for responsible pesticide application.

Assessment and conclusion by applicant:

The article reports the results of a 12-year field-scale monitoring program on the leaching of glyphosate and AMPA in Denmark. The analytical method 8270 applied between 2007 and 2010 showed insufficient recovery. The correction procedure by a constant factor of 2 is considered not appropriate in the context of the active substance approval under Regulation (EC) No 1107/2009. Further, it is discussed that measurements in the drainflow may origin from drainage of surface water as well as from groundwater, i.e. a clear conclusion about drained substance amounts cannot be drawn. As the overall results of the article may add valuable supplementary information to the data set.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:
Leaching of glyphosate and its degradation product AMPA was studied at a Danish experimental field site in Estrup, southern Jutland, in a 12-year field-scale monitoring program.

It is noted that analytical method changed through the period and that analyical issues are reported for the period 2007-2010, and results from this periode may therefore be less reliable.

The field site has a relatively shallow water table located 1 to 3 m below ground water surface, and the field site is systematically tile drained at an average of 1.1 m. Tile-drainage water from the cultivated area is directed to a monitoring well with a Thomson weir (30° V-notch) at the outlet of the drainage system in the northeastern corner of the field.

No detailed table results are available in the article, but results can be read on the following graph, and be put in relation with the application timings.

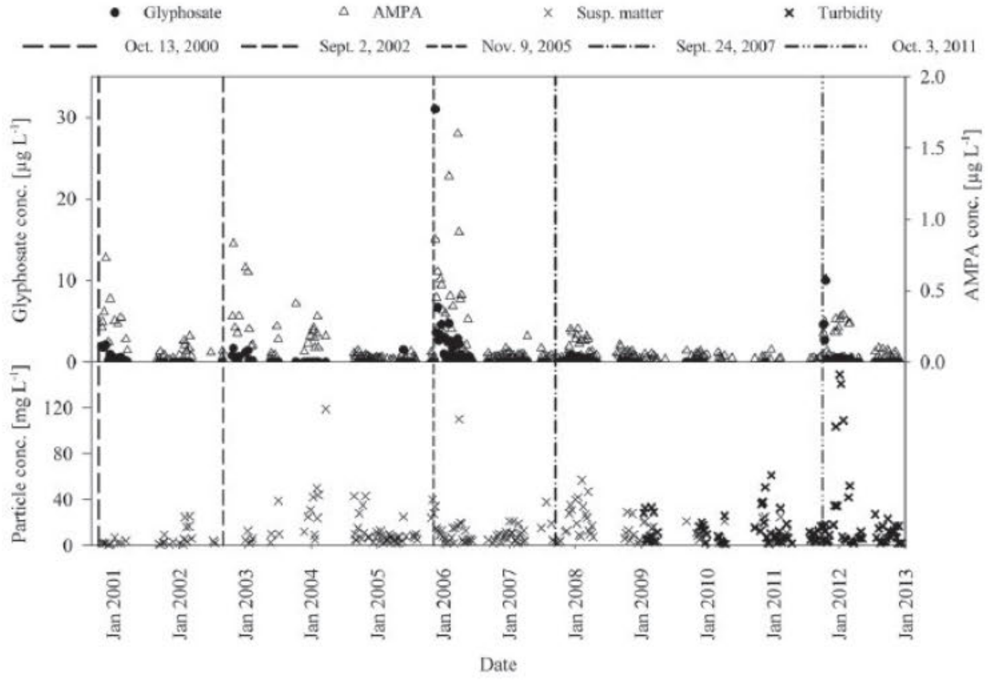


Fig. 2. Glyphosate (filled circles), aminomethylphosphonic acid (AMPA) (open triangles), and soil particle (crosses) concentrations in drainage samples and glyphosate application dates in the period 1 Sept. 2000 to 1 Jan. 2013 from the field site in Estrup, Denmark. The five glyphosate application dates are shown with different vertical lines. The particle concentration was determined as the amount of suspended matter through a 1.6-mm filter until 17 Mar. 2011 (thin crosses) until turbidity measurements were introduced on 22 Sept. 2010 (thick crosses). Glyphosate concentrations analyzed in the period from 1 July 2007 to 1 July 2010 have been corrected for method underestimation by multiplication by two according to Kjær et al. (2011b).

However, the different treatments (timing, addition of straw, different glyphosate salts) complicate a straightforward analysis. Also it is noted that the flow proportional samples were pooled on a weekly basis, they do not represent peak concentrations that may occur during the week.

Maximum measured concentration for glyphosate of 31 µg/L is observed in November 2005, 8 days after application 3, and 2 days after intense rain event of 21mm and increase of the groundwater table. It is worth noting that the application 3 was in a context of lower temperature compared to the other applications
Overall the authors considered that the results from this serie confirm their initial hypothesis that the timing of precipitation in relation to glyphosate application is a controlling factor for glyphosate leaching. In contrast, particle facilitated leaching of glyphosate ad AMPA could not be demonstrated by the authors' observations.

The results should however be considered carefully to evaluate potential leaching to groundwater.

As indicating by the study authors, "our results also highlight complications in relating the flux of pesticides to the groundwater based on measurements made in drain systems."

Additional information on this point is get from the full-text article:
"In this study, it is important to clarify that the registered drainage flow is only a portion of the flow to the groundwater. When the water table is above the drains, there is no guarantee that the drain flow is solely related to infiltration because it also captures groundwater, and the concentration in the drains may be a mixture of groundwater and infiltration. When the water table is below the drains, we may expect bypass flow of the drain system because preferential flow has also been associated with biopores other than in the drain system".

The article is considered reliable with restrictions.

Data point:	CA 7.5/022 CA 7.5/023 (Translation)
Report author	Martin, J. *et al*.
Report year	2013
Report title	Sugar Cane, Herbicides And water Pollution in Reunion Island: Achievements and Perspectives at the End of the First Decade of monitoring
Document No	Conference paper: 22nd Conference of COLUMA. International Days on Weed Control, Dijon, France, December 10-12, 2013 pp.641-651 ref.13
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities
Acceptability/Reliability:	Reliable with restrictions

BRGM, the French geological and hydrogeological survey, compiled data from three local agencies involved in water quality. The compilation included data from 247 sites monitored between May 1999 and January 2010. Positive results were found in 55% of the sites. Among the 398 substances checked, 73 were found and 65 were quantified: 35 of them were herbicides or herbicide degradates, and 17, were involved in sugarcane weeding. 1,811 results were positive, 1,407 results were quantified and 251 results had concentrations over the drinking water threshold (0.1 ppb). Sugarcane herbicides, including glyphosate, were responsible for 80% of the results over 0.1 ppb. Two sugarcane herbicides widely used in the past, atrazine and diuron, were responsible for 80% of the quantified results and 67% of the results over 0.1 ppb. Four herbicides currently in use have been found at concentrations over 0.1 ppb. They are being tested in the laboratory BRGM in order to assess the pollution risks for groundwater when applied on some native soils.

Materials and methods

OLE initiated the tracking of pesticides in freshwater in May 1999, the physico-chemical analyzes campaigns started in 1992 on 49 water points. The ARS, concerned about the sanitary quality of water intended for human consumption, did the same from the end of 2000 on 203 water points. The DEAL concerned with the quality of the surface water of 13 particular sites is the third actor.

The ‘Phytosanitary transfer’ compilation is ultimately based on a total of 384,627 analysis results of pesticide detection. This number includes all the OLE-DEAL analyzes and some of the ARS analyzes, those giving a positive result. The absence of ARS analyzes negative results preclude calculating absolute rates of positivity to a given substance. The period covered up to 2009 inclusive for OLE and DEAL with around a quarter of analyzes and until January 2010 for the ARS with about three quarters of the analyzes compiled.

With 18 water points common to ARS and OLE, the total number of sampling points amounts to 247, about three quarters ARS and a quarter OLE-DEAL. Those of the ARS relate for almost three quarters to ESO, while those of OLE-DEAL almost half relate to ESU. Overall, two thirds of the water points and analyzes concern ESOs. When compiling, the limits of quantification (LQ) of the AS, likely to change during the decade or between laboratories, have not been exhaustively identified. Some substances have been ‘detected’ without quantification, whereas within the meaning of the DCE a substance is considered ‘present’ if and only if it has been quantified: ‘proven’ pollution. Subsequently, the term ‘positive’ analyzes and ‘detected’ substances includes all the quantified and detected substances without quantification. Some ASs have unquantified detection rates for this period much more important than the average.

Results

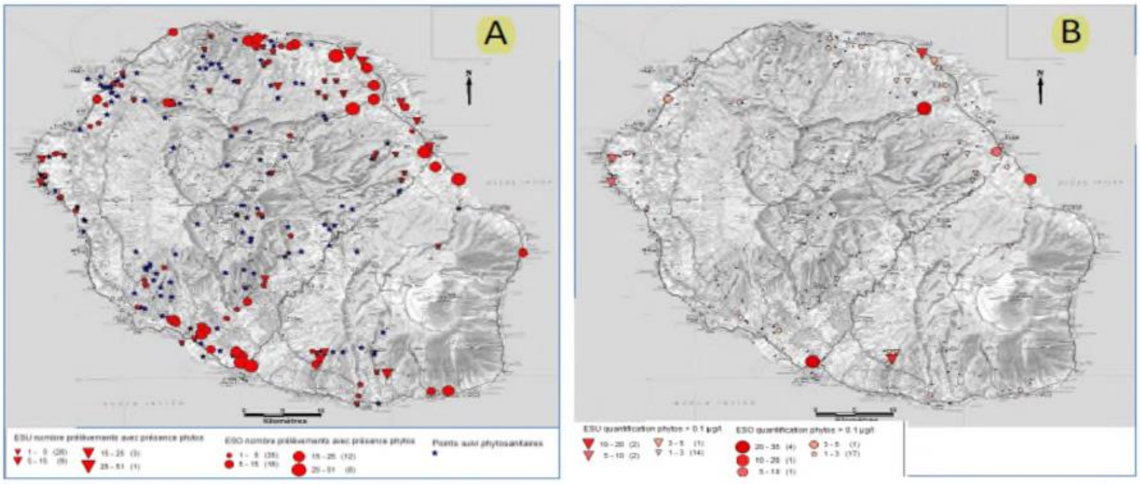
Regarding ARS, 43.8% of the water points were positive at least once to a pesticide (or metabolite) detected or quantified, while for the OLE-DEAL, this rate rises to 80.6% (55% globally).

Table 8.5-76 lists the 72 substances detected (including their metabolites) - 65 of which are present according to the meaning of the DCE - after 89,675 analyzes, values to be compared with the cumulation of 398 detected substances in more than 384,627 analyzes grouped together in this first decennial compilation (the negative analyzes of the ARS do not appear there). Noted are 1,811 positive analyzes, including 1,407 cases of proven pesticide presence and 251 case of exceeding the potability threshold of 0.1 µg/l. These results are graphically rendered, all substances combined, by the maps in Figure 8.5-53-A for detections, Figure 8.5-53-B for exceedances of the threshold of 0.1 µg/L (thereafter ‘exceedances’).

Figure 8.5-53: Monitoring pollution of freshwater by pesticides in Reunion Island, ARS + OLE + DEAL, period 1999-2010. ESU: surface water, ESO: groundwater.

A: Positive samples, B: > 0.1 µg/L results.

Monitoring of water pollution by pesticides, Reunion Island, 1999-2010. ESU: surface water, ESO: groundwater; A: positive results; B: results > 0.1 ppb.



Whether for ESO or ESU, these maps show the sites where pollution cases are recurring and those where they are occasional. The map of detections clearly shows the most exposed areas: the Northeast border (from Sainte-Rose to Sainte-Marie), and a part of the South-East border (between Saint- Leu and Saint-Pierre).

The map of exceedances reports about thirty sites victims of occasional pollution, as well as the ten or so sites that are victims of more frequent or even chronic pollution especially North of Saint- Pierre (BAC of Salette) and Sainte-Suzanne (BAC of Sainte-Vivienne) with more than 20 exceedances over the decade (for a frequency of 4 annual sampling in principle), and to a lesser extent Sainte-Anne (less than 20 exceedances over the decade).

Table 8.5-76: Pesticides in fresh waters (ESU + ESO) in Reunion, 1999-2010 period. Pesticides found in water, Reunion Island, 1999-2010.

#S	#H	CAS#	Phytosanitary Substances Detected or Quantified	Number of Analyzes	Number of Detections not Quantified	Number of Quantifications ≤ 0.1 µg	Number of Quantifications > 0.1 µg/l	For herbicides, main uses	status or year of withdrawal (*)
1	1	1	**desethylatrazine (DEA)**	1748	**66**	**525**	**150**	**Metabolite of atrazine**	
2	2	2	**diuron**	2012	43	136	15	**ex CAS**	**2008**
3	3	3	glyphosate	1054	0	1	9	TTG, CAS *et al*	Authorized
4	4	4	aminomethylphosphonic acid (AMPA)	1054	0	2	8	Metabolite of glyphosate	
5	5	5	hexazinone	1765	74	28	7	ex CAS	2007
6			DDE-4,4'	1148	0	0	6		
7			diazinon	1852	3	9	5		
8			DDD-4,4'	1150	0	0	5		
9			DDT-4,4'	1505	0	0	5		
10	6	6	bentazone	1549	14	13	4	Corn, meadow, peas, herbs, CAS tested	Authorized
11			endosulfan alpha	1901	0	0	4		
12	7	>>	2.4-MCPA	1417	0	0	3	TTG meadow, lawn	Authorized
13			endosulfan beta	1902	0	0	3		
14	8	7	**atrazine**	**1984**	79	271	2	Ex CAS	2003
15	9	8	metolachlore / S-metolachlore	1796	18	30	2	(ex CAS) + in CAS	Authorized
16	10	9	bromacil	1417	25	5	2	ex CAS	2003
17	11	10	2.4-D	1770	3	13	2	CAS	Authorized
18	12		metazachlore	1503	7	4	2	Cabbage, sunflowers, CAS tested	Authorized
19	13		aminotriazole	364	0	3	2	TTG, fruit trees, trees and bushes, corn	Authorized
20	14	11	metribuzine	1059	0	0	2	ex + in CAS	Authorized
21			oxadixyle	1769	4	20	1		
22	15		triclopyr	1547	1	7	1	TTG meadows (brush killer)	Authorized
23			cyprodinil	1149	1	3	1		
24	16		monuron	1061	3	3	1	Asparagus, vine	1994
25	17		isoproturon	1635	1	3	1	Cereals, lavender	Authorized
26			piperonyl butoxide	1096	1	1	1		
27			chlopyriphos ethyl	1906	2	3	1		
28	18		terbutryne	1069	0	0	1	Potatoes, peas, corn	2003
29			tebuconazole	356	2	0	1		
30			nonylphenols	250	1	0	1		
31	19	13	paraquat	718	0	0	1	TTG, ex CAS et al	2007
32	20		bromoxynil	1060	0	0	1	Meadows,, corn; CAS tested	
33	21		prometryne	1063	0	0	1	Lentils, carrots, leeks, celery	2007
34	22	14	**1- (3.4-dichlophenyl)-3-methylurea**	1054	20	30	0	Diuron metabolite	
35	23	(15)	alachlore	1939	3	6	0	Corn; CAS tested	2008
36	24		mecoprop	1414	2	5	0	Lawns	Authorized
37			anthraquinone	977	1	5	0		
38			cabendazime	1500	4	4	0		2009
39	25		oxadiazon	1794	0	4	0	TTG, fruit trees, wine, horticulture	Authorized
40	26		dichloprop-p (DDP)	1060	0	3	0	TTG, forests, meadows, lawns; CAS tested	Authorized
41			hch gamma	935	0	3	0		
42			imidaclopride	1056	5	2	0		
43	27	16	**deisopropylatrazine (DIA)**	**1067**	2	2	0	Metabolite of atrazine	
44	28		propyzamide	1194	1	2	0	Fruit trees, wine, forest, vegetables, horticulture	Authorized
45			mepiquat chlorure	356	1	2	0		
46			deltamethrine	1974	0	2	0		
47			fenirothion	1676	0	2	0		
48			Fipronil	1645	0	2	0		
49			permethrine	1097	0	2	0		
50	29	17	2.4, S-T	1062	0	2	0	Ex CAS	2003
51			thiabenzadole	968	0	2	0		
52			chloromequat chlorure	356	0	2	0		
53	30		acetochlore	976	4	1	0	Corn, CAS tested	(2007) 2013
54	31		ethofumsate	1062	1	1	0	Meadows, herbs	Authorized
55	32		Imazamethabenz	1057	1	1	0	Cereals	2007
56	33	>>	dicamba	976	1	1	0	TTG, meadows, ,awns, corn	Authorized
57			folpel	1663	0	1	0		
58			dinitrocresol	1572	0	1	0		
59			pentachlorophenol	1315	0	1	0		
60			DDT-2.4'	1151	0	1	0		
61			tolyfluanide	1062	0	1	0		
62			metalaxyle	1061	0	1	0		
63	34		dinoterbe	1058	0	1	0	Meadows, protein crops, corn	1997 (France)
64			azoxystrobine	974	0	1	0		
65			endosulfan	35	0	1	0		
66			metamidophos	8	0	1	0		
67			propoxur	1061	2	0	0		
68			temephos	1661	1	0	0		
69			fenpropidine	1416	1	0	0		
70			procymidone	1061	1	0	0		
71	35		metoxuron	1060	1	0	0	carrots	
72			propiconazole	1059	1	0	0		
73			spiroxamine	634	1	0	0		
			CUMULATED	89675	409	1176	251		
398	number of substances detected								

#S number of detected substances:, #H: herbicide-related, reported shaded, #HCAS: sugarcane-related, (x): non-approved CAS use, >>: post-2010 CAS use; TTG: general treatments; CAS: sugar cane, ex CAS: formerly CAS, in CAS: currently CAS, CAS et al. : use partly related to the CAS; (*) authorized is meant on 25 July 2013

N.B.: the number of analyzes includes all the OLE and DEAL analyzes but only the positive analyzes of the ARS.

Some of these ESO points are polluted by several substances at once with some cases of exceeding the threshold of 0.5 µg/L for the sum of the concentrations: 4 occurrences in Saint-Benoît and Sainte Anne. Still on the east coast, between Bras-Panon and Sainte-Suzanne, the ESU experienced in 2007 very intense pollution peaks, with sums of concentrations reaching 10 to 20 times the threshold value. These exceptional levels of pollution are to be linked to repeated heavy rains in the first half of 2007, probably erosive rains. That year, the cyclone Gamède, more active on the west coast, caused two occurrences of sums of concentrations 5 and 6 times the threshold of 0.5 µg/L. In the South, there are three cases of exceeding this threshold, two of which in very permeable terrain (very recent volcanic formations of the volcano of the Fournaise).

Table 8.5-76 indicates that among the 73 substances detected in the Reunion Island's fresh waters, 35 are herbicides or their metabolites, of which 17 (or 23.3%) are predominantly or partially related, currently or in the past to the weeding of cane. Table 8.5-77 details the impact of the 19 herbicides that have directly or via their metabolites exceeded the threshold of 0.1 µg/L; they alone are responsible for the 94% of proven pollution and 87% of exceedances. As a result, the remaining 6% of the remaining pollution is caused by other pesticides in larger number (52 substances). Cane or partially cane herbicides caused 91% of proven pollution and 80% of exceedances.

Table 8.5-77: Herbicides quantified above the threshold of potability (0.1 µg/L). Water pollution (ESU + ESO) in Reunion, period 1999-2010. Herbicides found in water at concentrations> 0.1 ppb, Reunion Island, 1999-2010.

H #	HCAS #		Quantification (Qt)		Quantifications> 0.1 µg/l		Qs/Qt
			Number of cases	%	Number of cases	%	%
		Reminder: All pesticides	1407	100.00%	251	100.00%	18%
		Among which herbicides	1320	93.8%	217	86.5%	16%
		Among which those linked to weeding of cane	1276	90.7%	201	80.1%	16%
1	1	Atrazine + DEA + DIA	950	67.5%	152	60.6%	16%
2	2	Diuron + its metabolite	181	12.9%	15	6%	8%
		Subtotal atrazine + diuron	1131	80.4%	167	66.5%	15%
3	3	Glyphosate + its metabolite (partially CAS)	20	1.4%	17	6.8%	85%
4	4	**Hexazinone (ex CAS)**	35	2.5%	7	2.8%	20%
5		Bentazone	17	1.2%	4	1.6%	24%
6		2.4-MCPA (meadows and soon CAS)	3	0.2%	3	1.2%	100%
7	5	**Metolachlore + S-metolachlore (CAS + miscellaneous)**	32	2.3%	2	0.8%	6%
8	6	**Bromacil (ex CAS)**	32	2.3%	2	0.8%	6%
9	7	**2.4-D (CAS + corn + meadows)**	15	1.1%	2	0.8%	13%
10		Metazachlore	6	0.4%	2	0.8%	33%
11		Aminotrazole	5	0.4%	2	0.8%	40%
12	8	**Metribuzine (CAS + tomatoes + potatoes)**	2	0.1%	2	0.8%	100%
		Subtotal (hexazinone + metibruzine	147	10.4%	26	10.4%	18%
13	9	Triclopyr (brush killer, borders CAS)	8	0.6%	1	0.4%	13%
14		Monuron	4	0.3%	1	0.4%	25%
15		Isoproturon	4	0.3%	1	0.4%	25%
16		Terbutryne	1	0.1%	1	0.4%	100%
17	10	Paraquat (partially ex CAS)	1	0.1%	1	0.4%	100%
18		Bromoxynil	1	0.1%	1	0.4%	100%
19		Prometryne	1	0.1%	1	0.4%	100%
		Sub-total (triclopyr – prometryne)	20	1.4%	7	2.8%	35%

CAS Sugar cane, #H Number of herbicides #HCAS: Number of CAS herbicides

Aftereffects of some Old Fashioned Cane Sugar Herbicides…

The two most frequent cases of exceedances concern two old herbicides massively used with sugar cane, atrazine - withdrawn in 2003 - and diuron - withdrawn in 2008; with their metabolites, they are responsible for 80% of cases of proven pollution or 66.5% of cases of exceedances of the potability threshold (0.1 µg/L) (Table 8.5-77). Glyphosate, for which we consider lacking better estimate that it would be used for half on sugar cane, comes in third position with a 1.4% contribution to proven pollution which amounts to 6.8% of cases exceeding the thresholds. These 3 herbicides are therefore responsible in their own right for 82% of proven pollution and 73% of cases of exceeding the threshold of potability during the decade.

The cases of exceedances of the threshold of potability related to the cases of proven presence give an average ratio of 18% for all pesticides and 16% for all herbicides or cane herbicides (Table 8.5-77). This ratio hides nevertheless significant variations: 6% for the metolachlor, 8% for diuron, 16% for atrazine, 20% for hexazinone and 85% for glyphosate.

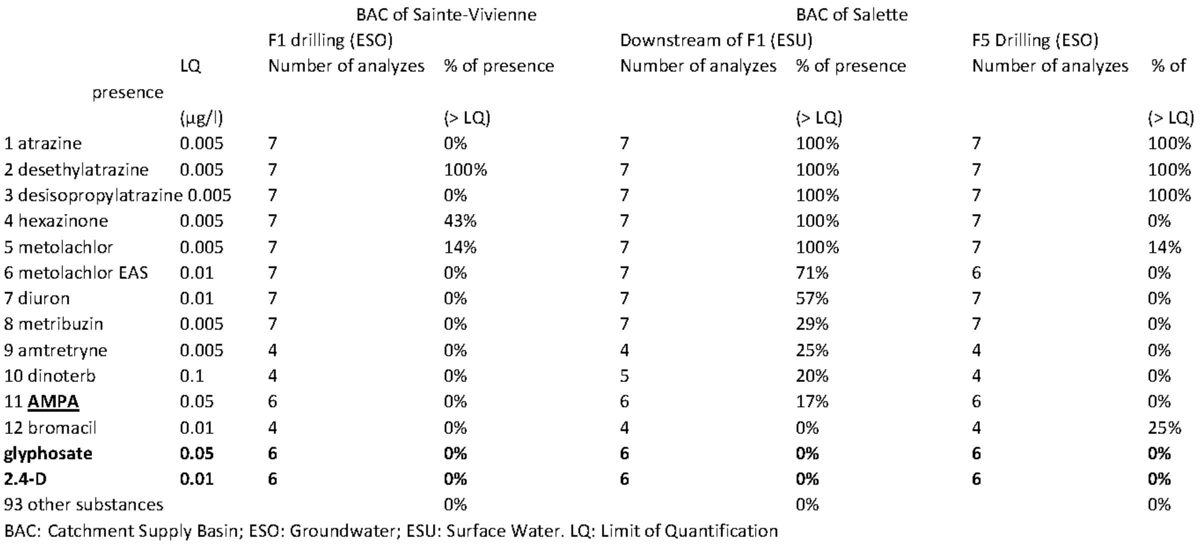
Of the 7 herbicides that exceeded the threshold one time, there is no herbicide dedicated to cane weeding. Two herbicides could nevertheless be used by cane growers: paraquat (banned since 2007) on glyphosate-type uses (preparation of the ground before planting, or associated with pre-emergence herbicides, or in treatment directed at the foot of the cane post-emergence): triclopyr, brush cutter approved on meadows or in general treatments of paths and borders, totally selective of grasses, sometimes used to devitalize the perennials at the edge of the fields, or sometimes even within localized treatments.

Particularly Persistent

As part of the Phytos Transfer Project, BRGM has undertaken to characterize the risks of diffuse pollution from the study of two of the most polluted priority BACs, that of Sainte- Vivienne, on the eastern very rainy slope (> 3m/year), and that of La Salette, on the western less rainy slope (<1m/year). Risks will be assessed from field surveys of agricultural practices and laboratory tests. These are aimed at determining the adsorption dynamics and degrading four cane herbicide, and ultimately their GUS (Groundwater ubiquity score) from soil samples that are agriculturally representative. These four herbicides are 2.4-D, S-metolachlor, metribuzin and glyphosate; historical herbicides still in use, they are widely used and have some instances of exceedances to their liabilities (respectively 2 + 2 + 2 + 17, Table 8.5-77). In this context, specific water samples were collected monthly from both BACs to track 106 pesticides or their metabolites (mainly herbicides) between September 2011 and April 2012. The list of 106 is not a strict subset of the list of 398 because it includes for example both metabolites metolachlor, absent from the list of 398.

Twelve substances were quantified, all related to herbicides, mainly cane herbicides (with the exception of dinoterbe, and partially glyphosate). Table 8.5-78 reports a single case of pollution with AMPA (glyphosate metabolite) in St. Vivienne ESU. Glyphosate is like metolachlor and metribuzin already an aged herbicide in terms of use, although at the time of atrazine it was probably less used than today, paraquat being available.

Table 8.5-78: The 12 pesticides present in the waters taken from the BACs of Sainte-Vivienne (municipality of Sainte-Suzanne) and La Salette (municipality of Saint-Pierre) between September 2011 and April 2012 as part of the BRGM Phyto Transfer Project (monthly remittances).



		BAC of Sainte-Vivienne		BAC of Salette			
		F1 drilling (ESO)		Downstream of F1 (ESU)		F5 Drilling (ESO)	
	LQ (µg/l)	Number of analyzes	% of presence (> LQ)	Number of analyzes	% of presence (> LQ)	Number of analyzes	% of presence (> LQ)
1 atrazine	0.005	7	0%	7	100%	7	100%
2 desethylatrazine	0.005	7	100%	7	100%	7	100%
3 desisopropylatrazine	0.005	7	0%	7	100%	7	100%
4 hexazinone	0.005	7	43%	7	100%	7	0%
5 metolachlor	0.005	7	14%	7	100%	7	14%
6 metolachlor EAS	0.01	7	0%	7	71%	6	0%
7 diuron	0.01	7	0%	7	57%	7	0%
8 metribuzin	0.005	7	0%	7	29%	7	0%
9 amtretryne	0.005	4	0%	4	25%	4	0%
10 dinoterb	0.1	4	0%	5	20%	4	0%
11 **AMPA**	0.05	6	0%	6	17%	6	0%
12 bromacil	0.01	4	0%	4	0%	4	25%
glyphosate	**0.05**	**6**	**0%**	**6**	**0%**	**6**	**0%**
2.4-D	**0.01**	**6**	**0%**	**6**	**0%**	**6**	**0%**
93 other substances			0%		0%		0%

BAC: Catchment Supply Basin; ESO: Groundwater; ESU: Surface Water. LQ: Limit of Quantification

Conclusion

The high inertia of pesticide pollution phenomena affecting freshwater resources can be explained by the average age of the groundwater, between their entry into the soil, their percolation in the unsaturated zone via draining rains and their removal from a source or borehole. As part of the Phytos Transfer Project, the BRGM estimated the average stay times of several situations in Reunion Island to often several decades. The case of the delayed impact of old sugarcane herbicides in Reunion Island is particularly demonstrative, in particular for atrazine and diuron, responsible for 67% of exceedances and 73% of detections.

However, the average age of water affects all herbicides in the same way. The risks of diffuse pollution are linked on the one hand to the quantities applied and on the other hand to the characteristics intrinsic properties of cross-products with the properties of surface soils and the conditions of application, including the prevailing weather conditions during the preceding days and the days following the spreading.

Assessment and conclusion by applicant:
The article summarizes the results of monitoring pesticides in groundwater and surface water conducted by the responsible authorities of Reunion Island. As the data were generated by authorities, it is assumed to be quality assured (even though no details on sample collection and analytical methods are reported). Application of herbicides to sugar cane on Reunion Island is considered only limited representative for European conditions.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:
No measured concentration are available from this study. Moreover, it should be noted the results are given for both groundwater and surface and cannot be separated. Overall two thirds of the 247 water points and analyses concern groundwater.
Glyphosate is reported to be the third more frequently detected pesticide above >0.1 µg/L in groundwater/surface water, although representing no more than 7 % of the total pesticide detection above the trigger.
The article is considered reliable with restrictions.

Data point:	CA 7.5/024
Report author	Mörtl, M. *et al*.
Report year	2013
Report title	Determination of glyphosate residues in Hungarian water samples by immunoassay
Document No	Microchemical Journal 107 (2013) 143–151
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities (Central Food Research Institute, Hungary)
Acceptability/Reliability:	Reliable with restrictions

An enzyme-linked immunosorbent assay (ELISA) for the detection of glyphosate was investigated for assay performance characteristics and was applied for determination of glyphosate contamination levels in selected surface and ground water resources in Hungary in 2010 and 2011. Advantages of the method include its simplicity (no laborious extraction) and specificity (cross-reactivity is below 0.1% for related compounds, e.g. aminomethyl-phosphonic acid, glufosinate). On the basis of our experiments, the practical limit of detection (LOD) ranged between 0.05 and 0.12 ng/mL. The standard curve was of sigmoid (logistic) characteristics, and it co-occurred with curves obtained for spiked surface water samples. Matrix effects were observed in tap water, possibly due to chlorination and/or heavy metal ions, e.g. copper and zinc. The method was applied for the analysis of 42 surface and ground water samples collected from Békés county in Hungary at 14 sampling sites in 2010 and 18 surface water samples collected from the Danube River and Lake Velencei in Hungary at 12 sampling sites in 2011. Exceedingly high glyphosate levels (nearly 1 ng/mL) were measured in 5 samples, and significant concentrations were determined in 16 cases (0.54-0.76 ng/mL) in 2010, while practically no contamination was found in 2011. The great contrast between the two sampling regimes is explained by differing agricultural locations, natural precipitation and, to a greater extent, catchment area characteristics, resulting in varying leaching or run-off of glyphosate to surface waters.

Materials and Methods

Reagents

The glyphosate analytical standard (Pestanal grade), Amberlite IR 120 strongly acidic cation exchange resin and all reagents were purchased commercially.

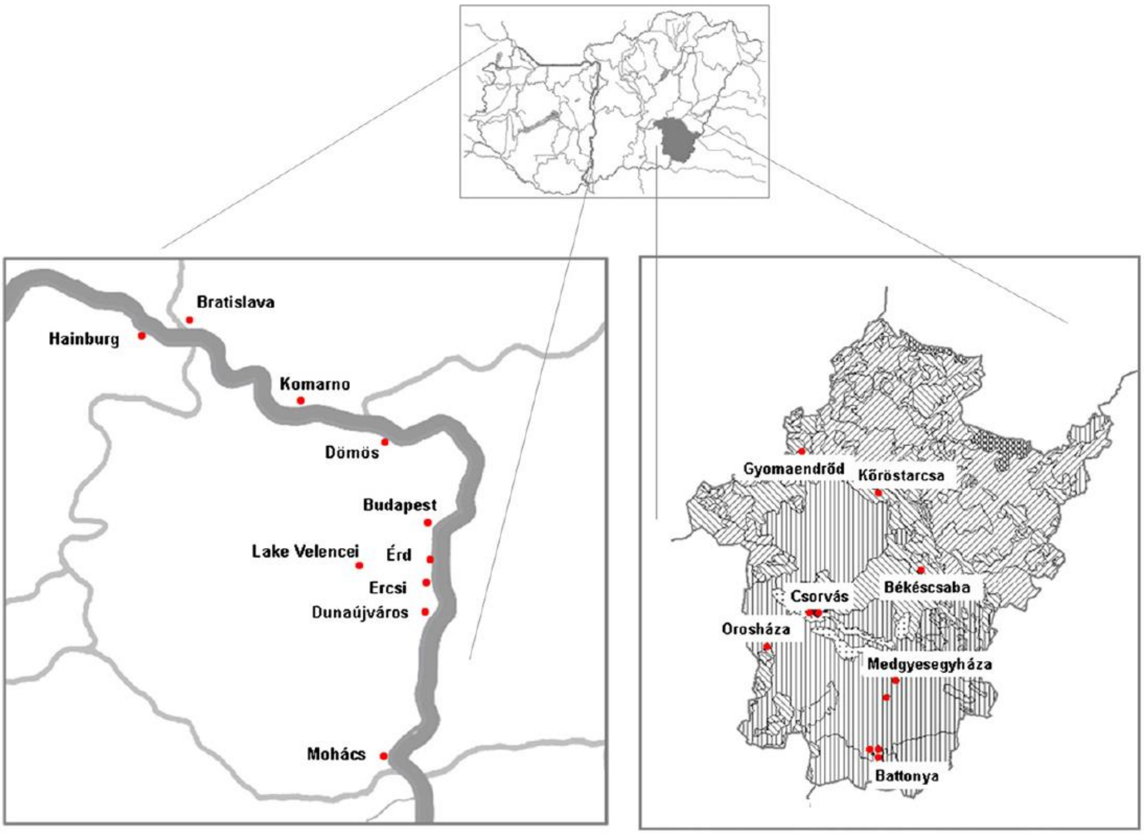
ELISA

For immunoanalytical detection of glyphosate, the commercially available ELISA method by Abraxis LLC was used.

Calibration, limits of detection and matrix effects

Calibration curves were established with standard solutions provided by Abraxis at five concentration levels between 0.075 and 4.0 ng/mL (0, 0.075, 0.2, 0.5, 1.0, 4.0 ng/mL), two replicates each. An analytical quality control solution (0.75 ng/mL) was also used. LODs, defined as glyphosate concentration causing 10 % decrease in the optical assay signal, i.e. 90 % B/B_0 (where B/B_0 is the signal obtained with the given sample divided by the maximum signal obtained with a sample containing no glyphosate), were determined in all experiments. For investigation of matrix effects, a stock solution of glyphosate (1.0 mg/ml) was prepared in MilliQ water. This solution was diluted to 0.1 µg/mL (spike solution). Solutions containing glyphosate at final concentrations (typically 0.075, 0.2, 0.5, 1.0, 4.0 ng/mL) were made by addition of appropriate amounts of spike solution to different water matrices.

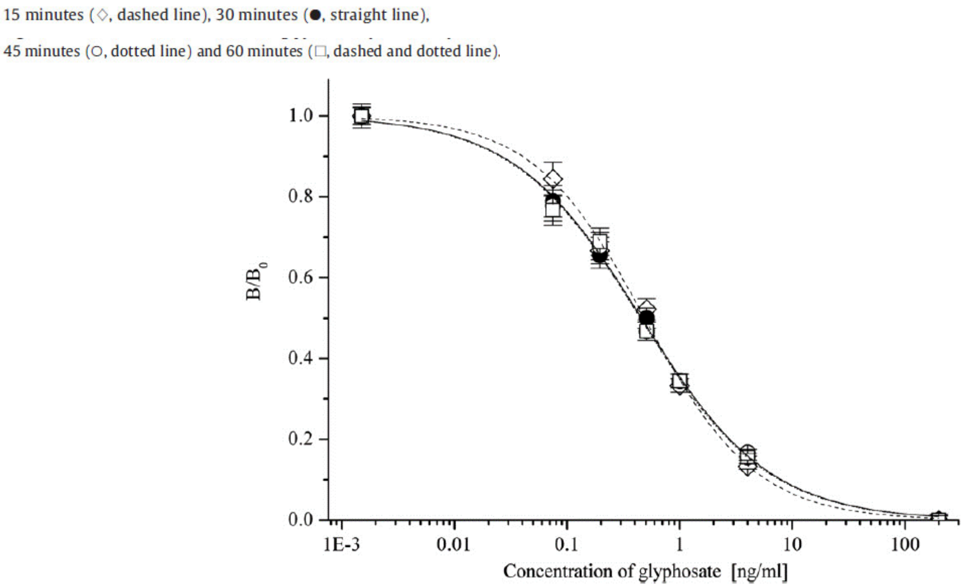
Figure 8.5-54: Sampling sites in Hungary along the Danube and in Békés county



Influence of sample preparation

The influence of different sample preparation steps proposed by Küsters *et al*. for drinking water has also been investigated. Briefly, for the cleanup of spiked water samples, the cation exchange resin Amberlite IR 120 was converted to sodium form. This, and all subsequent column regeneration steps after each sample, was carried out with a 4 M sodium chloride solution. Then, each sample was passed through the cation exchange column, followed by washing with deionized water. All eluates were collected in round bottom flasks and then evaporated to dryness. The residues obtained were dissolved in deionized water. After each sample preparation step, concentrations of glyphosate were determined by ELISA, with concentrations obtained corrected according to the volume change.

Figure 8.5-55: Standard calibration curve in the glyphosate-specific competitive ELISA, and the effect of preincubation



15 minutes (◇, dashed line), 30 minutes (●, straight line),

45 minutes (○, dotted line) and 60 minutes (□, dashed and dotted line).

Sample collection

Municipal water at the laboratory site (II. District, Budapest, Hungary) was used as tap water. Field samples were collected in amber glass bottles previously washed with aqueous hydrochloric acid (pH 2) and repeatedly rinsed with deionized water. During sampling, the bottles were rinsed twice with the water sampled, then filled and tightly capped. Samples were stored at 4°C in the dark. In the scope of a national environmental survey, 42 water samples (6 surface water and 36 ground water samples) were obtained on September 7-8, 2010, from 14 sampling sites in Békés county, Hungary. In addition, 18 surface water samples were collected on October 1, 2011, from 11 sampling sites along the Danube River and one site at Lake Velencei, Hungary. The sampling sites are depicted on Figure 8.5-54.

Figure 8.5-56: **Matrix effects in the glyphosate-specific competitive ELSA indicated by standard calibration curves obtained in assay matrix**

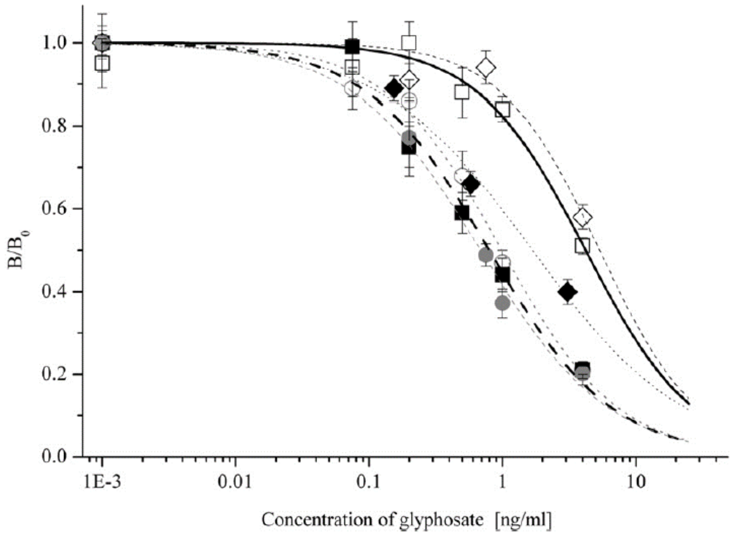
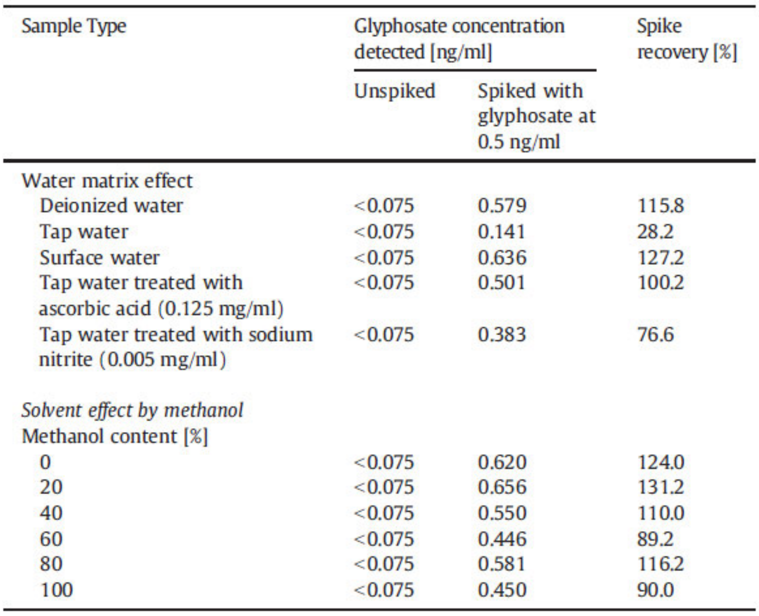


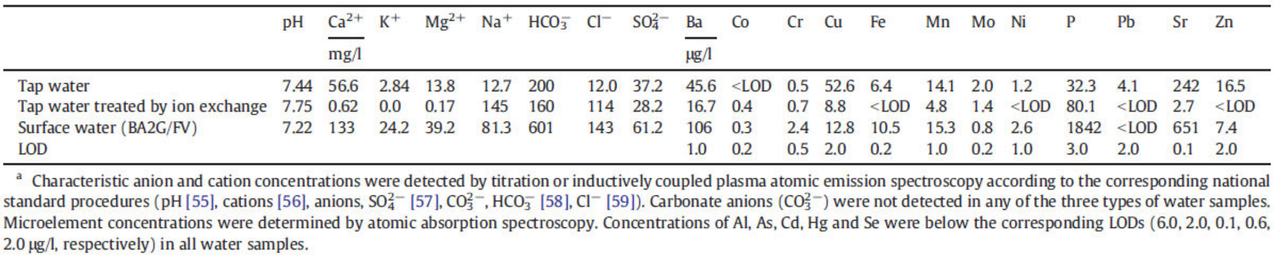
Fig. 3. Matrix effects in the glyphosate-specific competitive ELISA indicated by standard calibration curves obtained in assay matrix (○, gray dotted line), distilled water (●, gray dashed line), tap water (□, thick solid line), tap water treated by cation exchange and spiked (■, thick dashed line), tap water spiked and treated by cation exchange (◆, dotted line) and tap water spiked, treated by cation exchange, evaporated and resolved in distilled water (◇, dashed line).

Table 8.5-79: **Detected glyphosate concentrations and corresponding recoveries in unspiked and spiked water samples as a measure of matrix effects on ELISA performance**



Sample Type	Glyphosate concentration detected [ng/ml]		Spike recovery [%]
	Unspiked	Spiked with glyphosate at 0.5 ng/ml	
Water matrix effect			
Deionized water	<0.075	0.579	115.8
Tap water	<0.075	0.141	28.2
Surface water	<0.075	0.636	127.2
Tap water treated with ascorbic acid (0.125 mg/ml)	<0.075	0.501	100.2
Tap water treated with sodium nitrite (0.005 mg/ml)	<0.075	0.383	76.6
Solvent effect by methanol			
Methanol content [%]			
0	<0.075	0.620	124.0
20	<0.075	0.656	131.2
40	<0.075	0.550	110.0
60	<0.075	0.446	89.2
80	<0.075	0.581	116.2
100	<0.075	0.450	90.0

Table 8.5-80: Compositional characteristics of the water types studied[a]



	pH	Ca^{2+}	K^+	Mg^{2+}	Na^+	HCO_3^-	Cl^-	SO_4^{2-}	Ba	Co	Cr	Cu	Fe	Mn	Mo	Ni	P	Pb	Sr	Zn
		mg/l							µg/l											
Tap water	7.44	56.6	2.84	13.8	12.7	200	12.0	37.2	45.6	<LOD	0.5	52.6	6.4	14.1	2.0	1.2	32.3	4.1	242	16.5
Tap water treated by ion exchange	7.75	0.62	0.0	0.17	145	160	114	28.2	16.7	0.4	0.7	8.8	<LOD	4.8	1.4	<LOD	80.1	<LOD	2.7	<LOD
Surface water (BA2G/FV)	7.22	133	24.2	39.2	81.3	601	143	61.2	106	0.3	2.4	12.8	10.5	15.3	0.8	2.6	1842	<LOD	651	7.4
LOD									1.0	0.2	0.5	2.0	0.2	1.0	0.2	1.0	3.0	2.0	0.1	2.0

[a] Characteristic anion and cation concentrations were detected by titration or inductively coupled plasma atomic emission spectroscopy according to the corresponding national standard procedures (pH [55], cations [56], anions, SO_4^{2-} [57], CO_3^{2-}, HCO_3^- [58], Cl^- [59]). Carbonate anions (CO_3^{2-}) were not detected in any of the three types of water samples. Microelement concentrations were determined by atomic absorption spectroscopy. Concentrations of Al, As, Cd, Hg and Se were below the corresponding LODs (6.0, 2.0, 0.1, 0.6, 2.0 µg/l, respectively) in all water samples.

Results and Discussion

Assay performance

The Abraxis glyphosate ELISA kit applies the principle of the competitive immunoassay, with prior sample derivatization by acetic anhydride. A unique feature of the ELISA is that two key steps of the protocol are carried out simultaneously: the derivatized analyte is preincubated with glyphosate-specific antibodies, and the latter are bound to IgG-specific antibodies immobilized on the solid surface of the microwells of the ELISA plate. The competitive ELISA provides a sigmoid (logistic) standard curve downward with increasing glyphosate concentration (Figure 8.5-55). Typical analytical parameters of the immunoassay carried out in buffer were analyte concentration resulting in 50% inhibition of the assay signal (IC_{50}) at 0.66 ± 0.16 ng/mL, slope of the standard curve at the IC_{50} at 1.52 ± 0.76 ng/mL, and LOD at 0.05 ng/mL. This LOD value is the 90% B/B_0, commonly used to indicate sensitivity, which is the estimated minimum detectable concentration based on 90% binding (10 % inhibition) in the assay. The concentration of the first calibration standard was 0.075 ng/mL. Although levels between 0.05 ng/mL and 0.075 ng/mL are within the detectable range of the assay, as with any analytical technique (ELISA, GC, etc.), there must be valid calibration points on either side of a sample value to be considered a legally defensible, valid sample result. As the results for these samples were all below the first standard (0.075 ng/mL), Table 8.5-79 lists the results for the unspiked samples (with no glyphosate detected) as <0.075 ng/mL, rather than giving a (less exact) value below the calibration range of the assay. The ELISA is highly specific for glyphosate: cross-reactivities of related compounds, including main metabolites AMPA and glycine; glufosinate, an herbicide active ingredient of related chemical structure; and glyphosine, a withdrawn fungicide active ingredient of related chemical structure, were all below 0.1% as calculated at both the LOD and at the IC_{50} of each compound.

Table 8.5-81: **Detected glyphosate concentrations in surface and groundwater samples collected in Hungary in 2010 and 2011**

Sample code	Type of water	Sampling site	Glyphosate concentration detected (ng/ml)
2010 sampling regime			
BA1F/FV	Surface water	Battonya	0.12 ± 0.085
BA1G/FV	Surface water	Battonya	0.17 ± 0.013
BA2F/FV	Surface water	Battonya	0.27 ± 0.131
BA2G/FV	Surface water	Battonya	0.68 ± 0.090
BA3F/FV	Surface water	Battonya	0.66 ± 0.150
BA3G/FV	Surface water	Battonya	0.63 ± 0.070
CSP1/TV	Ground water	Csorvás	0.65 ± 0.130
CSP2/TV	Ground water	Csorvás	0.82 ± 0.040
CS1F/TV	Ground water	Csorvás	0.68 ± 0.120
KT2F/TV	Ground water	Kőröstarcsa	0.76 ± 0.040
KT2G/TV	Ground water	Kőröstarcsa	0.41 ± 0.040
MH2F/TV	Ground water	Medgyesegyháza	0.75 ± 0.080
BSZ1A/TV	Ground water	Békéscsaba	0.93 ± 0.080
BSZ1B/TV	Ground water	Békéscsaba	0.60 ± 0.050
BSZ1C/TV	Ground water	Békéscsaba	0.44 ± 0.001
BSZ1D/TV	Ground water	Békéscsaba	0.46 ± 0.107
BSZ1E/TV	Ground water	Békéscsaba	0.66 ± 0.100
BSZ1F/TV	Ground water	Békéscsaba	0.42 ± 0.009
GYN1A/TV	Ground water	Gyomaendrőd	0.33 ± 0.066
GYN1B/TV	Ground water	Gyomaendrőd	0.43 ± 0.069
GYN1C/TV	Ground water	Gyomaendrőd	0.98 ± 0.003
GYN1D/TV	Ground water	Gyomaendrőd	0.56 ± 0.260
GYN1E/TV	Ground water	Gyomaendrőd	0.33 ± 0.055
GYN1F/TV	Ground water	Gyomaendrőd	0.35 ± 0.012
GYN1G/TV	Ground water	Gyomaendrőd	0.63 ± 0.040
GYN1H/TV	Ground water	Gyomaendrőd	0.59 ± 0.040
GYN1I/TV	Ground water	Gyomaendrőd	0.25 ± 0.009
GYN1J/TV	Ground water	Gyomaendrőd	0.59 ± 0.110
GYN1K/TV	Ground water	Gyomaendrőd	0.87 ± 0.080
OŰ1A/TV	Ground water	Orosháza	0.39 ± 0.063
OK1A/TV	Ground water	Orosháza	0.39 ± 0.07
OK1D/TV	Ground water	Orosháza	0.38 ± 0.011
OK1E/TV	Ground water	Orosháza	0.33 ± 0.186
OK1F/TV	Ground water	Orosháza	0.35 ± 0.122
OK1H/TV	Ground water	Orosháza	0.31 ± 0.031
OK1G/TV	Ground water	Orosháza	0.66 ± 0.040
OK1I/TV	Ground water	Orosháza	0.96 ± 0.100
OK1B/TV/c	Ground water	Orosháza	0.58 ± 0.060
OK1C/TV/b	Ground water	Orosháza	0.30 ± 0.019
OK1K/TV	Ground water	Orosháza	0.33 ± 0.009
OK1L/TV	Ground water	Orosháza	0.33 ± 0.046
OK1M/TV	Ground water	Orosháza	0.54 ± 0.003
2011 sampling regime			
DH1/FV	Surface water	Hainburg	<LOD[a]
DB1/FV	Surface water	Bratislava	<LOD
DKM1/FV	Surface water	Komarno-bridge	<LOD
DKM2/FV	Surface water	Komarno-bridge	<LOD
DDO1/FV	Surface water	Dömös-riverbank	<LOD
DDO2/FV	Surface water	Dömös-riverbank	0.043 ± 0.009[b]
DL1/FV	Surface water	Luppa-island	<LOD
DL2/FV	Surface water	Luppa-island	<LOD
DDU1/FV	Surface water	Dunaújváros	<LOD
DKP1/FV	Surface water	Kopaszi gát-dam	<LOD
DKP2/FV	Surface water	Kopaszi gát-dam	0.035 ± 0.017
DED1/FV	Surface water	Érd	<LOD
DED2/FV	Surface water	Érd	<LOD
DER1/FV	Surface water	Ercsi	<LOD
DER2/FV	Surface water	Ercsi	<LOD
DDU2/FV	Surface water	Tököl-backwater	<LOD
DM1/FV	Surface water	Mohács	<LOD
V1/FV	Surface water	Lake Velencei	0.064 ± 0.021

[a] LOD is estimated to be 0.05 ng/ml (on the basis of 90% B/B_0) and 0.12 ng/ml (on the basis of the value and standard deviation of the upper plateau of the sigmoid standard curve).

[b] Detected values are near the LOD (on the basis of 90% B/B_0).

The effect of preincubation

Preincubation of the sample with the specific antibody is a key element in the achievable analytical sensitivity of the immunoassay. Longer preincubation of the antibodies with the free analyte (sample) allows antibody binding to approach equilibrium and should therefore favorably affect assay sensitivity. Results from the present study carried out to determine whether increasing the preincubation, up to 60 minutes, would provide an increase in sensitivity which would justify the additional analysis time. Thus, the effect of preincubation time with glyphosate at various concentrations (between 0.075 and 4.0 ng/mL) was tested. Experiments were carried out using four preincubation durations (ranging from 15 to 60 minutes) and are depicted in Figure 8.5-55. As seen on the resulting sigmoid curves, the duration of preincubation resulted in a moderate improvement in the reproducibility of the analytical standard curves, as those obtained with 30-60 minute preincubation were practically identical to each other. In consequence, the very slight improvement noted with the 45 minute preincubation, as opposed to the 30 minute preincubation, was not considered significant enough to justify the additional analysis time. Other assay parameters did not show dependence on the preincubation time of 15-60 minutes, i.e. the IC_{50} values were found to be 0.59, 0.46, 0.45 and 0.45 ng/mL at preincubation times of 15, 30, 45 and 60 minutes, respectively. Corresponding LOD values, calculated at 90% of the upper plateau of the sigmoid curve, were 0.069, 0.032, 0.025 and 0.022 ng/ml, respectively. The 30 minute preincubation resulted in a significant improvement in IC_{50} and LOD when compared to the 15 minute preincubation.

Solvent effect

In the present study, solutions containing various concentrations of methanol in deionized water were analyzed unspiked and spiked with 0.5 ng/ml of glyphosate, and achievable recoveries were recorded. Methanol (applied at 0%, 20%, 40%, 60%, 80% and 100%) did not produce false positive results up to 100 % in the ELISA (Table 8.5-79). This is due to the beneficial buffering effect of the assay medium allowing the use of sample solutions even in pure methanol, as the final solvent content is diluted to 20% in this case. Spiked samples with methanol concentrations up to 100% showed spike recoveries of 89.2-131.2%, with overestimation (recoveries above 100%) at low methanol content.

Matrix effects

In this study, no matrix effects were seen for surface water, but considerable matrix effects were observed for spiked tap water, with a curve shift towards higher concentrations (Figure 8.5-56). This matrix effect, however, was eliminated if tap water was processed by distillation or ion exchange, changing all cations to sodium ions, and then spiked. This indicated that the component(s) causing the matrix effect in tap water can be removed. Moreover, as the standard curve in distilled water runs closely to those in ion exchanged water and assay buffer, the assay is insensitive to ionic strengths between 0 (distilled water) and 0.41 M (phosphate buffered saline), due to the buffering effect seen for high organic solvent (methanol) tolerance as well. In contrast, applying ion exchange after spiking could not fully eliminate the matrix effect and resulted in a standard curve with an approximately 30% lower slope than that of the standard curve in assay buffer. After evaporation of water to dryness and solution of residue the curve obtained was practically the same as for tap water itself indicating that the component possibly causing the matrix effect is non-volatile, e.g. partly non-volatile disinfection by-products of chlorination.

To evaluate the possible effects of chlorine applied in water treatment, various water samples (deionized water, tap water, and surface water) were analyzed unspiked and spiked with 0.5 ng/mL of glyphosate, and achievable recoveries were recorded (Table 8.5-79). No false positives were detected in any of the water samples. Good spike recoveries were seen in deionized water and surface water samples. The spike recovery for tap water showed a biased low recovery (28.2%), due to matrix interference, possibly from chlorine. To test possible involvement of chlorine used for tap water purification, unspiked and spiked tap water samples were then treated with either ascorbic acid or with sodium nitrite (commonly used dechlorinating agents) at final concentrations of 0.125 and 0.005 mg/mL, respectively. The treated water samples were vortexed thoroughly and were then derivatized and analyzed by the ELISA protocol. As seen from the resultant data, treatment with ascorbic acid prior to analysis neutralized the matrix interferences from chlorinated tap water samples, allowing accurate analyte recovery. To exclude possible matrix interferences by ascorbic acid, unspiked samples were treated along with the glyphosate-spiked tap waters. These unspiked ascorbic acid treated tap water samples did not show any recovery. Treatment with sodium nitrite also resulted in the elimination of the matrix interference and improved recovery, although to a lesser extent.

To further differentiate between chemical and mineral composition of the water samples used, characteristics of tap water, ion exchanged tap water, and surface water are summarized in Table 8.5-80. There is only a slight difference in the composition of surface and tap water; concentrations of copper and zinc were higher in the tap waters than in the surface waters examined. Since spiked surface water samples did not show any matrix effects, the interference observed in tap water may arise from complex formation by glyphosate with the copper or zinc content of tap water. Organic matter content in water must also be taken into account, as it may act as a limiting factor of complex formation. In principle, ascorbic acid, used as a dechlorinating agent to eliminate matrix effects by chlorine (see above), could interact with the copper content in tap water (e.g. reducing Cu(II) to Cu(I), or forming chelates with Cu(II)) as established in quantitative antioxidant capacity assays. Biochemically important amino acids however, inhibit this catalytic autoxidation of ascorbic acid due to the high conditional stability constant of their Cu-complexes. Being a phosphonate derivative of glycine, glyphosate also shows higher affinity to Cu(II) ions than ascorbic acid. Therefore, an eliminatory effect of ascorbic acid on matrix effects caused by Cu(II) is not expected.

Analysis in field samples

The study area in the case of contamination of agricultural origin covered four settlements in Békés county (Kőröstarcsa,Medgyesegyháza, Csorvás, and Battonya). Both intensive and organic parcels were chosen in all four settlements (4 organic and 4 intensive), and the pasture was designated in Csorvás. Contamination of industrial origin was examined in three settlements in Békés county (Orosháza, Gyomaendrőd, and Békéscsaba) at five sites (Orosháza-Linamar, Orosháza-Közútkezelő, Orosháza-Üveggyár, Gyomaendrőd-Nagylapos, and Békéscsaba-Szennyvíztelep). The subsequent 2011 sampling regime focused on the Danube River and its catchment area. Altogether, 17 surface water samples were collected from the Danube River in the Middle and Lower Danube region from the Austrian-Slovakian border to the Hungarian-Croatian border, and one standing water sample from Lake Velencei.

Glyphosate content was determined in all surface and ground waters collected using the Abraxis ELISA method. The practical LOD was found to be 0.12 ng/mL as calculated from the value and standard deviation of the upper plateau of the sigmoid standard curve (as opposed to the 0.05 ng/ml LOD value determined from the 90% B/B_0 value and the concentration of the lowest analytical standard). A stunning difference between the results of the two sampling regimes in 2010 and 2011 was that while all samples collected in the first year contained detectable levels of glyphosate, only a slight proportion of the samples obtained in the second year had detectable glyphosate concentrations (Table 8.5-81). In 2010, severely or significantly contaminated samples represent half of the surface water samples obtained in the given sampling regime. In contrast, in 2011 glyphosate concentrations detected in the Danube River samples remained, in the vast majority, below the LOD of the assay (0.05 ppb) specified by the manufacturer on the basis of 90% B/B_0. Only the sample from Lake Velencei showed a concentration higher than the LOD (0.064 ng/ml), while two other samples from the Danube River (Dömös, Kopaszi gát) were near the LOD (0.043 and 0.035 ng/mL, respectively). There are at least two characteristic differences between the two sampling regimes in 2010 and 2011: sampling location and meteorological characteristics prior to and during sampling. Findings in the 2010 campaign of the present survey did not indicate a statistically significant difference in detected glyphosate concentrations in surface and ground water: detected glyphosate concentrations in surface water were 0.422 ± 0.271 ng/mL (with average concentrations in individual samples ranging between 0.12 and 0.68 ng/mL), while corresponding concentrations in ground water were found to be 0.537 ± 0.224 ng/mL (0.5 - 0.98 ng/ml). In our survey in 2011, in contrast to 2010, due to the drought period and the lack of rain events prior to sampling, glyphosate applied in September most likely remained bound to soil particles and was not leached from the fields by the date of sampling (Oct 1, 2011).

The sharp contrast between the contamination rates found in the two campaigns is likely largely due to regional differences (different catchment areas and agricultural circumstances), and partly by meteorological differences between the two years (a major difference in natural precipitation). The 2010 samples were collected in early autumn after a rainy summer. These findings are in agreement with glyphosate contamination reported in environmental water contamination studies. In the United States, surface water contamination has been reported due to run-off from agricultural areas or pesticide drift.

Conclusion

In conclusion, ELISA is a suitable and convenient method for glyphosate detection and has been successfully applied to surface and ground water samples. Although the lack of cross-reactivity with AMPA and the cost may hinder its widespread application, ELISA is still more cost-effective for routine analysis, especially in monitoring programs, as compared with traditional wet chemistry methods, if all sample preparation/measurement steps and the instrumental demand are all considered. In order to obtain more accurate results and eliminate matrix effects, characteristics of the water sample to be analyzed must be taken into account. As matrix effects were not experienced at all with surface water, the ELISA method appears to be readily applicable to surface water samples. Significant matrix effects were, however, experienced with tap water, indicating that the chlorine content of drinking water and/or the presence of multivalent cations may cause a considerable bias resulting in lower glyphosate content measured. Such effect was not eliminated by evaporation and subsequent resolution in water, yet was successfully eliminated by reducing agents such as ascorbic acid.

The level of glyphosate pollution in surface water detected in environmental studies may vary tremendously among locations and years of sampling, as glyphosate is strongly influenced by precipitation. Rain events result in the leaching of glyphosate from soil, due to its high-water solubility. In this way, glyphosate may contaminate surface water and locations distant from its application site. This effect was seen in the current study. In spite of the fact that cultivation of GT crops is prohibited in Hungary, glyphosate was found at significant concentrations in surface water and ground water samples after a rainy period in 2010. In contrast, samples from a different catchment area, the Danube River, after a dry period in 2011 were found not to be contaminated by this target analyte.

Assessment and conclusion by applicant:

The article describes a monitoring study where immunoassay analytical method was used. Several findings in different compartments (surface waters, ground water) were reported. Methods and results are sufficiently described.

The article is considered reliable.

Assessment and conclusion by RMS:

The article describes a monitoring study where immunoassay analytical method was used. In the scope of a national environmental survey, 42 water samples (6 surface water and 36 ground water samples) were obtained on September 7-8, 2010, from 14 sampling sites in Békés county, Hungary.

Methods and analysis (ELISA) are well described. The study authors concluded there was no matrix effects on the results of surface water. However, it should be noted that the recovery of the method (tested on spiked samples) in surface water was 127.7% (see Table 8.5-79). No indication on the recovery of the method for analyses of ground water samples is given. Also no information is given on the type of groundwater and the sampling method.

For samples from the Békés county, study authors indicate that both intensive and organic parcels were chosen in all four settlements (4 organic and 4 intensive), so as industrial site. However results are hard to relate to the different sites and cannot be related to any pressure of use of glyphosate.

The maximum ground water concentration reported for glyphosate is 0.98 µg/L ± 0.003.

The article is considered reliable with restrictions.

Data point:	CA 7.5/025
Report author	Sanchís, J. *et al*.
Report year	2012
Report title	Determination of glyphosate in groundwater samples using an ultrasensitive immunoassay and confirmation by on-line solid-phase extraction followed by liquid chromatography coupled to tandem mass spectrometry
Document No	Anal Bioanal Chem (2012) 402:2335–2345

Data point:	CA 7.5/026
Report author	Sanchís, J. *et al*.
Report year	2012
Report title	Erratum to: Determination of glyphosate in groundwater samples using an ultrasensitive immunoassay and confirmation by on-line solid-phase extraction followed by liquid chromatography coupled to tandem mass spectrometry
Document No	Anal Bioanal Chem (2012) 404:617

Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes
Acceptability/Reliability:	Reliable

Despite having been the focus of much attention from the scientific community during recent years, glyphosate is still a challenging compound from an analytical point of view because of its physicochemical properties: relatively low molecular weight, high polarity, high water solubility, low organic solvent solubility, amphoteric behaviour and ease to form metal complexes. Large efforts have been directed towards developing suitable, sensitive and robust methods for the routine analysis of this widely used herbicide. In the present work, a magnetic particle immunoassay (IA) has been evaluated for fast, reliable and accurate part-per-trillion monitoring of glyphosate in water matrixes, in combination with a new analytical method based on solid-phase extraction (SPE), followed by liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS), for the confirmatory analysis of positive samples. The magnetic particle IA has been applied to the analysis of about 140 samples of groundwater from Catalonia (NE Spain) collected during four sampling campaigns. Glyphosate was present above limit of quantification levels in 41% of the samples with concentrations as high as 2.5 µg/L and a mean concentration of 200 ng/L. Good agreement was obtained when comparing the results from IA and on-line SPE-LC-MS/MS analyses. In addition, no false negatives were obtained by the use of the rapid IA. This is one of the few works related to the analysis of glyphosate in real groundwater samples and the presented data confirm that, although it has low mobility in soils, glyphosate is capable of reaching groundwater.

Methods

Sample collection

Groundwater samples were collected by the Catalan Water Agency between May and September in 2007, 2008, 2009 and 2010. The samples were collected in 500-mL amber glass bottles. Then, 20-mL aliquot of each sample were separated and frozen during the transport to the laboratory and analysed immediately after sampling by the IA. The rest of the samples were frozen and stored in the dark in order to inhibit the degradation mechanism. A total of 139 samples from 69 wells located in 11 different sampling sites (water bodies) in Catalonia (Spain) were analysed. The number of samples varied between different campaigns: 18 samples from five different areas, 19 samples from eight areas, 37 samples from eight areas and 55 samples from ten different areas were collected during 2007, 2008, 2009 and 2010, respectively. The main characteristics of the sampling areas are summarised in Table 8.5-82. With the exception of one, all the areas studied presented a high impact from intensive agriculture and they were qualified as of high risk areas.

Chemicals

Analytical standards of glyphosate (reference 45521) and glyphosate-2-^{13}C (99% isotopic purity and reference 606502) were purchased from Sigma-Aldrich (Steinheim, Germany). The derivatisation agent FMOC-Cl (≥99.0% purity and reference 23814) and auxiliary reagents ethylenediaminetetraacetic acid (EDTA; 99.4–100.6% purity and reference E9884), sodium tetraborate ($Na_2B_4O_7$; 99% purity and reference 221732) and potassium hydroxide (KOH pellets, ≥85% purity and reference 221473) were also purchased from Sigma-Aldrich. HPLC-grade methanol, acetonitrile (ACN), ultra-pure water, dimethyl sulfoxide (DMSO) and formic acid and hydrochloric acid for analysis (25%) were supplied by Merck (Darmstadt, Germany). FMOC-Cl stock solution of 650 µM was prepared by dilution of 0.0168 g of FMOC-Cl in 100 mL of ACN. Tetraborate buffer was prepared by diluting 4 g of $Na_2B_4O_7$ in 500 mL of ultra-pure water. EDTA oversaturated solution was prepared by diluting 41.6 g of EDTA in 100 mL of ultra-pure water. All stock solutions were prepared weekly and stored at 4°C, with exception of FMOC-Cl stock solution, which was prepared daily.

Magnetic particle immunoassay

The glyphosate IA was developed and supplied by Abraxis LLC. This IA is based on polyclonal antibodies attached to paramagnetic particles, and the competitive reaction between derivatized glyphosate and derivatized enzyme labelled glyphosate for the antibody binding sites on the magnetic particles. The analysis procedure was performed in accordance with the operating manual accompanying the glyphosate kit. Very briefly, an aliquot of 250 µL of each sample was thoroughly mixed with 100 µL of diluted DMSO that served as derivatisation agent and incubated at room temperature for 10 min. After this period, 300 µL of derivatised sample and 500 µL suspended glyphosate antibody-coupled paramagnetic particles were mixed in a glass test tube and incubated for 30 additional minutes at room temperature. Incubation of another 30 min at room temperature followed after the addition of 250 µL of glyphosate enzyme conjugate. A magnetic field separator was then applied in order to separate any reagents unbound to the magnetic particles and keep hold of the bound reagents. Decanting of unwanted material took place after three washing cycles with deionised water; 500 µL of colour solution, containing the enzyme substrate (hydrogen peroxide) and the chromogen (3,3′,5,5′-tetramethylbenzidine), were added to the particles, and the mixture was incubated for 20 min at room temperature. The colour development reaction was stopped and stabilised by the addition of 500 µL of 2% sulphuric acid solution, and absorbance was then read at 450 nm using a photometer *Photometric Analyzer II* (Abraxis LLD, Warminster, PA) within 15 min after adding the stopping solution. Colour development was inversely proportional to glyphosate concentration. Standard calibration curves were prepared testing nine levels of increasing concentrations of glyphosate from 0.1 to 5 µg/L. The standard sigmoidal curves were fitted to a four-parameter equation according to the following formula:

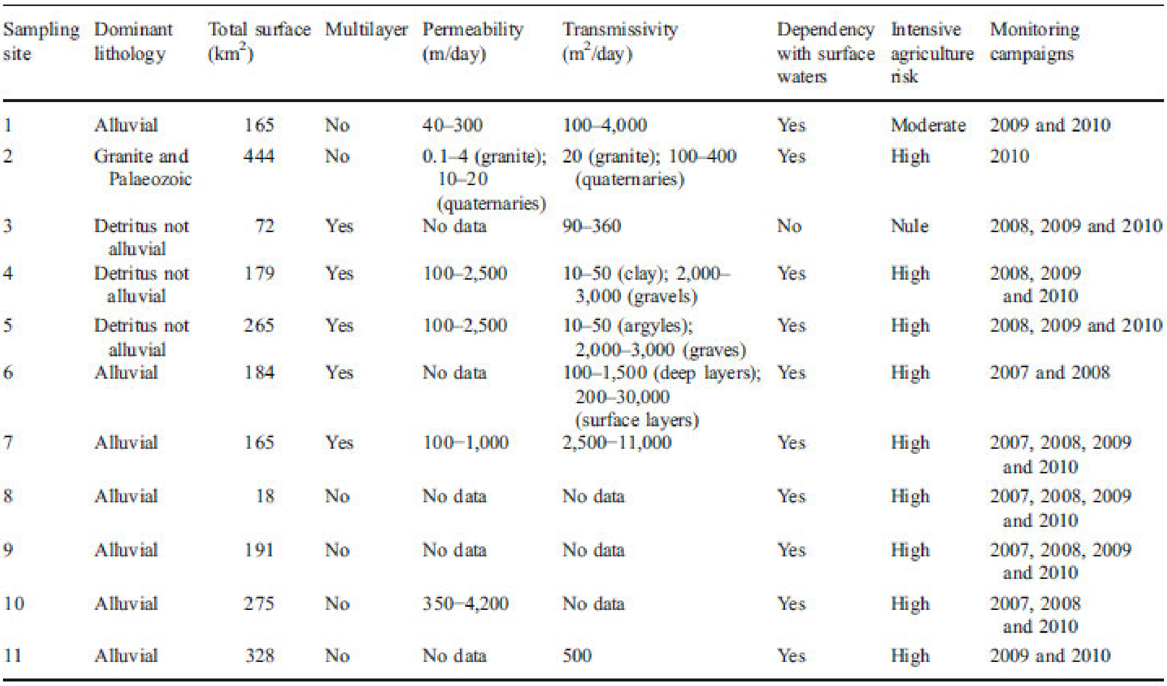
$$A = B + \frac{T - B}{1 + 10^{(\mathrm{LogEC_{50}} - \mathrm{LogC}) \times \mathrm{HS}}}$$

Where *A* is absorbance, *T* is the maximum absorbance value, *B* is the minimum absorbance value, EC_{50} is the concentration producing 50% of the maximum absorbance, *C* is the concentration and HS is the slope at the inflection point of the sigmoid curve. A standard curve was prepared with each set of samples analysed and two-matrix blank samples were analysed along with each sample set to determine possible interferences. No interferences were detected above the LOQ during the samples analysis. The average of at least three replicates was calculated and presented in this work.

Immunoassay evaluation

The recoveries and the matrix effects on the IA were previously studied and reported. Nevertheless, the matrix interference can be quite variable depending on the different types of water. For this reason, the first step of this work was to evaluate the suitability of the IA for the different types of ground water and river water selected in this study. Therefore, the different types of water as well as ultra-pure water, and tap water, free on glyphosate were fortified with glyphosate in a wide range of concentrations covering from 25 to 10 µg/L, were assayed after derivatization using the IA procedure described above, and the standard curves were fitted for the different types of water.

Table 8.5-82: General characteristics of sampling areas



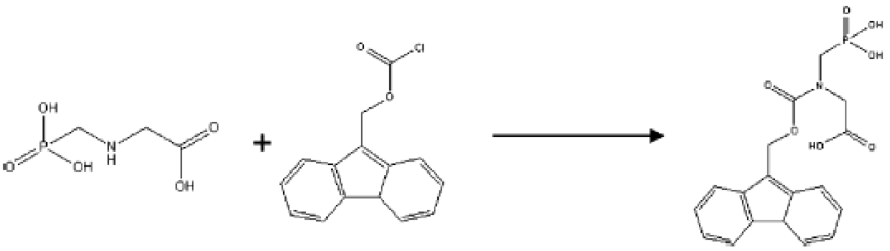
Sampling site	Dominant lithology	Total surface (km^2)	Multilayer	Permeability (m/day)	Transmissivity (m^2/day)	Dependency with surface waters	Intensive agriculture risk	Monitoring campaigns
1	Alluvial	165	No	40–300	100–4,000	Yes	Moderate	2009 and 2010
2	Granite and Palaeozoic	444	No	0.1–4 (granite); 10–20 (quaternaries)	20 (granite); 100–400 (quaternaries)	Yes	High	2010
3	Detritus not alluvial	72	Yes	No data	90–360	No	Nule	2008, 2009 and 2010
4	Detritus not alluvial	179	Yes	100–2,500	10–50 (clay); 2,000–3,000 (gravels)	Yes	High	2008, 2009 and 2010
5	Detritus not alluvial	265	Yes	100–2,500	10–50 (argyles); 2,000–3,000 (graves)	Yes	High	2008, 2009 and 2010
6	Alluvial	184	Yes	No data	100–1,500 (deep layers); 200–30,000 (surface layers)	Yes	High	2007 and 2008
7	Alluvial	165	Yes	100–1,000	2,500–11,000	Yes	High	2007, 2008, 2009 and 2010
8	Alluvial	18	No	No data	No data	Yes	High	2007, 2008, 2009 and 2010
9	Alluvial	191	No	No data	No data	Yes	High	2007, 2008, 2009 and 2010
10	Alluvial	275	No	350–4,200	No data	Yes	High	2007, 2008 and 2010
11	Alluvial	328	No	No data	500	Yes	High	2009 and 2010

In a previous work, the possible interference of structurally related compounds was evaluated. In the present work, this study was extended and the possible cross reactivity of other organic pollutants commonly found in groundwater from these sampling areas was studied. The compounds included here were triazine compounds (atrazine, desethyl atrazine and terbuthylazine), phenylurea compounds (diuron and linuron) and organophosphates (fenitrothion, diazinon, malathion and dimethoate) and measured with the IA. The cross-reactivity values were calculated according to the equation:

Immunoreactivity equivalents = (IC_{50} glyphosate/IC_{50} tested compounds) x 100

In addition, 30 blind prepared samples in assay buffer and 30 blind prepared samples in groundwater free of glyphosate were evaluated in triplicates, in order to assess the accuracy, precision and possible false negative and positive detected by the IA.

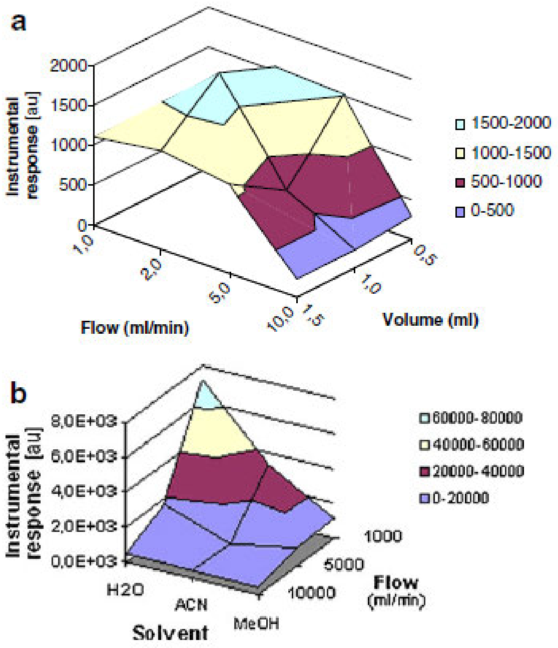
Figure 8.5-57: Chemical reaction between glyphosate and FMOC-Cl



Sample preparation for the instrumental analysis

Four millilitres of water samples were placed in an amber vials, were spiked with ^{13}C-glyphosate subrogate standard and were acidified with HCl 6 M to pH = 1.0. The acidified samples were stirred during 1 h in order to break the metal-glyphosate complexes that may happen under real environmental conditions. After this time, the presence of glyphosate is assumed to be in free form and the samples were neutralised with KOH 6 M. Derivatisation of the samples was performed according to the method previously described by Hanke *et al*. Very briefly, 1 mL of FMOC-Cl 650 µM in ACN and borate buffer (1:1) were added to the samples, and the mixture was stirred during 2 h at room temperature. Then the samples were acidified to pH 3 with formic acid, and 0.5 mL of aqueous EDTA (1.1 M) was added in order to prevent further metal complexation of glyphosate. The derivatised glyphosate (gly-FMOC) incorporates a fluorenylmethyloxycarbonyl group bounded to the glyphosate's amine group (Figure 8.5-57). The stability of gly-FMOC stored at 4°C during 12 h was proved. However, drastic loses of signal were detected when derivatized samples were stored overnight. Therefore, instrumental analysis was always carried out within the 12 h after derivatization.

Figure 8.5-58: Instrumental signals (in arbitrary units) obtained during the optimization of the on-line extraction: (a) Extraction step with three volumes of CAN with formic acid at four different flow rates; (b) Washing step with three solvents at three different flow rates



On-line extraction procedure

Derivatised water samples were loaded onto C18EC (Spark Holland, Emmen, The Netherlands) SPE cartridges previously conditioned with 2 mL of methanol and equilibrated with 1 mL of water at 2 mL/min. Derivatised samples (2 mL) were loaded at a slower flow rate (2 mL/min) with 1 mL ACN (0.1% formic acid) as transfer solvent. SPE cartridges were then washed with 0.5 mL of water at 1 mL/min flow rate. Elution was carried out using the mobile phase solvents. Following the elution step, and in order to avoid sample carry over, multiple valve and clamp washes were carried out with water.

Liquid chromatography coupled to tandem mass spectrometry

LC was performed using the Symbiosis Pico system (Spark Holland, Emmen, The Netherlands) equipped with a 5-mL sample loop. The chromatographic separation was achieved with a LC column Synergy 4 µ Hydro-RP 50×2.0 mm, 4 µm (Phenomenex, reference 00B- 4375-B0). Mobile phase composition consisted of (A) ammonium acetate (2.5 mM, pH=9.0) and (B) methanol. The elution gradient conditions for the LC mobile phase started with 10% eluent B, maintained isocratic during 1 min, increasing to 90% of eluent B in 1 min and holding for 1 min more. Initial conditions were reached in 1 min and re-equilibration was achieved in 2 min. The flow rate was kept at 0.2 mL/min through the total chromatographic run. As pointed elsewhere, the presence of ammonium acetate and pH = 9 are needed in order to obtain a good chromatographic shape of gly-FMOC although high concentrations of the modifier decreased the S/N ratio.

The Symbiosis Pico LC system was coupled to a 4000QTRAP hybrid triple quadrupole-linear ion trap mass spectrometer equipped with a Turbo Ion Spray source from Applied Biosystems-Sciex (Foster City, California, USA), employed in the negative electrospray ionisation mode (ESI (−)).

Simple reaction monitoring was used in order to obtain the required quantification points for confirmation. Quantification was performed with the Analyst software version 1.5. Optimal instrumental were set as follows: curtain gas (CUR)=40; collision gas (CAD): high; ion spray (IS)=−4,500 V; source temperature (TEM): 390; ion source gas 1 (GS1): 60; ion source gas 2 (GS2): 50.

Results

Optimisation of LC-MS/MS

Due to the previous experience in our group, a Synergy Hydro-RP (50 ×2 mm, 4 µm) analytical column was selected. For the mobile phase, different compositions and solvents were tested including water, methanol, acetonitrile and ammonium acetate (2.5 mM, pH = 9.0). Solvents used for the mobile phase were methanol and ammonium acetate, and the elution gradient was optimised by varying the percentage of organic solvent throughout the run. The optimised gradient was selected in order to obtain the best signal-to-noise ratio. The use of ammonium acetate was crucial for the gly-FMOC peak shape and retention time.

For the optimization of MS/MS conditions, a solution of gly-FMOC at a concentration of 1 mg/L was infused in order to select the two most relevant transitions of product ions. Once identification of the most abundant fragment ions was achieved, as well as the ionisation parameters for each transition, full-scan chromatograms were obtained, indicating the retention of derivatised glyphosate. Flow injection analysis was then used, in order to optimise the ion source conditions in the mass spectrometer, namely the ion source TEM, IS voltage, CUR, GS1 and GS2 and CAD.

Optimization of on-line SPE

The type of sorbent, injection volume, sample loading and wash solvent were investigated in order to improve the on-line extraction process. Different sorbent types were studied; C_{18}EC, C_{18}HD, HLB, Hysphere Resin GP and Varian polymer phase PLRPs. Best recovery was achieved with C_{18}EC with a mean value of 89% being slightly better than C_{18}-HP cartridges (mean value, 68%), and Resin GP cartridges (mean value, 62%).

Injection volume tests were performed with partial injections on a 5-mL sample loop in order to check for breakthrough in the range of 20–2,500 µL. No break- through volume was found at 2,500 µL, which was the maximum admitted amount using partial loop injection. Therefore, 2.5 mL was set as injection volume. Cartridge activation, sample loading and cartridge washing steps were also optimised. Different volumes and flow rates of methanol were tested to optimise cartridge activation and final conditions were 2 mL of methanol at 2 mL/min flow rate. Six different solvents methanol, ACN, water, ammonium acetate 2.5 mM at pH=9.0, ACN (0.1% formic acid) and water (0.1% formic acid) were tested in order to select the optimal elution solvent. Different volumes of ACN (0.1% formic acid) were evaluated at different flow rates. As can be seen in Figure 8.5-58a, the highest signal was obtained when the transfer solvent was 2 mL of acidified ACN at 2 mL/min followed by 1 mL of ACN at 2 mL/min for equilibration. Finally, the washing step was also optimised using different solvents and flow rates, obtaining the maximum instrumental response using 0.5 mL of water at a flow rate of 1 mL/min. Finally, cartridge elution was performed by the gradient elution. The recovery of gly-FMOC was calculated from the peak area obtained for the most intense transition.

On-line SPE-LC-MS/MS method validation

The method was validated according to the EU Decision 2002/657/EC. Blank groundwater was spiked at three concentrations levels: 80.0, 200 and 400 ng/L. Six replicates of each concentration were analysed at each concentration levels. The intraday reproducibility was calculated resulting in 15%, 12% and 8%, respectively.

Criteria for the LOQ was established as the lowest concentration fulfilling all of the following criteria: (1) bias from the calibration curve less than 25%, (2) relative standard deviation of four replicates below 19%, (3) peak shapes acceptable and (4) signal-to-noise ratio at least 10. Method limit of detection and method limit of quantification (MLOQ) were found to be 3.2 and 9.6 ng/L, respectively. The decision limit (CCα) was defined as the lowest concentration level at which the method is able to discriminate the gly-FMOC presence, with a statistical certainty of 99%. By analysing 20 blanks, CCα was estimated as 1.6 ng/L. The detection capability (CCβ) was defined as the smallest concentration of gly-FMOC that may be detected, identified and/or quantified in a sample with an error probability of β. By analysing 20 samples spiked at CCα, CCβ was established as 3.1 ng/L.

Linearity was assessed by constructing a seven-point calibration curve (ranging between 50 and 500 ng/L) in triplicate. Least-square linear regression analysis was performed by plotting the peak area of the analyte over the analyte concentration. R^2 of 0.99925 was achieved.

In order to assess the possible carryover of the method blank samples were analysed after analysis of groundwater samples fortified at 5 µg/L. In all these cases, blank samples showed values for glyphosate under the LOQ. Therefore, carryover could be considered negligible.

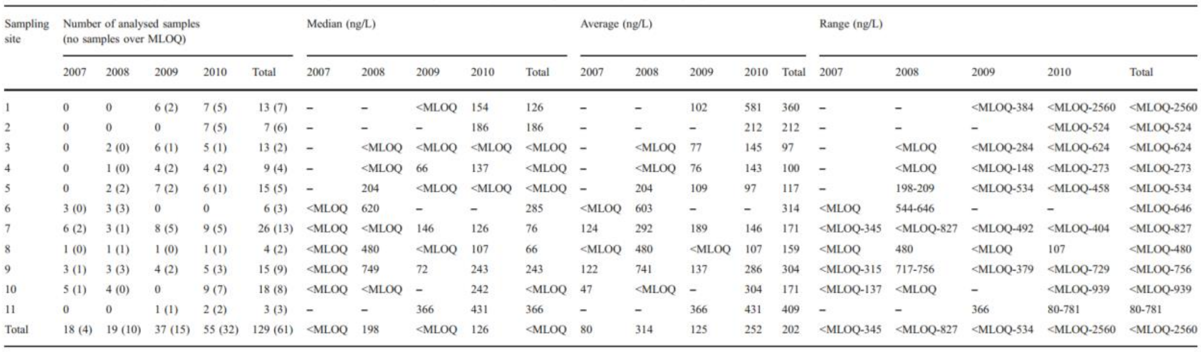
Immunoassay performance and specificity

The IA intra-assay precision was evaluated by determining the variation (CV%) between replicates assayed at various concentrations on the standard curves; as can be seen, good precision was shown by the IA with CV% of 13.4. Good agreement was found between fortified blank natural waters and the standard curve prepared in assay buffer and no significant changes on slopes were found. The recovery percentages range from 93% to 105% and 92% to 102% for groundwater and river water, respectively.

Very low cross reactivity was found for glyphosine and glufosinate, and no cross reactivity was found with other related compounds such as AMPA, in agreement with previous studies. No interference was found with other organic pollutants studied here, including other organophosphate compounds.

Sixty blind samples were prepared spiking glyphosate concentrations in the range between 0 and 4 µg/L. Thirty of these samples were prepared in assay buffer, and 30 samples more were prepared in a real groundwater samples free in glyphosate. The samples were analysed by magnetic particle immunoassay. The results of this test showed that no false negatives or false positives were obtained by the IA, very good correlation was obtained between the results obtained using the IA and the concentrations of fortification with coefficient of correlation R^2 = 0.9907 in assay buffer and R^2 = 0.9816 in groundwater. In addition, slight tendency to overestimation was observed in groundwater.

Table 8.5-83: Summary of glyphosate concentrations in groundwater samples analysed during four sampling campaigns



Sampling site	Number of analysed samples (no samples over MLOQ)					Median (ng/L)					Average (ng/L)					Range (ng/L)				
	2007	2008	2009	2010	Total	2007	2008	2009	2010	Total	2007	2008	2009	2010	Total	2007	2008	2009	2010	Total
1	0	0	6 (2)	7 (5)	13 (7)	–	–	<MLOQ	154	126	–	–	102	581	360	–	–	<MLOQ-384	<MLOQ-2560	<MLOQ-2560
2	0	0	0	7 (5)	7 (6)	–	–	–	186	186	–	–	–	212	212	–	–	–	<MLOQ-524	<MLOQ-524
3	0	2 (0)	6 (1)	5 (1)	13 (2)	–	<MLOQ	<MLOQ	<MLOQ	<MLOQ	–	<MLOQ	77	145	97	–	<MLOQ	<MLOQ-284	<MLOQ-624	<MLOQ-624
4	0	1 (0)	4 (2)	4 (2)	9 (4)	–	<MLOQ	66	137	<MLOQ	–	<MLOQ	76	143	100	–	<MLOQ	<MLOQ-148	<MLOQ-273	<MLOQ-273
5	0	2 (2)	7 (2)	6 (1)	15 (5)	–	204	<MLOQ	<MLOQ	<MLOQ	–	204	109	97	117	–	198-209	<MLOQ-534	<MLOQ-458	<MLOQ-534
6	3 (0)	3 (3)	0	0	6 (3)	<MLOQ	620	–	–	285	<MLOQ	603	–	–	314	<MLOQ	544-646	–	–	<MLOQ-646
7	6 (2)	3 (1)	8 (5)	9 (5)	26 (13)	<MLOQ	<MLOQ	146	126	76	124	292	189	146	171	<MLOQ-345	<MLOQ-827	<MLOQ-492	<MLOQ-404	<MLOQ-827
8	1 (0)	1 (1)	1 (0)	1 (1)	4 (2)	<MLOQ	480	<MLOQ	107	66	<MLOQ	480	<MLOQ	107	159	<MLOQ	480	<MLOQ	107	<MLOQ-480
9	3 (1)	3 (3)	4 (2)	5 (3)	15 (9)	<MLOQ	749	72	243	243	122	741	137	286	304	<MLOQ-315	717-756	<MLOQ-379	<MLOQ-729	<MLOQ-756
10	5 (1)	4 (0)	0	9 (7)	18 (8)	<MLOQ	<MLOQ	–	242	<MLOQ	47	<MLOQ	–	304	171	<MLOQ-137	<MLOQ	–	<MLOQ-939	<MLOQ-939
11	0	0	1 (1)	2 (2)	3 (3)	–	–	366	431	366	–	–	366	431	409	–	–	366	80-781	80-781
Total	18 (4)	19 (10)	37 (15)	55 (32)	129 (61)	<MLOQ	198	<MLOQ	126	<MLOQ	80	314	125	252	202	<MLOQ-345	<MLOQ-827	<MLOQ-534	<MLOQ-2560	<MLOQ-2560

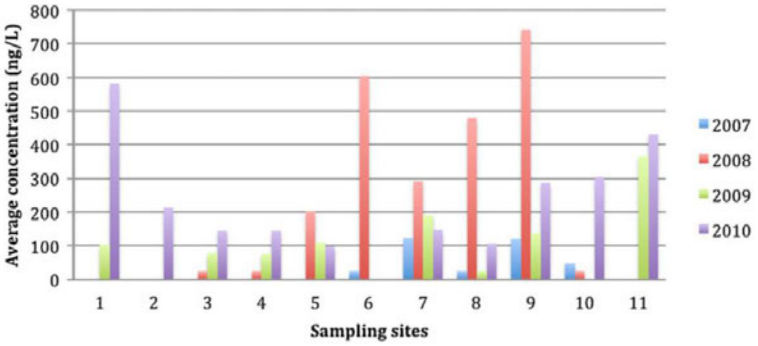
Finally, all the samples of the last sampling campaign were analysed in parallel by means of the magnetic particle IA and on-line SPE-LC-MS/MS. The average relative error between the IA analyses and the confirmation method was lower than 12%.

Applicability of the method
Glyphosate was investigated in 139 samples, and it was detected at quantifiable levels in 61 samples (47%). Table 8.5-83 summarises the median concentration, average and range of concentrations along the different campaigns. All samples were analysed using the magnetic particle immunoassay, and positive samples were confirmed by instrumental analysis. No false negatives were found using the immunoassay. The concentrations of glyphosate range from MLOQ to 2.6 µg/L, and the average was 202 ng/ L (samples under limit of quantification were computed as half the MLOQ for the average calculation). Mean concentrations of glyphosate are presented in Figure 8.5-59. In general, in terms of average concentrations, slight differences were obtained along the sampling campaigns, which range from 97 ng/L for the cleanest site to 409 ng/L. As it was expected, more contaminated areas (sites 6, 9 and 11) were found in those regions of thriving agriculture activity. However, the higher value was achieved in 2010, in site no. 1, which corresponds to an area with moderate agricultural activity. In addition, a significant difference was obtained compared with the same site during 2009 campaign. In this case, the presence of glyphosate can be related to their increasing use as herbicide for non-agricultural applications, such as, the control of weeds on margins or streams and drains, around buildings, railways, roads and industrial areas.

All sampling campaigns were carried out during the application season but, in some of the sampling areas (1, 3, 4 and 11), an increasing trend was observed along the different campaigns, and in others, such as, 5, 7, 8 and 9, the higher average concentrations were obtained during the first sampling campaign in 2008. In this sense, it should be mentioned that the degradation of glyphosate is highly variable according to the environmental conditions. The degradation of glyphosate in surface water has been reported to be very fast. Whereas, in groundwater glyphosate is rapidly adsorbed to organic matter, precipitated and then can be retained in the soil where half-life can be longer than 2 years. In addition, the mobility and leaching capability of glyphosate also depend on the type of soil. Borggaard *et al*. reported that the different glyphosate forms can be moved by leaching through uniform gravelly soils and in structured soils with macro-pores, being determinant other factors such as rain precipitations, timing, tillage and vegetation. Therefore, the results showing the higher concentrations can be associated to sites where the sampling was carried out immediately after glyphosate application in the area. In addition, glyphosate can be accumulated in soil leaching by precipitation. This fact can partially explain high concentrations in some areas during 2008, such as sites 5 and 7, which coincides with the onset of spring rains in 2008 after 3 years of heavy drought that could have favoured the dissolution of glyphosate retained in the soil. After these high levels in the 2008 campaign, during the 2009 and 2010, campaigns registered a progressive decrease.

The presence of glyphosate in groundwater has been exiguously reported, and very few works have been carried out to study this presence. In most of previous studies, no quantifiable levels of glyphosate were found in groundwater, even in areas where surface water is found to contain the herbicide. However, it should be pointed out that these studies were carried out with analytical methods presenting LOQ in the range of micrograms per litre, and the present study use a, IA capable to detect glyphosate at pictogram-per-millilitre range without sample pre-treatment, just derivatisation, and an on-line SPE-LC-MS/MS method for confirmation of the glyphosate at nanogram-per-litre range. Second, in this study the sampling campaigns were carried out during the peak season of glyphosate application in those areas, in order to investigate main areas susceptible of glyphosate accumulation in soils. These areas should be determined and controlled in order to follow the behaviour and dissolution of this herbicide under certain environmental conditions as after rains.

Figure 8.5-59: Average concentrations of the sampled areas during four sampling campaigns



Conclusion
The magnetic particle IA for glyphosate analysis from Abraxis LLC was proved to be a suitable, sensitive and cost-effective method for the fast ultra-trace screening analysis of a large number of real groundwater samples. The here presented IA is the most sensitive in the literature for the analysis of glyphosate. In addition, a new methods based on on-line SPE-LC-MS/MS was developed and validated as rapid confirmatory analytical method for glyphosate analysis at ultra-trace level.

The good performance of these analytical approaches, as well as, the applicability of the combined methodology for the analysis of glyphosate in groundwater has been proved using the approach for the analysis of groundwater from 11 different areas in Catalonia. The results showed a 41% of the samples presenting quantifiable concentrations of glyphosate when were sampled. In addition, the results of this study corroborate the hypothesis of previous studies pointing that glyphosate may exhibit certain grade of mobility in soils. This is the first that experimental data about glyphosate reaching groundwater provided. Despite the tendency of glyphosate of being immobilised in soils, aquifer contamination with glyphosate has been demonstrated to happen because of its intensive use. Higher concentrations for 2008 were registered and it was linked to 2008 spring precipitations finishing with a 3-year drought period. Since the environmental source of glyphosate is certainly related to agricultural practices, runoff to surface waters is very likely to occur. Therefore, the potential ecological impact of this contamination should be taken in consideration in a more global view. Although the levels reported in this work are relatively low, their variability is significant through space and time, and an increase tendency has been observed in some sampling points, underpinning the importance of further analysis of glyphosate and their degradation products in groundwater samples.

Assessment and conclusion by applicant:
The article presents an analytical method to determine glyphosate in groundwater samples from Catalonia / Spain. Glyphosate findings in the respective groundwater samples are presented. Methods and results are well described. Maximum concentration of glyphosate measured at 2560 ng/L in 2010. The article is considered reliable.

Assessment and conclusion by RMS:
This study was previously sutmitted for AIR II renewal, and have been reviewd in the RAR 2015. RMS evaluation from the RAR 2015 is reported below.

The article reports that a total of 129 groundwater samples from wells located in 11 different sampling sites in Catalonia, Spain, were collected by the Catalan Water Agency between May and September in 2007, 2008, 2009 and 2010. With the exception of one, all the areas studied presented a high impact from intensive agriculture. The samples were analysed by an immunoassay in the first step and to some extent by a LC-MS/MS measurement in the second step. The concentrations of glyphosate range from method limit of quantification (MLQQ) to 2.6 µg/L, the average was 202 ng/L (for the average calculation, samples under limit of quantification were computed as half the MLQQ).

In the publication, it is pointed out that more contaminated areas were found in regions of thriving agriculture activity. However, the highest concentration of glyphosate was measured in sampling site no. 1, which corresponds to an area with only moderate agricultural activity. Therefore, the presence of glyphosate in groundwater cannot exclusively be related to the use as herbicide for agricultural applications. Other sources of glyphosate, e.g. the control of weeds on streams and drains, around railways, roads, sports fields and industrial areas have to be considered as well.

The pathways of glyphosate into groundwater are not investigated by the authors. With the aid of a literature review it is shown that glyphosate can be moved by leaching through uniform gravelly soils and structured soils with macro-pores. Furthermore, glyphosate can be accumulated in soil by precipitation. Spring rains after years of heavy drought could then have favoured the dissolution of glyphosate retained in soil. Due to the fact that surface waters exist in 10 out of 11 sampling sites, surface run-off and/or drainage into these waters with subsequent bank filtration into groundwater cannot be excluded.

The study is considered reliable.

Data point:	CA 7.5/027
Report author	Bruchet, A. *et al.*
Report year	2011
Report title	Natural attenuation of priority and emerging contaminants during river bank filtration and artificial recharge
Document No	European Journal of Water Quality 42 (2011) 123-133
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities
Acceptability/Reliability:	Reliable with restrictions

The fate of various emerging contaminants as well as priority pollutants from the European Union Water Framework directive was examined along a complex combination of natural and engineered processes used to produce drinking water downstream of a major metropolitan area. The sampling points examined comprised Seine river water downstream of the Paris area, water from a primary well after bank filtration, water from a secondary well influenced by an artificial recharge process and water from the mixture of secondary wells after drinkingwater treatment. More than 80 organic contaminants includingglyphosate and AMPA, were monitored during five campaigns. River bank filtration and to a lesser extent artificial recharge clearly decreased the variety of contaminants, in particular glyphosate and AMPA were reduced from <0.1 – 0.12 µg/L and 0.25 – 0.65 µg/L, respectively, in the river to <0.1 µg/L in both the primary and secondary wells.

Materials and methods

Study site

The aquifer studied (Figure 8.5-60) is located along the Seine river, downstream of Paris and its urban wastewater plants. In particular, it is located downstream of a wastewater plant that treats the effluents from 6.5 million people at a rate of 2 million m^3/day. This aquifer covers an area of 40 km^2 and comprises 36 primary and secondary wells. The primary wells are located mostly along the river, naturally re-supplied under anoxic conditions through river bank filtration. The primary wells output is pumped and re-infiltrated through a sand-gravel artificial basin (under slightly aerobic conditions) to recharge secondary production wells. Water from the secondary wells is further treated in a drinking water plant that comprises settling with addition of powdered activated carbon, sand filtration, ozonation and final disinfection with chlorine. The plant production is equal to 144 000 m^3/day.

The following points were sampled (grab samples) on five occasions during September and October 2008:

(1) the Seine raw water,

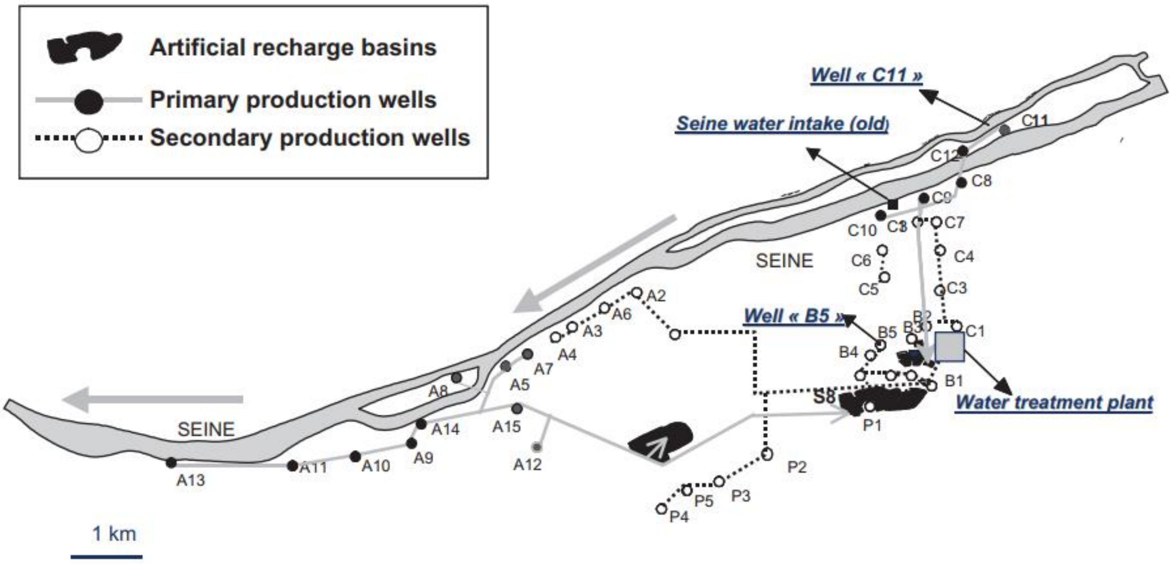
(2) primary production well C11 (one of the C wells in Figure 8.5-60) which is located on a small island on the Seine river and hence directly influenced by the river after bank filtration,

(3) secondary well B5 (one of the B wells in Figure 8.5-60) which is influenced by the main artificial recharge basin. However, due to the direction of underground flows, this well is also influenced by other areas of the aquifer and,

(4) the treated water at the outlet of the drinking water plant.

The sampling period covered both low flow conditions (220 m^3/s) and higher flow rates (up to 343 m^3/s).

Figure 8.5-60: **Description of study site showing the four sampling points. Flow of the river is from right to left.**



Analytical methods

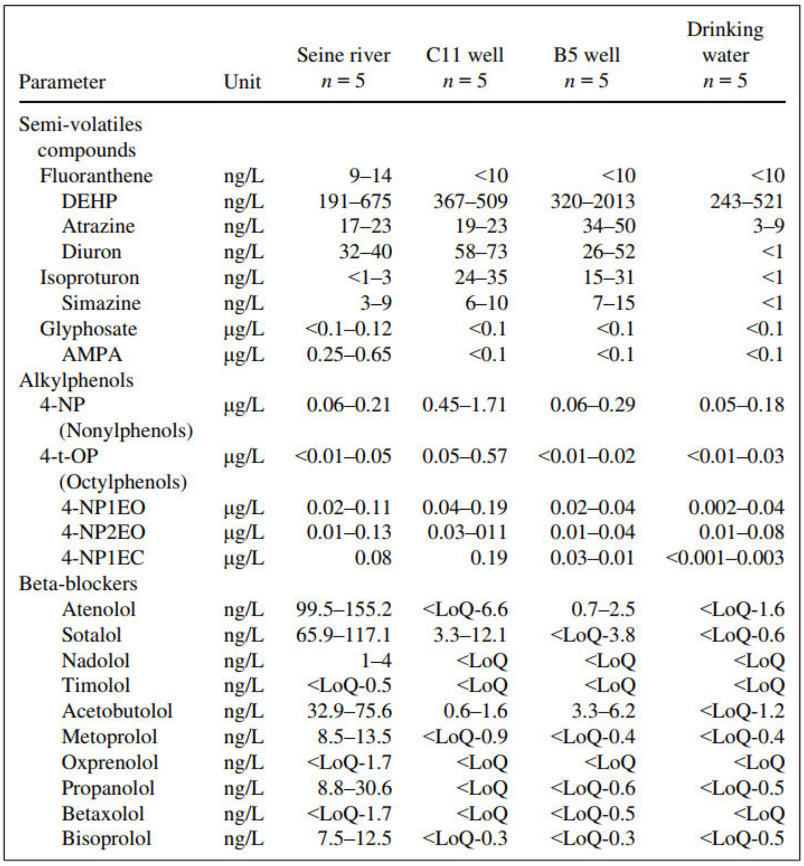
A wide array of analytical methods was used to cover most priority pollutants and emerging contaminants. Volatile organic compounds (VOC's) were determined by Purge and Trap gas chromatography-mass spectrometry (GC/MS). Glyphosate and AMPA were determined by FMOC derivatization-HPLC-fluorescence.

Results and Discussion

Although the sampling point on the Seine river is located downstream of a metropolitan area with 11 million people, most EU priority compounds were never detected.

The only pesticide or degradate found at a level exceeding 0.1 µg/L in the Seine river is **glyphosate** (on one occasion) and its degradate **AMPA** (systematically in the range 0.25-0.65 µg/L). AMPA can also be present as a wastewater contaminant, from household detergent use. These two compounds are totally removed by bank filtration, in accordance with previous observations and do not reappear in the aquifer.

Table 8.5-84: **Fate of priority and emerging contaminants during bank filtration (C11), artificial recharge (B5) and drinking water treatment.**



Parameter	Unit	Seine river $n = 5$	C11 well $n = 5$	B5 well $n = 5$	Drinking water $n = 5$
Semi-volatiles compounds					
Fluoranthene	ng/L	9–14	<10	<10	<10
DEHP	ng/L	191–675	367–509	320–2013	243–521
Atrazine	ng/L	17–23	19–23	34–50	3–9
Diuron	ng/L	32–40	58–73	26–52	<1
Isoproturon	ng/L	<1–3	24–35	15–31	<1
Simazine	ng/L	3–9	6–10	7–15	<1
Glyphosate	µg/L	<0.1–0.12	<0.1	<0.1	<0.1
AMPA	µg/L	0.25–0.65	<0.1	<0.1	<0.1
Alkylphenols					
4-NP (Nonylphenols)	µg/L	0.06–0.21	0.45–1.71	0.06–0.29	0.05–0.18
4-t-OP (Octylphenols)	µg/L	<0.01–0.05	0.05–0.57	<0.01–0.02	<0.01–0.03
4-NP1EO	µg/L	0.02–0.11	0.04–0.19	0.02–0.04	0.002–0.04
4-NP2EO	µg/L	0.01–0.13	0.03–011	0.01–0.04	0.01–0.08
4-NP1EC	µg/L	0.08	0.19	0.03–0.01	<0.001–0.003
Beta-blockers					
Atenolol	ng/L	99.5–155.2	<LoQ-6.6	0.7–2.5	<LoQ-1.6
Sotalol	ng/L	65.9–117.1	3.3–12.1	<LoQ-3.8	<LoQ-0.6
Nadolol	ng/L	1–4	<LoQ	<LoQ	<LoQ
Timolol	ng/L	<LoQ-0.5	<LoQ	<LoQ	<LoQ
Acetobutolol	ng/L	32.9–75.6	0.6–1.6	3.3–6.2	<LoQ-1.2
Metoprolol	ng/L	8.5–13.5	<LoQ-0.9	<LoQ-0.4	<LoQ-0.4
Oxprenolol	ng/L	<LoQ-1.7	<LoQ	<LoQ	<LoQ
Propanolol	ng/L	8.8–30.6	<LoQ	<LoQ-0.6	<LoQ-0.5
Betaxolol	ng/L	<LoQ-1.7	<LoQ	<LoQ-0.5	<LoQ
Bisoprolol	ng/L	7.5–12.5	<LoQ-0.3	<LoQ-0.3	<LoQ-0.5

In the river, glyphosate was found at <0.1 – 0.12 µg/L, and AMPA at 0.25 – 0.65 µg/L: but, in both the primary well and the secondary well, concentrations of both substances were <0.1 µg/L, as they were in the drinking water samples. (It is worth noting that "<0.1 µg/L" indicates LOQ, and not an absolute concentration – using it as a basis for determining the removal rate for AMPA would give a removal rate of 85%, and 17% for glyphosate; whereas, it is clear from the context that removal is more likely to be 100%. Indeed, the authors state that "both these compounds are totally removed by bank filtration" in this case.

Conclusion

The present study allowed most priority substances from the EU Water Framework Directive to be measured, and also a wide variety of emerging substances in a surface water downstream of a major metropolitan area that treats the majority of its urban wastewaters (the Seine river downstream of Paris). The study site selected allowed the fate of the substances detected to be observed, during their infiltration into an aquifer primarily re-supplied by natural bank filtration. The fate of the substances reaching the aquifer was monitored along a natural recharge process and at the outlet of a drinking water plant treating a mixture of boreholes from this aquifer.

In a system influenced by urban wastewaters downstream of a major metropolitan area, a drinking water produced by a complex combination of natural bank filtration, artificial recharge, clarification with powdered activated carbon addition, ozonation and chlorination, complies with the current legislation. In particular, glyphosate and AMPA were reduced, by the bank filtration process, from <0.1 – 0.12 µg/L and 0.25 – 0.65 µg/L, respectively, in the river, to <0.1 µg/L in the primary and secondary wells. It is also worth noting that "<0.1 µg/L" indicates LOQ, and not an absolute concentration – using it as a basis for determining the removal rate for AMPA would give a removal rate of 85%, and 17% for glyphosate; whereas, it is clear from the context that removal is more likely to be 100%. Indeed, the authors state that "both these compounds are totally removed by bank filtration" in this case.

Assessment and conclusion by applicant:
The article describes a monitoring experiment with glyphosate and AMPA among different other substances from Seine river and a drinking water production area downstream of the Paris urban area. The study is well described, the analytical methods used are sufficient.

With respect to glyphosate and AMPA, the study sheds light on the effectiveness of the water treatment train employed for a major surface water to drinking water plant, where the primary treatment process is bank filtration. In this case, it is clear that bank filtration has been shown to be an effective process to remove glyphosate and AMPA to <0.1 µg/L from water destined to be drinking water.

The article is considered reliable.

Assessment and conclusion by RMS:
This study describes monitoring experiment in the area of Paris, FR. The sampling points examined comprised Seine river water downstream of the Paris area, water from a primary well after bank filtration, water from a secondary well influenced by an artificial recharge process and water from the mixture of secondary wells after drinkingwater treatment.
More than 80 organic contaminants including glyphosate and AMPA, were monitored during five campaigns.

Grab samples were taken on five occasions during September and October 2008.

The only pesticide or degradate found at a level exceeding 0.1 µg/L in the Seine river is glyphosate (on one occasion) and its degradate AMPA (systematically in the range 0.25-0.65 µg/L).

This study evidenced that the river bank filtration and to a lesser extent artificial recharge clearly decreased the variety of contaminants, in particular glyphosate and AMPA were reduced from <0.1 – 0.12 µg/L and 0.25 – 0.65 µg/L, respectively, in the river to **<0.1 µg/L in both the primary and secondary wells.** It is concluded that these two compounds are totally removed by bank filtration, in accordance with previous observations and do not reappear in the aquifer.
It is however considered a particular context of bank filtration and is considered reliable with restriction.

Data point:	CA 7.5/028
Report author	[redacted]
Report year	2011
Report title	Investigation of the potential glyphosate groundwater contamination in Lombardia region (North Italy)
Report No	BVL No. 2310280
Document No	
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

Glyphosate concentrations above the drinking water limit were detected in five groundwater monitoring sites from the Lombardia region (North Italy), all collected during the May 2007 monitoring campaign, and all located in the South East part of the region. In order to investigate these groundwater detects, all accessible information (including information on methods and tools implemented or used by ARPA Lombardia for planning monitoring programs and also information on the analytical method) was requested from the responsible authorities (ARPA-Lombardia) and checked. Detailed information on soil characteristics, technical and hydrogeological information was also gathered, and a site inspection carried out. In addition, parallel samples from contaminated sites, and from surrounding areas where piezometers were available, were collected to assess residues levels, characterize the water, and to investigate possible different analytical methods. In four of the sites, the glyphosate content of the additional samples taken more than 3 years after the reported detections did confirm the findings, highlighting the persistence of the groundwater contamination. Site inspections have revealed that findings could be attributed to artificial influences, as inflow of surface water and mud/sediment or point source contamination. For one of the five wells, investigations are still ongoing to confirm some assumptions of possible contamination such as infiltration from a stream or infiltrating wastewater.

Generally, it can be noted that the conditions of the wells were not suitable for the collection of groundwater quality samples for the assessment of a possible contamination of plant protection products at trace concentrations

Materials and Methods

The clarification of the reported glyphosate findings was done in stepwise procedure. In the first part of the study, all accessible information (including information on methods and tools implemented or used by ARPA Lombardia for planning monitoring programs and also information on the analytical method) was requested from the responsible authorities (ARPA Lombardia) and checked. As this information was insufficient to clarify the findings, detailed information on soil characteristics, technical and hydrogeological information was gathered, and a site inspection carried out to verify the well status and inspect the well surrounding. Local authorities or the owners of the wells were also contacted.

As the available information did not allow to assess the quality of the analyses and the water sampling method, parallel samples from contaminated sites, and from surrounding areas where piezometers were available, were collected to assess residues levels, characterize the water, and to investigate the impact of a different analytical method: the analytical method used by ARPA Lombardia (FMOC-Cl derivatization with HPLC:fluorescence detector) was implemented in the laboratories of the University of Piacenza and compared with method using FMOC-Cl derivatization followed by LC/MS/MS (method LOD of 0.02 µg/L).

Results and discussion

The table below provides an overview of the findings and the result of the assessment

Table 8.5-85: Overview on findings of glyphosate and results of the assessments

Site	Date of findings	Glyphosate level (µg/L)	Cause of the findings	Date of re-sampling	Glyphosate level (µg/L)
Pandiono (CR)	10 May 2007	0.9	Inflow of surface water	28 Nov 2010	< LOQ
Trigolo (CR)	22 May 2007	0.2	Point source contamination	28 Nov 2010	0.252
Caselle Lurani (LO)	08 May 2007	0.2	Point source contamination	30 Nov 2010	0.163
Asola (MN)	05 June 2007	0.7	Investigation still ongoing	16 Oct 2010	0.525
San Benedetto (MN)	06 June 2007	1.2	Point source contamination	12 Jan 2011	1.375

<u>Pandino</u>: The inspection of the monitoring well showed that the piezometer was not sealed and that surface water and mud from the adjacent areas were standing between the cast iron manhole and the piezometer, and could thus flow into the well.

<u>Trigolo</u>: The owner of the site explained that during the investigation period he weeded the stretch of land around the piezometer with a glyphosate containing herbicide to facilitate access. A careful inspection of the site showed that the base of the piezometer was not well isolated and could thus lead to preferential flows.

Asola: Investigations are ongoing to confirm hypotheses of possible contamination such as infiltration of rainwater from paved surfaces and drainages

Casselle Lurani: The old well (more than one century) is located in a private courtyard of a farm, and is not completely sealed. Surface water from the courtyard can enter directly into the well from the manhole. The farmer uses the well to wash the spray equipment and tractor next to the well.

San Benedetto: the well is located in the courtyard in front of the product and sprayer storage of a company applying herbicides on railways. The area next to the well is used to clean and maintain the trucks used for herbicide application.

The results of the analysis of the samples taken more than 3 years after the reported detect did confirm the levels observed in 2007 in the wells from Trigolo, Caselle Lurani, Asola and San Benedetto, demonstrating the persistence of the contamination.

Conclusion

The detailed investigation has allowed plausible explanations of the origin of the glyphosate findings at 4 of the 5 locations. In one location, the investigation is still ongoing. In all cases, the origin of the glyphosate concentrations could be allocated to surface inflow or to point source contamination. Up until now, there was not a single case for which the findings could be correlated with the normal and proper use of glyphosate in the field.

Assessment and conclusion by applicant:

The article elucidates reported glyphosate concentrations above the drinking water limit (0.1 µg/L) detected in May 2007 in North Italy (Lombardia region). Methods and results are sufficiently described. The article is considered reliable.

Assessment and conclusion by RMS:

This study was previously sutmitted for AIR II renewal, and have been reviewed in the RAR 2015. RMS evaluation from the RAR 2015 is reported below.

It has to be noted that glyphosate findings exceeding the limit concentration 0.1 µg/L have been measured in groundwater aquifers at 5 locations in Italy. A detailed investigation has allowed plausible explanations of the origin of the glyphosate findings at 4 of the 5 locations. Thereby, the origin of the glyphosate concentrations could be allocated to surface inflow or to point source contamination. In one location the investigation is still ongoing. Until now, the findings could not be correlated with the normal and proper use of glyphosate in the field.

The study is considered reliable.

Data point:	CA 7.5/029 CA 7.5/030 (Translation)
Report author	[redacted]
Report year	2010
Report title	Evaluatie van metingen van glyfosaat en AMPA in grondwater in Nederland (Evaluation of glyphosate and AMPA measurements in groundwater in The Netherlands)
Report No	Report 354
Document No	BVL No. 2310284
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No (no experimental work performed)
Acceptability/Reliability:	Reliable

Glyphosate and AMPA detects were mentioned in two reports (RIVM, 2007 and Royal Haskoning, 2008), summarising the residues of plant protection products in Dutch groundwater. Before conducting an on-site investigation, information about the site characteristics, analytical method and data processing were gathered remotely and evaluated. The investigation showed that the protection of the well was poor at 2 sites and medium at 5 sites, and that surface water inflow or contamination by spray drift cannot be excluded at these locations. Uncertainty about sample processing was observed for 2 sites. For 6 (out of the 10) glyphosate detects, no plausible explanation could be found based on this investigation. It should be noted that no special attention was given to the AMPA detects, as this compound is considered as a non-relevant metabolite in The Netherlands, and the 0.1 µg/L trigger does thus not apply.

Materials and Methods

The clarification of the reported glyphosate and AMPA findings was done in stepwise procedure. In a first step information on the analytical method, sampling and data processing, and on the characteristics well surroundings were gathered and evaluated. The second step involved an on-site investigation with a special focus on the protection of the well.

Results and discussion

Glyphosate was found in 6 out of the 189 measurements (3.71% of all measurements) carried out in one report (2008, Royal Haskoning), and 4 out of 691 measurements (0.58% of all measurements) carried out in the second report (2007, RIVM). Table 8.5-86 summarizes available information about the different locations investigated. The locations 1-10 related to the 2008 report, locations 11 to 14 to the 2007 report.

Table 8.5-86: Overview on findings of glyphosate/AMPA and results of the assessments

Location	Concentration (µg/L)	Date	Description	Groundwater body	Land use in surrounding area	Well protection[1]	Sample processing[2]
1. South Limburg, Vaals	0.16 glyphosate	8th October 2007	Spring near Sinselbeek	Chalk South Limburg	Agriculture / Nature (forest)	+/-	+
2. South Limburg, Valkenburg	0.13 glyphosate	11th October 2007	Spring on plateau near Geul	Chalk South Limburg	Agriculture / Nature (forest)	+/-	+
3. Central Limburg, Maasbracht	0.20 glyphosate 0.12 AMPA	11th July 2007	Semi-deep groundwater (6-8 m)	Maas Deep Channel	Agriculture	-	+
4. North Limburg, Tegelen,	0.12 glyphosate	19th Sept. 2007	Semi-deep groundwater (13-15 m)	Maas Sand	Agriculture	+/-	+
5. North Limburg, Nuland,	0.62 glyphosate 0.23 AMPA	1st October 2007	Shallow groundwater (2 m)	Maas Deep Channel	Agriculture/ Groundwater protection area	+	+
6. North Limburg, Laarbeek,	0.13 glyphosate	23rd October 2007	Shallow (phreatic) groundwater (2-3 m)	Maas Sand	Agriculture	+	+
7 Central Limburg, Grathem,	0.17 AMPA	17th October 2007	Semi-deep groundwater (3 m)	Maas Deep Channel	Recreation (bungalow park)	+/-	+
8. North Limburg, Broekhuizn	0.17 AMPA	24th Sept. 2007	Semi-deep groundwater (8-10 m)	Maas Sand	Agriculture	+/-	+
9. North Limburg, Gennep,	0.17 AMPA	15th August 2007	Semi-deep groundwater (8-10 m)	Maas Sand	Urban area	-	-
	0.13 AMPA		Deep groundwater (18-20 m)				
10 North Brabant, Eindhoven,	0.29 AMPA	3rd October 2007	Semi-deep groundwater (3 m)	Maas Sand	Car park / sports grounds	+	Uncertain bottle code
11. South Holland, Noordwijkerhout	0.99 glyphosate	2003-04	Shallow (< 7 m)		Agricultural (bulbs), residential district	+	
12. North Holland, Texel	4.74 glyphosate	2006	Shallow (< 7 m)		Agricultural	+	
13. Groningen, Hoogezand	0.47 glyphosate	2006	10 m deep		Agricultural	+	
14. Groningen, Winschoten	0.32 glyphosate	2006	10 m deep		Agricultural	+	

[1] On the basis of inspection on location, + signifies good protection of the well, +- signifies that the appearance of surface translocation or drift is unlikely but cannot be excluded, - signifies a likely chance of drift or surface translocation.

[2] On the basis of insights into possible errors which occurred during the processing of the samples and the analysis of the data, + signifies no indication that errors have occurred, - signifies that possible errors have occurred.

The results show that at least 2 sites (Maasbracht and Gennep) showed a poor well protection that surface water influx cannot be excluded. At five other sites, the well wasn’t fully protected either (2 springs, and 3 sites where the covers did not fully close) and it is conceivable that contact with surface water my occur. Uncertainty related to the data processing was evidenced at 2 sites. For 6 of the 10 sites at which glyphosate was detected, no explanation could be found during this investigation.

It should be noted that numerous AMPA detects were reported from the 2007 studies, but not investigated in his report. AMPA is considered as a non-relevant metabolite in The Netherlands and the 0.1 µg/L trigger does thus not apply.

Conclusion

This has evidenced a potential contact between ground and surface water due to a bad sealing of the well cover for 7 wells, and uncertainty related to data processing in 2 sites. No explanation for 6 out of the 10 glyphosate detects could be found within the remit of this study.

Assessment and conclusion by applicant:

The article elucidates findings of glyphosate and AMPA in groundwater in The Netherlands. The methods and results are sufficiently described.
The article is considered reliable.

Assessment and conclusion by RMS:

This study was previously sutmitted for AIR II renewal, and have been reviewd in the RAR 2015. RMS evaluation from the RAR 2015 is reported below.

At 6 out of 189 sampling locations glyphosate was measured above the detection limit and drinking water threshold of 0.1 µg/L carried out in one report (Royal Haskoning, 2008), and at 4 out of 691 measurements carried out in a second report (RIVM, 2007). The results show that some wells were not fully protected and it is conceivable that contact with surface water may occur. Uncertainty related to the data processing was evidenced as well. For 6 sites at which glyphosate was detected, no explanation could be found during this investigation. Irrespective of the pathways of glyphosate into groundwater and the uncertainty related to the data processing, it remains unclear if the findings can be correlated with the normal and proper use of glyphosate in the field.

The study is considered reliable.

B.8.5.4. Monitoring data in surface water

New studies/assessments

Data point:	CA 7.5/001
Report author	[redacted]
Report year	2020
Report title	Collection of public monitoring data for European countries for the compartments soil, water, sediment and air for Glyphosate, AMPA and HMPA
Document No	110057-1
Guidelines followed in study	Methodology is based on the Groundwater Monitoring guideline document (Gimsing *et al*., 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations') Minimum quality criteria of monitoring data described by the FOCUS Ground Water Work Group chapter 9.5 (European Commission, 2014)
Deviations from current test guideline	None
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

The report provides information about the outcome of a search for readily accessible and available monitoring data in European countries at a regional/national level for the time period 1995-2019. The main focus was on the time period 2012-2019 while earlier years are already covered by existing data. The search included raw data, requested from regional/national authorities or downloadable from their websites, as well as aggregated data extracted from reports compiled by authorities.

Data from 14 European countries were considered: Austria, Belgium, Denmark, France, Germany, Hungary, Ireland, Italy, The Netherlands, Poland, Romania, Spain, Sweden and the United Kingdom. The countries represent the major markets of products containing glyphosate sold in the EU. The data compilation included the active substance glyphosate and its metabolites AMPA and HMPA, in the soil, groundwater, surface water, tidal water, drinking water, sediment and air environmental compartments.

As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities and other bodies of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were not actually included in any of the monitoring programs.

Surface Water Compartment Conclusion
A large surface water public monitoring dataset was compiled, comprising raw datasets from 10 countries (AT, BE, DK, ES, FR, IE, IT, NL, SE and UK) and aggregated datasets from published reports for 8 countries (AT, DE, DK, ES, HU, IE, IT and NL). Collectively these cover a wide range of pedoclimatic and hydrological settings typically spanning more than a decade.

I. MATERIALS AND METHODS

The general methodology of data collection of public monitoring data and minimum quality criteria is based on existing guideline documents for groundwater monitoring programs. The underlying principles have been applied to all environmental compartments, especially where no specific guidance is at hand. Data search, acquisition and processing approaches are described below. The same approach was applied for each country, compartment and substance. Country specific adaptations to the general procedure were made

in order to generate a harmonized database. The data collected for this report refers to third party organization data regarding all environmental compartments (SOIL, GW, SW, TD, DW, SD, AIR) and was further differentiated into the two different data types, i.e. raw data and aggregated data. Aggregated data refers to information provided in publicly available reports, e.g. from environmental agencies or research institutes. Such reports might hold only summary information on substance findings over space and time and may intersect with the raw data. Raw data refers to mid to long term time series of data that are provided on request by e-mail or by database from governmental authorities and are therefore recognized as official monitoring data. These datasets hold the information of sampling values, quality information (sampling, treatment, limit of detection - LOD, limit of quantification - LOQ) as well as information of location and time of sampling.

The following data source types were investigated in order to collect monitoring data:

- E-mail requests: a general e-mail was sent to the national responsible authorities with regard to the required information.

- Governmental webpages: the official webpages of the national responsible authorities were searched for information regarding available reports and datasets.

- Public online databases: available data from online databases were downloaded as provided by the webpages of governmental authorities and other institutions.

The data search resulted in a very heterogeneous collection of tabular data and reports in different formats and structure. Data were processed into a harmonized tabular format by selecting relevant information and adapting data organisation. In general, the complete datasets were included in the final harmonized database as provided by the authorities, but obvious duplicates were deleted. In general, all entries for the digital database were checked for consistency and plausibility. For the raw data it was assumed that information was already subjected to critical scrutiny by the respective organization. For the aggregated data the same assumption was made with quality assurance of the data (mostly summaries) being the responsibility of the authors of the respective reports.

II. RESULTS AND DISCUSSION

The final data collection of raw data and aggregated data is summarised for each compartment and each country in Table 8.5-87.

Surface water

- Austria (AT)
  - Raw monitoring data from national authorities for surface water were downloaded from the H2OFachdatenbank.
  - Aggregated monitoring data from reports published by national authorities for surface water were downloaded from several sources.

- Belgium (BE)
  - Raw monitoring data for surface water for both Flanders and Wallonia compiled by the Belgian association for the plant protection products industry were received *via* e-mail.
  - An additional dataset by the Flemish EPA was received for surface water in Flanders.
  - No aggregated monitoring data from reports published by national authorities were considered in case of the compartment surface water, because of the good data availability by raw data.

- Germany (DE)
  - Raw monitoring data from national authorities for surface water were provided by the regional authorities of Brandenburg, Bavaria, Bremen, Mecklenburg-Vorpommern, North

Rhine – Westphalia, Rhineland-Palatinate, Schleswig-Holstein, Saxony-Anhalt, Hesse, the state of Baden-Württemberg, and the state of Saxony.
  - Additionally, data were received for the large river systems Elbe and Rhine.
  - The regional authority in Mecklenburg-Vorpommern also provided data on tide waters.
  - Aggregated monitoring data from reports published by national authorities for surface water were downloaded from the German EPA, the LAWA, the environmental authority of Mecklenburg-Vorpommern, and the states of Rhineland-Palatinate, Schleswig-Holstein and Thuringia.

- Denmark (DK)
  - No raw monitoring data from national authorities for surface water in Denmark were identified.
  - Aggregated monitoring data from reports published by national authorities for surface water were downloaded from the National Center for Environment and Energy (DCE).

- Spain (ES)
  - Raw monitoring data from national authorities for surface water were provided from the Ministry of Agriculture, Fisheries and Food after contacting the Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA) *via* e-mail.
  - Aggregated monitoring data from reports published by national authorities refers to two reports from Madrid Polytechnical University and a non-governmental organization (Ecologistas en Acción).

- Europe (EU)
  - Raw monitoring data from on the European level were found from the International Commission for the Protection of the Rhine and Danube River.
  - Aggregated monitoring data from reports were found from RIWA-Maas and the World Health Organization as well as from the International Commissions for the Protection of the Rhine.

- France (FR)
  - In France, monitoring data for surface water are published by the Public Water Information Service (eaufrance). Raw monitoring data from national authorities for surface water were downloaded from NAIADES.
  - No aggregated monitoring data from reports published by national authorities were considered, because of the very good data cover by the raw monitoring data.

- Hungary (HU)
  - Raw monitoring data from national authorities for surface water were not available.
  - Aggregated monitoring data from reports published by national authorities for surface water were obtained in form of a peer-reviewed paper of the National Agricultural Research and Innovation Centre published in Journal of Chemistry.

- Ireland (IE)
  - Raw monitoring data from national authorities for surface water were provided by the Irish EPA *via* e-mail.
  - Aggregated monitoring data from reports published by national authorities for surface water were downloaded from the Irish EPA.

- Italy (IT)
  - Raw monitoring data from national authorities for surface water were downloaded from the regional environment agencies (ARPA) of the regions of Lombardia, Toscana, Veneto and Umbria.
  - The provincial environmental agency (APPA) of the province of Trento and the regional environment agencies of the regions of Emilia-Romagna, Marche, Venetia and the region

    of Pimento provide raw data for measurements in surface water, but no explicit data on glyphosate.
  - Aggregated monitoring data from reports published by national authorities for surface water were downloaded from ISPRA.

- The Netherlands (NL)
  - Raw monitoring data from national authorities for surface water were downloaded from the Water Dutch Quality Portal. Raw monitoring data for surface water in the Netherlands were also provided by RIWA Rhine *via* e-mail.
  - Aggregated monitoring data from reports published by national authorities for surface water were downloaded from RIVM and VROM. Aggregated monitoring date from reports for surface water were also provided by and downloaded from the Association of River Waterworks RIWA.

- Poland (PL)
  - The responsible authorities for monitoring data in Poland are the Polish Geological Institute and the Chief Inspectorate Of Environmental Protection. The latter authority confirmed by e-mail that in Poland there is currently no public monitoring of glyphosate or its metabolites in surface water.

- Romania (RO)
  - The responsible authority for monitoring data is the Ministry of Water and Forests. The Water Resources Management Directorate confirmed on behalf of the Ministry of Water and Forests that no public monitoring of glyphosate or its metabolites is carried out in any water compartment in Romania.

- Sweden (SE)
  - Raw monitoring data from national authorities in Sweden for surface water were provided by SLU *via* e-mail. Additional raw monitoring data for surface water were directly downloaded from the SLU homepage. Moreover, SLU provided another database containing raw data for surface water issued from other sources than national monitoring, e.g. regional monitoring and private wells. This dataset was separately processed.
  - Aggregated monitoring data from reports published by national authorities for surface water were not identified. However, aggregated national monitoring data in tabular form for surface water were downloaded from the SLU homepage.

- United Kingdom (UK)
  - Raw monitoring data from national authorities for surface water were downloaded from the Environment Agency for England, and were provided *via* e-mail by the Scottish EPA for Scotland. For tide waters, data were available for England from UK's EPA webpage.
  - No aggregated monitoring data from reports were provided.

Table 8.5-87: Overview of public monitoring data availability of raw data (R) and aggregated data (A)

Country	Soil	Water				Sediment	Air
		Ground	Surface	Tidal	Drinking		
Austria	-	R, A	R, A	-	A	-	-
Belgium	-	R	R	-	A (Flanders)	-	-
Denmark	-	R, A	A	-	A	-	-
France	-	R	R	-	A	R	-
Germany	R (Brandenburg)	R, A	R, A	R	R (Schleswig-Holstein), A	-	-

Hungary	-	A (one research article)	A (one research article)	-	-	-	-
Ireland	-	R, A	R, A	-	R, A	-	-
Italy	-	R (Lombardia), A	R, A	-	-	-	-
The Netherlands	-	R, A	R, A	-	R	-	-
Poland	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Romania	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Spain	-	R, A	R, A	-	A	-	-
Sweden	-	R, A	R	-	R, A	R	-
UK England	-	R	R	R	A	-	-
UK Northern Ireland	-	R	-	-	-	-	-
UK Scotland	-	-	R	-	-	-	-
UK Wales	-	-	R	-	A	-	-

R raw data available; A aggregated data from reports available; - no raw or aggregated data available

III. CONCLUSIONS

The collection of public monitoring data for glyphosate, AMPA and HMPA in soil, groundwater, surface water, drinking water, tide water, sediment and air resulted in a comprehensive database of ‘raw monitoring data from national authorities’ and ‘aggregated monitoring data from reports published by national authorities’. As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were actually not included in any of the monitoring programs.

A large surface water public monitoring dataset was compiled, comprising raw datasets from 10 countries (AT, BE, DK, ES, FR, IE, IT, NL, SE and UK) and aggregated datasets from published reports for 8 countries (AT, DE, DK, ES, HU, IE, IT and NL). Collectively these cover a wide range of pedoclimatic and hydrological settings typically spanning more than a decade.

Assessment and conclusion by applicant:
The study describes the collection process of public monitoring data for European countries for the compartment soil, water, sediment and air for Glyphosate, AMPA and HMPA.
The study is considered valid.

Assessment and conclusion by RMS:

This report describes the methodology employed for collection of monitoring data for Glyphosate, AMPA and HMPA. The data collection refers to third party organization data regarding all environmental compartments (Soil, GW, SW, TD, DW, SD, AIR), as described for GW in FOCUS 2014 and Gimsing *et al*. 2019. Two different data types were collected, *i.e.* raw data from national authorities and aggregated data from publicly available reports (from environmental agencies or research institute).

The general search strategy was similar for each compartment, country and substance. All details of data acquisition are given in the report, and all data sources are carefully listed and described.
Although the process can clearly not be reproduced, and cannot be checked in details for exhaustiveness, the search strategy is clearly exposed and considered acceptable.

For surface water compartment, data from 10 countries were collected. Raw data set from 10 countries (AT, BE, DK, ES, FR, IE, IT, NL, SE and UK) and aggregated data from 8 countries were eventually collected (AT, DE, DK, ES, HU, IE, IT and NL). Three countries confirmed (PL, HU and RO) that the target substances are not including in national monitoring programs.

Findings from this data collection and corresponding analysis are given in a separate report; see [redacted] 2020 below.

The study (surface water part) is considered acceptable.

Data point:	CA 7.5/002
Report author	[redacted]
Report year	2020
Report title	Glyphosate (GLY) and the primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA): Public monitoring data assessment and interpretation
Report No	EnSa-20-0322
Document No	-
Guidelines followed in study	Groundwater monitoring guideline document (Gimsing *et al.*, 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations'); Article 5 of Directive 2009/90/EC - Technical specifications for chemical analysis and monitoring of water status.
Deviations from current test guideline	Not relevant
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary

The report provides information about the outcome of an analysis of public monitoring data comprising environmental concentrations of glyphosate (GLY) and its primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA) collated from readily available public monitoring databases held by national/regional environment agencies. This data collection and analysis was designed to expand previous reviews to include other compartments and supplement them for surface water, groundwater and drinking water. Public monitoring data from the following Member States (MS) were assessed for the water, sediment and soil compartments: Austria (AT), Belgium (BE), Denmark (DK), France (FR), Germany (DE), Ireland (IE), Italy (IT), Netherlands (NL), Spain (ES), Sweden (SE) and the United Kingdom (UK). Three MS, namely Poland (PL), Hungary (HU), and Romania (RO) confirmed that they do not conduct analyses for GLY, AMPA and HMPA in any environmental compartment. No data for HMPA was identified for any MS or compartment. Note that at the time the study was started the UK was a Member State and is referred to as a Member State throughout the report.

Analyses of the large spatial and temporal dataset of measured concentrations occurring in several environmental compartments, namely surface water, groundwater, drinking water, tidal water, sediment and soil, were conducted to assess their state. This analysis not only sought to assess the state of the environmental compartment but also to consider the potential impacts this might have on biota, ecosystems and human health by using regulatory endpoints and thresholds from a range of European (EU) Directives. These included the Water Framework Directive (Directive 2000/60/EC) and associated Groundwater (2006/118/EC), Drinking Water (1998/83/EC) and Priority Substances (2008/105/EC28) Directives in addition to the Plant Protection Products Directive (1107/2009/EC).

Surface water

Surface water (SW) data from AT, BE, DE, ES, FR, IT, SE, UK and two large transboundary catchments relating to the Rhine and Danube river basins were analysed for compliance with a range of regulatory endpoints and thresholds. The SW data were assessed against a RAC of 400 µg/L for GLY and 1200 µg/L for AMPA. Additional analyses against MS specific annual average (AA) and Maximum Allowable Concentration (MAC) EQS values were also undertaken.

Glyphosate

The large GLY public monitoring dataset (>291 000 samples collected from >13 800 sampling sites) was dominated by data sourced from France (~65%) with smaller contributions from Belgium (9%), Germany (~8.5%), the Netherlands (~5.6%) and Spain (~4.9%).

Detection of GLY above the limit of quantification (>LOQ) in SW samples was ~40% which compares well with the ~31% of samples from the previous data collection, with the apparent increase likely a function of improving LOQs. Compliance with the GLY RAC of 400 µg/L was extremely high (99.994% of samples; 99.90% of sites) and the very occasional exceedances (0.006% of samples; 0.10% of sites) were largely on separate non-consecutive occasions (0.003% of samples being consecutive). MS results for DE and FR are consistent with other published examples. A small number of high maximum concentrations in the dataset were confirmed to be outliers and once excluded indicated a maximum concentration of 57 µg/L, which is well below the RAC. Assessment of the spatial distribution of locations that exceed the GLY RAC did not indicate any specific pattern or bias. No EU-wide EQS values, annual average (AA) or maximum allowable concentration (MAC), were available for assessment as broader ecosystem endpoints. Consideration of the MS GLY surface water data against MS EQS values indicates that the presence of GLY is not expected to have any adverse impacts on ecosystems with a near total compliance (99.987%) across the large EQS-MAC dataset (~228 000 samples from ~9 000 sites) with very few exceedances (0.013% of samples; 0.22% of sites) identified. Similarly, 100% compliance for the large EQS-AA dataset (~11 000 years from ~1 600 sites) is indicated with no exceedances identified. These EQS results are consistent with national and regional published results for France, and Flanders in Belgium.

AMPA

The large AMPA public monitoring dataset (>269 000 samples collected from >12 400 sampling sites) was dominated by French data (~68.3%) with smaller contributions from Belgium (~9.6%), Germany (~9.0%) and the Netherlands (~5.9%). Detection of AMPA >LOQ in SW samples was ~64% which compares well with the ~50% of samples in the previous data collection, likely a function of improving LOQs. Compliance with the AMPA RAC of 1200 µg/L was very high (99.999% of samples; 99.976% of sites) with infrequent exceedances (0.001% of samples from 0.024% of sites) occurring on 3 separate non-consecutive occasions. MS results for FR are consistent with other published examples. A small number of high maximum concentrations were confirmed to be outliers and once excluded indicated a maximum concentration of 224.4 µg/L, which is well below the RAC. Assessment of the spatial distribution of locations of AMPA exceedance of the RAC did not indicate any specific pattern or bias. It should be borne in mind that AMPA may originate from sources other than GLY, for example detergents. No EU-wide EQS values, AA or

MAC, were available for assessment as broader ecosystem endpoints. Consideration of the MS AMPA surface water data against MS EQS values indicates that the presence of AMPA, from GLY or other sources, is not expected to have any impacts with 100% compliance for the large EQS-MAC (~218 000 samples from ~9 000 sites) and EQS-AA (~10 000 years from ~1 400 sites) datasets. The EQS results are consistent with national and regional published results for France, and Flanders in Belgium.

HMPA
No monitoring data were available for HMPA.

Understanding Sources of Exposure

In order to gain a better understanding of the sources and drivers of current residues in the environment further attention was paid to the surface water compartment given the richness of the dataset available and the fact that residues in this compartment may arise from several use environments, for example urban, railway and arable.

Regression tree models (RTM) were developed for a case study focusing on France to predict the number (total and consecutive) and rate of exceedance (%) of 0.1 µg/L in surface waters using predictor variables describing sources of GLY/AMPA and factors affecting emission and detection, for example the extent of different landcovers, GLY sales and extent of Urban Waste Water Treatment emissions in the catchment of the monitoring points. These RTMs indicate that urban areas and urban waste water treatment works emissions were the most important drivers in the rate of exceedance as well as the number of exceedances, total and consecutive. They also demonstrated that arable (to a lesser extent) and permanent crops (to even smaller extent than arable) were important factors in GLY and AMPA detection.

Consideration of published relevant literature which explores the source apportionment of GLY and AMPA in aquatic environments reinforced the conclusions drawn from assessment of the public monitoring data. GLY and AMPA concentrations appeared to be generally larger from urban sources than from diffuse agricultural ones. With respect to urban sources, use on railways/roads seemed to result in the highest residues, while garden use resulted in lower residues in comparison to amenity use. In addition, from urban sources AMPA concentrations were often greater than glyphosate and likely to be derived from other compounds like detergents. Storm events often gave rise to large spikes in concentration in agricultural settings, and even more so where there was an urban contribution. If the sampling location was downstream of urban, or major infrastructure (rail or roads) then the GLY and AMPA residues were mostly likely not to have come from agricultural uses. These observations mirror that of the RTMs.

Surface Water Compartment Conclusion
No information on HMPA was available. Analysis of the large GLY and AMPA surface water datasets indicates they are both frequently detected above the LOQ, however, compliance against regulatory endpoints and thresholds is extremely high with the frequency of exceedance being very low. The environmental concentrations typically encountered do not pose a risk for biota or ecosystems.

I. MATERIALS AND METHODS

An integral part of potentially understanding the patterns of exposure highlighted by the public monitoring data is where products containing GLY were used and the extent of usage. Assessment of usage of GLY and other sources of AMPA considered published data and summaries. The dataset analysed comprised individual surface water analysis records as well as existing aggregated analyses extracted from reports sourced from regional/national environment agencies (see [redacted], 2020, CA 7.5/001). The surface waterbodies captured by the dataset included streams, rivers, canals and lakes. They did not include transitional brackish water bodies which were included in a separate section. The approach taken for the data processing was precautionary in that it preserved samples in the analysis where there was any doubt regarding their reliability. As such the number of records excluded from the analysis were small (*n*=8 672), especially relative to the total number of samples (*n*=569 400) prior to removal. Similarly, no attempt to remove outliers prior to the analysis or calculation of statistics was undertaken despite the presence of extreme values being present in the datasets. In order to explore the extreme nature of some of the values included in the surface water dataset and assess the implications for this analysis, an outlier analysis was performed on the combined EU dataset. The development of Regression Tree models was also undertaken for the French surface water public monitoring dataset. These models sought to predict the exceedance rate (%) of the arbitrarily defined regulatory threshold of 0.1 µg/L as well as the number of exceedances through relating them to descriptors of the catchment upstream of each monitoring location.

Table 8.5-88: Summary of Environmental Quality Standards (EQS), average annual (AA) and maximum allowable concentration (MAC) utilised for the different Member States

Member State	GLY		AMPA	
	EQS-AA	EQS-MAC	EQS-AA	EQS-MAC
	µg/L			
AT - Austria	NA	NA	NA	NA
BE - Belgium (Wallonia)	28	70	450	45200
BE - Belgium (Flanders)	NA	64	NA	800
BE - Belgium (Combined)[1]	28	64	450	800
DK - Denmark	NA	NA	450	45200
EU - Transboundary (Danube/Rhine)	NA	NA	NA	NA
FR - France	28	70	452	45200
DE - Germany	28	NA	96	NA
IE - Ireland	60	NA	NA	NA
IT - Italy	NA	70[2]	NA	45200[2]
NL - Netherlands	77	NA	79.7	NA
ES- Spain	NA	NA	NA	NA
SE- Sweden	NA	100	NA	500
UK – United Kingdom	196[3]	398[3]	NA	NA
EU Combined Dataset	NA	NA	NA	NA

NA – Not available as not defined

[1] - Lowest value taken from each federal region to define a worst case set of national values

[2] - Italian law (Legislative Decree 172, 2015) stipulates that where an EQS value has not been set for an individual pesticide a value of 0.1 µg/L should be used for both parent and metabolites unless a scientific justification is presented for an alternate value. In this case alternate values adopted by France have been used as this is the only other southern Zone MS to have set such values

[3] - These are 90th percentiles, applied as maximum values in the first instance in a precautionary approach.

Analysis and assessment of the data against thresholds was undertaken using the statistical software R (R Core Team, 2019) and graphs produced with the R package ggplot2 (Wickham, 2009). The average annual (AA) value for comparison against the MS EQS-AA (Environmental Quality Standard), where available, was calculated in accordance with Article 5 of Directive 2009/90/EC, namely technical specifications for chemical analysis and monitoring of water status, whereby values denoted as being below the limit of quantification (LOQ) are set to half the LOQ when calculating the arithmetic mean. This rule was also applied to the data denoted as being below the limit of detection (LOD). An additional rule was also applied whereby 12 values were required for any one year for this calculation. This was considered to be consistent with the monthly sampling intensities laid down in the Water Framework Directive (2000/60/EC) for priority substances (PS). For surface water the monitoring data was evaluated against the following thresholds and endpoints:

- Ecotoxicological endpoint: Regulatory Acceptable Concentration (RAC) of 400 µg/L for GLY and 1200 µg/L for AMPA.
- Ecosystem endpoint: Environmental quality standards (EQS) where these were proposed/available (see Table 8.5-88) at a Member State level, comprising annual average EQS (EQS-AA) and maximum allowable concentration (EQS-MAC); No values for these endpoints have been set at a European level.

- Evaluation threshold: The data were also evaluated against a threshold of 0.1 µg/L for comparative purposes with other published evaluations despite there being no regulatory requirement to present such data.

II. RESULTS AND DISCUSSION

Glyphosate Product Sales/Usage

The data presented in Figure 8.5-61 were derived from annual sales data submitted by registrants to the national authorities, in many instances reported under the Sustainable Use Directive (Directive 2009/128/EC). Sales/usage data (see Figure 8.5-61) indicated that annual amounts in recent years for some MS are very small e.g. DK where these range between ~300 and ~1 900 kg a.s.. For many MS these amounts were below 3 000 tonnes (see Figure 8.5-61b) while in others they were large e.g. ES where >10 000 tonnes were sold annually. The following trends in available sales/usage were evident for the data in the last 5 years:

- Increasing in ES, UK and the combined 11 MS for which monitoring data is available;
- Static or possibly decreasing in AT, BE, DK, FR, NL and SE
- Decreasing in DE
- No data for IE and IT

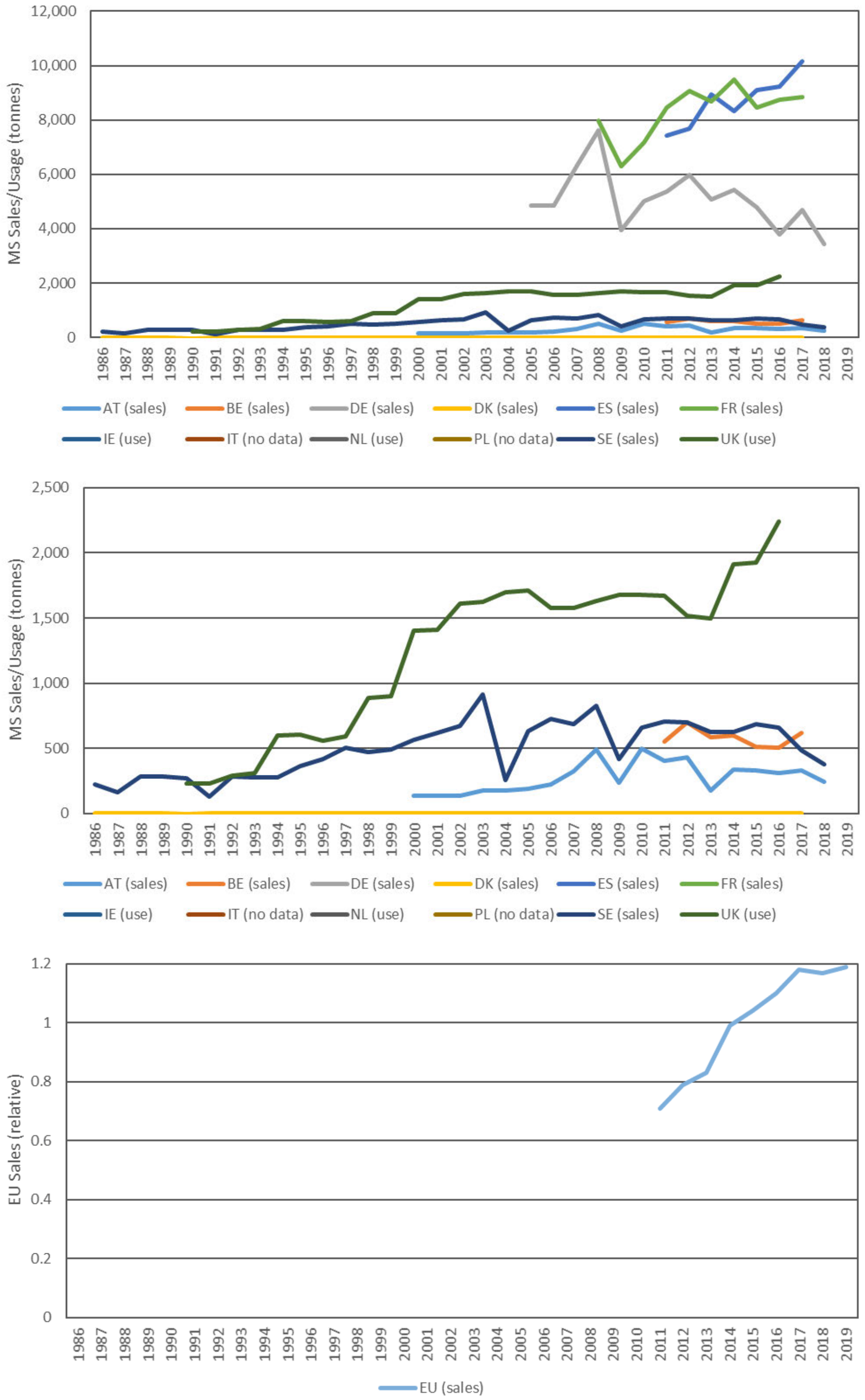
Little data on railway, urban/amenity/amateur usage was identified. Evaluation of the product sales in the FR BNVD dataset for 2017 suggests that approximately 14% of sales were to the amateur/amenity sector (see Table 8.5-89).

Table 8.5-89: Summary of glyphosate sales volumes in France differentiated by key user groups (ANSES, 2019)

Year	**Units**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**
Agricultural	tonnes	5157	5798	6731	7075	6616	7753	6930	7151	6951
	%	80.3	80.5	79.5	78.1	76.3	81.7	82.0	82.0	86.1
Amateur/amenity	tonnes	1264	1407	1739	1987	2057	1733	1522	1570	1125
	%	19.7	19.5	20.5	21.9	23.7	18.3	18.0	18.0	13.9
Total	tonnes	6421	7205	8470	9062	8673	9486	8452	8721	8076

Railway usage was documented for a number of MS for 2017 and indicated that applications of GLY may be as low as ~1 tonne (DK) up to ~60 tonnes (IT), typically representing only a few percent of total GLY sales.

Figure 8.5-61: **Illustration of glyphosate (GLY) sales/usage in Member States targeted by the monitoring for (a) all sales/usage tonnage (b) those with sales/usage below 2500 tonnes/annum and (c) all MS for which monitoring data was identified. The European sales figures are expressed relative to the average of those years and as such is a relative value for illustrative purposes only.**



(a)

(b)

(c)

Other Sources of AMPA

It was emphasized that AMPA may be derived from other parent compounds used in both industrial and household applications, including detergents, fire retardants, anti-corrosives, anti-scaling agents and complexing agents in the textile industry. ECHA REACh registrations indicated that these compounds may be included in water softeners, polishes and waxes, washing and cleaning products, coating products, cosmetics, personal care products, water treatment products, textile treatment products, dyes, leather treatment products, paper chemicals, amongst others. The usage classes for such compounds (see Table 8.5-90) suggested that these compounds would contribute meaningfully to loads of AMPA in the environment, especially where specific industries, for example paper or textile, emit effluent.

Table 8.5-90: Summary of REACh registration tonnage and published estimates for key phosphonates that break down in the aquatic environment to form AMPA (*after* JRC, 2015b)

Parent Compound Name	**Parent Compound ID**	**Main Use (in Europe)**	**EU Tonnage Class tonnes/annum**[2]	**Number AMPA molecules**[1]
Amino tris(methylenephosphonate)	ATMP (CAS 6419-19-8)	Industrial boilers/cooling	10000-100000	1
Diethylenetriamine penta(methylenephosphonate)	DTPMP (CAS 15827-60-8)	Detergents	1000-10000	3
Ethylenediamine tetra(methylenephosphonate)	EDTMP (CAS 1429-50-1)	Laundry detergents	10-100	2
Hexamethylenediamine tetra(methylenephosphonate)	HDTMP (CAS 38820-59-6)	Industrial boilers/cooling	No current registration	2

[1] - Number of AMPA molecules that can potentially be formed from one molecule of each compound.

[2] - https://echa.europa.eu/, accessed March 2020.

The total volume of phosphonates used in Europe was found to not be well documented, but estimated to be in the range of 10,000-50,000 tons/year on an active acid basis, of which 12,000 tons of ATMP, HDTMP and DTPMP were used in household detergents and cleaning products (JRC, 2015b). AMPA is poorly removed in sewage treatment works and consequently household and industrial emissions containing detergents were considered likely to contain AMPA, leading the JRC to conclude that “the AMPA load from detergents should not be underestimated in surface water, if compared to the indirect contamination that could occur following the use of glyphosate” (JRC, 2015b).

Monitoring Data Assessment

Glyphosate

Temporally the GLY (see Figure 8.5-62) data indicated some bias at a MS level with fewer samples typically collected in the winter and spring months resulting in a unimodal distribution. In some MS, notably FR and SE, the data had a potentially bimodal distribution with data collection in spring and autumn, during key agricultural and hard surface usage periods, being greater than at other times of the year. The spatial distribution of GLY public monitoring locations for MS where data was collected was biased (see Figure 8.5-64). For some MS, e.g. DE, IT and ES, this was a function of data only arising from some provincial/regional environment agencies while for others, e.g. the UK, this was likely a function of spatial targeting. The input data collated for analysis of GLY residues in SW were dominated by data sourced from France (~65.4%) with smaller contributions from Belgium (~9%), Germany (~8.5%), the Netherlands (~5.6%) and Spain (~4.9%).

Across all MS the GLY public monitoring dataset compiled comprised >291 000 samples collected from >13 800 sampling sites (see Table 8.5-91). Detection of GLY above the limit of quantification (LOQ) in SW was ~40%, ranging from as low as 6.5% in BE to as high as 67.5% in SE, relative to a varying LOQ with an average of 0.15 µg/L (min: 0.01 – max: 1000 µg/L). These compared well with the previous data collection ([redacted], 2012, CA 7.5/013 and 2016, CA 7.5/010) where ~31% of samples were found to have detected GLY (see Table 8.5-95).

Compliance with the GLY RAC of 400 µg/L was extremely high (99.994% of samples; 99.90% of sites), ranging from 100% (e.g. in AT) to 99.44% (UK), with exceedances being extremely rare (16 samples from 23 sites; 0.006% of samples from 0.10% of sites). MS results for DE and FR were consistent with other published analyses, using predicted no effect concentration (PNEC) thresholds. When exceedances occurred, they occurred largely on separate non-consecutive occasions (0.003% of samples; see Table 8.5-96). The spatial distribution of the GLY exceedance locations (see Figure 8.5-64) did not indicate any specific patterns or bias.

Maximum measured concentrations up to 91 600 µg/L were reported, however, these extreme values were considered likely erroneous as they would be difficult to generate from GLY containing products in real world water bodies short of a major pollution incident having occurred and gone unreported. The 99th percentile concentration (see Table 8.5-93), the concentration that 99% of samples are below, was 2.3 µg/L and the RAC represents the 99.987th percentile value. In line with the precautionary data processing approach adopted in this study possible outliers were not removed from the dataset prior to analysis. However, an additional analysis step was conducted to identify likely outliers in the dataset and the implications of these for the analysis assessed. This identified 58 outliers which if excluded, suggest the maximum concentration would be 57.0 µg/L which is well below the RAC and as such 100% compliance with the RAC would be expected (see Table 8.5-93).

No EU-wide EQS values, AA or MAC, were available for analysis of the combined EU dataset. Consideration of the MS GLY surface water data against available MS EQS-MAC (see Table 8.5-92) and EQS-AA (see Table 8.5-97) endpoints, indicated that the presence of GLY was not expected to have any impacts with near total compliance (99.987% of samples) across the large EQS-MAC dataset (~228 000 samples from ~9 000 sites) with very few exceedances (0.013% of samples; 0.22% of sites) identified. In all cases the values exceeding the MAC were classed as likely outliers in the combined EU dataset. Similarly, 100% compliance for the large EQS-AA dataset (~11 000 years from ~1 600 sites) was indicated with no exceedances identified. These results were considered to be consistent with national published results for Flanders in BE, and France, using regional/national EQS values.

In order to compare these detailed GLY results with published aggregated results, assessment against the arbitrarily defined regulatory threshold of 0.1 µg/L was also undertaken. Detection above the threshold of 0.1 µg/L was ~23% of samples (~54.0% of sites), ranging from 3.4% in AT to 57.5% in BE. These results compared well with the aggregated values extracted from reports (see Table 8.5-94) which ranged from 0.2% in AT to 22.9% of samples in DE. Similarly, these results compared well with the previous data collection where ~21% of samples were found to exceed 0.1 µg/L.

Annual and monthly investigations of sampling effort and compliance were also documented within the report. These have not been summarised as they do not alter the conclusions of the primary study, instead providing additional detail should this be required.

Figure 8.5-62: **Bar chart of surface water monthly glyphosate (GLY) sampling effort**

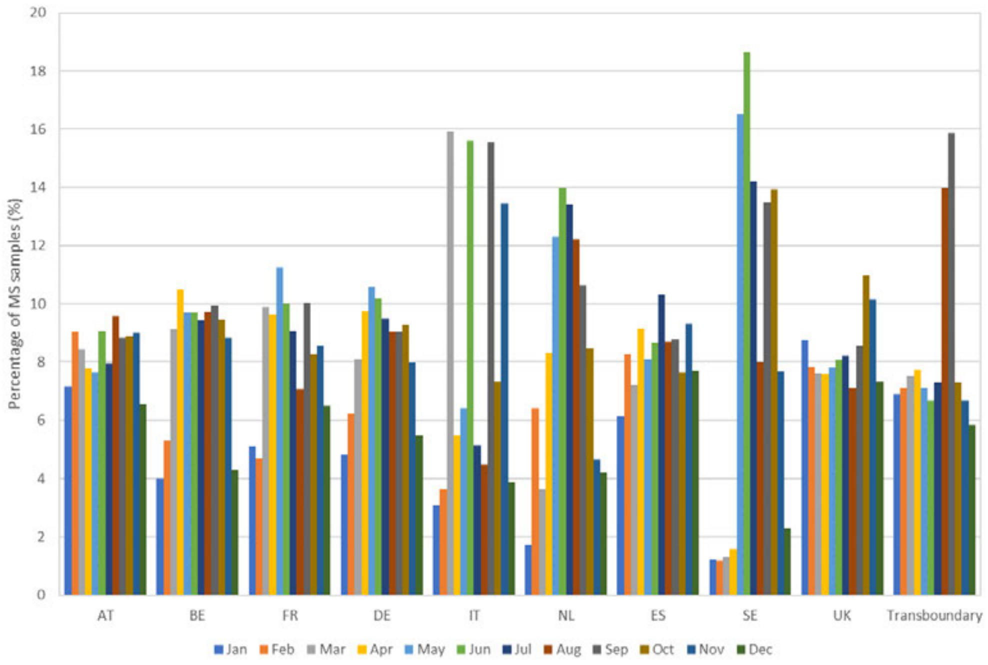


Figure 8.5-63: **Bar chart of surface water monthly AMPA sampling effort**

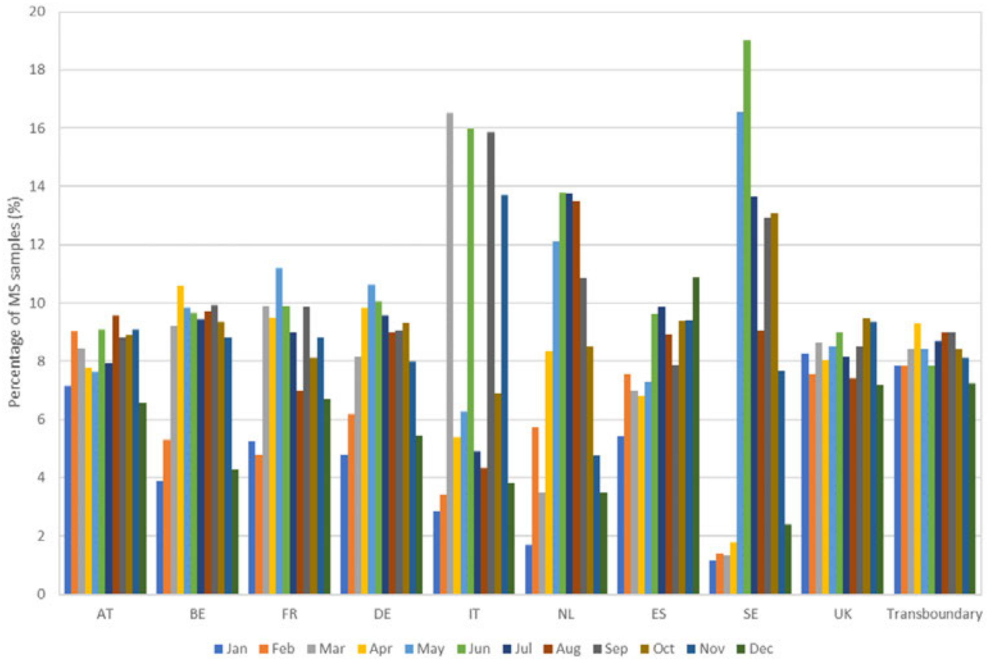


Figure 8.5-64: **Map illustrating the distribution of glyphosate (GLY) surface water (SW) sampling locations. Also illustrated are the number of exceedances of the SW regulatory acceptable concentration (RAC) at each location.**

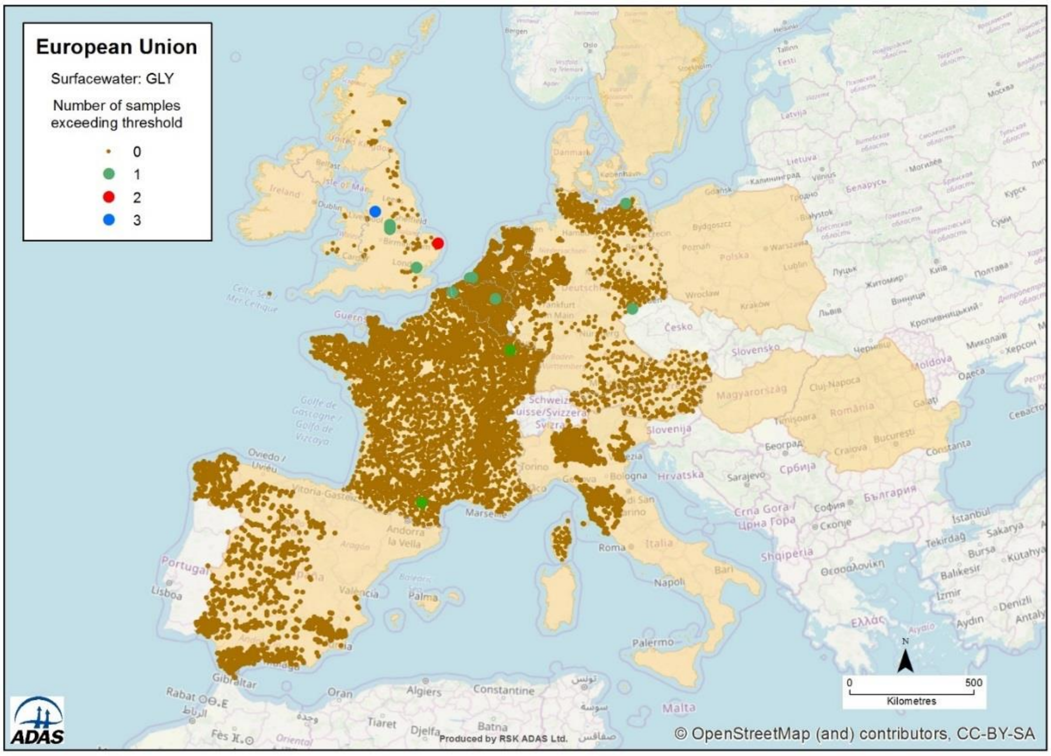
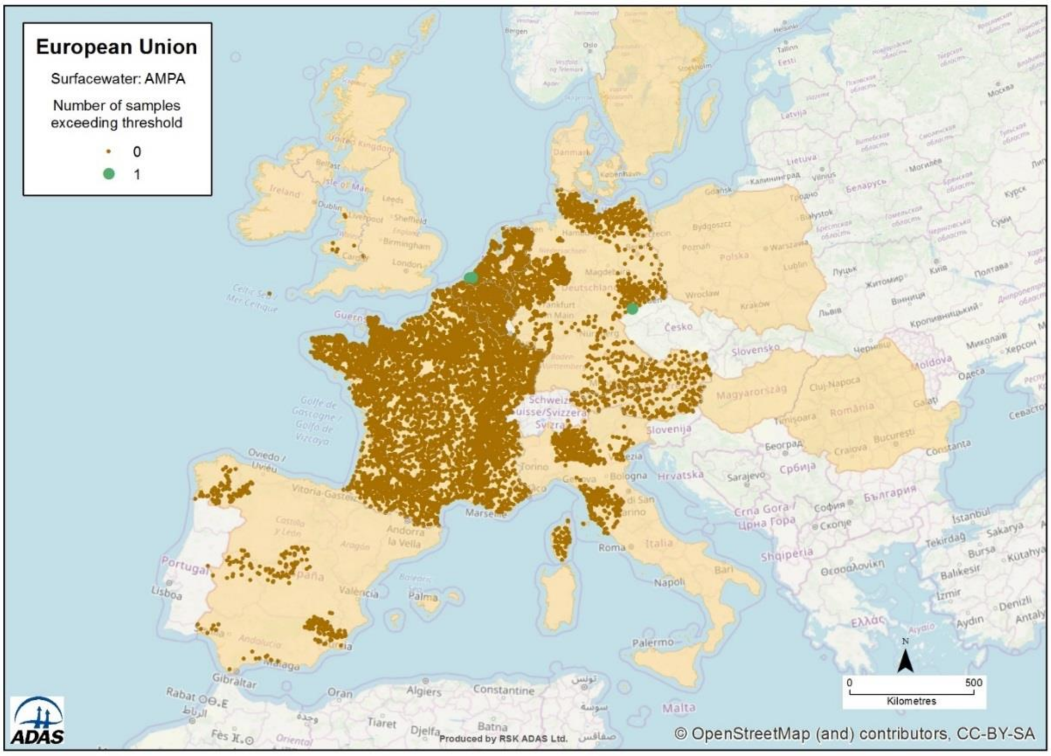


Figure 8.5-65: **Map illustrating the distribution of AMPA surface water (SW) sampling locations. Also illustrated are the number of exceedances of the SW regulatory acceptable concentration (RAC) at each location.**



AMPA

Temporally the AMPA (see Figure 8.5-63) data indicated some bias at a MS level with fewer samples typically collected in the winter and spring months resulting in a unimodal distribution. In some MS, notably FR and SE, the data had a potentially bimodal distribution with data collection in spring and autumn, during key agricultural and hard surface usage periods, being greater than at other times of the year. The spatial distribution of AMPA public monitoring locations for MS where data was collected was biased (see Figure 8.5-65). For some MS, e.g. DE, IT and ES, this was a function of data only arising from some provincial/regional environment agencies while for others this was likely a function of spatial targeting. The French data dominated the combined dataset (~68.3%) with smaller contributions from Belgium (~9.6%), Germany (~9.0%) and the Netherlands (~5.9%).

Across all MS the AMPA public monitoring dataset compiled comprised >269 000 samples collected from >12 400 sampling sites (see Table 8.5-91). Detection of AMPA >LOQ in all SW was ~64%, ranging at a MS level from as low as ~24.1% in AT to as high as ~87.7% in BE, relative to a varying LOQ with an average of 0.07 µg/L (min: 0.01 – max: 10 µg/L). These results were similar to the previous data collection where ~50% of samples were found to detect AMPA (see Table 8.5-95).

Compliance with the AMPA RAC of 1200 µg/L was very high (99.999% of samples; 99.976% of sites), ranging at a MS level from 100% (e.g. in AT) to 99.98% (NL), with infrequent exceedances (3 samples from 3 sites; 0.001% of samples from 0.024% of sites) occurring on 3 separate non-consecutive occasions (see Table 8.5-96). This observation was consistent with a published analysis using a PNEC threshold for France. The spatial distribution of the AMPA exceedance locations (see Figure 8.5-65) did not indicate any specific patterns or bias. It was highlighted that AMPA may originate from sources other than GLY, for example detergents.

Maximum measured concentrations up to 230 000 µg/L were reported, however, these extreme values were considered to likely be anomalous. The 99th percentile concentration, the concentration that 99% of samples are below, was 5.81 µg/L (see Table 8.5-93) while the RAC was the 99.999th percentile concentration. An additional analysis step was conducted to identify likely outliers in the dataset and the implications assessed. This identified 3 outliers in the combined EU dataset which if excluded, indicated the maximum concentration would be 224.4 µg/L which is well below the RAC and as such 100% compliance with the RAC would be expected (see Table 8.5-93).

No EQS values, AA or MAC, were available for assessment of the combined EU dataset. Consideration of the MS AMPA surface water data against EQS-MAC (see Table 8.5-92) and EQS-AA (see Table 8.5-97) endpoints indicates that the presence of AMPA from GLY or other sources was not expected to have any impacts as there was 100% compliance with the large EQS-MAC (zero exceedances of ~218 000 samples from ~9000 sites) and EQS-AA (zero exceedances in ~10 000 data years from ~1 400 sites) datasets compiled. These results were considered to be consistent with published results for Flanders in BE, and France, which reported compliance against EQS values.

In order to compare these AMPA results with aggregated results from published reports, assessment against the arbitrarily defined regulatory threshold of 0.1 µg/L was also undertaken. Detection above the threshold of 0.1 µg/L was ~47.5% of samples (~67.6% of sites), ranging from 16.3% in AT to 77.7% of samples in BE. These results were comparable with aggregated values extracted from reports (see Table 8.5-94) which range from ~44.4% in IT to ~91.7% of samples in the NL. Similarly, these results compare well with the previous data collection where ~41% of samples were found to exceed 0.1 µg/L (see Table 8.5-95).

Annual and monthly investigations of sampling effort and compliance were also documented within the report. These have not been summarised as they do not alter the conclusions of the primary study, instead providing additional detail should this be required.

Table 8.5-91: Member State and combined European dataset public monitoring summaries for glyphosate (GLY) and AMPA in surface water

MS	Substance	Number of Sites	Number of Samples	Years	LOQ (µg/L)	Samples with LOQ≤0.1 µg/L		Detected above LOQ		Detected >0.1 µg/L		Detected >RAC[1]		Measured Concentration (µg/L)[2]
					Mean (min - max)	Sites	Samples	Samples	%	Samples	%	Samples	%	Median (min - max)
AT	AMPA	314	4507	2003 - 2015	0 05 (0 04 - 0 50)	314	4505	1086	24 1	735	16 3	0	0 000	0 03 (0 007 - 3 8)
AT	GLY	316	4508	2003 - 2015	0 05 (0 04 - 0 50)	316	4506	292	6 5	155	3 4	0	0 000	0 03 (0 015 - 3 6)
BE	AMPA	842	25957	2001 - 2019	0 06 (0 02 - 1 0)	842	25836	22653	87 7	20069	77 7	0	0 000	0 59 (0 017 - 199 0)
BE	GLY	849	26364	2001 - 2019	0 06 (0 02 - 1 0)	849	26115	16710	64 0	15012	57 5	0	0 000	0 17 (0 013 - 139 0)
DE	AMPA	1639	24309	1996 - 2019	0 07 (0 01 - 0 41)	1600	23624	18154	76 8	15406	65 2	1	0 004	0 20 (0 000 - 5000 0)
DE	GLY	1714	24898	1996 - 2019	0 05 (0 01 - 0 20)	1643	23731	9011	38 0	4383	18 5	0	0 000	0 05 (0 005 - 171 0)
DK	AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DK	GLY	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ES	AMPA	323	2457	2012 - 2018	0 09 (0 03 - 0 20)	323	2453	1521	62 0	1471	60 0	0	0 000	0 24 (0 030 - 81 9)
ES	GLY	1172	14234	2006 - 2018	0 09 (0 00 - 100)	1170	13226	4373	33 1	2960	22 4	0	0 000	0 05 (0 000 - 100 0)
EU Transboundary	AMPA	3	361	2007 - 2017	0 39 (0 03 - 5 0)	3	345	325	94 2	248	71 9	0	0 000	0 20 (0 030 - 5 0)
EU Transboundary	GLY	72	493	2002 - 2017	0 09 (0 01 - 5 0)	72	479	135	28 2	23	4 8	0	0 000	0 05 (0 010 - 5 0)
FR	AMPA	7185	183708	2000 - 2019	0 06 (0 01 - 10 0)	7172	182539	107537	58 9	73679	40 4	0	0 000	0 10 (0 005 - 164 0)
FR	GLY	7410	190660	2000 - 2019	0 06 (0 01 - 10 0)	7378	189879	69589	36 6	33607	17 7	1	0 001	0 05 (0 005 - 558 0)
IE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
IE	GLY	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
IT	AMPA	688	5349	2011 - 2019	0 08 (0 01 - 0 10)	688	5349	2785	52 1	2178	40 7	0	0 000	0 10 (0 002 - 79 2)
IT	GLY	701	5611	2007 - 2019	0 08 (0 01 - 0 10)	701	5611	1977	35 2	1063	18 9	0	0 000	0 10 (0 000 - 26 0)
NL	AMPA	1014	15984	1995 - 2018	0 13 (0 03 - 1 00)	944	12812	10225	79 8	9239	72 1	2	0 016	0 22 (0 000 - 230000 0)
NL	GLY	1019	16230	1995 - 2018	0 05 (0 01 - 0 50)	904	11082	6169	55 7	4661	42 1	2	0 018	0 20 (0 000 - 40000 0)
SE	AMPA	393	5663	1997 - 2018	0 20 (0 03 - 2 00)	383	4117	2019	49 0	1421	34 5	0	0 000	0 00 (0 000 - 36 0)
SE	GLY	400	5703	1997 - 2018	0 05 (0 02 - 1 00)	395	5658	3817	67 5	2329	41 2	0	0 000	0 08 (0 000 - 370 0)
UK	AMPA	13	850	1996 - 2017	0 11 (0 10 - 1 00)	13	835	252	30 2	251	30 1	0	0 000	0 10 (0 100 - 4 4)
UK	GLY	151	2882	1996 - 2017	7 07 (0 05 - 1000)	145	2663	864	32 4	814	30 6	13	0 488	0 10 (0 050 - 91600 0)
EU Combined	AMPA	12414	269145	1995 - 2019	0 07 (0 01 - 10 0)	12282	262415	166557	63 47	124697	47 5	3	0 001	0 10 (0 000 - 230000 0) 0 10 (0 000 – 224 4)[3]
EU Combined	GLY	13804	291583	1995 - 2019	0 15 (0 00 - 1000)	13573	282950	112937	39 91	65007	23 0	16	0 006	0 05 (0 000 - 91600 0) 0 05 (0 000 – 57 0)[3]

[1] RAC = Regulatory Acceptable Concentration of 400 µg/L for glyphosate and 1200 µg/L for AMPA

[2] Values <LOQ and <LOD are treated as equal to LOQ and LOD as a precautionary estimate of the median

[3] Statistics with outliers excluded;

ND = None identified within the timeframe

Table 8.5-92: Summary of Maximum Allowable Concentration (MAC) Environmental Quality Standard (EQS) statistics for those Member States (MS) where such a threshold is available

Substance	**GLY**					**AMPA**				
Member State	**BE**	**FR**	**IT**	**SE**	**UK**	**BE**	**FR**	**IT**	**SE**	**UK**
EQS-MAC Threshold (µg/L)	**64**	**70**	**70**	**100**	**398**	**800**	**45200**	**45200**	**500**	**NA**
Number of Sites	849	7378	701	395	145	842	7172	688	383	NA
Number of Samples	26115	189879	5611	5658	2663	25836	182539	5349	4117	NA
Number of samples > threshold	10[1]	3[1]	0	3[1]	13[1]	0	0	0	0	NA
% of samples > threshold	0.04	0.0016	0.00	0.05	0.49	0.00	0.00	0.00	0.00	NA
Number of sites > threshold	5	3	0	3	10	0	0	0	0	NA
% of sites > threshold	0.59	0.041	0.00	0.76	6.9	0.00	0.0	0.0	0.00	NA
Maximum number of samples > threshold at a single site	5	1	0	1	3	0	0	0	0	NA
Maximum number of consecutive samples > threshold at a single site	2	1	0	1	3	0	0	0	0	NA

[1] All of these samples are classed as outliers in the combined EU dataset

Table 8.5-93: Summary statistics for glyphosate (GLY) and AMPA surface water concentration data considering the influence of outliers

Compound	**Outlier Status**	**Concentration (µg/L)**										**Percentile of RAC**	**Number of outliers**
		Minimum	**Mode**	**25th Percentile**	**Median**	**Mean**	**75th Percentile**	**90th Percentile**	**95th Percentile**	**99th Percentile**	**Maximum**		
GLY	Included	0	0.05	0.048	0.05	1.76	0.105	0.342	0.671	2.3	91600	99.9897	NA
	Excluded	0	0.05	0.048	0.05	0.20	0.105	0.34	0.67	2.23	57	100	58
AMPA	Included	0	0.05	0.05	0.1	1.41	0.34	1	2	5.81	230000	99.9989	NA
	Excluded	0	0.05	0.05	0.1	0.49	0.34	1	2	5.80	224.4	100	3

NA – Not applicable as not considered

Table 8.5-94: Summary of monitoring data aggregated in reports for glyphosate (GLY) and AMPA in surface water

MS	Substance	Number of reports identified	Reports with data relating to threshold						Maximum value (µg/L)
			Number of reports	Date range	Number of samples	Threshold (µg/L)	Samples above threshold	% samples above threshold	
AT	AMPA	2	0	NA	NA	3.0	NS	NS	3.7
	GLY	3	1	2011 - 2013	1852	0.1	4	0.22	8.1
BE	AMPA[7]	1	1	2004-2016	NS	28[4]	0	0.0	NS
	GLY[7]	1	1	2004-2016	NS	28[4]	0	0.0	NS
DE	AMPA[6]	ND	ND	ND	ND	ND	ND	ND	ND
	GLY[6]	1	1	2005-2015	3557	100[2]	1	0.03	NS
	AMPA	9	4	2004-2008	647	0.1	360	55.6	16.2
	GLY	12	4	2004-2008	647	0.1	148	22.9	16
DK	AMPA	1	0	NA	NA	NS	NA	NA	0.12
	GLY	1	0	NA	NA	NS	NA	NA	0.11
ES	AMPA	1	0	NA	NA	0.1	NA	NA	NA
	GLY	2	0	NA	NA	0.1	NA	NA	27.3
EU Transboundary	AMPA	2	0	NA	NA	NS	NA	NA	6.0
	GLY	2	0	NA	NA	NS	NA	NA	1.0
FR	AMPA[5]	1	1	2007-2017	137467	452[4]	0	0.0	NS
	GLY[5]	1	1	2007-2017	137518	28[4]	1	0.001	NS
	AMPA[5]	1	1	2007-2017	137467	45200[3]	0	0.0	NS
	GLY[5]	1	1	2007-2017	137518	70[3]	5	0.004	NS
	AMPA[5]	1	1	2007-2017	137467	60[2]	1[1]	0.001[1]	NS
	GLY[5]	1	1	2007-2017	137518	60[2]	1[1]	0.001[1]	NS
IE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	2	1	2007-2015	790	NS	0	0	NS
IT	AMPA	8	7	2007-2016	9212	0.1	4094	44.4	NS

Table 8.5-94: Summary of monitoring data aggregated in reports for glyphosate (GLY) and AMPA in surface water

MS	Substance	Number of reports identified	Reports with data relating to threshold						Maximum value (µg/L)
			Number of reports	Date range	Number of samples	Threshold (µg/L)	Samples above threshold	% samples above threshold	
	GLY	8	8	2007-2016	9340	0.1	1799	19.3	NS
NL	AMPA	25	7	2007-2018	1497	0.1	1372	91.7	7.9
	GLY	27	8	2007-2018	1576	0.1	305	19.4	1.1
SE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
UK	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND

ND – No data identified

NS – Not specified

[1] - Number/Percentage of sites where the annual average concentration exceeds the threshold

[2] – PNEC

[3] – Maximum allowable concentration (MAC) environmental quality standard (EQS)

[4] – Average annual (AA) concentration EQS

[5] - ANSES (2019) publication

[6] - Szöcs *et al*. (2018) publication

[7] - VMM (2017) publication

Table 8.5-95: **Summary of glyphosate (GLY) and AMPA analyses in surface water in Europe (*after* [redacted], 2016, CA 7.5/010)**

Country	**Compound**	**Date**	**Sites**	**Samples**	**Detected (samples)**		**Samples ≥ 0.1 µg/L**		**Max Conc**	**LoQ (LoD)**
		Range	**No.**	**No.**	**No.**	**%**	**No.**	**%**	**µg/L**	**µg/L**
Austria	AMPA	2001-02	?	345	≥90	≥26	90	26	3.4	?
Belgium (Flanders and Wallonia)	GLY F	2007-15	≥131	6802	5510	81	1628	23.9	139	0.02-0.4
	AMPA F	2007-15	≥132	6801	6256	92	3844	56.5	47	0.02-0.4
	GLY W	2001-14	≥171	6118	≥961	≥15.7	961	15.7	15.5	(0.05)
	AMPA W	2007-14	≥171	5891	≥148	≥86.6	≥148	≥86.6	35.8	(0.025-0.1)
Czech Republic	GLY	2010-14	≥290	6358	2547	40	≤2476	≤38.9	52	0.025-1.0
	AMPA	2010-14	≥236	4845	3185	65.7	≤3020	≤62.3	83	0.05-10
Denmark	GLY	2004-13	≥20	370	281	76	<281	<76	2.7	0.01-0.1
	AMPA	2004-13	≥20	363	296	81	<269	<81	0.28	0.01-0.2
Finland	GLY	2007-11	4	82	5	6.1	5	6.1	0.9	0.1
	AMPA	2007-11	4	84	14	16.7	≤13	≤15.5	0.22	0.05
France	GLY	97-2012	≥2003	91044	27999	30.7	19505	21.4	88	0.01-2.5
	AMPA	98-2012	≥2001	80817	42855	53	36053	44.6	106	0.01-0.25
Germany	GLY	97-2013	>204	≥2018	831	41	≤712	≤35	4.7	0.02-1.5
	AMPA	97-2013	≥71	≥1362	≤837	61.4	≤719	52.8	1.4	0.05-0.5
Ireland	GLY	2005-12	≥256	≥2544	142	5.6	≤142	≤5.6	186	0.08-0.1/20
	AMPA	2010-12	≥70	870	2	0.2	≥2	≥0.2	>200	20
Italy (Lombardia Region)	GLY	2005-12	≥274	2851	754	26.4	673	23.6	37.6	0.1
	AMPA	2008-12	≥274	2229	1386	62.2	1386	62.2	393	0.1
Norway	GLY	97-2015	12	98	88	89.8	≤71	≤72	0.93	0.01-0.05
	AMPA	97-2015	12	98	90	91.8	≤59	≤60	0.54	0.01-0.05
Slovakia	GLY	2006-14	≥142	5018	835	16.6	775	15.4	4.2	0.05-0.5
Spain	GLY	2009-14	≥343	5418	1847	34	1218	22	3400	0.03-30
	AMPA	2012-14	≥84	830	543	65	534	64	9.2	0.05-0.2
Sweden	GLY	2000-14	≥21	1439	442	30.7	≤433	≤30	370	<0.06-<1
	AMPA	2000-14	≥22	1418	320	22.6	≤312	≤22	36	<0.07-<1

Table 8.5-95: **Summary of glyphosate (GLY) and AMPA analyses in surface water in Europe (*after* [redacted], 2016, CA 7.5/010)**

Country	Compound	Date	Sites	Samples	Detected (samples)		Samples ≥ 0.1 µg/L		Max Conc	LoQ (LoD)
		Range	No.	No.	No.	%	No.	%	µg/L	µg/L
Switzer-land	GLY	2006	5	≥10	≥8	80	1	≤10	0.1	0.0007
	AMPA	2006	5	≥11	≥11	100	≥3	27	0.29	0.0008
Nether-lands	GLY	2006-14	≥373	9316	≥1223	≥13	≤1223	≤13	0.14	?
	AMPA	2006-14	≥373	9270	≥1358	≥15	≤1358	≤15	0.07	?
UK	GLY	93-2015	≥102	3916	754	19.2	754	19.2	8.2	0.1-1
Danube	GLY	2013	68	68	5	7.3	0	-	0.07	0.03
	AMPA	2013	68	68	66	97	≤66	≤97	0.96	0.03
Total	**GLY**	**93-2015**	**≥4419**	**≥143470**	**444232**	**31**	**30858**	**21**	**0.07-3400**	**0.01-2.5**
	AMPA	**97-2015**	**≥3543**	**≥115302**	**≥57457**	**50**	**≥47876**	**41**	**0.07-393**	**0.01-0.5**

Table 8.5-96: **Summary of sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA in surface water for the combined EU dataset**

Statistic/Threshold	GLY			AMPA		
	RAC: 400 µg/L	EQS-MAC: NA µg/L	Threshold : 0.1 µg/L	RAC: 1200 µg/L	EQS-MAC: NA µg/L	Threshold : 0.1 µg/L
Number of sites	13573	NA	13573	12282	NA	12282
Number of samples	282950	NA	282950	262415	NA	262415
Number of samples > threshold	16	NA	65007	3	NA	124697
% of samples > threshold	0.006	NA	23.0	0.001	NA	47.5
Number of sites > threshold	13	NA	7332	3	NA	8298
% of sites > threshold	0.10	NA	54.0	0.024	NA	67.6
Number of consecutive samples > threshold	8	NA	48663	0	NA	112759
% of samples that are consecutive samples > threshold	0.003	NA	17.2	0.0	NA	42.97
Maximum number of samples > threshold at a single site	3	NA	348	1	NA	399
Maximum number of consecutive samples > threshold at a single site	1	NA	202	1	NA	264

NA – Not available for EU analysis

Table 8.5-97: Summary of Annual Average (AA) Environmental Quality Standard (EQS) statistics for those Member States (MS) where such a threshold is available

MS	Substance	Number of Sites	Number of Years	Number of Sites with 12 Samples per Year	Number of Data Years with 12 Samples per Year	Number of Sites > AA-EQS	Percent of Sites > AA-EQS	Number of Years > AA-EQS	Percent of Years > AA-EQS
BE	AMPA	842	2871	215	1461	0	0.0	0	0.0
	GLY	849	2945	219	1526	0	0.0	0	0.0
FR	AMPA	7172	29143	1049	8147	0	0.0	0	0.0
	GLY	7378	30132	1195	8963	0	0.0	0	0.0
DE	AMPA	1600	3453	273	1001	0	0.0	0	0.0
	GLY	1643	3482	281	1017	0	0.0	0	0.0
NL	AMPA	944	2896	60	286	0	0.0	0	0.0
	GLY	904	2471	65	273	0	0.0	0	0.0
UK	AMPA	NA	NA	NA	NA	NA	NA	NA	NA
	GLY	145	289	39	149	0	0.0	0	0.0

ND – No data identified

Understanding Sources of Exposure

Regression Tree Modelling

The development of Regression Tree models was undertaken for the French surface water public monitoring dataset as this data comprises the majority of the surface water dataset available across the EU and has sub-national GLY sales data available. Regression trees are highly visual means of exploring datasets to assess underlying relationships which makes them good for risk communication purposes. These models sought to predict the exceedance rate (%) of the arbitrarily defined regulatory threshold of 0.1 µg/L as well as the number of exceedances through relating them to descriptors of the catchment upstream of the monitoring location.

Urban areas were identified as the most important predictor variable for both the GLY exceedance rate and the number of consecutive GLY exceedances while the urban wastewater treatment capacity was the most important for the absolute number of GLY failures. Similarly, arable land cover was identified as an important landcover but to a lesser extent, for the exceedance rate (~0.6), the number of exceedances (~0.75) and the number of consecutive exceedances (~0.68).

Urban areas were identified as the most important predictor variable for the AMPA exceedance rate while the urban wastewater treatment capacity was the most important for both the number of consecutive AMPA exceedances and the absolute number of AMPA failures. Similarly, arable land cover was identified as an important landcover but to a lesser extent, for the exceedance rate (~0.53), the number of exceedances (~0.72) and the number of consecutive exceedances (~0.53). It should be borne in mind that AMPA may originate from sources other than GLY, for example detergents.

These models clearly outlined the importance of the urban landcover and urban waste water treatment works capacity in their catchment on high rates of exceedance expressed in diverse ways. The importance of arable landcover was also demonstrated along with permanent crops to a much lesser extent.

Source Apportionment Appraisal

An assessment of source apportionment was conducted through review of peer reviewed literature. With respect to assessing monitoring data for surface water: the glyphosate and AMPA concentrations appeared to be generally larger from urban sources than from diffuse agricultural ones. With respect to urban sources, use on railways/roads seemed to result in higher residues, while garden use resulted in lower residues in comparison to amenity use. In addition, from urban sources AMPA concentration were often greater than glyphosate and likely to be derived from detergents, and phosphonates used in water treatment processes, as well as from glyphosate used in urban environments. Storm events often gave rise to large spikes in concentration in agricultural settings, and even more so where there was an urban contribution. Generally, where the glyphosate route to water bypassed soil, glyphosate residues may be transported into water. If the sampling location was downstream of urban, or major infrastructure (rail or roads) then the glyphosate and AMPA residues were mostly likely not to have come from agricultural uses. These findings echoed that of the regression tree modelling.

III. CONCLUSIONS

The analysis of the large surface water dataset for GLY and AMPA indicated they are both frequently detected above the LOQ in this compartment. However, compliance with regulatory acceptable concentrations and environmental quality standards was very high with few exceedances measured. Most of these exceedances were considered to be anomalous. It should also be borne in mind that AMPA may originate from sources other than GLY, for example detergents. The environmental concentrations typically encountered in this environmental compartment do not pose a risk for biota or ecosystems.

Assessment and conclusion by applicant:

The report describes the analysis of public monitoring data for key European countries for the compartments soil, water and sediment for Glyphosate and AMPA. The maximum GLY concentration in SW of 91.6 mg/L was likely anomalous and once outliers were identified and excluded would be 57.0 µg/L. The GLY RAC represented the 99.987th percentile value in the distribution of measured SW GLY concentrations.

The maximum AMPA concentration in SW of 230.0 mg/L was likely anomalous and once outliers were identified and excluded would be 224.4 µg/L. The AMPA RAC represented the 99.999th percentile value in the distribution of measured SW AMPA concentrations.

The available data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in the surface water compartment.

The study is considered valid.

Assessment and conclusion by RMS:

An extended surface water monitoring data set was collected throughout 10 EU countries and analysis of these data have been proposed by the study authors to assess what they call "the state of all environmental compartments" and "consider the impacts this state might have on biota, ecosystems and human health via drinking water". The present summary focuses on surface water results, and analysis for other compartment can be found in the relevant corresponding section.
Results are given for each country, and for the whole combined EU data set.

Analyzing and assessing such public surface water monitoring data is a difficult exercise, since many information shall be available to set into context and interpret the findings, and relate them to GLY containing products use at the scale of the upstream catchment.
The conclusions of the study authors is that GLY and AMPA residues are frequently detected in surface water, but these are such that they do not pose risk to the environment. If indeed the results show very few exceedance of the RAC and other Environmental Quality Standard, any straightforward risk assessment conclusions based on these findings should be regarded with caution, as key information are lacking to get a clear picture of what these data capture in terms of use pressure and temporal percentile.

Please also note that applicant proposes an assessment based on a RAC of 400 µg/L. However, the RAC proposed for risk assessment by RMS is 100 µg/L. In this case, this will not change significantly the overall conclusion on the % compliance of the RAC.

Data handling
A first step of data handling was performed to exclude unusable raw data that often comes with national databases extraction (analysis uncompleted, data not validated, data not attributed to any location, no indication of the LOD/LOQ, no indication of the measurements unit...).The data exluded at this step were excluded in the applicant's analysis reported in Table 8.5-91.

An additional analysis step was conducted by the study authors to identify likely outliers in the dataset and the implications of these for the analysis assessed, this is discussed by RMS hereunder in its conclusions on the results

Spatial distribution of the data
The whole data sets represents >291 000 samples collected from >13 800 sampling sites. However, the spatial distribution of these sampling is heterogeneous throughout EU MS for which data are available (Figure 8.5-64 and Figure 8.5-65**Figure 8.5-72**). Study authors indicated that for some MS (DE, IT and ES) this is due to data only arising from some regional environmental agencies, while in some other case (UK), this is due to specific spatial targeting. Data from FR, which represents about 65% of surface water sample contribution, are homogeneously distributed throughout the territory. However, all sample sites with available results are plotted on the maps; while regularity of sampling for each site is not known, additional information on the French data set from 1999 to 2013 available in [redacted] 2016, indicates that several sites may provide only very few data over the whole period (see RMS comments hereunder on the sampling effort).
Please also note that the sampling points from Sweden are not plotted on the Figure 8.5-64 and Figure 8.5-65since spatial distribution of the Swedish sampling points is not known.

Exhaustiveness of the data – consistence of the data sets.
As indicated in RMS comments on [redacted] (2020, CA7.5/001), the exhaustiveness of the data collated could not be checked by RMS, and should be appreciated at MS level. However, review of the open literature articles may provide additional information on the lack of consistence of the data set for surface water. For Italy for instance, the article Di Guardo A., 2018 (CA7.5/036) reports results from the Lombardia monitoring program for the period 2008-2014, with maximum concentration of 108 µg/L in 2014 and 38 µg/L in 2008, which are apparently not included in the present [redacted], 2020 review. The

maximum value of 38 µg/L (37.4 µg/L) appears in the table after [redacted], 2016 (but this table still does not include the maximum value of 108 µg/L in 2014).

Temporal distribution of the data - sampling effort
Analysis of the global sampling effort is provided by study authors, indicated an unimodal distribution of data collection (*i.e* fewer samples in the winter and spring months) for some MS, and a bimodal distribution (data collection in spring and autumn during key use periods being greater than at other times of the year) for other MS (*e.g.* FR and SE).

However, no information is given on the multi-year sampling pattern of sites, neither of the annual number of measurements. This is key information to be provided, since the sampling effort can be very different from a site to another. The study of [redacted] (2016), focusing on the results from the French public monitoring between 1999 and 2013, showed that more than third of stations for which sampling results are available were in fact monitored for one single year other the 15 year period studied (36 % and 32% for AMPA and glyphosate, respectively). Less than 15% of the stations have been monitored for 7 years or more out of 15.

Waterbodies characteristics and relation to pressure of use
One of the main issue dealing with public monitoring it is that these do not, in all cases, allow having a picture of the kind of water bodies included in monitoring programs.
As underlined by study authors, it is "likely that the size of the waterbodies monitored in public monitoring programs would be larger than edge of field waterbodies utilised in the typical risk assessment of PPPs in the EU." It is however acknowledged by RMS that further detailed information on the water bodies' characteristics may be available in some of the national monitoring programs, but cannot be handled here. This may be requested and analysed at MS level for product registration.

As for ground water, the surface water sampling sites cannot in all cases be related to any use pattern of the active substance. No sufficient information at each site location is available to evaluate the proportion of sampling sites that are really located down gradient of area where the active substance is used, or even just likely to be used. It is however acknowledged by RMS that this may be handled in some of the national monitoring programs, but cannot be consistently included here at EU scale. However, this influence might be limited in the case of glyphosate, considering the spread and diversity of uses of glyphosate containing products (including agricultural and non-agricultural uses, professional and non professional uses).

Understanding the sources of contamination
Study authors proposed an assessment based on regression tree models, to investigate the proportion of the urban and agricultural GLY sources potentially driving exceedance of 0.1 µg/L.
Authors indicate that "the regression tree models developed sought to predict the rate of exceedance, the percentage of exceedance of all valid samples, as well as total number of exceedances in surface water, using predictor variables describing sources and factors, for example the extent of different landcovers, GLY sales and extent of Urban Waste Water Treatment emissions in the catchment of the monitoring point"
These RTMs indicate that urban areas and urban waste water treatment works emissions were the most important drivers in the rate of exceedance as well as the number of exceedances, total and consecutive. They also demonstrated that arable (to a lesser extent) and permanent crops (to even smaller extent than arable) were important factors in GLY and AMPA detection.
This may be an interesting analysis but could not be reveiew in detail by RMS, and is not considered further.

Conclusions and findings
The study (surface water part) is considered acceptable.

Maximum values and outliers

It is noticeable that maximum values arising from these monitoring data in surface water are not clearly presented. Indeed only maximum values within the whole period per MS are indicated in Table 8.5-91. Annual maximum value for each member state are not reported; although summary tables of glyphosate and AMPA analyses are presented for each MS in Appendix 2 of the report, the maximum values are not included in these.

Note that in the report of [redacted], 2016, which results are reported here in Table 8.5-95 for comparison, maximum values are given per year in each member states. However, if the collected data in [redacted], 2016 overlaps those from the present study, they do not include the most recent data (stops in 2012, 2015 depending on MS).

Authors of the present study indicate that possible outliers were not removed from the dataset prior to analysis. An additional analysis step was conducted to identify likely outliers in the dataset and the implications of these for the analysis assessed. This identified 58 (or 56) outliers for GLY and 3 outliers for AMPA, which, when removed, gives a maximum concentration throughout EU for GLY of 57 µg/L. However, no explanation on this additional step is provided and no details are given on the values excluded (locations, level of concentrations) neither any justification for considering these outliers. From the Table 8.5-91, where maximum GLY concentration for the whole period is reported for each MS, it can be seen that some values considered outlier by study authors (i.e. >57 µg/L) are encountered in several MS, and range from 100 µg/L to 91 600 µg/L (other extreme values such as 40 000 µg/L also reported). While RMS acknowledges the values such as 40 000 or 91 600 µg/L can be considered erroneous, lower maximum values (between 100 µg/L and 558 µg/L) may not be considered outliers.

Further information are required as data gap to clarify the method used for outlier removal, and the detailed of the exluded values. Although the influence of removing the data considered outliers by applicant been proved to have no significant impact on the overall conclusions on rate of compliance with the RAC, it has to be ckecked that no reliable higher maximum concentration could be retained from this data set. The maximum value of 57 µg/L excluding outliers reported by study authors should be considered with caution, without further information on the values considered "outliers".

Level of quantification

The GLY public monitoring dataset represents >291 000 samples collected from >13 800 sampling sites, and is dominated by data sourced from France (~65%) with smaller contributions from Belgium (9%), Germany (~8.5%), the Netherlands (~5.6%) and Spain (~4.9%). Detection of GLY above the limit of quantification (>LOQ) in SW samples on the overall dataset is ~40% which compares well with the ~31% of samples from the previous data collection ([redacted], 2012; 2016), with the apparent increase likely a function of improving LOQs.

The AMPA public monitoring dataset represents >269 000 samples collected from >12 400 sampling sites, and is dominated by French data (~68.3%) with smaller contributions from Belgium (~9.6%), Germany (~9.0%) and the Netherlands (~5.9%). Detection of AMPA >LOQ in SW samples is ~64% which compares well with the ~50% of samples in the previous data collection ([redacted], 2012; 2016), likely a function of improving LOQs.

The monitoring data were compared to ecotoxicological endpoint (RAC), ecosystems endpoints (Environmental Quality Standard values, when defined at MS level) and to the thresholds of 0.1 µg/L for cases where surface water is taken for drinking water.

Results are summarized below, but these should always be regarded keeping in mind the limitations and comments made by RMS above.

Ecotoxicological risk assessment

Comparison with Regulatory Acceptable Concentration (RAC) of 400 µg/L for GLY and 1200 µg/L for AMPA (RAC values proposed by the applicant)

Study authors report high compliance with the GLY RAC of 400 µg/L (99.994% of samples; 99.90% of sites), ranging from 100% (e.g. in AT) to 99.51% (UK), with exceedances being extremely rare (16 samples from 13 sites; 0.006% of samples from 0.10% of sites).

Analysis of the RAC exceedance was performed by study authors based on a RAC value of 400 µg/L (note this RAC is not the retained RAC for risk assessment by RMS, see paragraph below). The exceedences of the 400 µg/L threshold represented 16 samplings including outliers, occurred on 13 different sites, and largely on separate non-consecutive occasions (0.003% of samples are consecutive samples; see Table 9.5-99). However since no data are available on the sampling regularity of the 13 sites where exceedances are found, the relevance of such assessment is hard to evaluate. Also in table 9.5-99, RMS does not see what could be the difference between row 7 ("number of consecutive samples > thresholds') and row 10 ("maximum number of consecutive samples > thresholds at a single site").

Note that the RAC eventually retained for risk assessment is 100 µg/L and not 400 µg/L as proposed by applicant. Since detailed results of maximum concentrations are not available, the analysis and the % compliance cannot be updated by RMS. However, considering that about 58 samples considered "outliers" by applicant are above 57 µg/L (applicant indicated the maximum concentration is 57 µg/L when excluding outliers), the overall compliance with any lower RAC would not be significantly different than the one presented by applicant.

Ecosystem risk assessment

Comparison with EQS-MAC (Environmental Quality Standard – Maximum Allowable Concentration)

For both GLY and AMPA, study authors analysis reports very few exceedance of the EQS-MAC in MS where such threshold is defined; *i.e.* less than 1% in BE, FR and SE, about 7% in UK (see Table 8.5-97). All sample results found to be > MAC are indicated by authors as being those identified as outliers. However, the definition of an outlier, and the justification for considering those values as outliers is not clear (see RMS comments on this topic above).

Comparison with EQS-AA (Environmental Quality Standard – Average Annual Concentration)

The average annual concentration (AA) value for comparison against the MS EQS-AA, where available, was indicated to be calculated in accordance with Article 5 of Directive 2009/90/EC. Details of the calculation was not provided and was not checked by RMS. Study authors indicated that only sampling sites with 12 sampling event within a year were selected for calculating this AA.

Proportion of sites fulfilling this latter criteria is 25% of sites in BE, 15% of sites in FR, 17% of sites in DE, 6.5% of sites in NL and 27% of sites in UK.

As a results, for both GLY and AMPA, there were no sites showing average annual concentration >EQS-AA in the MS where such trigger is defined. However, there is no indication whether the selected sites fulfilling the criteria for calculating the annual average concentration are located in areas where glyphosate is used. No further analysis of spatial distribution of these sites and their potential relation to glyphosate containing product use is proposed in the study.

Comparison with drinking water threshold of 0.1 µg/L

Detection above the threshold of 0.1 µg/L for glyphosate was ~23% of samples (~54.0% of sites), ranging from 3.4% in AT to 57.5% in BE. These results compare well with the previous data collection ([redacted], 2012; 2016) where ~21% of samples were found to exceed 0.1 µg/L. Details of these results per MS are available in the table results reported below.

RMS notes that this comparison is reported for information. Among the sampling locations, the proportion of location potentially intended to supply drinking water is unknown. No indication on this was further given in the report, and it is not known whether exceedance of the 0.1 µg/L trigger is observed in particular conditions. It could be assumed that the level of exceedance will be lower for larger water bodies from which drinking water is abstracted, and it may be expected that the exceedance rates given are a worst-case for drinking water abstraction locations, but this cannot be asserted unless the analysis is actually done.

Detailed results of thresholds exceedance per Member States.

For completeness, MS monitoring data summaries taken from appendix 2 of the report are reported below:

Table A. 1: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for Austria

SW Metric	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: NA**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: NA**
Number of Sites	314	314	NA	316	316	NA
Number of Samples	4505	4505	NA	4506	4506	NA
Number of samples > threshold	735	0	NA	155	0	NA
% of samples > threshold	16.3	0.0	NA	3.4	0.0	NA
Number of sites > threshold	110	0	NA	44	0	NA
% of sites > threshold	35.0	0.0	NA	13.9	0.0	NA
Max number of samples > threshold at a single site	37	0	NA	26	0	NA
Max number of consecutive samples > threshold at a single site	30	0	NA	8	0	NA

Table A. 2: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for Belgium

SW Metric BE	AMPA			GLY		
Threshold (µg/L)	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: 800 µg/L**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: 64 µg/L**
Number of Sites	842	842	842	849	849	849
Number of Samples	25836	25836	25836	26115	26115	26115
Number of samples > threshold	20069	0	0	15012	0	10
% of samples > threshold	77.68	0.00	0.00	57.48	0.00	0.04
Number of sites > threshold	715	0	0	623	0	5
% of sites > threshold	84.92	0.00	0.00	73.38	0.00	0.59
Max number of samples > threshold at a single site	200	0	0	202	0	5
Max number of consecutive samples > threshold at a single site	198	0	0	202	0	2

Table A. 7: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for France

SW Metric	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: 45200 µg/L**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: 70 µg/L**
Number of Sites	7172	7172	7172	7378	7410	7378
Number of Samples	182539	182539	182539	189879	190660	189879
Number of samples > threshold	73679	0	0	33607	1	3
% of samples > threshold	40.4	0.0	0.00	17.7	0.0	0.00158
Number of sites > threshold	4873	0	0	4246	1	3
% of sites > threshold	67.9	0.0	0.0	57.5	0.0	0.041
Max number of samples > threshold at a single site	399	0	0	112	1	1
Max number of consecutive samples > threshold at a single site	109	0	0	33	1	1

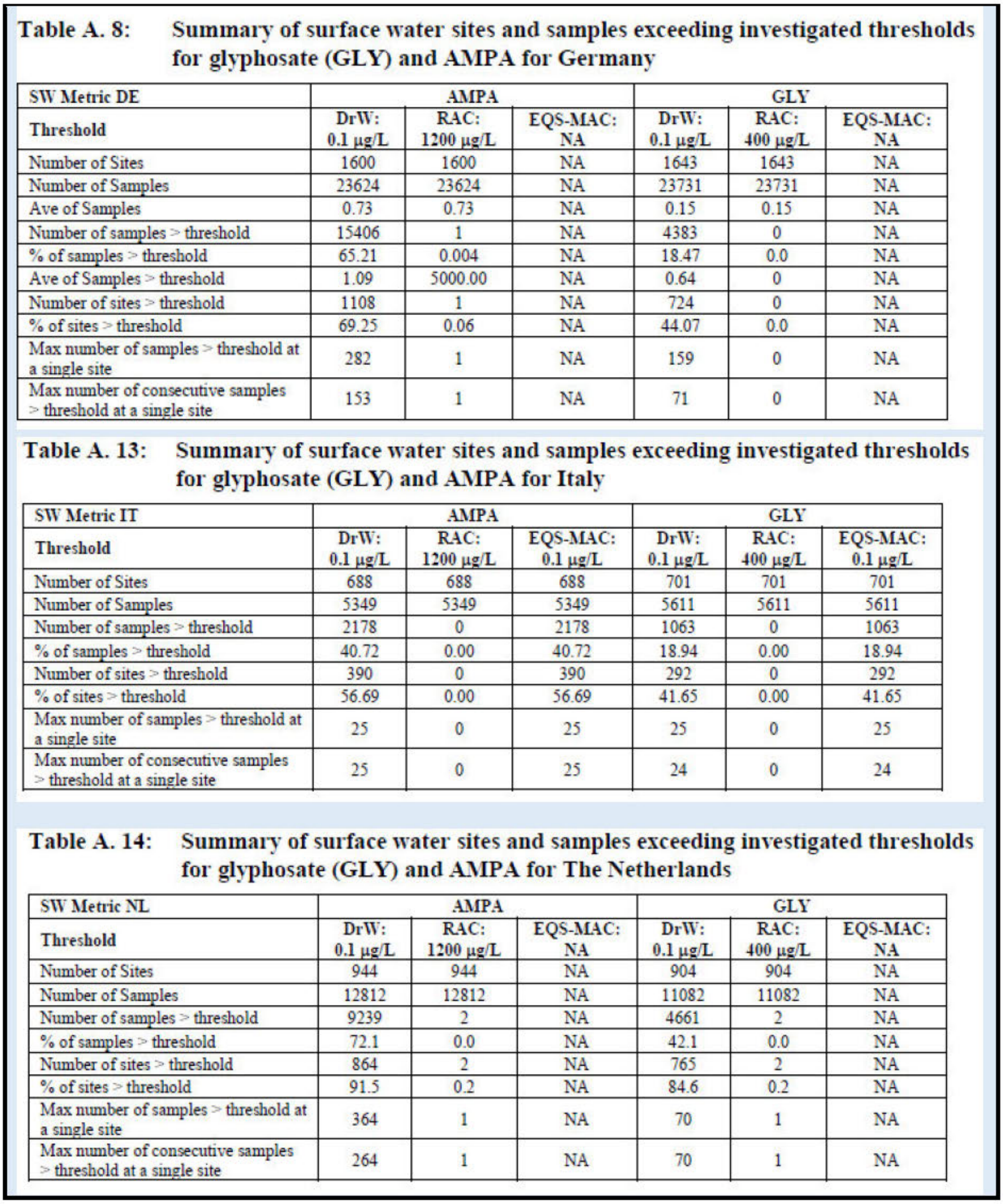


Table A. 8: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for Germany

SW Metric DE	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: NA**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: NA**
Number of Sites	1600	1600	NA	1643	1643	NA
Number of Samples	23624	23624	NA	23731	23731	NA
Ave of Samples	0.73	0.73	NA	0.15	0.15	NA
Number of samples > threshold	15406	1	NA	4383	0	NA
% of samples > threshold	65.21	0.004	NA	18.47	0.0	NA
Ave of Samples > threshold	1.09	5000.00	NA	0.64	0	NA
Number of sites > threshold	1108	1	NA	724	0	NA
% of sites > threshold	69.25	0.06	NA	44.07	0.0	NA
Max number of samples > threshold at a single site	282	1	NA	159	0	NA
Max number of consecutive samples > threshold at a single site	153	1	NA	71	0	NA

Table A. 13: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for Italy

SW Metric IT	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: 0.1 µg/L**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: 0.1 µg/L**
Number of Sites	688	688	688	701	701	701
Number of Samples	5349	5349	5349	5611	5611	5611
Number of samples > threshold	2178	0	2178	1063	0	1063
% of samples > threshold	40.72	0.00	40.72	18.94	0.00	18.94
Number of sites > threshold	390	0	390	292	0	292
% of sites > threshold	56.69	0.00	56.69	41.65	0.00	41.65
Max number of samples > threshold at a single site	25	0	25	25	0	25
Max number of consecutive samples > threshold at a single site	25	0	25	24	0	24

Table A. 14: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for The Netherlands

SW Metric NL	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: NA**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: NA**
Number of Sites	944	944	NA	904	904	NA
Number of Samples	12812	12812	NA	11082	11082	NA
Number of samples > threshold	9239	2	NA	4661	2	NA
% of samples > threshold	72.1	0.0	NA	42.1	0.0	NA
Number of sites > threshold	864	2	NA	765	2	NA
% of sites > threshold	91.5	0.2	NA	84.6	0.2	NA
Max number of samples > threshold at a single site	364	1	NA	70	1	NA
Max number of consecutive samples > threshold at a single site	264	1	NA	70	1	NA

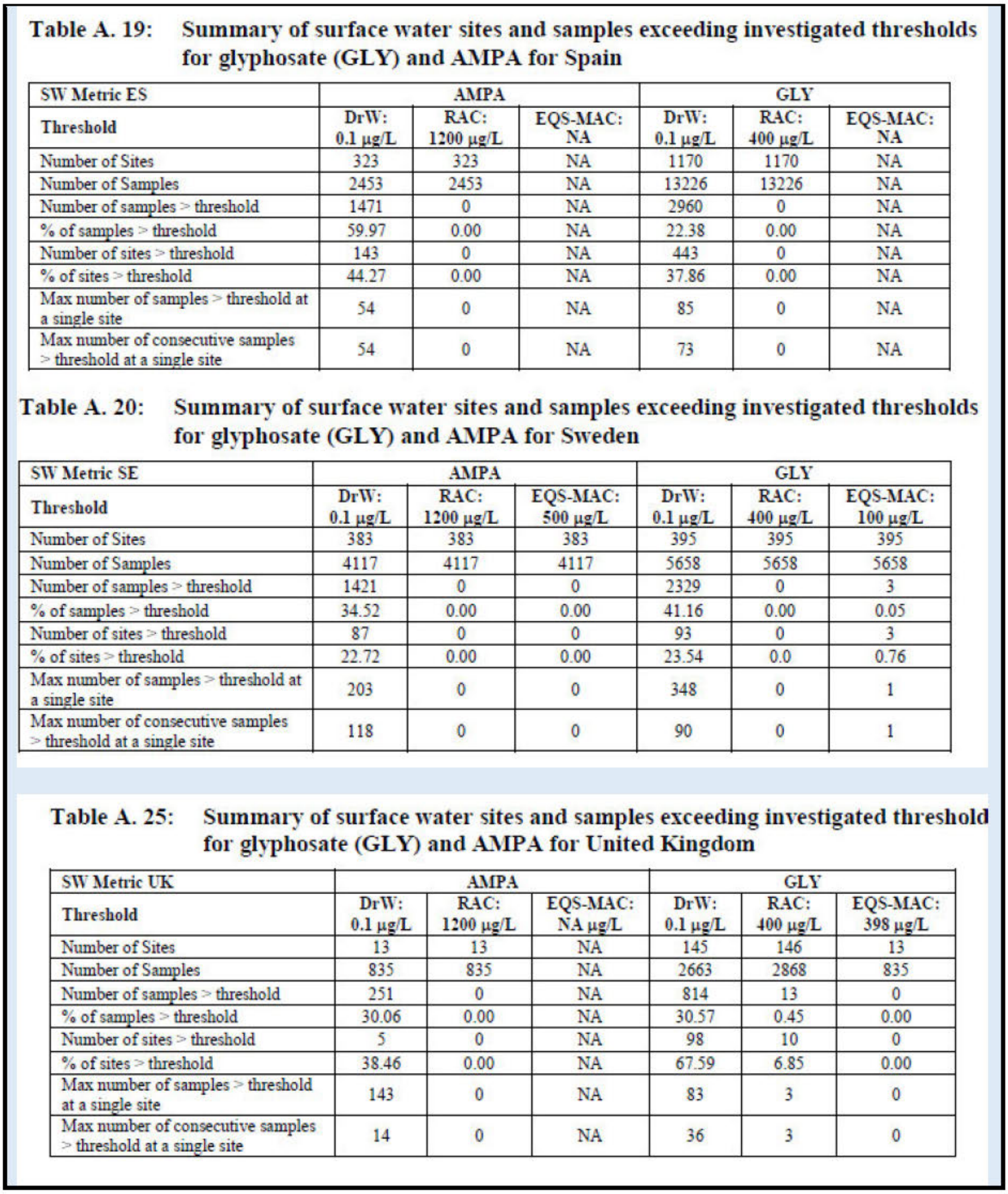


Table A. 19: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for Spain

SW Metric ES	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: NA**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: NA**
Number of Sites	323	323	NA	1170	1170	NA
Number of Samples	2453	2453	NA	13226	13226	NA
Number of samples > threshold	1471	0	NA	2960	0	NA
% of samples > threshold	59.97	0.00	NA	22.38	0.00	NA
Number of sites > threshold	143	0	NA	443	0	NA
% of sites > threshold	44.27	0.00	NA	37.86	0.00	NA
Max number of samples > threshold at a single site	54	0	NA	85	0	NA
Max number of consecutive samples > threshold at a single site	54	0	NA	73	0	NA

Table A. 20: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for Sweden

SW Metric SE	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: 500 µg/L**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: 100 µg/L**
Number of Sites	383	383	383	395	395	395
Number of Samples	4117	4117	4117	5658	5658	5658
Number of samples > threshold	1421	0	0	2329	0	3
% of samples > threshold	34.52	0.00	0.00	41.16	0.00	0.05
Number of sites > threshold	87	0	0	93	0	3
% of sites > threshold	22.72	0.00	0.00	23.54	0.0	0.76
Max number of samples > threshold at a single site	203	0	0	348	0	1
Max number of consecutive samples > threshold at a single site	118	0	0	90	0	1

Table A. 25: Summary of surface water sites and samples exceeding investigated threshold for glyphosate (GLY) and AMPA for United Kingdom

SW Metric UK	AMPA			GLY		
Threshold	**DrW: 0.1 µg/L**	**RAC: 1200 µg/L**	**EQS-MAC: NA µg/L**	**DrW: 0.1 µg/L**	**RAC: 400 µg/L**	**EQS-MAC: 398 µg/L**
Number of Sites	13	13	NA	145	146	13
Number of Samples	835	835	NA	2663	2868	835
Number of samples > threshold	251	0	NA	814	13	0
% of samples > threshold	30.06	0.00	NA	30.57	0.45	0.00
Number of sites > threshold	5	0	NA	98	10	0
% of sites > threshold	38.46	0.00	NA	67.59	6.85	0.00
Max number of samples > threshold at a single site	143	0	NA	83	3	0
Max number of consecutive samples > threshold at a single site	14	0	NA	36	3	0

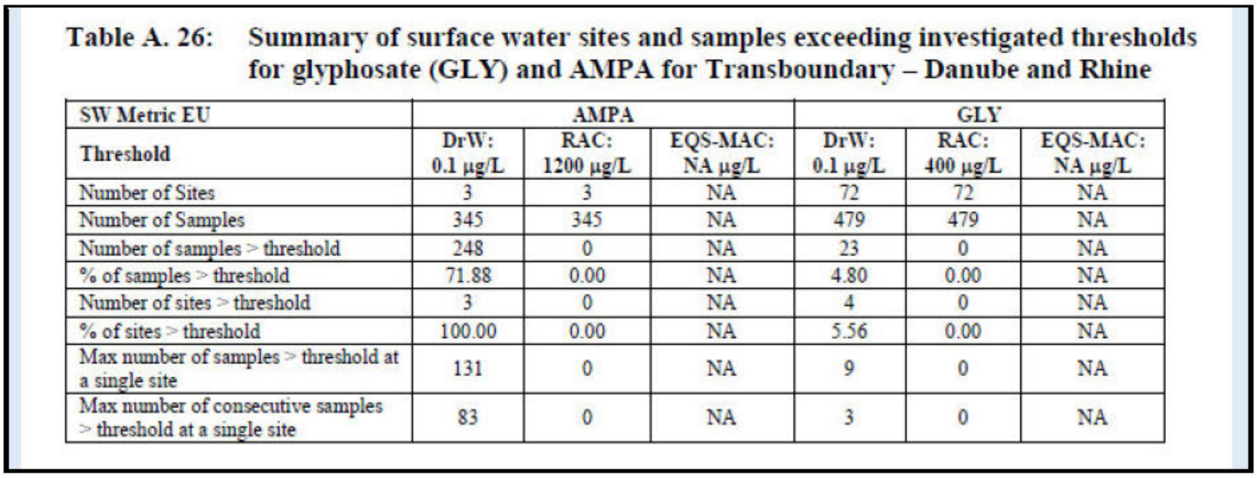


Table A. 26: Summary of surface water sites and samples exceeding investigated thresholds for glyphosate (GLY) and AMPA for Transboundary – Danube and Rhine

SW Metric EU	AMPA			GLY		
Threshold	DrW: 0.1 µg/L	RAC: 1200 µg/L	EQS-MAC: NA µg/L	DrW: 0.1 µg/L	RAC: 400 µg/L	EQS-MAC: NA µg/L
Number of Sites	3	3	NA	72	72	NA
Number of Samples	345	345	NA	479	479	NA
Number of samples > threshold	248	0	NA	23	0	NA
% of samples > threshold	71.88	0.00	NA	4.80	0.00	NA
Number of sites > threshold	3	0	NA	4	0	NA
% of sites > threshold	100.00	0.00	NA	5.56	0.00	NA
Max number of samples > threshold at a single site	131	0	NA	9	0	NA
Max number of consecutive samples > threshold at a single site	83	0	NA	3	0	NA

Data point:	CA 7.5/031
Report author	[redacted]
Report year	2019
Report title	Mitigating glyphosate levels in surface waters: Pilot catchment details and monitoring results
Report No	-
Document No	-
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary

A 5-year mitigation study on glyphosate was performed for the years 2014-2018 to evaluate the effect of mitigation measures to reduce glyphosate loads in surface water. A representative pilot study catchment in Europe, containing mainly agricultural land uses, was monitored two years before (baseline monitoring) and three years after the implementation of mitigation measures.

Basic information such as land-use, connectivity to the river, gross emission of glyphosate, location of other potential sources and erosion mitigating measures was inventoried. Using this data, priority zones within the study area were selected for the implementation of erosion and glyphosate loss mitigating measures.

To discern between runoff sources and point sources, event-based and time-integrated monitoring was established. The monitoring period consists of a baseline period during which no measures were implemented and no communication to farmers was carried out, and a mitigation period after which the mitigation measures were installed. The monitored stretch of river was also just (50 m) downstream of a sewage outlet, serving four villages (2475 inhabitants) and an industrial laundry. A small number of samples were taken within and around this outlet, and it was clear that this was a significant source of glyphosate, and even more so of AMPA.

Communication with farmers in the study area was done by meetings and workshops, and 15 farmers in the priority zones with a significant impact on the pesticide load to surface water were encouraged to enter a voluntary erosion control program supported by the local government. During 2016 and 2017, 11 grassed buffer strips were installed. In addition, 22 biofilters were built by farmers to mitigate point sources of pesticides.

During runoff events, the load intensity was substantially higher compared to baseflow load. After the implementation of the mitigation measures, the loads almost halved from 4-5 g/h to 2-3 g/h. Mitigation measures seemed to have had impact on the event loads. Baseflow loads close to 1 g/h were not influenced by mitigation measures. Over the mitigating period, number and intensity of point sources reduced from 8 to 1 and from 100 µg/L to less than 20 µg/L. Point sources decreased over the period 2014-2018 in number as well as concentration. Influx of glyphosate during rainfall events decreased over the period 2014-2017.

The study strongly suggested that even in a predominantly agricultural area, urban sources of glyphosate and AMPA are still likely to be significant and also that agricultural point losses (point sources) are significant sources of glyphosate/AMPA which can be substantially reduced with appropriate targeted education. Risk profiling and targeted mitigation measures can significantly reduce rain-driven losses of glyphosate/AMPA from treated fields.

I. MATERIALS AND METHODS

Study area

The selection of the study area focused on small agricultural catchments in the region of Haspengouw (Flanders, Belgium). A subcatchment of the Cicindria river was selected as the study area (72% agriculture, 11% residential, 6% airport, 6% forest/natural) because of its high potential erosion, relatively high measured concentration of glyphosate, its potential for the installation of mitigation measures and the high relative contribution (39%) of the selected study area to the total gross emission of glyphosate of the Cicindria catchment. These factors point to a high probability that mitigation measures in the study area would have a measurable effect on the levels of glyphosate in surface water.

Glyhposate loads to the river from agriculture

A map of the gross emission of glyphosate within the catchment area was constructed by combining detailed crop maps with the result of a farmer survey. Emission factors for different transport routes (drift, direct losses, volatilisation, interception, erosion, drainage and leaching) were calculated. Emission to surface water was calculated as the sum of drift, direct losses, erosion and drainage, based on the yearly use and the emission factors. Glyphosate chemical properties used for the calculations of the gross emission were a DT_{50} in soil of 12 d and K_{OC} of 28700 mL/g.A 6.5 km stretch of the river was selected (catchment size 1075 ha), and a theoretical risk map was constructed in order to prioritize between fields and farmers to target to reduce glyphosate loads to surface water in the most efficient way.

The highest risk for losses of glyphosate was based on the calculated glyphosate gross emission and the connectivity of the field to the Cinidria. This theoretical risk map was validated by the local water board and priority zones for the implementation of erosion and glyphosate loss mitigating measures in the study area were created.

Other potential sources in the area

There are two main discharge points of residential wastewater (which are potential other sources mainly for AMPA) in the Cicindria in the vicinity of the pilot area: one for the small village of Kerkom that discharges into the investigated river stretch and one larger point for 4 villages and the industrial laundry just upstream of the study area. At this moment, the contribution of these sources to the glyphosate and AMPA load to the river cannot be quantified. To do this, additional measurements (grab samples) at these locations were taken. The results indicate that the impact of the larger upstream discharge on the glyphosate load coming into the study area is potentially large.

Communication with the relevant stakeholders

In total, 15 farmers in the priority zones with a significant impact on the pesticide load to surface water were encouraged to enter a voluntary erosion control program supported by the government. Starting in 2015, information meetings about the monitoring campaign, the importance of implementing measures, the influence of point sources, and the correct use of pesticides were held.

Analytical conditions

The monitoring set-up consisted of a flow meter to monitor water level and flow velocity at the upstream and the downstream monitoring location of the selected stretch of the Cinidria, a rain gauge at the downstream location and two samplers at both locations. An event-based and time-integrated monitoring was established to monitor the glyphosate concentrations and loads to the river, and to discern between runoff sources and point sources. Time-paced samples are taken every two hours and collected in one bottle for every 24 hours. Event samples are taken once a discharge threshold was exceeded. These were taken every 15 minutes and collected in a sample bottle for every 90 minutes. Samples of the refrigerated time paced samplers were collected on a weekly basis, whole event samples were collected and frozen within 24 hours.

To determine glyphosate and AMPA concentrations in the water samples, a 10 mL sample was spiked with internal standards ($^{13}C_2{}^{15}N$-glyphosate, $^{13}C^{15}N$-AMPA), acidified with 6 M HCL and the mixture was allowed to react for 1 hour. Afterwards it was neutralised with 6 M KOH. Borate buffer (5% sodiumtetraborate in water) and a solution of FMOC (fluorenylmethyloxycarbonylchloride) in acetonitrile was added for derivatisation. The mixture was allowed to react for 30 minutes and the reaction was stopped by adding formic acid. The mixture was diluted with 12.5 mL water and EDTA solution was added. Analytes were extracted by solid phase extraction using 200 mg Oasis HLB cartridges conditioned with methanol and 0.1% formic acid. After elution, the cartridge was washed twice with formic acid. A second rinsing was done with methylene chloride. Analytes were eluted with methanol; the extract was evaporated to nearly dryness and reconstituted in 1:9 methanol/mobile phase A.

Analysis was done by UPLC-MS/MS. Limit of quantification was 50 ng/L.

The load of glyphosate was calculated by combining the concentration and discharge measurements, as based on concentration only it is not possible to assess the glyphosate fluxes. Difference between the upstream load and the downstream load was calculated to assess the load that enters the river over the study area.

II. RESULTS AND DISCUSSION

All event and time integrated monitoring results are presented in the appendices. In 2016, eleven new buffer strips were installed in the pilot catchment, all in the priority zones. Most of the buffer strips were 9 m wide, three of them were 21 m wide. For 2017, 4 new buffer strips were planned. From 2017, famers were obliged to use 50 % drift-reducing nozzles. Further changes in agricultural practice (like crop rotation, tillage and cropping techniques) were introduced. Use of glyphosate by residents was prohibited since July 2017.

The tables below provide a summary of the results obtained for 2014-2018 including mean, standard deviation, median and 90th percentile for the upstream and downstream glyphosate load, the upstream and downstream discharge, and the glyphosate influx over the study area.

The results for 2015 correspond rather well with the results obtained for 2014. In both years, the influx under baseflow conditions was clearly lower than the influx under rain event flow conditions. In 2014 the average influx was for both conditions (baseflow and rain event) higher than in 2015.

The results for 2016 were in line with the results obtained in 2014 and 2015. In all years, the influx under baseflow conditions was clearly lower than the influx under rain event flow conditions.

The results for 2017 confirmed that the influx from the catchment was considerably higher during rainfall events compared to baseflow conditions. The results from 2016 indicated a decrease in the loads and influxes compared to the previous years and that decreasing tendency was continued in 2017. The average influx under baseflow conditions was lower in 2017 than in the years before and also the loads in the river (upstream and downstream) were clearly lower than the years before. The lower loads were a combined effect of lower concentrations and lower discharge (less rainfall in 2017). The average influx during rainfall events in 2017 was similar as in 2016, and lower than in 2014-2015. Most of the events in 2017 involved lower fluxes than events in 2016. It was mainly the single high flux rainfall event on the 9th of August that increased the 2017 event flux average to the level of 2016. The median value of the event fluxes in 2017 was lower than the median value for 2016.

In 2018 only 3 events could be analysed for calculating the influx from the study area. The calculated flux during events was lower than in the previous years. The calculated influx during non-event conditions was in line with results from previous years, and higher than in 2017. The results for 2018 should be interpreted carefully because of the extremely dry conditions and the low amount of available data.

Over the 5 years, a decreasing trend can be observed for the influx of glyphosate during rainfall events. The results show a difference between the years in the baseline period (2014-2015) and in the period after measures (2017-2018). This is a combined effect of changes in the management (agricultural practice, mitigation measures), variations in climatic conditions and changes in glyphosate use.

Table 8.5-98: Summary of the results obtained for the upstream and downstream glyphosate load, discharge and the glyphosate influx. All data related to non-event conditions

Non-event conditions		Glyphosate load (g)		Discharge average (m³/s)		Influx (g/h)
		Down-stream	Up-stream	Down-stream	Up-stream	Load Down-Up
2014 (N = 11)	**Mean**	36	14	0.053	0.033	0.9
	StDev	17	5	0.009	0.002	0.7
	Median	33	13	0.051	0.033	0.7
	90th percentile	55	21	0.065	0.036	1.6
2015 (N = 10)	**Mean**	38	22	0.065	0.042	0.6
	StDev	13	7	0.012	0.012	0.4
	Median	36	21	0.062	0.037	0.7
	90th percentile	57	33	0.082	0.053	1.1
2016 (N = 14)	**Mean**	41	25	0.101	0.061	0.9
	StDev	13	13	0.018	0.014	0.5
	Median	44	22	0.093	0.062	0.9
	90th percentile	53	34	0.121	0.079	1.5
2017 (N = 12)	**Mean**	30	21	0.058	0.041	0.4
	StDev	8	9	0.008	0.012	0.3
	Median	29	22	0.059	0.045	0.4
	90th percentile	39	29	0.068	0.047	0.8
2018 (N = 10)	**Mean**	29	10	0.049	0.018	0.8
	StDev	13	6	0.014	0.009	0.5
	Median	26	10	0.045	0.014	0.7
	90th percentile	42	17	0.066	0.029	1.1

Table 8.5-99: Summary of the results obtained for the upstream and downstream glyphosate load, discharge and the glyphosate influx. All data related to event conditions

Event conditions		Glyphosate load (g)		Discharge average (m³/s)		Influx (g/h)
		Down-stream	Up-stream	Down-stream	Up-stream	Load Down-Up
2014 (N = 8)	**Mean**	64	38	0.444	0.184	4.7
	StDev	62	55	0.463	0.122	2.5
	Median	38	11	0.285	0.194	4.3
	90th percentile	147	122	0.836	0.302	7.5
2015 (N = 8)	**Mean**	104	73	0.223	0.136	3.3
	StDev	54	43	0.107	0.084	1.9
	Median	91	61	0.193	0.112	3.1

Table 8.5-99: Summary of the results obtained for the upstream and downstream glyphosate load, discharge and the glyphosate influx. All data related to event conditions

Event conditions		Glyphosate load (g)		Discharge average (m^3/s)		Influx (g/h)
		Down-stream	Up-stream	Down-stream	Up-stream	Load Down-Up
	90th percentile	163	130	0.308	0.191	5.5
2016 (N = 7)	Mean	73	45	0.252	0.139	2.5
	StDev	32	19	0.132	0.077	1.1
	Median	66	48	0.196	0.114	2.6
	90th percentile	112	66	0.378	0.216	3.6
2017 (N = 6)	Mean	34	16	0.235	0.095	2.6
	StDev	25	12	0.070	0.020	2.3
	Median	22	13	0.230	0.088	1.8
	90th percentile	66	27	0.306	0.117	4.9
2018 (N = 3)	Mean	55	56	0.430	0.351	0.8
	StDev	41	43	0.522	0.507	0.3
	Median	52	47	0.223	0.136	0.7
	90th percentile	97	105	0.918	0.806	1.0

III. CONCLUSIONS

The number of findings of point losses decreased over the years with 6 and 7 possible point loss detections per year in the baseline period (2014-2015) to 2 to 3 per year in the mitigation period (2016-2018). Maximum concentration observed in point losses decreased over the years from over 100 µg/L to less than 20 µg/L. The load intensity of glyphosate decreased with time, and the loads almost halved from 4-5 g/h to 2-3 g/h after the implementation of measures. Mitigation measures did not have impact on baseflow loads close to 1 g/h.

The estimated yearly influx (based on 2014 dataset) of glyphosate under low flow conditions is about 7 kg/year and the influx under rain event flow conditions was about 4 kg/year. This means that about a third of the loads enter the river during events, which occured only 10% of the time.

The baseline concentrations in the upstream location were on average 5.6 µg/L and in the downstream location on average 6.5 µg/L. Baseline concentration in the downstream location was consistently higher than in the upstream location indicating also an influx during non-event conditions.

The communication to the farmers with information meetings proved to be successful with 11 installations of buffer strips in 2016 and 4 more in 2017.

In order to have a lasting effect on glyphosate load in the river, the interactions with the different stakeholders in the area need to be maintained and strengthened. Communication and sensitisation is crucial to have actor involvement in decreasing the loads to the river.

Assessment and conclusion by applicant:
The study investigates the effect of mitigation measures on loads of glyphosate and AMPA in surface water in a small agricultural catchment in the region of Haspengouw (Belgium) over five years. The study strongly suggested that even in a predominantly agricultural area, urban sources of glyphosate and AMPA are still likely to be significant and also that agricultural point losses (point sources) are significant sources of glyphosate/AMPA which can be substantially reduced with appropriate targeted education. Risk profiling and targeted mitigation measures can significantly reduce rain-driven losses of glyphosate/AMPA from treated fields.

The study methods and results as well as the analytical procedures are properly reported.

The study is considered valid.

Assessment and conclusion by RMS:

The study described a 5-year mitigation study on glyphosate, performed for the years 2014-2018 to evaluate the effect of mitigation measures to reduce glyphosate loads in surface water.

RMS indicates that it is a very well documented and detailed study with many information and results that are not easy to summarize. The study is considered acceptable.

RMS notes that the results presented in the study summary are expressed as loads. The summary does not provide information on concentration and/or threshold exceedence. However, many detailed information are available in the full-text report. Some additional relevant information are reported below.

The following points can be retained:
The study catchment in Belgium, containing mainly agricultural land uses (72%), was monitored two years before (baseline monitoring) and three years after the implementation of mitigation measures.

An event-based and time-integrated monitoring was established to monitor the glyphosate concentrations and loads to the river, and to discern between runoff sources and point sources. Time-paced samples are taken every two hours and collected in one bottle for every 24 hours. Event samples are taken once a discharge threshold was exceeded. These were taken every 15 minutes and collected in a sample bottle for every 90 minutes. In order to distinguish between the different pathways, the samples collected during the monitoring campaign are split into 3 groups:

- Samples affected by point losses (e.g. 24h time integrated samples showing elevated concentrations in dry periods)
- Samples collected under low flow condition (24h time integrated samples)
- Samples collected under high flow condition upon rainfall events (≈2h time integrated samples).

Quantification of the contribution of sources others than agriculture

It is indicated in the study report that there are two main discharge points of residential wastewater within the pilot area. In 2017, 3 occasions samples were taken just before the sewage discharge (upstream of the investigated stretch), inside the sewage collector and downstream of the sewage discharge to get a first estimate of the potential contribution of the sewage outlet to the loads of glyphosate and AMPA."
The results are reported below;

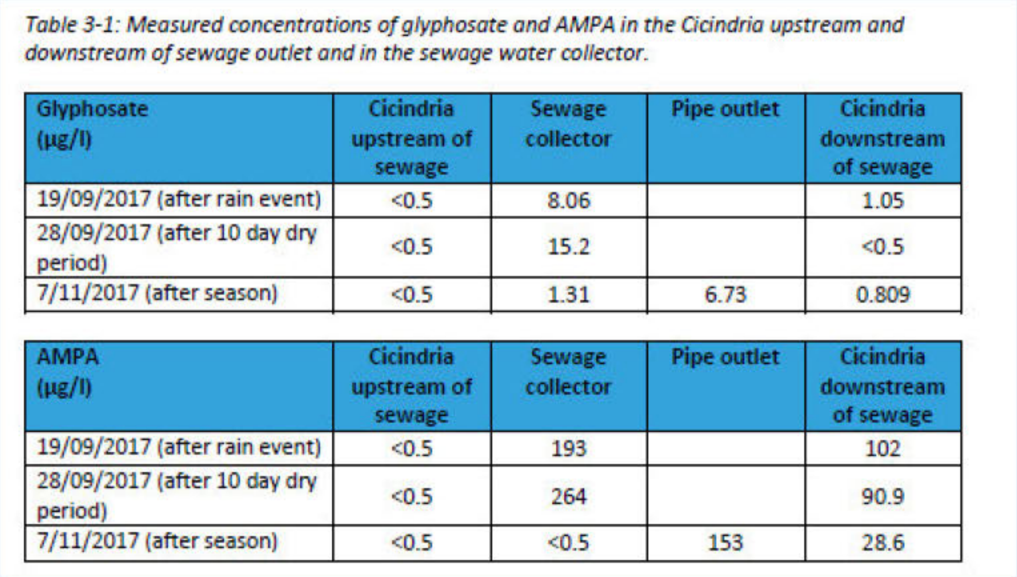


Table 3-1: Measured concentrations of glyphosate and AMPA in the Cicindria upstream and downstream of sewage outlet and in the sewage water collector.

Glyphosate (µg/l)	Cicindria upstream of sewage	Sewage collector	Pipe outlet	Cicindria downstream of sewage
19/09/2017 (after rain event)	<0.5	8.06		1.05
28/09/2017 (after 10 day dry period)	<0.5	15.2		<0.5
7/11/2017 (after season)	<0.5	1.31	6.73	0.809

AMPA (µg/l)	Cicindria upstream of sewage	Sewage collector	Pipe outlet	Cicindria downstream of sewage
19/09/2017 (after rain event)	<0.5	193		102
28/09/2017 (after 10 day dry period)	<0.5	264		90.9
7/11/2017 (after season)	<0.5	<0.5	153	28.6

These results indicate that the concentration of glyphosate and AMPA is globally higher downstream of the sewage outlet compared to upstream Also the measured concentrations inside the sewage water collector or from the small pipe outlet suggest that these sources contribute to the observed rise in concentration.

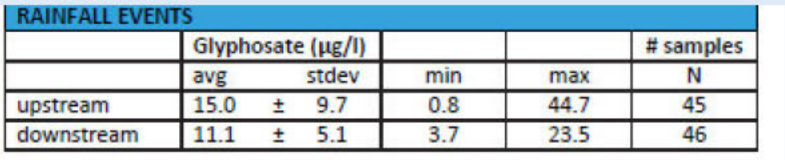
Since these measurements are all located upstream of the study area, there is no implication for the calculated loads of ghyphosate from the study area.

Evolution of glyphosate influx during rain events In all year from 2014 to 2018, the glyphosate influx under baseflow conditions was lower than the influx under rain event flow conditions. However, over the 5 years, a decreasing trend can be observed for the influx of glyphosate during rainfall events. The results show a difference between the years in the baseline period (2014 2015) and in the period after measures (2017 2018). This is a combined effect of changes in the management (agricultural practice, mitigation measures), variations in climatic conditions and changes in glyphosate use.

Mean concentration measured under event flow condition

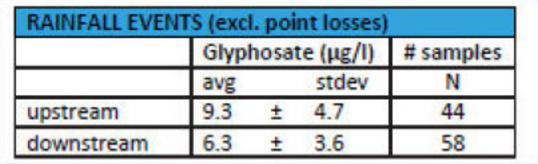
Concentration results not reported in the summary are available in the full text report. However, the range of min max concentrations are only given for year 2015. After 2016, only the mean and SD are given. However all results for all measure event concentration are available in appendix G of the full text report. Due to time constraint RMS could not check all results to get min-max values.

2015:



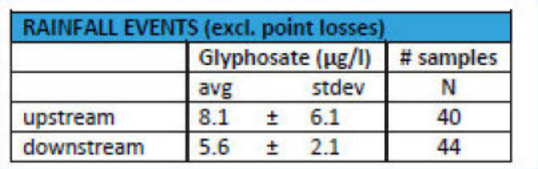
RAINFALL EVENTS						
	Glyphosate (µg/l)					# samples
	avg		stdev	min	max	N
upstream	15.0	±	9.7	0.8	44.7	45
downstream	11.1	±	5.1	3.7	23.5	46

2016



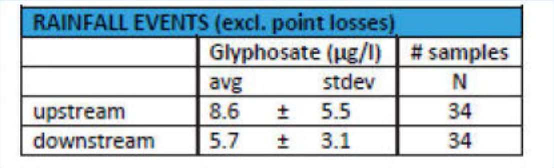
RAINFALL EVENTS (excl. point losses)				
	Glyphosate (µg/l)			# samples
	avg		stdev	N
upstream	9.3	±	4.7	44
downstream	6.3	±	3.6	58

2017



RAINFALL EVENTS (excl. point losses)				
	Glyphosate (µg/l)			# samples
	avg		stdev	N
upstream	8.1	±	6.1	40
downstream	5.6	±	2.1	44

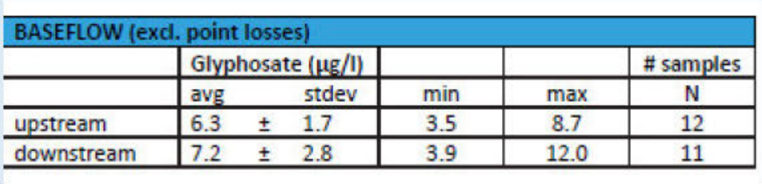
2018



RAINFALL EVENTS (excl. point losses)				
	Glyphosate (µg/l)			# samples
	avg		stdev	N
upstream	8.6	±	5.5	34
downstream	5.7	±	3.1	34

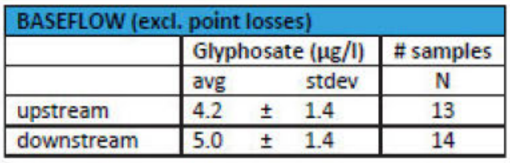
Mean concentrations measured under baseflow condition

2015



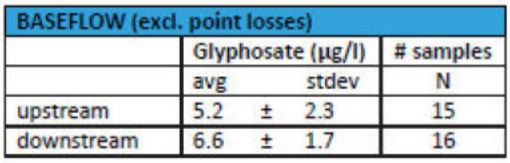
BASEFLOW (excl. point losses)						
	Glyphosate (µg/l)					# samples
	avg		stdev	min	max	N
upstream	6.3	±	1.7	3.5	8.7	12
downstream	7.2	±	2.8	3.9	12.0	11

2016



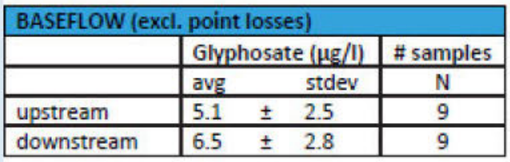
BASEFLOW (excl. point losses)				
	Glyphosate (µg/l)			# samples
	avg		stdev	N
upstream	4.2	±	1.4	13
downstream	5.0	±	1.4	14

2017



BASEFLOW (excl. point losses)				
	Glyphosate (µg/l)			# samples
	avg		stdev	N
upstream	5.2	±	2.3	15
downstream	6.6	±	1.7	16

2018



BASEFLOW (excl. point losses)				
	Glyphosate (µg/l)			# samples
	avg		stdev	N
upstream	5.1	±	2.5	9
downstream	6.5	±	2.8	9

Evolution of point source contamination

The number of findings of point losses decreased over the years with 6 and 7 possible point loss detections per year in the baseline period (2014-2015) to 2 to 3 per year in the mitigation period (2016-2018). It is noted that a measurement is considered a point loss if there is no rainfall in the sampling period and the concentration exceeds 10 µg/L.

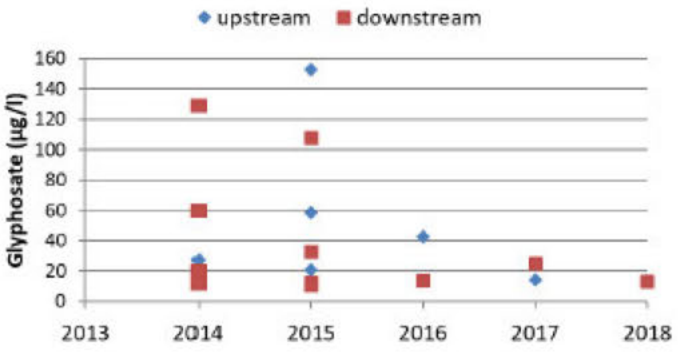


Figure 3-13: Measured concentrations related to point sources for the period 2014 to 2018.

Targeted communication and continuous sensitization have resulted in an increase in implemented measures. Point sources have decreased over the period 2014-2018 in number as well as concentration.

Data point:	CA 7.5/008
Report author	[redacted]
Report year	2019a
Report title	Phase 1: Traitements et analyses statistiques sur les données SOES UIPP 2008 - 2014 Analyses des données de suivi de glyphosate et de l'AMPA dans les eaux de France Période 2008-2014 (Processing and statistical analysis of the 2008-2014 SOES UIPP data. Analysis of the 2008-2014 water monitoring data for glyphosate and AMPA in France.)
Document No	REA-DOC-026
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No, but likely conducted by COFRAC approved testing facilities
Acceptability/Reliability:	Acceptable

The study is relevant for multiple subchapters. Only data about surface water monitoring were left in the following summary. Ground water data are summarized in the relvant section.

Executive Summary

This report is an update of a previous report "Analysis of monitoring data for glyphosate and AMPA in French waters in the period 1997-2013" ([redacted], 2016, CA 7.5/009). It includes the 2014 monitoring data for glyphosate and AMPA in ground and surface waters (extracted from the SOES UIPP database in July 2017). The dataset extracted from the SOES UIPP database is analysed in several ways.

Number of measurements and monitoring stations

At the combined national and French overseas level, the entire dataset for surface waters consists of 148561 analyses, of which 74271 are for AMPA and 74290 are for glyphosate. The number of unique stations is 3006 for the whole dataset. The present study only considers data from mainland France. Therefore, the surface water database selected for the study comprises 148295 analyses (74138 for AMPA and 74157 for glyphosate) from 2980 stations (Table 8.5-100).

Both glyphosate and AMPA were monitored every year between 2008 and 2014 in surface waters and groundwater. The majority of stations extracted from the $SOES_{uipp}$ database have both AMPA and glyphosate monitoring data.

I. MATERIAL AND METHODS

Table 8.5-100: Number of analyses for glyphosate and AMPA performed during 2008-2014 period

Year	Total $SOES_{uipp}$ data points	AMPA	Glyphosate	Year	Total $SOES_{uipp}$ data points	AMPA	Glyphosate
GroundwatGroundwater				**Surface water**			
2008	1 421 369	7048	7246	2008	2 074 007	4862	4862

2009	2 446 506	11662	11783	2009	4 000 041	7559	7559
2010	2 833 373	12514	12663	2010	4 428 556	10001	10001
2011	3 136 242	13258	13396	2011	5 100 025	12456	12457
2012	1 887 369	6106	6373	2012	5 123 717	11395	11417
2013	2 122 877	6811	6808	2013	7 039 438	13067	13066
2014	2 431 470	6850	6846	2014	6 944 879	14798	14795
TOTAL	**16 279 206**	**64249**	**65115**	**TOTAL**	**34 710 663**	**74138**	**74157**

Surface water

For surface water, the number of analyses has constantly increased between 2008 and 2014 (except in 2012). The number of analyses increased threefold across seven years with 14700 analyses for each substance in 2014.

For surface water monitoring (Figure 8.5-67**Figure 8.5-23**), there was a gradual increase in stations monitoring for glyphosate and AMPA between 2008 and 2014. There were 909 stations in 2008 and 2154 in 2014 monitoring both AMPA and glyphosate.

Figure 8.5-66: Evolution of the annual number of surface water analyses carried out for AMPA and glyphosate.

Figure 8.5-67: **Number of stations involved in the surface water monitoring of (a) AMPA and (b) glyphosate**

(a) (b)

II. RESULTS AND DISCUSSION

Multi-year continuity analysis

Based on the number of years of monitoring, this section looks at the continuous measurements within the time period and therefore on the ability to draw conclusions in terms of how the multi-annual trends evolved. Taking into account the inter- and intra-annual climatic variability as well as crop rotations, it is necessary to have several years of monitoring data to assess such trends and this does not necessarily require data to be based on consecutive years.

<u>Surface water</u>

For surface waters the number of stations for which monitoring is carried out over the seven years is greater than for groundwater with 22% of stations carrying out measurements. The percentage of stations monitoring for one year is 25%. The results are similar for AMPA and glyphosate. However, the surface water stations performed more systematic measurements in comparison to groundwater monitoring stations.

Table 8.5-101: **Number of years of surface water monitoring for stations between 2008-2014**

	AMPA		**Glyphosate**	
No of years	**No of stations**	**% of stations**	**No of stations**	**% of stations**
One year	731	25%	751	25%
2 years	340	11%	339	11%
3 years	209	7%	210	7%
4 years	170	6%	170	6%
5 years	467	16%	467	16%
6 years	389	13%	389	13%
7 years	655	22%	655	22%
Total no of stations	2961	-	2981	-

Analysis of the annual number of measurements

The examination of the continuity of research across multiple years includes an assessment of the annual number of monitoring data. The data are presented as seven ranges to reflect the number of measurements made per station per year: 1 p.a; 2-3 p.a; 4-5 p.a; 6-9 p.a; 10-14 p.a; 15-49 p.a; >50 p.a.

Surface water

For surface water monitoring stations, the number of measurements per station and per year is generally greater than seen for groundwater. Except in 2008 where the number of analyses per station was mostly 4-5 per year, the number of monitoring events per station was mostly 6-9 per year (for 50%-61% of stations across all years). Between 5% and 15% of stations carried out more than 10 monitoring events per year, and this could correspond to a monthly measurement schedule. No station performed as many as 50 measurements a year. In contrast to groundwater, the number of stations with sampling doubled between 2008 and 2014.

Assessment of the multi-year trend in measurements greater than LOQ (code 1)

In this section, the results of the quantifiable analytical results of glyphosate and AMPA are studied i.e. those results where the concentration of the target molecule is reported as being greater than the limit of quantification (LOQ). The measured concentration values are compared against the regulatory values provided for the provision of drinking water: greater or equal to 0.1 µg/L for drinking water and greater or equal to 2 µg/L for water destined for drinking water.

AMPA

The percent of annual measurements for AMPA > LOQ in groundwater is low (< 5% in all years studied, Table 8.5-102. The lowest such values for AMPA were in 2008-2010 with 0.7-0.9%. From 2013 to 2014, this value for AMPA is *ca.* 2.5% of analyses. In mainland France, fewer than 100 analyses for AMPA exceeded 0.1 µg/L in any one year, except in 2011 where there were 133 exceedances. The concentrations greater than 0.1 µg/L were always <1.1% in groundwater over the seven years of the study. Fewer than five analyses per year exceeded the 2 µg/L limit.

The annual percentage of AMPA measurements >LOQ in surface water were much higher than in groundwater. These vary between 46% and 62.5% with a median quantification rate of 54% (AMPA is detected in more than half of the measurements). Concentrations of AMPA are often > 0.1 µg/L with 33.2% - 53.6% of measurements exceeding this threshold. Concentrations for AMPA >2 µg/L comprise <3% (between 106 and 268 values p.a.) of samples.

Table 8.5-102: Annual measurements above LOQ for AMPA

	2008	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Surface water							
Number of analyses	4862	7559	10001	12456	11395	13067	14798
Number of analyses with conc.> LOQ	2557	3887	4597	7789	6148	7307	7983
% >LOQ (code remarque = 1)	**52.6%**	**51.4%**	**46.0%**	**62.5%**	**54.0%**	**55.9%**	**53.9%**
Number of analyses > LOQ and >= 0.1 µg/L	2130	3389	4068	6681	4054	4348	4913
% of analyses > LOQ and >=0.1 µg/l	**43.8%**	**44.8%**	**40.7%**	**53.6%**	**35.6%**	**33.3%**	**33.2%**
Number of analyses > LOQ and >= 2 µg/L	106	190	172	268	176	162	191
% of analyses > LOQ and >=2 µg/L	**2.18%**	**2.51%**	**1.72%**	**2.15%**	**1.54%**	**1.24%**	**1.29%**

Glyphosate

The annual percentage of measurements > LOQ in surface waters vary between 25.3% and 39.1% with a median quantification rate of 32.3% (indicating that glyphosate is detected in one third of analyses). As well as being identified as higher than LOQ, the analyses were often > 0.1 µg/L (14-21.7% of measurements compared to the whole dataset). In addition, <1% (between 25 and 52 values p.a.) of analyses were >2 µg/L.

Table 8.5-103: Annual measurements above LOQ for glyphosate

	2008	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
	Surface water						
Number of analyses	4862	7559	10001	12457	11417	13066	14795
Number of analyses with conc. > LOQ	1550	1936	2535	4026	4189	5048	5791
% >LOQ (code remarque = 1)	**31.9%**	**25.6%**	**25.3%**	**32.3%**	**36.7%**	**38.6%**	**39.1%**
Number of analyses > LOQ and >= 0,1 µg/L	1051	1404	1757	2697	1937	2004	2072
% of analyses > LOQ and >=0,1 µg/L	**21.6%**	**18.6%**	**17.6%**	**21.7%**	**17.0%**	**15.3%**	**14.0%**
Number of analyses > LOQ and >= 2 µg/L	25	43	36	52	40	41	47
% of analyses > LOQ and >=2 µg/L	**0.5%**	**0.6%**	**0.4%**	**0.4%**	**0.4%**	**0.3%**	**0.3%**

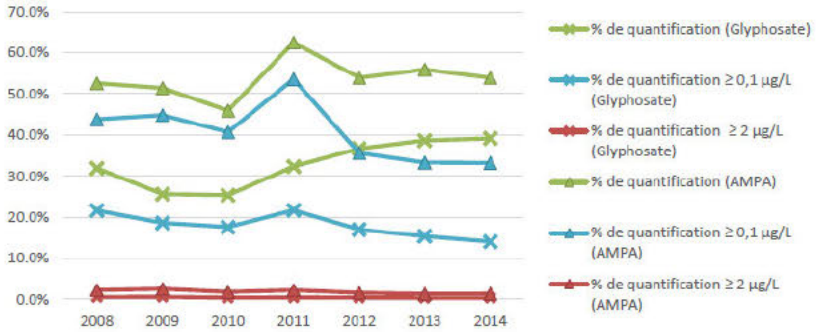
Comparison of concentration levels (greater than LOQ) of AMPA and glyphosate

Surface water

For surface waters, the annual percentage of measurements with concentrations > 0.1µg/L for AMPA varied between 33% and 54%, whilst for glyphosate the variability was less, between 15% and 22% of analyses (Figure 8.5-68)

There appears to be a correlation between the annual percentages for AMPA and glyphosate as they both follow similar trends between years. They generally decrease over the period 2008-2014. Values for annual % of measurements for concentrations >2 µg/L were always low and below 0.6% for glyphosate and 2.5% for AMPA.

Figure 8.5-68: Examining the trend in yearly % of measurements in surface water with respect to regulated concentrations



Maximum concentrations, 90th, 95th and 99th percentiles

The measured concentrations of AMPA and glyphosate in surface waters each year for the period 2008-2014 are described according to their maximum value and their 90th, 95th and 99th percentiles (Table 8.5-104 to Table 8.5-107**Table 8.5-40**).

The glyphosate and AMPA maximum concentrations vary between the years, covering a range of ~1 to 3369 µg/L. There is no logical explanation for these maximum concentration values. Hypotheses put forward are:

- The maximum value can be due to pollution events upstream from the monitoring station with minimal dilution.
- This maximum value could simply be erroneous (transcription error, unit error, etc.)

The 99th percentile concentrations range between 1.6 and 26.3 µg/L.
The 95th percentile concentrations range between 0.3 and 2.9 µg/L. While the 90th percentile concentrations range between 0.2 and 1.2 µg/L.

The data shows opposite trends for surface water and groundwater as follows:

- For surface water, glyphosate maximum concentrations during 2008-2014 are less than those measured for AMPA in all percentile assessments.
- On the contrary, groundwater maximum glyphosate concentrations during 2008-2014 are higher than those for AMPA in all percentile assessments.

The surface water concentrations for both AMPA and glyphosate tend to decrease in all percentiles since 2009.

Table 8.5-104: Annual summary of maximum concentrations (µg/L)

	Period	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Surface water								
AMPA	3369	20.3	33.5	106	3369	80	59.1	61.4
Glyphosate	2237	17.3	19.7	21	2237	66	37.9	558

Table 8.5-105: Annual summary of 90th percentile concentrations (µg/L)

	Period	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Surface water								
AMPA	0.91	1.11	1.20	1.02	1.04	0.88	0.68	0.73
Glyphosate	0.45	0.54	0.70	0.55	0.53	0.42	0.32	0.34

Table 8.5-106: Annual summary of 95th percentile concentrations (µg/L)

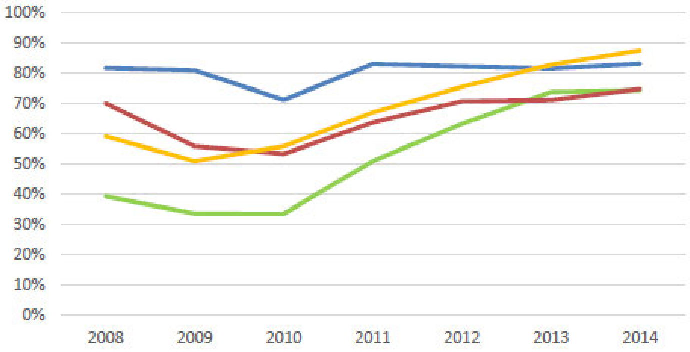
	Period	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Surface water								
AMPA	1.50	1.74	1.97	1.68	1.65	1.40	1.20	1.21
Glyphosate	0.74	0.84	1.19	0.89	0.81	0.71	0.55	0.56

Table 8.5-107: Annual summary of 99th percentile concentrations (µg/L)

	Period	2008	2009	2010	2011	2012	2013	2014
Surface water								
AMPA	4.17	4.70	4.80	4.57	5.16	4.04	3.85	2.90
Glyphosate	2.11	2.85	3.49	2.34	2.22	1.90	1.70	1.80

Assessment of quantification (concentrations greater than LOQ) with respect to monitoring stations
For surface water, AMPA is measured and quantified in ~80% of monitoring stations quoted compared to ~70% for glyphosate (Figure 8.5-69).

Figure 8.5-69: Surface water Red- % of stations with glyphosate concentrations measured/quantified; Blue- % of stations with AMPA concentrations measured/quantified; Yellow: % of stations with glyphosate concentrations measured/quantified less than/equal to 0.1 µg/L; Green- % of stations with AMPA concentrations measured/quantified less than/equal to 0.1 µg/L



Seasonal assessment of quantifications (concentrations greater than LOQ)

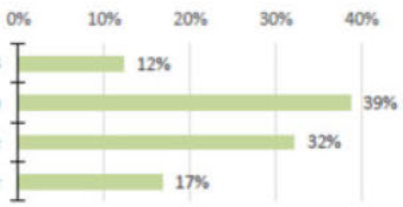
For surface water, the measurements are taken during spring for glyphosate and summer for AMPA (which aligns well with the main usage of the active substance). In fact, on average a third of measurements occur between April and June as well as July and September.

Figure 8.5-70: Surface water distribution of glyphosate from the dataset

	2008	2009	2010	2011	2012	2013	2014	2008-14
Jan to Mar	24%	13%	17%	17%	26%	10%	18%	18%
Apr to Jun	24%	28%	37%	31%	38%	29%	39%	32%
Jul to Sep	42%	33%	28%	32%	29%	42%	25%	33%
Oct to Dec	11%	25%	19%	20%	7%	19%	18%	17%
No of quantifications	395	402	440	608	422	426	320	3 013

Figure 8.5-71: Surface water distribution of AMPA from the dataset

	2008	2009	2010	2011	2012	2013	2014	2008-2014
Jan to Mar	16%	7%	7%	18%	18%	11%	13%	12%
Apr to Jun	45%	35%	42%	13%	38%	40%	41%	39%
Jul to Sep	31%	32%	31%	30%	32%	33%	28%	32%
Oct to Dec	8%	25%	20%	37%	12%	16%	19%	17%
No of quantifications	203	170	178	199	221	241	148	1360



III. CONCLUSIONS

The present study only considers data from mainland France. The surface water database selected for the study comprises 148295 analyses (74138 for AMPA and 74157 for glyphosate) from 2980 stations.

For groundwater, the database consists of 129364 analyses, of which 64249 are for AMPA and 65115 are for glyphosate. The number of distinct water quality monitoring stations is 14831 for the whole database (France mainland only).

Both glyphosate and AMPA were monitored every year between 2008 and 2014 in surface waters and groundwater. The majority of stations extracted from the SOES$_{\text{uipp}}$ database have both AMPA and glyphosate monitoring data. The analysis focusses on those concentrations measured/detected which are above the LOQ, then assesses from those measurements which are ≤ 0.1 µg/L and greater than 2.0 µg/L. The surface water concentrations for both AMPA and glyphosate tend to decrease in all percentiles since 2009.

For surface water, glyphosate maximum concentrations during 2008-2014 are less than those measured for AMPA in all percentile assessments.

Assessment and conclusion by RMS:
Please note that the original report is written in French and that only the present summary is available in English.

This report focuses on data from the French public monitoring data during the period 2008-2014.
It is an update of the report [redacted], 2016, which was focusing on time period 1999-2013.

Pease refer to [redacted], 2016 for more detailed analysis from RMS.

Data point:	CA 7.5/032
Report author	[redacted]
Report year	2019b
Report title	Phase 3 et 4: Traitements et analyses statistiques sur les données SOES UIPP 2008 - 2014 Analyses des données de surveillances sur 6 territoires témoins. Synthêse des données sur l'ensemble des territoires viticoles. (Phase 3 and 4: Statistical analysis of SOES UIPP data 2008 - 2014 Analysis of surveillance data for 6 control regions. Synthesis of data for all wine production regions.)
Document No	REA-DOC-026
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No, but likely conducted by COFRAC approved testing facilities
Acceptability/Reliability:	Acceptable

Executive Summary

This report is an update of a previous report "Analysis of monitoring data for glyphosate and AMPA in French waters in the period 1997-2013" ([redacted], 2016, CA 7.5/009). It includes the 2014 monitoring data for glyphosate and AMPA in ground and surface waters, extracted from the SOES UIPP database in July 2017. The report also looked at the monitoring of AMPA and glyphosate in surface waters associated with six wine growing regions across France.

The study assessed the number of water quality monitoring stations in each area, the regularity of the monitoring (number of samples per year per station) and compared the frequency of quantification and exceedance of drinking water thresholds (0.1 µg/L and 2 µg/L) for both AMPA and glyphosate. Data were also examined in relation to seasonality and trends across the seven-year monitoring period.

The representativeness of stations and associated analysis results presented for the 6 vineyard areas are very limited. There are three areas where four stations monitor the water quality. Estimating water quality of an area from a limited number of sampling points can introduce bias into the interpretation. In addition, the placement of some sampling stations in some areas limits robust estimates of pollution in the area of the vineyard.

For the three other vineyards the number and position of the stations gives a better indication of the level of contamination by glyphosate and AMPA in these areas. However, certain stations should be excluded, because even though they are strictly located in the area, the information generated reflects the conditions and contaminants of much larger areas than the vineyards studied.

In comparison to the analysis made at national level (Phase 1), the frequency of quantification of AMPA was less at the monitoring stations associated with the vineyards (5-20% less). The quantifications of AMPA and glyphosate generally followed the same overall variations year on year. In the vineyard stations the quantifications >0.1 µg/L represented one third of the data; those greater than 2 µg/L of AMPA represent 1-3% of data.

I. MATERIAL AND METHODS

Size of database

At national scale
At the national level the entire dataset for surface waters consists of 148561 analyses for AMPA and glyphosate, across the whole of France including Guadeloupe. The number of unique stations is 3006. The present study focusses on analysis of data from mainland France. Therefore, the database selected for the study comprises 148295 analyses (74138 for AMPA and 74157 for glyphosate) from 2980 stations for the study of surface waters.

At the scale of the 6 winegrowing regions studied
Phases 3 and 4 focus on presenting AMPA and glyphosate residues in surface waters associated with 6 vineyards distributed across France, namely:

- Languedoc – Hérault et Picpoul de Pinet;
- Champagne;
- Coteaux de Saumur;
- Entre deux mers;
- Beaujolais village;
- Cognac.

The number of monitoring stations sampling each year is very variable, in part a function of the differing size of the vineyard regions:

- Picpoul de Pinet et Hérault Languedoc – 4-12 stations
- Champagne - 17-20 stations;
- Coteaux de Saumur - 1-3 stations
- Entre deux mers – 1-3 stations
- Beaujolais village - 1 monitoring station
- Cognac – 38-74 stations (except 2008, 14 stations)

Data for glyphosate and AMPA were generated by the same number of monitoring stations for each region. The number of analyses for glyphosate and AMPA being very similar, within one or two values for the 6 vineyards for the 7 years studied, except for the Cognac vineyard in 2012 (290 analyses for glyphosate compared to 315 for AMPA). For most vineyards, the average number of analyses per station year is between 3 and 5. Some stations have only 1 or no analyses in certain years whilst others had more than 7-8 analyses per year in certain years. The overall average for all vineyards is between 5 and 7 analyses per station per year. These analyses include data across all SANDRE codes of reliability (1 = > LOQ; 2 = < LOD; 7 = >LOD but <LOQ – substance present but not possible to quantify accurately; 10= <LOQ [since 2007]).

II. RESULTS AND DISCUSSION

Multi-year continuity analysis
This analysis looked at continuity of analyses within the time period and therefore at the ability to draw conclusions in terms of multi-annual trends, based on the number of years of monitoring. Due to the inter and intra-annual climatic variability and crop rotations, it is necessary to have several years of monitoring to analyse trends.

Multi-year data may not use consecutive years, thus a station monitoring for 5 years may have non-consecutive years e.g. 2008, 2009, 2010, 2013, 2014). These data show that monitoring is very regular at stations located in the vineyards of Beaujolais village, Champagne and Entre deux mers. For the vineyards of Cognac and Picpoul de Pinet, the number of stations is relatively higher compared to other vineyards (except Champagne), however their monitoring is fairly irregular with more than a third of the stations monitoring for 4 years or less. For Coteaux de Saumur, monitoring was less regular with fewer stations present in this area.

- For Beaujolais-Village, there was one station monitoring every year for seven years for both AMPA and glyphosate (100% of all stations in the area).
- For Champagne, for both AMPA and glyphosate, out of 22 stations: two stations monitored in just one year (9.1% of all stations in the area); one station monitored for two, three and five years (4.5%); 17 stations monitored for seven years (77.3%).
- For Cognac, for both AMPA and glyphosate, out of 77 stations: two stations monitored in just one year (2.6%); 10 stations monitored for two years (13.0%); one station monitored for three years (1.3%), 26 stations monitored for four years (33.8%); two stations monitored for five years (2.6%); 22 stations monitored for six years (28.6%) and 14 stations monitored for seven years (18.2%).
- For Coteaux de Saumur, for both AMPA and glyphosate, out of four stations: one station monitored in one and three years (25%); two stations monitored for five years (50%).
- For Entre deux mers, for both AMPA and glyphosate, out of three stations: two stations monitored for six years (66.7%) and one station station monitored for seven years (33.3%).
- For Picpoul de Pinet et Hérault Languedoc, for both AMPA and glyphosate, out of 13 stations: three stations monitored for two years (23.1%); one station monitored for four years (7.7%); four stations monitored for five years (30.8%); one station monitored for six years (7.7%) and four stations monitored for seven years (30.8%).

Analysis of the annual number of monitoring data

The examination of the continuity of monitoring across multiple years includes the annual number of monitoring data. The data are presented as seven ranges to reflect the number of monitoring events made per station per year: 1 per annum (p.a.); 2-3 p.a.; 4-5 p.a.; 6-9 p.a.; 10-14 p.a.; 15-49 p.a.; >50 p.a.

In the Beaujolais, Coteaux de Saumur, Champagne and PicPoul de Pinet vineyards, the number of monitoring events for both glyphosate and AMPA by station and by year is generally 6 to 9 per year. At the Entre deux mers and Cognac vineyards, the data are less frequent, mostly between 4 and 5 monitoring events per station per year.

Review of the trend in quantifications

In this section, the results of the analytical results of glyphosate and AMPA >LOQ are assessed. The quantified concentrations are compared against the regulatory values provided for the provision of drinking water: ≥0.1 µg/L for potable water and ≥ 2 µg/L for water which is to be made potable.

Table 8.5-108: Annual summaries of AMPA quantifications for all (a) and individual (b – g) vineyard regions

(a) Combined 120 stations for 6 vineyards							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	189	331	277	521	530	652	662
Number > LOQ	123	152	91	201	162	308	245
% > LOQ	**65%**	**46%**	**33%**	**39%**	**31%**	**47%**	**37%**
Number ≥ 0.1 µg/L	96	111	74	155	93	181	141
% ≥ 0.1 µg/L	**51%**	**34%**	**27%**	**30%**	**18%**	**28%**	**21%**
Number ≥ 2 µg/L	2	3	7	8	9	7	7
% ≥ 2 µg/L	**1%**	**1%**	**3%**	**2%**	**2%**	**1%**	**1%**
(b) Beaujolais village							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	6	6	6	8	6	6	6
Number > LOQ	0	2	4	6	5	5	3
% > LOQ	**0%**	**33%**	**67%**	**75%**	**83%**	**83%**	**50%**
Number ≥ 0.1 µg/L	0	2	2	5	4	4	2
% ≥ 0.1 µg/L	**0%**	**33%**	**33%**	**63%**	**67%**	**67%**	**33%**
Number ≥ 2 µg/L	0	0	0	0	0	0	0
% ≥ 2 µg/L	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**
(c) Champagne							

Table 8.5-108: Annual summaries of AMPA quantifications for all (a) and individual (b – g) vineyard regions

Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	82	124	114	120	129	126	115
Number > LOQ	52	71	28	49	47	62	38
% > LOQ	**63%**	**57%**	**25%**	**41%**	**36%**	**49%**	**33%**
Number ≥ 0.1 µg/L	41	50	20	44	23	27	10
% ≥ 0.1 µg/L	**50%**	**40%**	**18%**	**37%**	**18%**	**21%**	**9%**
Number ≥ 2 µg/L	0	1	1	0	1	0	0
% ≥ 2 µg/L	**0%**	**1%**	**1%**	**0%**	**1%**	**0%**	**0%**
(d) Coteaux de Saumur							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	12	-	14	26	14	25	41
Number > LOQ	11	-	11	20	12	24	29
% > LOQ	**92%**	**-**	**79%**	**77%**	**86%**	**96%**	**71%**
Number ≥ 0.1 µg/L	11	-	11	20	6	13	22
% ≥ 0.1 µg/L	**92%**	**-**	**79%**	**77%**	**43%**	**52%**	**54%**
Number ≥ 2 µg/L	0	-	0	0	0	0	0
% ≥ 2 µg/L	**0%**	**-**	**0%**	**0%**	**0%**	**0%**	**0%**
(e) Cognac							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	56	164	86	297	315	400	413
Number > LOQ	43	64	25	90	71	157	137
% > LOQ	**77%**	**39%**	**29%**	**30%**	**23%**	**39%**	**33%**
Number ≥ 0.1 µg/L	27	45	25	63	39	91	83
% ≥ 0.1 µg/L	**48%**	**27%**	**29%**	**21%**	**12%**	**23%**	**20%**
Number ≥ 2 µg/L	0	2	3	6	6	5	7
% ≥ 2 µg/L	**0%**	**1%**	**3%**	**2%**	**2%**	**1%**	**2%**
(f) Entre deux mers							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	4	13	6	15	15	24	24
Number > LOQ	4	8	3	10	7	23	20
% > LOQ	**100%**	**62%**	**50%**	**67%**	**47%**	**96%**	**83%**
Number ≥ 0.1 µg/L	4	7	3	7	6	20	16
% ≥ 0.1 µg/L	**100%**	**54%**	**50%**	**47%**	**40%**	**83%**	**67%**
Number ≥ 2 µg/L	0	0	0	0	0	0	0
% ≥ 2 µg/L	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**
(g) Picpoul de Pinet et Hérault Languedoc							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	29	24	51	55	51	71	63
Number > LOQ	13	7	20	26	20	37	18
% > LOQ	**45%**	**29%**	**39%**	**47%**	**39%**	**52%**	**29%**
Number ≥ 0.1 µg/L	13	7	13	16	15	26	8
% ≥ 0.1 µg/L	**45%**	**29%**	**25%**	**29%**	**29%**	**37%**	**13%**
Number ≥ 2 µg/L	2	0	3	2	2	2	0
% ≥ 2 µg/L	**7%**	**0%**	**6%**	**4%**	**4%**	**3%**	**0%**

Compared to the analyses at the national scale (Phase 1), the frequencies of quantification of AMPA (Table 8.5-108) are lower at the vineyard monitoring stations (5% to 20% less) than nationally, except for 2008 where the frequency of quantification at national scale was 53% of all the analyses but was 65% of the analyses across the 120 stations associated with the six vineyards.

For these 120 stations the quantifications ≥0.1 µg/L for AMPA represent a third of the data (except for 2008) against 33% to 54% for the national database. The quantifications ≥2 µg/L for AMPA represent 1-3% of data between 2008 and 2014 (the same order of magnitude as at national scale).

AMPA quantification rates across the different vineyards vary, although for the Beaujolais-Village, Coteaux de Saumur and Entre deux mers vineyards, care should be taken with interpretation as these data are based solely on analyses carried out with just 1 to 3 water quality stations.

For the Beaujolais-Village, Coteaux de Saumur and Entre deux mers vineyards, there is no quantification greater than the 2 µg/L limit. For these three vineyards the percentage of quantification and of quantification greater than 0.1 µg/L are greater than the combined statistics of the 120 stations, probably due to the small number of monitoring stations for these vineyards on which this data is based. This is particularly true for the years 2010 to 2013. For Coteaux de Saumur, the rate of quantification of AMPA is greater than 70% for all the years (except 2009 where no data are available) and that of the exceedances of the 0.1 µg/L limit is also greater than 70% for half of the years studied. For Entre deux mers, the level of quantification of AMPA is > 80% for three years and the rate of quantification greater than 0.1 µg/L is 50% for five of the seven years.

For the Champagne vineyard, the level of quantification of AMPA is closer to that of the 120 stations taken as a whole, although the frequencies of exceedances of 0.1 and 2 µg/L limits are less (three exceedances of 2 µg/L across the seven years).

For stations situated in Cognac, the water quality data have rates of quantification of AMPA less than 40% (except in 2008) and the levels of quantification for concentrations > 0.1 µg/L were between 20 and 30% which are slightly lower than across the 120 stations of all six vineyards.

The Picpoul de Pinet et Hérault Languedoc vineyard is the area with the highest level of quantification of AMPA at concentrations >2 µg/L (levels ≥4% in four of the studied years).

Table 8.5-109: Annual summaries of glyphosate quantifications for all (a) and individual (b – g) vineyard regions

(a) Combined 120 stations for 6 vineyards							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	189	331	277	521	508	652	662
Number > LOQ	106	113	58	110	132	271	166
% > LOQ	**56%**	**34%**	**21%**	**21%**	**26%**	**42%**	**25%**
Number ≥ 0.1 µg/L	73	86	44	76	77	134	66
% ≥ 0.1 µg/L	**39%**	**26%**	**16%**	**15%**	**15%**	**21%**	**10%**
Number ≥ 2 µg/L	3	4	3	8	3	3	2
% ≥ 2 µg/L	**2%**	**1%**	**1%**	**2%**	**1%**	**0.5%**	**0.3%**
(b) Beaujolais village							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	6	6	6	8	6	6	6
Number > LOQ	2	0	2	2	2	2	5
% > LOQ	**33%**	**0%**	**33%**	**25%**	**33%**	**33%**	**83%**
Number ≥ 0.1 µg/L	2	0	0	0	1	0	1
% ≥ 0.1 µg/L	**33%**	**0%**	**0%**	**0%**	**17%**	**0%**	**17%**
Number ≥ 2 µg/L	0	0	0	0	0	0	0
% ≥ 2 µg/L	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**
(c) Champagne							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	82	124	114	120	129	125	115
Number > LOQ	53	55	28	35	68	80	46
% > LOQ	**65%**	**44%**	**25%**	**29%**	**53%**	**64%**	**40%**
Number ≥ 0.1 µg/L	38	44	21	33	36	32	15
% ≥ 0.1 µg/L	**46%**	**35%**	**18%**	**28%**	**28%**	**26%**	**13%**
Number ≥ 2 µg/L	3	3	1	3	1	0	0
% ≥ 2 µg/L	**4%**	**2%**	**1%**	**3%**	**1%**	**0%**	**0%**
(d) Coteaux de Saumur							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	12	-	14	26	14	25	41
Number > LOQ	5	-	8	11	4	16	12
% > LOQ	**42%**	**-%**	**57%**	**42%**	**29%**	**64%**	**29%**
Number ≥ 0.1 µg/L	5	-	6	10	0	2	1
% ≥ 0.1 µg/L	**42%**	**-%**	**43%**	**38%**	**0%**	**8%**	**2%**
Number ≥ 2 µg/L	0	-	0	0	0	0	0
% ≥ 2 µg/L	**0%**	**-%**	**0%**	**0%**	**0%**	**0%**	**0%**
(e) Cognac							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	56	164	86	297	293	401	413
Number > LOQ	36	50	9	45	41	137	77
% > LOQ	**64%**	**30%**	**10%**	**15%**	**14%**	**34%**	**19%**
Number ≥ 0.1 µg/L	19	36	9	24	30	75	42
% ≥ 0.1 µg/L	**34%**	**22%**	**10%**	**8%**	**10%**	**19%**	**10%**
Number ≥ 2 µg/L	0	1	2	5	2	3	1
% ≥ 2 µg/L	**0%**	**1%**	**2%**	**2%**	**1%**	**1%**	**0%**
(f) Entre deux mers							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Number of analyses	4	13	6	15	15	24	24
Number > LOQ	3	6	0	3	4	12	9
% > LOQ	**75%**	**46%**	**0%**	**20%**	**27%**	**50%**	**38%**
Number ≥ 0.1 µg/L	2	4	0	3	3	8	3
% ≥ 0.1 µg/L	**50%**	**31%**	**0%**	**20%**	**20%**	**33%**	**13%**
Number ≥ 2 µg/L	0	0	0	0	0	0	0
% ≥ 2 µg/L	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**
(g) Picpoul de Pinet et Hérault Languedoc							
Years	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**

Table 8.5-109: Annual summaries of glyphosate quantifications for all (a) and individual (b – g) vineyard regions

Number of analyses	29	24	51	55	51	71	63
Number > LOQ	7	2	11	14	13	24	17
% > LOQ	**24%**	**8%**	**22%**	**25%**	**25%**	**34%**	**27%**
Number ≥ 0.1 µg/L	7	2	8	6	7	17	4
% ≥ 0.1 µg/L	**24%**	**8%**	**16%**	**11%**	**14%**	**24%**	**6%**
Number ≥ 2 µg/L	0	0	0	0	0	0	1
% ≥ 2 µg/L	**0%**	**0%**	**0%**	**0%**	**0%**	**0%**	**2%**

For glyphosate (Table 8.5-109), as for AMPA, the frequencies of quantification are less for the vineyard stations (5-20% less) when compared to the national scale. The exceptions are for 2008 and 2009 where the frequencies of quantification at national scale were 40% and 26%, compared to 56% and 34%. These findings were the same for the frequencies of quantification of concentrations greater than 0.1 µg/L and 2 µg/L.

As for AMPA, glyphosate quantification rates across the different vineyards vary, although for the Beaujolais-Village, Coteaux de Saumur and Entre deux mers vineyards, care should be taken when interpreting these data as they are based solely on analyses carried out with just 1 to 3 water quality stations.

For the Beaujolais-Village, Coteaux de Saumur and Entre deux mers vineyards, there is no quantification of glyphosate (or AMPA) greater than the 2 µg/L limit. For Beaujolais-Village, the rate of quantification of glyphosate ranged from 25% to 33%. There were two atypical years: 2009 with no quantification of glyphosate and 2014 where it was quantified in 5 or 6 samples.

For the stations in Coteaux de Saumur and Entre deux mers, there was a large variation between years in the rates of quantification: between 0% and 43% for Coteaux de Saumur and between 0% and 75% for Entre deux mers. Again, this was probably due to the small number of monitoring stations for these vineyards on which this data is based. For Entre deux mers, quantifications greater than 0.1 µg/L were observed in one-fifth to one-third of the data, depending on the year.

For Champagne, the rates of quantification of glyphosate are greater than when considering the rates of quantification of the 120 stations as a whole (> 40% in 2009 and 2014, and > 50% in 2008, 2012 and 2013). Also, for five of the seven years, more than a quarter of quantifications of glyphosate are greater than 0.1 µg/L. Several exceedances of 2 µg/L were seen.

For Cognac, frequencies of quantification of glyphosate in the water quality data > 0.1 µg/L were comparably less (5% -10%) than across the 120 stations studied for the six vineyards. There were some exceedances of the 2 µg/L limit.

The rates of quantification for glyphosate in Picpoul de Pinet et Hérault Languedoc were less than those at the other vineyards. Less than a quarter of the analyses exceeded the 0.1 µg/L drinking water limit and none exceeded 2 µg/L.

Maximum concentrations and 90th, 95th and 99th percentile concentrations

Overall, the maximum concentrations, and 90th, 95th and 99th percentiles are greater for AMPA than for glyphosate except for data associated with the Champagne vineyard. For Beaujolais, Coteaux de Saumur and Entre deux mers, the maximum concentrations never exceed 2 µg/L.

For Cognac, AMPA concentrations in excess of 50 µg/L were observed for four of the seven years and concentrations for glyphosate exceeded 10 µg/L in two years.

In Picpoul de Pinet et Hérault Langeudoc the maximum concentrations below 10 µg/L while in Champagne, the maximum concentrations exceed 10 µg/L.

There appears to be no logical explanation for the maximum concentrations. It is hypothesized that:

- The maximum value is caused by occasional point source pollution events upstream of the monitoring station with no dilution.
- The value is possibly an anomalous value in the database, e.g. a data transcription error, incorrect unit, etc.

Seasonality of quantifications
Quantifications of AMPA and glyphosate were studied according to their distribution by season and application timing to the vines. Autumn is defined as 15th October to 15th December, Winter is 1st February to 15th March, Spring is 15th March to 31st May and summer is 15th June to 31st July. Times not included in these seasonal definitions are defined as “the rest of the year”.

Glyphosate is mainly applied between March and June. Analytical quantifications of glyphosate occurred mainly in the Spring. For AMPA, quantifications were mostly seen in the summer and “rest of the year”. The fewest quantifications of both glyphosate and AMPA were in winter.

III. CONCLUSIONS

Phases 3 and 4 assess the presence of AMPA and glyphosate in surface waters associated with six vineyards across France in Beaujolais village, Champagne, Cognac, Coteaux de Saumur, Entre deux mers and Picpoul de Pinet et Languedoc-Hérault.

The number of water quality monitoring stations in each area was variable: 1 to 3 stations per year for Beaujolais village, Entre deux mers and Coteaux de Saumur; 10 to 20 stations for Picpoul de Pinet et Languedoc-Hérault and Champagne and more than 30 stations per year for Cognac. The same is true for the regularity of monitoring (number of samples per year per station). Regular monitoring occurred at stations located in Beaujolais Village, Champagne and Entre deux mers. For Cognac and Picpoul de Pinet et Languedoc-Hérault the number of stations is relatively high compared to the other vineyards but the monitoring is more irregular.

In comparison to the analysis made at national level (Phase 1), the frequency of quantification of AMPA was less at the monitoring stations associated with the vineyards (5-20% less). The quantifications of AMPA and glyphosate generally followed the same overall variations year on year. In the vineyard stations the quantifications >0.1 µg/L represented one third of the data; those greater than 2 µg/L of AMPA represent 1-3% of data.

The representativeness of stations and the analysis results of the actual vineyards themselves are very limited. For three vineyards there are four stations monitoring the water quality. Estimating the water quality of an area from a limited number of sampling points can introduce bias in the interpretation (point source pollution close to sampling count, inappropriate siting of the station, errors in sampling).

In addition, the placement of some sampling stations in certain areas does not allow good estimates of pollution arising from the vineyard. For example, in Beaujolais (area 393 km^2), the only station of the area is situated on the Saône (which drains many thousands of km^2) upstream from the confluence of the Ardière which is the only water course that traverses the vineyard. The water quality observed at this sampling point is therefore largely independent of applications made in the Beaujolais village vineyard.

Also, for Coteaux de Saumur, two of the four stations in the area are on the Loire and the two others are downstream of Thouet which drains a basin much bigger than that of the vineyard.

For Entre deux mers, three stations are all sited to the East/South east of the area and one is situated on the Dropt which drains a basin much bigger than the vineyard.

For the three other vineyards the number and position of the stations gives a better estimate of the levels of contamination by glyphosate and AMPA in these areas.

Assessment and conclusion by applicant:

The report describes the results of a surface water monitoring study for glyphosate and AMPA for six wine growing areas across France. The work looks at the contextualisation of monitoring data with reference to frequency of quantification and exceedance of regulatory drinking water limits for each vineyard.

The study is considered valid.

Assessment and conclusion by RMS:

Please note that the original report is written in French and that only the present summary is available in English.

This report focuses on data from the French public monitoring data during the period 2008-2014, these data are however also reported in [redacted] 2019a. The purpose of the present report is to further focus on the findings of GLY and AMPA in surface water for this 7 years period in the area of six vineyards across France.

Results and conclusions from this report should be considered with caution, for the reasons exposed by study authors:

- The representativeness of stations are very limited in some cases: There are three areas where less than 3 stations monitor the water quality.
- The regularity of inter- and intra-annual sampling is not always met: monitoring is very regular at stations located in the vineyards of Beaujolais village, Champagne and Entre deux mers. For the vineyards of Cognac and Picpoul de Pinet, the monitoring if rather irregular with more than a third of the stations monitoring for 4 years or less. In terms of annual frequency, most of the stations have been monitored less than 5 times a year.

The study is considered acceptable.

Data point:	CA 7.5/033
Report author	[redacted]
Report year	2018a
Report title	Etude environnementale du Glyphosate et de l'AMPA à l'échelle des 10 points de surveillance les plus préoccupants pour le Glyphosate et pour l'AMPA. Analyse des suivis du Glyphosate et de l'AMPA en lien avec les bassins versants drainés par les stations de mesures et l'occupation des sols. Etudes des stations sur le glyphosate. (Environmental Study of Glyphosate and AMPA for the 10 most concerning locations for Glyphosate and AMPA. Analysis of Glyphosate and AMPA monitoring data with respect to their drained river areas and land use. Glyphosate Studies.)
Document No	Envilys Report Version 1 (2018)
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted

GLP/Officially recognised testing facilities	No, but likely conducted at COFRAC accredited testing facilities
Acceptability/Reliability:	Acceptable

Executive Summary

This document presents the water quality records of eight surface water quality monitoring stations. These stations were shortlisted from the SOES UIPP 2008-2014 dataset as they have reported the highest median and mean concentration values for glyphosate. These stations are also the only ones that can provide glyphosate data for 5 years between 2008 and 2014 (not necessarily over five consecutive years).

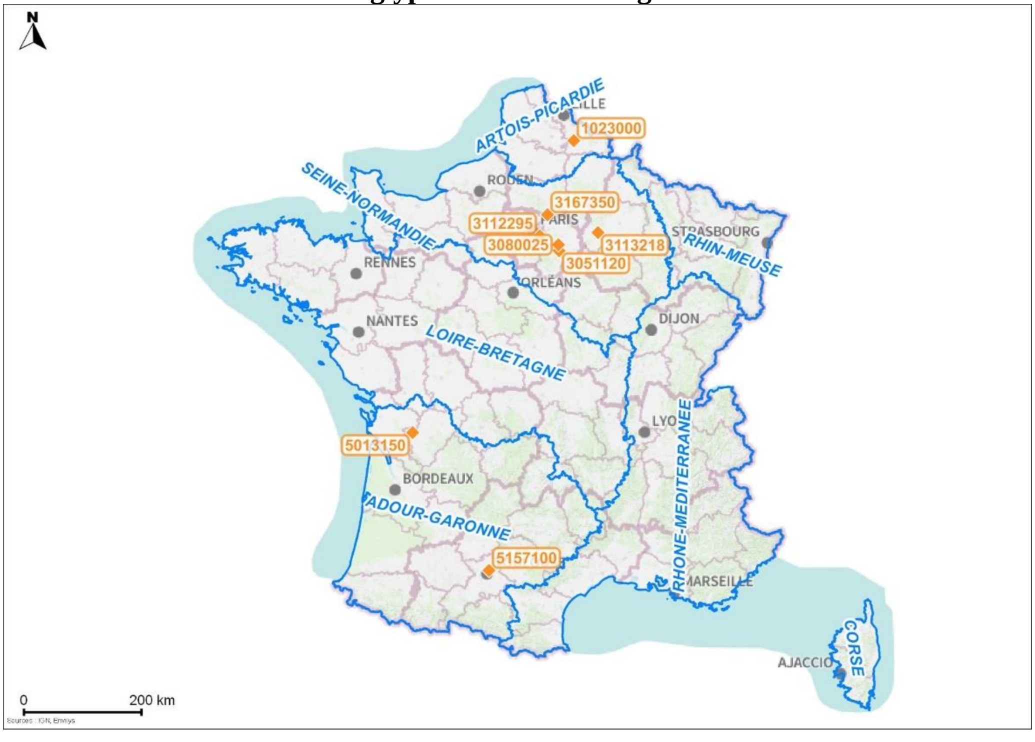
I. MATERIAL AND METHODS

The eight selected glyphosate monitoring stations are listed in Table 8.5-110 and their locations are shown in Figure 8.5-72. Each station record is split and presented over 3 parts, with each describing the regional landscape and hydrology, the rainfall and climate, and the water quality.

Table 8.5-110: List of 8 glyphosate monitoring stations

Station	Station Name	Name of surface water body	Agency
1023000	L'Erclin à Iwuy	L'Erclin	AEAP
3051120	Ru de Courtenain à Fontenailles	L'Almont	AESN
3080025	Yvron à Courpalay	L'Yvron	AESN
3112295	Morbras à Sucy en Brie	Le Morbras	AESN
3113218	Le ruisseau de Cubersault à Coizard-Joches	Le ruisseau de Cubersault	AESN
3167350	Ver sur Launette	La Launette	AESN
5013150	Terrier Raboin	Le Tourtrat	AEAG
5157100	St Caprais	La Sausse	AEAG

Figure 8.5-72: Location of the glyphosate monitoring stations



II. RESULTS AND DISCUSSION

Station 1 - L’Erclin à Iwuy (01023000)

River	L’Erclin	Number of water quality stations in the catchment	1
Catchment size (km^2)	161.598	Length of river (km)	69.97
Number of municipalities	38	Region	Nord

Landscape
The catchment is mostly agricultural (~88%) with 80% of the area comprised of arable land and 7% grassland (but no vineyards). The remaining ~11% are urban areas.

Rainfall
According to the meteorological data from the Météo France station at St Quentin, the average annual rainfall is 702.6 mm recorded over 122.5 rain days. The climate is temperate and rainfall occurs uniformly spread throughout the year, even in the summer months when the heaviest downpours occur.

Water quality
There were 35 glyphosate measurements taken between 13/02/2008 and 15/12/2014 (Table 8.5-111). The mean and median concentrations of glyphosate were 0.9 µg/L and 0.7 µg/L, respectively. The measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 7.2 µg/L) on two occasions. Approximately 92% glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 41 AMPA measurements taken between 13/02/2008 and 15/12/2014 with the maximum concentration reported being 8.5 µg/L. The mean and median concentrations of AMPA were 5.6 µg/L and 2.4 µg/L, respectively. There were 7 analyses for AMPA that exceeded the threshold of 10 µg/L (20% of measurements), 17 that exceeded 5 µg/L (17% of measurements) and 22 measurements exceeded the threshold of 2 µg/L (54% of measurements).

Table 8.5-111: Summary of glyphosate and AMPA concentration data at L’Erclin à Iwuy

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0 1	0.1 – 2	2-5	5-10	10-50	>50
GLY	0102300	35	13/02/2008	15/12/2008	0.932	0.672	7.22	1	32	1	1	na	na
AMPA	0102300	41	13/02/2008	15/12/2008	2.75	2.07	8.5	na	19	15	7	na	na

Ave = Average; Med = median; Max = maximum; NA – No Data

Station 2 - Ru de Courtenain à Fontenailles (03051120)

River	L’Almont	Number of stations	1
Area covered (km^2)	71.66	Length of river (km)	42.209
Number of municipalities	10	Region	Seine et Marne

Landscape
The catchment is mostly agricultural with ~63% of the area comprised of arable land (but no vineyards), 1% grassland, 29% natural areas and the remaining 6% urban areas.

Rainfall
According to the meteorological data from the Météo France station at Melun, the average annual rainfall is 676.9 mm recorded over 117.2 rain days. The climate is temperate and rainfall is uniformly distributed throughout the year. The least rainy month is February and the rainiest period is between May and October.

Water quality
There were 26 glyphosate and AMPA measurements taken between 17/09/2008 and 11/04/2014 (Table 8.5-112). The mean and median concentrations of glyphosate were 1.2 µg/L and 0.5 µg/L, respectively. The measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 4.2 µg/L) on seven occasions. Approximately 69% glyphosate measurements were between 0.1 µg/L and 2 µg/L.

The mean and median concentrations of AMPA were 10.8 µg/L and 4 µg/L, respectively. There were ten analyses for AMPA that exceeded the threshold of 5 µg/L (38% of measurements) and 21 records exceeded 2 µg/L (81% of measurements). Two measurements exceeded 50 µg/L. The AMPA concentrations seemed to increase during the 2013-2014 period.

Table 8.5-112: Summary of glyphosate and AMPA concentration data at Ru de Courtenain à Fontenailles

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	03051120	26	17/09/2008	04/11/2014	1.17	0.531	4.18	1	18	7	na	na	na
AMPA	03051120	26	17/09/2008	04/11/2014	10.8	4.04	61.4	na	5	11	3	5	2

na – no data; Ave – average; Med – Median; Max – Maximum

Station 3 – Yvron à Courpalay (03080025)

River	L'Yvron	Number of stations	1
Area covered (km^2)	156.986	Length of river (km)	85.358
Number of municipalities	24	Region	Seine-et-Marne

Landscape
The catchment is mostly agricultural with ~90% of the area comprised of arable land (but no vineyards). Natural areas cover 8% of the total area with urban areas making up the remaining 2%.

Rainfall
According to the meteorological data from the Météo France station at Melun, the average annual rainfall is 676.9 mm recorded over 117.2 rain days. The climate is temperate with rainfall spread quite homogeneously throughout the year. The least rainy month is February while May and October register the most rainfall.

Water quality
There were 31 glyphosate measurements taken between 15/07/2008 and 11/11/2014 (Table 8.5-113). The mean and median concentrations of glyphosate were 2 µg/L and 0.8 µg/L, respectively. The measured concentrations exceeded the threshold of 10 µg/L (maximum concentration of 13.1 µg/L) twice and the threshold of 2 µg/L eleven times. Approximately 83% glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 30 AMPA measurements taken between 15/07/2008 and 11/11/2014. The mean and median concentrations of AMPA were 3.1 µg/L and 1.1 µg/L, respectively. There were seven analyses of AMPA that exceeded the threshold of 5 µg/L (23% of measurements). Approximately 60% of AMPA measurements were between 0.1 µg/L and 2 µg/L. The concentrations of AMPA seemed to decrease during the 2013-2014 period.

Table 8.5-113: Summary of glyphosate and AMPA concentration data at Yvron à Courpalay

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50

GLY	03080025	31	15/07/2008	11/11/2014	1.96	0.752	13.1	3	17	9	na	2	na
AMPA	03080025	30	15/07/2008	11/11/2014	3.14	1.13	13	3	18	2	4	3	3

na – no data; Ave – average; Med – Median; Max – Maximum

Station 4 – Morbras à Sucy en Brie (03112295)

River	Le Morbras	Number of stations	1
Area covered (km^2)	50.06	Length of river (km)	30.637
Number of municipalities	17	Region	Seine-et-Marne, Seine-St-Denis, Val-de-Marne

Landscape
The catchment is characterized by a high coverage (49%) of urban areas plus 6% parks and gardens. Natural areas (26%) are at the head of the catchment. Agricultural area (19%) extend over the whole catchment and include 15% cropped arable land.

Rainfall
According to the meteorological data from the Météo France station at d'Orly, the average annual rainfall is 616.6 mm recorded over 109.7 rain days. The climate is temperate and rainfall occurrence is homogeneous throughout the year. The least rainy month is February while the months of May, August and October register the most rainfall.

Water quality
There were 34 glyphosate measurements taken between 16/07/2008 and 13/05/2014 (Table 8.5-114). The mean and median concentrations of glyphosate were 0.9 µg/L and 0.5 µg/L, respectively. The measured concentrations exceeded the thresholds of 5 µg/L (maximum concentration of 9.9 µg/L) and 2 µg/L on one and two occasions, respectively. Approximately 85% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 36 AMPA measurements taken between 16/07/2008 and 07/07/2014. The mean and median concentrations of AMPA were both 1.3 µg/L. There were 6 analyses of AMPA that exceeded the threshold of 5 µg/L (17% of measurements) and 14 records exceeded 2 µg/L (17% of measurements). Approximately 81% of AMPA measurements were between 0.1 µg/L and 2 µg/L.

Table 8.5-114: Summary of glyphosate and AMPA concentration data at Morbras à Sucy en Brie

Compound	**Station**	**Number analyses**	**Start date**	**End date**	**Ave**	**Med**	**Max**	**Measured concentrations (µg/L)**					
								<0.1	**0.1 – 2**	**2-5**	**5-10**	**10-50**	**>50**
GLY	03112295	34	16/07/2008	13/05/2014	0.879	0.474	9.88	3	29	1	1	na	na
AMPA	03112295	36	16/07/2008	07/07/2014	1 3	1.31	3.6	1	29	6	na	na	na

na – no data; Ave – average; Med – Median; Max – Maximum

Station 5 – Le ruisseau de Cubersault à Coizard-Joches (03113218)

River	Le ruisseau de Cubersault	Number of stations	1
Area covered (km^2)	29.992	Length of river (km)	14.188
Number of municipalities	9	Region	Marne

Landscape
The catchment is predominantly agricultural with ~66% of the area comprised of arable land, 1% grassland and 4% mixed agricultural and natural areas. Vineyard coverage is 14%, natural areas 10% and urban areas make up 4% of the remaining catchment area.

Rainfall

According to the meteorological data from the Météo France station at Troyes, the average annual rainfall is 644.8 mm recorded over 114.5 rain days. The climate is temperate coastal, with considerable rainfall during the spring and autumn. Summer is the least rainy season but thunderstorm and hailstone events can occur.

Water quality
There were 31 glyphosate measurements taken between 06/08/2008 and 06/04/2014 (Table 8.5-115). The mean and median concentrations of glyphosate were 1.1 µg/L and 0.8 µg/L, respectively. The measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 4.6 µg/L) on four occasions. Approximately 81% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 27 AMPA measurements taken between 06/08/2008 and 06/04/2014. The mean and median concentrations of AMPA were 0.8 µg/L and 0.7 µg/L, respectively. There was one analysis of AMPA that exceeded the threshold of 2 µg/L. Approximately 89% of measurements were between 0.1 µg/L and 2 µg/L. The concentrations of AMPA and glyphosate seemed to decrease during the 2011-2014 period.

Table 8.5-115: Summary of glyphosate and AMPA concentration data at *Le ruisseau de Cubersault à Coizard-Joches*

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	03113218	31	06/08/2008	06/04/2014	1.14	0.831	4.59	2	25	4	na	na	na
AMPA	03113218	27	06/08/2008	06/04/2014	0.816	0.747	2.59	2	24	1	na	na	na

na – no data; Ave – average; Med – Median; Max – Maximum

Station 6 – Ver sur Launette (03167350)

River	La Launette	Number of stations	1
Area covered (km^2)	39.949	Length of river (km)	28.013
Number of municipalities	12	Region	Oise, Seine-et-Marne

Landscape
The catchment is mostly agricultural with ~71% of the area comprised of arable land (but no vineyards) and 2% grasslands. Natural areas cover 29% of the total area and urban areas make up the remaining ~19% of the catchment area.

Rainfall
According to the meteorological data from the Météo France station at Roissy-en-France, the average annual rainfall is 693.6 mm recorded over 116.8 rain days. The climate is temperate with rainfall spread homogeneously during the year. The least rainy month is February while the months of May, October and December register the most rainfall.

Water quality
There were 38 glyphosate measurements taken between 21/07/2008 and 24/11/2014 (Table 8.5-116). The mean and median concentrations of glyphosate were 1 µg/L and 0.9 µg/L, respectively. The measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 2.9 µg/L) on four occasions. Approximately 87% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 35 AMPA measurements taken between 21/07/2008 and 24/11/2014. The mean and median concentrations of AMPA were 4.1 µg/L and 3.7 µg/L, respectively. There were 10 analyses of AMPA that exceeded the threshold of 5 µg/L (29% of measurements) and 28 records exceeded 2 µg/L (80% of measurements). The highest AMPA concentrations were measured during the 2009-2012 period.

Table 8.5-116: Summary of glyphosate and AMPA concentration data at Ver sur Launette

Compound	**Station**	**Number analyses**	**Start date**	**End date**	**Ave**	**Med**	**Max**	**Measured concentrations (µg/L)**					
								<0.1	**0.1 – 2**	**2-5**	**5-10**	**10-50**	**>50**
GLY	03167350	38	21/07/2008	24/11/2014	0 964	0.923	2.86	1	33	4	na	na	na
AMPA	03167350	35	21/07/2008	24/11/2014	4.11	3.69	15.9	NA	7	18	9	1	na

na – no data; Ave – average; Med – Median; Max – Maximum

Station 7 – Terrier Raboin (05013150)

River	Le Tourtrat	Number of stations	2
Area covered (km^2)	68.498 km^2	Length of river (km)	24.286
Number of municipalities	12	Region	Charente, Charente-Maritime

Landscape
The catchment is mostly agricultural with ~88% of the area comprised of arable land, 27% mixed arable and natural areas and 24% vineyards interspersed with and surrounded by arable land. Urban areas make up the remaining 3% of the catchment area.

Rainfall
According to the meteorological data from the Météo France station at Cognac, the average annual rainfall is 777.1 mm recorded over 117 rain days. The climate is oceanic "Aquitaine" with considerably more rainfall between October and January than the summer which is the least rainy season.

Water quality
There were 25 glyphosate measurements taken between 13/05/2008 and 24/11/2014 (Table 8.5-117). The mean and median concentrations of glyphosate were 2.2 µg/L and 0.8 µg/L, respectively. The measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 11 µg/L) on nine occasion (36% of measurements). Approximately 52% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 29 AMPA measurements taken between 18/03/2008 and 24/11/2014. The mean and median concentrations of AMPA were 28.7 µg/L and 5.7 µg/L, respectively. There were 19 analyses of AMPA that exceeded the threshold of 2 µg/L and the maximum concentration of AMPA recorded was 106 µg/L in 2010.

Table 8.5-117: Summary of glyphosate and AMPA concentration data at Terrier Raboin

Compound	**Station**	**Number analyses**	**Start date**	**End date**	**Ave**	**Med**	**Max**	**Measured concentrations (µg/L)**					
								<0.1	**0.1 – 2**	**2-5**	**5-10**	**10-50**	**>50**
GLY	05013150	25	13/05/2009	24/11/2014	2.22	0.81	11	3	13	4	4	1	na
AMPA	05013150	29	18/03/2009	24/11/2014	28.7	5.7	106	na	10	4	3	4	8

na – no data; Ave – average; Med – Median; Max – Maximum

Station 8 – St Caprais (05157100)

River	La Sausse	Number of stations	1
Area covered (km^2)	114.937	Length of river (km)	152.196
Number of municipalities	24	Region	Haute-Garonne

Landscape
The catchment is mostly agricultural with ~74% of the area comprised of arable land (no vineyards), 11% mixed arable and natural areas and ~4% natural areas. Urban areas make up the remaining ~11% of the catchment area.

Rainfall
According to the meteorological data from the Météo France station at Toulouse-Blagnac, the average annual rainfall is 638.3 mm recorded over 95.7 rain days. The climate is temperate akin to a Mediterranean climate whereby spring is wettest and summer the driest seasons.

Water quality
There were 25 glyphosate measurements taken between 16/03/2008 and 27/11/2014 (Table 8.5-118). The mean and median concentrations of glyphosate were 0.9 µg/L and 0.5 µg/L, respectively. The measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 3.6 µg/L) on four occasions. Approximately 76% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 27 AMPA measurements taken between 16/03/2008 and 27/11/2014. The mean and median concentrations of AMPA were 2.6 µg/L and 1.5 µg/L, respectively. There were eleven analyses of AMPA that exceeded the threshold of 2 µg/L (40% of measurements) and 16 measurements were between 0.1 µg/L and 2 µg/L (60% measurements).

Table 8.5-118: Summary of glyphosate and AMPA concentration data at St Caprais

Compound	**Station**	**Number analyses**	**Start date**	**End date**	**Ave**	**Med**	**Max**	**Measured concentrations (µg/L)**					
								<0.1	**0.1 – 2**	**2-5**	**5-10**	**10-50**	**>50**
GLY	05157100	25	16/03/2009	27/11/2014	0.866	0.53	3.6	2	19	4	na	na	na
AMPA	05157100	27	16/03/2009	27/11/2014	2.65	1.5	11	na	16	7	3	1	na

na – no data; Ave – average; Med – Median; Max – Maximum

III. CONCLUSIONS

This document presents the water quality records of eight surface water quality monitoring stations. These stations were shortlisted from the SOES UIPP 2008-2014 dataset as they have reported the highest median and mean concentration values for glyphosate. These stations are also the only ones that can provide glyphosate data for 5 years between 2008 and 2014 (not necessarily over five consecutive years).

Analytics are not described but the analyses were likely conducted by COFRAC accredited laboratories.

Assessment and conclusion by applicant:
The study describes results from analyses of 8 water quality monitoring stations with elevated glyphosate concentrations. Analytics are not described but the analyses were likely conducted by COFRAC accredited laboratories.

The study is considered valid.

Assessment and conclusion by RMS:

This study provides details on 8 stations from the French public monitoring stations where elevated concentrations of glyphosate were found. These stations are indicated to be selected within the 2008-2014 dataset as they have reported the highest median and mean concentration values for glyphosate. These stations are also the only ones that can provide glyphosate data for 5 years between 2008 and 2014 (not necessarily over five consecutive years).

RMS underlines that the selection process of the 8 stations is not further detailed in the report. For instance, it is not clear whether the mean concentration criteria used for selection of the sites is calculated on an annual basis, or on the whole period 2008-2014.

The report provides detail on the monitoring location (name of the river, size of the catchment area, length of the river within the catchment area), on the landcover of the catchment area, on weather data and gives the water quality results for each station (number of sampling, mean, median, number of exceedance of the Thresholds of 0.1 µg/L, 2 µg/L or 10 µg/L). However, no further analysis is performed, for instance on the influence of the land cover, or of the weather data.

Summary table below gives an overview of the main results of glyphosate concentration from the 8 stations.

Station	Number of analysis	GLY Mean [µg/L]	GLY Median [µg/L]	Number of analysis exceeding the thresholds			Maximum concentration [µg/L]
				2 µg/L	5 µg/L	10 µg/L	
1	35	0.9	0.7	2	-	-	7.2
2	36	1.2	0.5	7	-	-	4.2
3	31	2	0.8	11	-	2	13.1
4	34	0.9	0.5	2	1	-	9.9
5	31	1.1	0.8	4	-	-	4.6
6	38	1	0.9	4	-	-	2.9
7	25	2.2	0.8	9	-	-	11
8	25	0.9	0.5	4	-	-	3.6

The study is considered acceptable.

Data point:	CA 7.5/034
Report author	[redacted]
Report year	2018b
Report title	Etude environnementale du Glyphosate et de l'AMPA à l'échelle des 10 points de surveillance les plus préoccupants pour le Glyphosate et pour l'AMPA. Analyse des suivis du Glyphosate et de l'AMPA en lien avec les bassins versants drainés par les stations de mesures et l'occupation des sols. Etudes des stations sur l'AMPA. Environmental Study of Glyphosate and AMPA for the 10 most concerning locations for Glyphosate and AMPA. Analysis of Glyphosate and AMPA monitoring data with respect to their drained river areas and land use. AMPA Studies.
Document No	Envilys Report Version 1 (2018)
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No, but likely conducted at COFRAC accredited testing facilities.
Acceptability/Reliability:	Acceptable

Executive Summary

This document presents the water quality records of ten surface water quality monitoring stations. These stations were shortlisted from the SOES UIPP 2008-2014 dataset as they have reported the highest median and mean concentration values for AMPA. These stations are also the only ones that can provide AMPA data for 5 years between 2008 and 2014 (not necessarily over five consecutive years).

I. MATERIAL AND METHODS

The 10 selected AMPA monitoring stations are listed in Table 8.5-119 and their locations are shown in Figure 8.5-73. Each station record is split and presented over 3 parts, with each describing the regional landscape and hydrology, the rainfall and climate, and the water quality.

Table 8.5-119: List of 10 AMPA monitoring stations

Station	Station Name	River Name	Agency
1075000	La Becque de Steenwerck à Steenwerck	La Becque de Steenwerck	AEAP
1089000	L'Yser à Bambecque	L'Yser	AEAP
3051120	Ru de Courtenain à Fontenailles	L'Almont	AESN
3051250	Ru d'Ancoeur à St Ouen en Brie	L'Almont	AESN
3129440	Boué	Le Morteau	AESN
3167350	Ver sur Launette	La Launette	AESN
4143150	Sangueze à Le Pallet	La Sanguèze	AELB
5013150	Terrier Raboin	Le Tourtrat	AEAG
6169050	Alenya	L'Agulla de la Mar	AERMC
6196948	Raumartin	Le Raumartin	AERMC

Figure 8.5-73: Location of the AMPA monitoring stations

II. RESULTS AND DISCUSSION

Station 1 - La Becque de Steenwerck à Steenwerck (01075000)

River	La Becque de Steenwerck	Number of stations	1
Area covered (km^2)	69.908	Length of river (km)	63.795
Number of Municipalities	9	County/Region	Nord

Landscape

The catchment is mostly agricultural with ~90% of the area comprised of arable land (but no vineyards) and urban areas (10%).

Rainfall

According to the meteorological data from the Météo France station at Lille-Lesquin, the average annual rainfall is 742.5 mm recorded over 127.4 rain days. The climate is temperate oceanic and downpours are a regular occurrence all year.

Water quality

There were 36 glyphosate measurements taken between 22/07/2008 and 23/12/2014 (Table 8.5-120). The mean and median concentrations of glyphosate were 0.6 µg/L and 0.5 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 2.2 µg/L) on one occasion. Approximately 92% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 41 AMPA measurements taken between 18/02/2008 and 23/12/2014. The mean and median concentrations of AMPA were 5.6 µg/L and 2.4 µg/L, respectively. There were 8 analyses of AMPA that exceeded the threshold of 10 µg/L (20% of measurements) and 17 records exceeded 5 µg/L (41% of measurements).

Table 8.5-120: Summary of glyphosate and AMPA concentration data at La Becque de Steenwerck à Steenwerck

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	01075000	36	22/07/2008	23/12/2014	0 553	0.477	2.22	2	33	1	na	na	na
AMPA	01075000	41	18/02/2008	23/12/2014	5.57	2.42	40.3	4	16	4	9	8	na

na – no data; Ave – average; Med – Median; Max - Maximum

Station 2 - L'Yser à Bambecque (01089000)

River	L'Yser	Number of stations	1
Area covered (km^2)	378.628	Length of river (km)	277.353
Number of Municipalities	46	County/Region	Nord

Landscape
The region is mostly agricultural with ~97% of the area comprised of arable land (but no vineyards) with 1% grasslands and the remaining areas being urban areas.

Rainfall
According to the meteorological data from Météo France station at Dunkerque, the average annual rainfall is 697.8 mm recorded over 121.6 rain days. The climate is temperate oceanic and heavy rainfall is a regular occurrence during autumn and the beginning of winter.

Water quality
There were 30 glyphosate measurements taken between 20/02/2008 and 17/10/2014 (Table 8.5-121). The mean and median concentrations of glyphosate were 0.7 µg/L and 0.4 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 2.2 µg/L) on one occasion. Approximately 55% glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 30 AMPA measurements taken between 20/02/2008 and 17/06/2014. The mean and median concentrations of AMPA were 4.3 µg/L and 1.6 µg/L, respectively. There were 6 analyses of AMPA that exceeded the threshold of 10 µg/L (20% of measurements) and 14 that exceeded 5 µg/L (46% of measurements).

Table 8.5-121: Summary of glyphosate and AMPA concentration data at L'Yser à Bambecque

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	01089000	30	20/02/2008	17/10/2014	0.671	0.41	5.03	4	25	na	1	na	na
AMPA	01089000	30	20/02/2008	17/06/2014	4.25	1.57	18.4	na	16	5	3	6	na

na – no data; Ave – average; Med – Median; Max - Maximum

Station 3 - Ru de Courtenain à Fontenailles (03051120)

River	L'Almont	Number of stations	1
Area covered (km^2)	71.66	Length of river (km)	42.209
Number of Municipalities	10	County/Region	Seine-et-Marne

Landscape
The catchment is mostly agricultural with ~63% of the area comprised of arable land (but no vineyards) and 1% grasslands. Natural landcover accounts for 29% of the total area and urban areas make up the remaining 6%.

Rainfall

According to the meteorological data from the Météo France station at Melun, the average annual rainfall is 676.9 mm recorded over 117.2 rain days. The climate is warm and temperate with rainfall spread quite homogeneously throughout the year. The least rainy month is February while May and October register the most rainfall.

Water quality
There were 26 glyphosate and AMPA measurements taken between 17/09/2008 and 04/11/2014 (Table 8.5-122). The mean and median concentrations of glyphosate were 1.2 µg/L and 0.5 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 4.2 µg/L) on seven occasions. Approximately 69% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

The mean and median concentrations of AMPA were 10.8 µg/L and 4 µg/L, respectively. There were 10 analyses of AMPA that exceeded the threshold of 5 µg/L (38% of measurements) and 21 records exceeded 2 µg/L (81% of measurements). Two measurements exceeded 50 µg/L. The concentrations of AMPA seemed to increase during the 2013-2014 period.

Table 8.5-122: Summary of glyphosate and AMPA concentration data at Ru de Courtenain à Fontenailles

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	03051120	26	17/09/2008	04/11/2014	1.17	0.531	4.18	1	18	7	na	na	na
AMPA	03051120	26	17/09/2008	04/11/2014	10.8	4.04	61.4	na	5	11	3	5	2

na – no data; Ave – average; Med – Median; Max - Maximum

Station 4 - Ru d'Anoeur à St Ouen en Brie (03051250)

River	L'Almont	Number of stations	2
Area covered (km^2)	101.391	Length of river (km)	60.622
Number of Municipalities	16	County/Region	Seine-et-Marne

Landscape
The catchment is comprised predominantly of agricultural and natural vegetation with 67% and 27% of the area, respectively (but not vineyards). The urban areas comprise 9% of the catchment area.

Rainfall
According to the meteorological data from Météo France station at Dunkerque, the average annual rainfall is 697.8 mm recorded over 121.6 rain days. The climate is temperate oceanic and heavy rainfall is a regular occurrence during autumn and the beginning of winter.

Water quality
There were 33 glyphosate measurements taken between 17/09/2008 and 04/11/2014 (Table 8.5-123). The mean and median concentrations of glyphosate were 0.6 µg/L and 0.5 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 2.6 µg/L) on one occasion. Approximately 88% glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 34 AMPA measurements taken between 17/09/2008 and 04/11/2014. The mean and median concentrations of AMPA were 3.4 µg/L and 1.8 µg/L, respectively. There were 6 analyses of AMPA that exceeded the threshold of 5 µg/L (17% of measurements) and 14 records exceeded 2 µg/L (41% of measurements). The concentrations of AMPA seemed to increase during the 2013-2014 period.

Table 8.5-123: Summary of glyphosate and AMPA concentration data at Ru d'Ancoeur à St Ouen en Brie

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	03051250	33	17/09/2008	04/11/2014	0.592	0.5	2.56	3	29	1	na	na	na
AMPA	03051250	34	17/09/2008	04/11/2014	3.36	1.79	16.9	1	16	8	2	4	na

na – no data; Ave – average; Med – Median; Max - Maximum

Station 5 - Boué (03129440)

River	Le Marteau	Number of stations	1
Area covered (km^2)	37.31	Length of river (km)	51.283
Number of Municipalities	8	County/Region	Aisne

Landscape

The catchment is covered with grasslands (47%) on the right river bank and with woodland and natural vegetation (46%) on the left river bank (but not vineyards). Urban areas make up 9% of the catchment, of which 3% are gardens and parks.

Rainfall

According to the meteorological data from the Météo France station at Cognac, the average annual rainfall is 702.6 mm recorded over 122.5 rain days. The climate is warm and temperate, with abundant rainfall uniformly distributed throughout the year.

Water quality

There were 28 glyphosate measurements taken between 09/07/2008 and 18/05/2014 (Table 8.5-124). The mean and median concentrations of glyphosate were 0.3 µg/L and 0.2 µg/L, respectively. Measured concentrations never exceeded the threshold of 2 µg/L while 75% of glyphosate measurements were between 0.1 and 2 µg/L.

There were 33 AMPA measurements taken between 09/07/2008 and 18/05/2014. The mean and median concentrations of AMPA were 7 µg/L and 3.8 µg/L, respectively. There were 13 analyses of AMPA that exceeded the threshold of 5 µg/L (39% of measurements) and 25 records exceeded 2 µg/L (76% of measurements). The concentrations of AMPA seemed to decrease during the 2012-2014 period.

Table 8.5-124: Summary of glyphosate and AMPA concentration data at Boué

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	03129440	28	09/07/2008	18/05/2014	0 265	0.185	0.83	7	21	na	na	na	na
AMPA	03129440	33	09/07/2008	18/05/2014	6.98	3.77	24	4	4	12	5	8	na

na – no data; Ave – average; Med – Median; Max - Maximum

Station 6 - Ver sur Launette (03167350)

River	La Launette	Number of stations	1
Area covered (km^2)	39.949	Length of river	28.013
Number of Municipalities	12	County/Region	Oise, Seine-et-Marne

Landscape

The catchment is mostly agricultural with ~71% of the area comprised of arable land (but no vineyards) and with 2% grasslands. Natural vegetation covers 29% of the total area and urban areas make up the remaining ~19%.

Rainfall

According to the meteorological data from the Météo France station at Roissy-en-France, the average annual rainfall is 693.6 mm recorded over 116.8 rain days. The climate is warm and temperate with rainfall spread quite homogeneously throughout the year. The least rainy month is February while May and October register the most rainfall.

Water quality
There were 38 glyphosate measurements taken between 21/07/2008 and 24/11/2014 (Table 8.5-125). The mean and median concentrations of glyphosate were 1 µg/L and 0.9 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 2.9 µg/L) on four occasions. Approximately 87% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 35 AMPA measurements taken between 21/07/2008 and 24/11/2014. The mean and median concentrations of AMPA were 4.1 µg/L and 3.7 µg/L, respectively. There were 10 analyses of AMPA that exceeded the threshold of 5 µg/L (29% of measurements) and 28 records exceeded 2 µg/L (80% of measurements). The highest concentrations of AMPA were measured during the 2009-2012 period. The concentrations of AMPA seemed to increase during the 2013-2014 period.

Table 8.5-125: Summary of glyphosate and AMPA concentration data at Ver sur Launette

Compound	**Station**	**Number analyses**	**Start date**	**End date**	**Ave**	**Med**	**Max**	**Measured concentrations (µg/L)**					
								<0.1	**0.1 – 2**	**2-5**	**5-10**	**10-50**	**>50**
GLY	03167350	38	21/07/2008	24/11/2014	0 964	0.923	2.86	1	33	4	na	na	na
AMPA	03167350	35	21/07/2008	24/11/2014	4.11	3.69	15.9	na	7	18	9	1	na

na – no data; Ave – average; Med – Median; Max - Maximum

Station 7 - Sangueze à Le Pallet (04143150)

River	La Sangueze	Number of stations	1
Area covered (km^2)	159.643	Length of river (km)	138.416
Number of Municipalities	8	County/Region	Loire-Atlantique, Maine-et-Loire

Landscape
The catchment is predominantly agricultural with ~92% of the area comprised of arable land of which 32% are field crops, 23% are areas of mixed arable and natural landcover, 20% improved grass and 17% vineyards. Urban areas make up 4% of the remaining catchment area.

Rainfall
According to the meteorological data from the Météo France station at Nantes, the average annual rainfall is 819.5 mm recorded over 119.1 rain days. The climate is temperate oceanic with frequent rainfall and occasional heavy storm events. The rainiest period is winter.

Water quality
There were 34 glyphosate measurements taken between 14/04/2008 and 03/12/2014 (Table 8.5-126). The mean and median concentrations of glyphosate were 0.7 µg/L and 0.3 µg/L, respectively. Measured concentrations exceeded the threshold of 5 µg/L (maximum concentration of 6.1 µg/L) on one occasion. Approximately 67% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 40 AMPA measurements taken between 10/03/2008 and 03/12/2014. The mean and median concentrations of AMPA were 12.1 µg/L and 5.1 µg/L, respectively. There were 14 analyses of AMPA that exceeded the threshold of 10 µg/L (35% of measurements) and 27 records exceeded 2 µg/L (67% of measurements).

Table 8.5-126: Summary of glyphosate and AMPA concentration data at Sangueze à Le Pallet

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	04143150	34	14/04/2010	03/12/2014	0.69	0.27	6.07	8	23	2	1	na	na
AMPA	04143150	40	10/03/2010	03/12/2014	12.1	5.12	48.4	na	13	7	6	14	na

na – no data; Ave – average; Med – Median; Max - Maximum

Station 8 - Terrier Raboin (05013150)

River	Le Tourtrat	Number of stations	2
Area covered (km^2)	68.498	Length of river (km)	24.286
Number of Municipalities	12	County/Region	Charente, Charente-Maritime

Landscape
The catchment is mostly agricultural with ~88% of the area comprised of arable land, of which 27% is mixed arable land and natural areas and 24% vineyards interspersed between and surrounded by arable land. Urban areas make up 3% of the remaining catchment area.

Rainfall
According to the meteorological data from the Météo France station at Cognac, the average annual rainfall is 777.1 mm recorded over 117 rain days. The climate is of the oceanic "Aquitaine" type with frequent rainfall spread between October and January while summer is the least rainy season.

Water quality
There were 25 glyphosate measurements taken between 13/05/2008 and 24/11/2014 (Table 8.5-127). The mean and median concentrations of glyphosate were 2.2 µg/L and 0.8 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 11 µg/L) on nine occasion (36% of measurements). Approximately 52% glyphosate measurements were between 0.1 µg/L and 2 µg/L.

There were 29 AMPA measurements taken between 18/03/2009 and 24/11/2014. The mean and median concentrations of AMPA were 28.7 µg/L and 5.7 µg/L, respectively. There were19 analyses for AMPA that exceeded the threshold of 2 µg/L and the maximum concentration of AMPA recorded was 106 µg/L in 2010.

Table 8.5-127: Summary of glyphosate and AMPA concentration data at Terrier Raboin

Compound	Station	Number analyses	Start date	End date	Ave	Med	Max	Measured concentrations (µg/L)					
								<0.1	0.1 – 2	2-5	5-10	10-50	>50
GLY	05013150	25	13/05/2009	24/11/2014	2.22	0.81	11	3	13	4	4	1	na
AMPA	05013150	29	18/03/2009	24/11/2014	28.7	5.7	106	na	10	4	3	4	8

na – no data; Ave – average; Med – Median; Max - Maximum

Station 9 - Alenya (06169050)

River	L'Agulla de la Mar	Number of stations	1
Area covered (km^2)	53.852	Length of river (km)	18.879
Number of Municipalities	14	County/Region	Pyrénées-Orientales

Landscape
The majority of the catchment is involved in wine production (44%) while a further 41% of the area is used for other agriculture. Urban areas make 10% of the remaining catchment area.

Rainfall

According to the meteorological data from the Météo France station at Perpignan, the average annual rainfall is 557.6 mm recorded over 54 rain days. The climate is 'Mediterranean' with frequent wet weather in autumn and winter and dryer conditions in the summer, notably August. This region is subject to periodic downpours over just a couple of hours.

Water quality

There were 38 glyphosate measurements taken between 25/02/2008 and 03/12/2014 (Table 8.5-128). The mean and median concentrations of glyphosate were 0.6 µg/L and 0.2 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 6.1 µg/L) on two occasions. Approximately 82% of glyphosate measurements are between 0.1 µg/L and 2 µg/L.

There were 34 AMPA measurements taken between 25/02/2008 and 09/06/214. The mean and median concentrations of AMPA were 4.7 µg/L and 2.9 µg/L, respectively. There were nine analyses of AMPA that exceeded the threshold of 2 µg/L (26% of measurements; maximum concentration of 24.3 µg/L recorded in 2014). Approximately 50% of AMPA measurements were between 0.1 µg/L and 2 µg/L.

Table 8.5-128: Summary of glyphosate and AMPA concentration data at Alenya

Compound	**Station**	**Number analyses**	**Start date**	**End date**	**Ave**	**Med**	**Max**	**Measured concentrations (µg/L)**					
								<0.1	**0.1 – 2**	**2-5**	**5-10**	**10-50**	**>50**
GLY	06169050	38	25/02/2008	03/12/2014	0 592	0.231	7.4	5	31	1	1	na	na
AMPA	06169050	34	25/02/2008	09/06/2014	4.69	2.93	24.3	na	8	17	6	3	na

na – no data; Ave – average; Med – Median; Max - Maximum

Station 10 - Raumartin (06196948)

River	La Raumartin	Number of stations	1
Area covered (km^2)	26.369	Length of river (km)	9.829
Number of Municipalities	8	County/Region	Bouches-du-Rhône

Landscape

The catchment is quite diverse in terms of landcover. Urban areas make up 27% of the total area largely in the lower portions of the catchment. The mid portion of the catchment is dominated by vineyards while natural areas comprise 46 of the remainder of the catchment.

Rainfall

According to the meteorological data from the Météo France station at Marignane, the average annual rainfall is 515.4 mm recorded over 53.2 rain days. The climate is "Mediterranean" with a very short wet season in autumn and early Winter. A very dry period occurs between June and August.

Water quality

There were 16 glyphosate and AMPA measurements taken between 23/02/2008 and 29/06/2014 (Table 8.5-129). The mean and median concentrations of glyphosate were 0.5 µg/L and 0.3 µg/L, respectively. Measured concentrations exceeded the threshold of 2 µg/L (maximum concentration of 2.2 µg/L) on one occasion. Approximately 81% of glyphosate measurements were between 0.1 µg/L and 2 µg/L.

The mean and median concentrations of AMPA were 6.3 µg/L and 2.2 µg/L, respectively. There were 9 analyses of AMPA that exceeded the threshold of 2 µg/L (47% of measurements; maximum concentration of 25.2 µg/L recorded in 2014). None of the records were less than 0.1 µg/L and numerous peaks in the measurements were observed above 5 µg/L between 2012 and 2014.

Table 8.5-129: Summary of glyphosate and AMPA concentration data at Raumartin

Compound	**Station**	**Number analyses**	**Start date**	**End date**	**Ave**	**Med**	**Max**	**Measured concentrations (µg/L)**					
								<0.1	**0.1 – 2**	**2-5**	**5-10**	**10-50**	**>50**

GLY	06196948	16	23/02/2010	29/06/2014	0.468	0.267	2.22	2	13	1	na	na	na
AMPA	06196948	16	23/02/2010	29/06/2014	6 3	2.22	25.2	na	7	5	1	3	na

na – no data; Ave – average; Med – Median; Max - Maximum

III. CONCLUSIONS

This document presents the water quality records of ten surface water quality monitoring stations. These stations were shortlisted from the SOES UIPP 2008-2014 dataset as they have reported the highest median and mean concentration values for AMPA. These stations are also the only ones that can provide AMPA data for 5 years between 2008 and 2014 (not necessarily over five consecutive years).

Analytics are not described but the analyses were likely conducted by COFRAC accredited laboratories

Assessment and conclusion by applicant:

The study describes results from analyses of 10 water quality monitoring stations with elevated AMPA concentrations. Analytics are not described but the analyses were likely conducted by COFRAC accredited laboratories.

The study is considered valid.

Assessment and conclusion by RMS:

This study provides details on 10 stations from the French public monitoring stations where elevated concentrations of AMPA were found. It is very simiar to the previous one ([redacted], 2018a, CA 7.5/033) but focused on elevated concentration of AMPA rather than Glyphosate. These stations are indicated to be selected within the 2008-2014 dataset as they have reported the highest median and mean concentration values for AMPA. These stations are also the only ones that can provide glyphosate data for 5 years between 2008 and 2014 (not necessarily over five consecutive years).

RMS underlines that the selection process of the 10 stations is not further detailed in the report. For instance, it is not clear whether the mean concentration criteria used for selection of the sites is calculated on an annual basis, or on the whole period 2008-2014.

The report provides detail on the monitoring location (name of the river, size of the catchment area, length of the river within the catchment area), on the land cover of the catchment area, on weather data and gives the water quality results for each station (number of sampling, mean, median, number of exceedance of the Thresholds of 0.1 µg/L, 2 µg/L, 10 µg/L or 50 µg/L). However, no further analysis is performed, for instance on the influence of the land cover, or of the weather data.

Summary table below gives an overview of the main results for AMPA analysis from the 10 stations.

Station	Number of analysis	Mean [µg/L]	Median [µg/L]	Number of analysis exceeding the thresholds				Maximum concentration [µg/L]
				2 µg/L	5 µg/L	10 µg/L	50 µg/L	
1	41	5.6	2.4	1	-	-	-	2.2
2	30	4.3	1.6	5	5	6	-	18.4
3	26	10.8	4.04	11	3	5	2	61.4
4	34	3.36	1.79	8	2	4	-	16.9
5	33	6.98	3.77	12	5	8	-	24
6	35	4.11	3.69	18	9	1	-	15.9
7	40	12.1	5.12	7	6	14	-	48.4
8	29	28.7	5.7	4	3	4	-	106
9	34	4.69	2.93	17	6	3	-	24.3
10	16	6.3	2.22	5	1	3	-	25.2

The study is considered acceptable.

Data point:	CA 7.5/009
Report author	[redacted]
Report date	2016
Report title	Analyse des données de suivi du glyphosate et de l'AMPA dans les eaux de France - Période 1997-2013 (Analysis of monitoring data for glyphosate and AMPA in French waters – Time period 1997-2013)
Document No	Rapport_AMPA_Glyphosate_1997-2013(V3)
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No, but likely conducted by COFRAC approved testing facilities
Acceptability/Reliability:	Acceptable

The study is relevant for multiple subchapters. The summary is provided in the groundwater monitoring subchapter of this document.

However, summary concerning surface water part are reported again below.

I. MATERIAL AND METHODS

Surface water

There is a trend of stations to increasingly monitor for AMPA and glyphosate in surface water over time (Figure 8.5-74, Figure 8.5-75 and Figure 8.5-76).

Figure 8.5-74: Annual progression in the number of analyses for glyphosate and AMPA in surface water

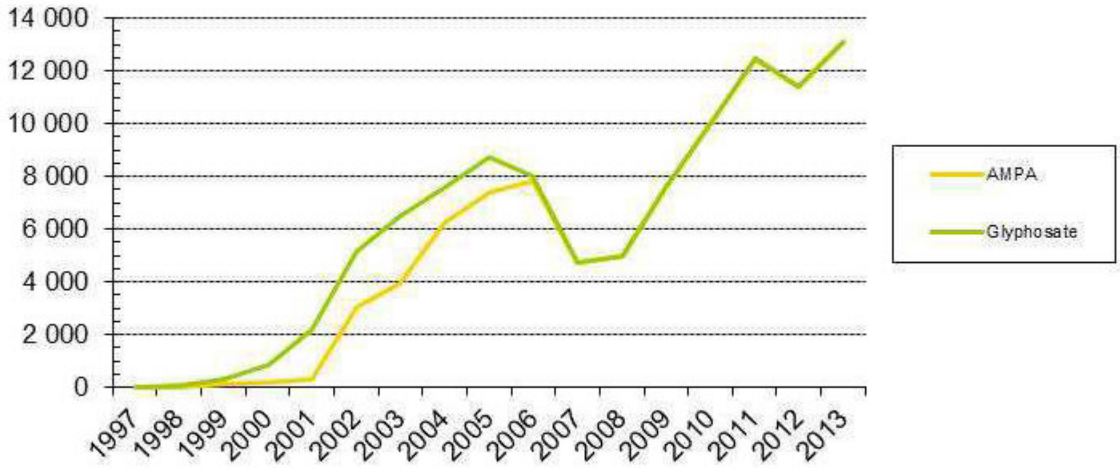


Figure 8.5-75: **Evolution of the number of stations monitoring for AMPA in surface waters (left axis: Number of stations as bar chart; right axis: Share of stations of the IFFEN database as a line chart)**

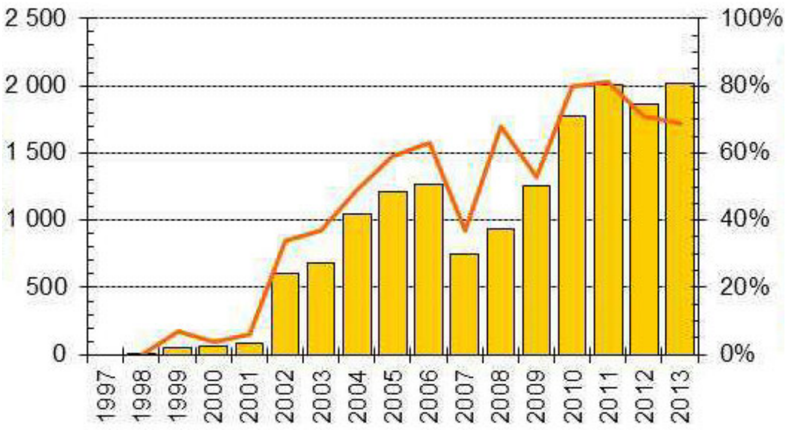
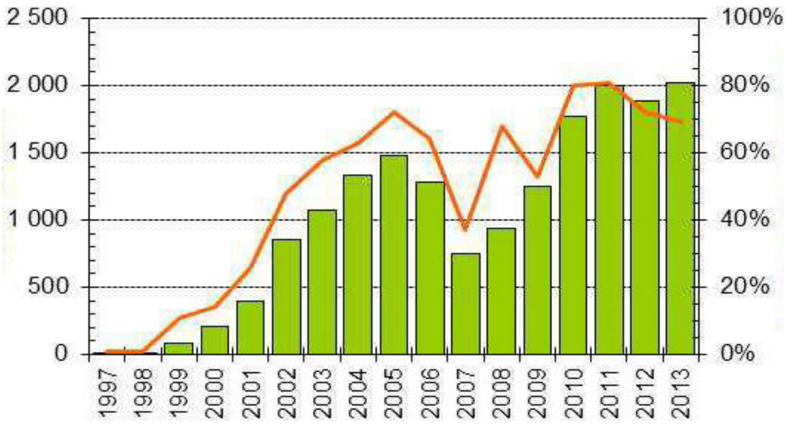


Figure 8.5-76: **Evolution of the number of stations monitoring for glyphosate in surface waters (left axis: Number of stations as bar chart; right axis: Percent of stations of the IFFEN database as a line chart)**

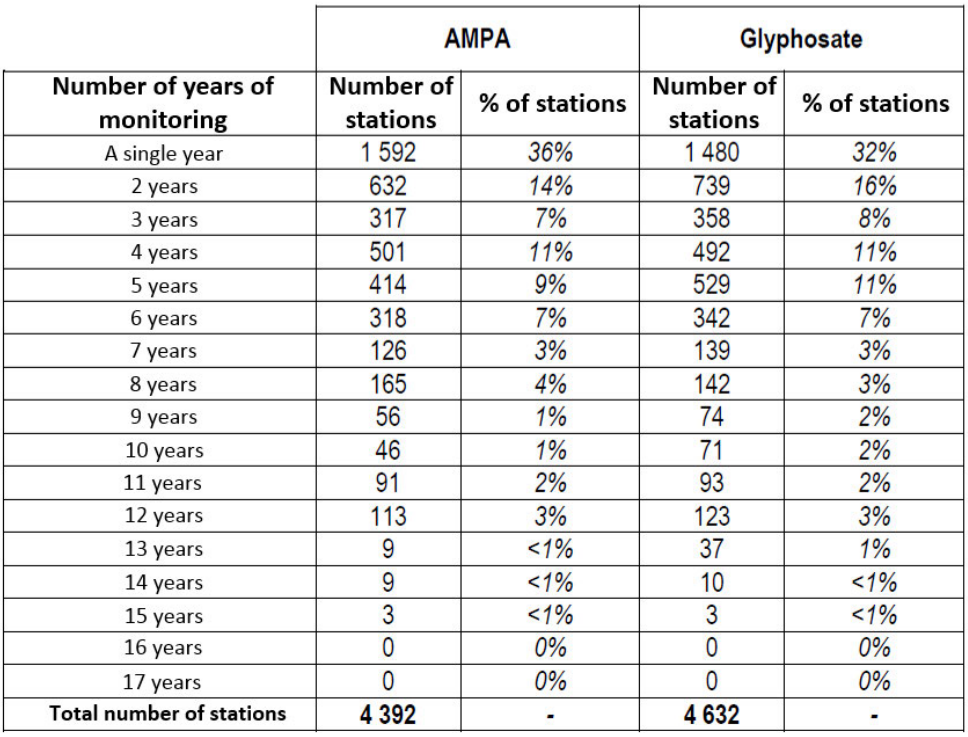


Multi-year continuity analysis of measurements

Based on the number of years of monitoring, an assessment was conducted to look at the continuous measurements within the time period and therefore on the ability to draw conclusions in terms of how the multi-annual trends evolve. It is worth noting that the stations are ordered by years of monitoring without the monitoring being necessarily in consecutive years (e.g. a station may be included in 5 years, corresponding to 1999, 2005, 2010, 2011, 2012).

In the case of surface waters, while the monitoring duration may theoretically be up to 17 years (1997-2013), the actual monitoring duration is up to 15 years at a maximum. Some stations are monitored only during a single year (36% and 32% for AMPA and glyphosate, respectively) while 30% and 34% of stations have 5 or more years, for AMPA and glyphosate, respectively (Table 8.5-130).

Table 8.5-130: Number of years of monitoring of 'surface water' stations on the 1999-2013 period



	AMPA		Glyphosate	
Number of years of monitoring	**Number of stations**	**% of stations**	**Number of stations**	**% of stations**
A single year	1 592	36%	1 480	32%
2 years	632	14%	739	16%
3 years	317	7%	358	8%
4 years	501	11%	492	11%
5 years	414	9%	529	11%
6 years	318	7%	342	7%
7 years	126	3%	139	3%
8 years	165	4%	142	3%
9 years	56	1%	74	2%
10 years	46	1%	71	2%
11 years	91	2%	93	2%
12 years	113	3%	123	3%
13 years	9	<1%	37	1%
14 years	9	<1%	10	<1%
15 years	3	<1%	3	<1%
16 years	0	0%	0	0%
17 years	0	0%	0	0%
Total number of stations	**4 392**	**-**	**4 632**	**-**

Analysis of the frequency of measurements within a monitoring year
The multi-year continuity analysis comprises an analysis of the frequency of measurements within a year of monitoring.

For surface waters, annual measurement frequencies are higher. There is a general increase from 2-3 times a year in 2000 to 6-9 times in the later years (2011 - 2013).

II. RESULTS AND DISCUSSION

Assessment of the multi-year trend in measurements higher than LOQ

In surface waters, the annual glyphosate quantification rate (Table 8.5-132) varies around 30% during the 2000-2012 period; without a clear tendency toward increase or decrease. Quantification rates ≥2 µg/L are typically <1%.

Quantification rates of AMPA in surface waters (Table 8.5-42) vary around a median of 54%. Quantification rates ≥2 µg/L are typically <3%.

Table 8.5-131: Quantification rates of AMPA in surface water

Year/Statistics	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Surface water																	
Number of analyses		2	108	218	291	3050	3974	6280	7382	7810	4714	4954	7600	10001	12456	11395	13067
Number >LOQ		0	63	106	179	1602	2351	3449	4355	3995	2030	2558	3893	4597	7789	6148	7307
% >LOQ		0%	58.3%	48.6%	61.5%	52.5%	59.2%	54.9%	59.0%	51.2%	43.1%	51.6%	51.2%	46.0%	62.5%	54.0%	55.9%
Number ≥0.1 µg/L		0	63	94	157	1453	2282	3284	4161	3865	1908	2130	3393	4068	6681	4054	4134
% ≥0.1 µg/L		0%	58.3%	43.1%	54.0%	47.6%	57.4%	52.3%	56.4%	49.5%	40.5%	43.0%	44.6%	40.7%	53.6%	35.6%	31.6%
Number ≥2 µg/L		0	1	2	5	50	200	141	222	219	68	106	190	172	268	176	162
% ≥2 µg/L		0%	0.9%	0.9%	1.7%	1.6%	5.0%	2.2%	3.0%	2.8%	1.4%	2.1%	2.5%	1.7%	2.2%	1.5%	1.2%

Table 8.5-132: Quantification rates of glyphosate in surface water

Year/Statistics	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Surface water																	
Number of analyses	4	51	289	840	2218	5172	6452	7589	8740	7989	4714	4954	7600	10001	12457	11417	13066
Number >LOQ	3	39	105	282	594	1903	2112	2713	2979	2114	1048	1551	1938	2535	4026	4189	5048
% >LOQ	75.0%	76.5%	36.3%	33.6%	26.8%	36.8%	32.6%	35.7%	34.1%	26.5%	22.2%	31.3%	25.5%	25.3%	32.3%	36.7%	38.6%
Number ≥0.1 µg/L	3	39	103	249	563	1715	2022	2553	2837	1963	947	1051	1406	1757	2697	1937	1873
% ≥0.1 µg/L	75.0%	76.5%	35.6%	29.6%	25.4%	33.2%	31.3%	33.6%	32.5%	24.6%	20.1%	21.2%	18.5%	17.6%	21.7%	17.0%	14.3%
Number ≥2 µg/L	0	2	5	7	17	52	62	38	73	37	26	25	43	36	52	40	40
% ≥2 µg/L	0%	3.9%	1.7%	0.8%	0.8%	1.0%	1.0%	0.5%	0.8%	0.5%	0.6%	0.5%	0.6%	0.4%	0.4%	0.4%	0.3%

Table 8.5-133: Maximum concentrations recorded per year (in µg/L)

	Period	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Surface water																		
AMPA	3369			5.05	2.99	4.2	48.9	48.1	17	30	27.5	16.5	20.3	33.5	106	3369	80	59.1
Glyphosate	3257	1.5	3.4	35	6.36	41	40.6	3257	50	17	34	28	17.3	19.7	21	2237	66	37.9

Table 8.5-134: 90th percentile concentrations recorded per year (in µg/L)

	Period	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Surface water																		
AMPA	1.1			1.05	0.91	0.93	0.89	1.66	1.2	1.3	1.3	1	1.11	1.2	1.1	1.04	0.88	0.68

Glyphosate	0.6	1.23	0.86	0.92	0.72	0.7	0.73	0.8	0.62	0.8	0.66	0.65	0.54	0.7	0.59	0.53	0.42	0.32

Table 8.5-135: **95th percentile concentrations recorded per year (in µg/L)**

	Period	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Surface water																		
AMPA	1.7			1.24	1.13	1.56	1.44	2.71	1.8	2	2.1	1.5	1.74	1.97	1.79	1.65	1.4	1.2
Glyphosate	0.95	1.37	1.22	1.63	1.3	1.2	1.25	1.3	0.93	1.13	1.08	1.27	0.84	1.19	0.95	0.81	0.71	0.55

Table 8.5-136: **99th percentile concentrations recorded per year (in µg/L)**

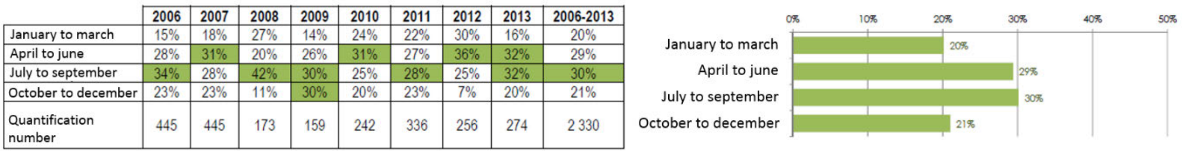
	Period	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Surface water																		
AMPA	4.6			3.06	2	2.59	4.22	6.25	3.45	4.47	5.73	3.77	4.7	4.8	4.67	5.16	4.04	3.85
Glyphosate	2.83	1.47	3.1	11.7	3.22	5.54	4.4	4.6	2.3	3.64	3.29	4.41	2.85	3.49	2.36	2.22	1.9	1.7

Analysis of measurement results by Department
An analysis of the geographical breakdown of the preceding results is also presented. This does not alter the primary observations.

Analysis of a smaller dataset composed of higher-frequency measurements
Complementary investigations were carried out by limiting the type of data used to only the higher-frequency monitoring programmes. Observations that complement preceding sections are presented.

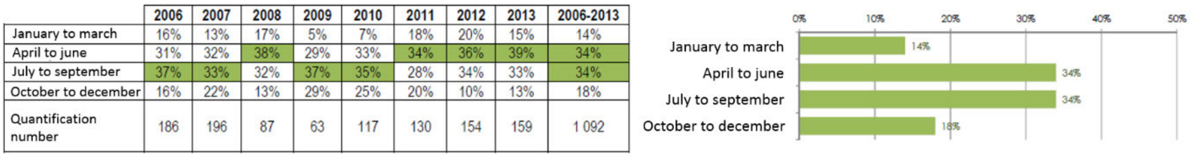
Analysis of the seasonality of the quantifications, based on a subset composed of higher-frequency measurements
For surface water (Figure 8.5-77 and Figure 8.5-78) there is a clear relationship between quantifications and spring and summer periods. This is consistent with the pattern of glyphosate usage, showing diffuse pollution directly linked to periods of use.

Figure 8.5-77: Seasonal distribution of AMPA quantification in surface water - smaller dataset



	2006	2007	2008	2009	2010	2011	2012	2013	2006-2013
January to march	15%	18%	27%	14%	24%	22%	30%	16%	20%
April to june	28%	31%	20%	26%	31%	27%	36%	32%	29%
July to september	34%	28%	42%	30%	25%	28%	25%	32%	30%
October to december	23%	23%	11%	30%	20%	23%	7%	20%	21%
Quantification number	445	445	173	159	242	336	256	274	2 330

Figure 8.5-78: Seasonal distribution of Glyphosate quantification in surface water - smaller dataset



	2006	2007	2008	2009	2010	2011	2012	2013	2006-2013
January to march	16%	13%	17%	5%	7%	18%	20%	15%	14%
April to june	31%	32%	38%	29%	33%	34%	36%	39%	34%
July to september	37%	33%	32%	37%	35%	28%	34%	33%	34%
October to december	16%	22%	13%	29%	25%	20%	10%	13%	18%
Quantification number	186	196	87	63	117	130	154	159	1 092

Surface Water Load calculations
When available, streamflow data for the stations were used in combination with the concentration measurements to calculate loads. This analysis is useful to put the analysis based on concentration measurements into perspective. This was conducted for stations with at least monthly monitoring data in 2012 or 2013. Of the 64 stations with suitable concentration data 9 had associated streamflow data. Concentration data were treated as monthly averages, where more than one value was present monthly averages were calculated. Daily flow data were summed to produce a corresponding monthly flow total. Monthly load calculations were summed and normalised by the catchment area to produce loads in g/year/km^2.

Glyphosate loads vary (Table 8.5-137**Erreur ! Source du renvoi introuvable.**), depending on the watershed, between 0.67 and 31 g/year/km². The AMPA loads vary between 13 and 94 g/year/km².There is a lack of consistency between the calculated loads of AMPA and glyphosate: in 7 cases out of 9, AMPA loads are much higher than glyphosate, with a ratio of 1.3 to 20.7.

Table 8.5-137: Glyphosate and AMPA loads from 9 stations

Monitoring station	Associated Hydro Station	AMPA Load (g/km^2)	Glyphosate Load (g/km^2)	AMPA/GLY Ratio
03091000	H5091010	13	19	0.7
03109000	H5321010	38	29	1.3

04131500	M3823010	31	10	3.2
04134700	M5300010	16	6	2.5
04155500	N3511610	28	31	0.9
04207400	J7214010	60	5	13
04179500	J3821820	13	4	3
04211000	J7483010	94	9	10.7
04216000	J9300611	14	0.67	20.7

Analysis of 6 AOC vineries

An analysis of AMPA and Glyphosate measurements, over the years, for stations associated with 6 vineyards is also presented.

III. CONCLUSIONS

Glyphosate was monitored in surface waters since 1997. AMPA was monitored in surface waters since 1998. The dataset extracted from the $\text{IFEN}_{\text{uipp}}$ database was analysed, for each substance, in terms of 1) the volume of individual measurements and 2) the number of stations contributing to the measurements, on an annual basis.

The dataset for surface waters consists of 93302 and 103583 analyses, for AMPA and glyphosate, respectively. There were 4392 and 4632 stations associated with the monitoring, for AMPA and glyphosate, respectively.

For surface waters:

- Less than a third of stations monitored between 1997 and 2013 show measurements with quantifications of AMPA that are not >0.1 µg/L.
- During the period 1997-2013, 38% of stations do not show quantification of glyphosate above 0.1 µg/L.

Assessment and conclusion by applicant:

The report describes the analyses of both surface water and groundwater for glyphosate and AMPA across France during the monitoring period of 1997-2013. The data analysis focusses on those concentrations measured/detected which are quantified above 0.1 µg/L.

The study is therefore considered valid.

Assessment and conclusion by RMS:

Please note that the original report is written in French and that only the present summary is available in English.

This report focuses on data from the French public monitoring data during the period 1997-2013. Therefore the raw data used in this study are *de facto* included in the data collection and analysis conducted in [redacted] (2020).
This study however gives additional relevant information on the sampling sites for surface water monitoring and notably on the sampling regularity (multi year continuity analysis and annual number of sampling) and its effect on interpretation of the results.

Indeed, though the dataset corresponds in theory to 17 years of AMPA and glyphosate monitoring (1999-2013) in surface water, no station is monitored on an annual basis within the 17-year period. At best, some stations are monitored for 15 years for glyphosate (less than 1%). For surface water, most stations cannot contribute to a multi-year analysis, with 50 and 48% of stations monitored for only a single or two years for AMPA and glyphosate, respectively. Less than 15% of the stations have been monitored for 7 years or more out of 15.

With regard to the frequency of sampling within a year in surface water, the frequency varies between 2-3 times a year in 2000 to 6-9 times in the later years (2011 - 2013).

Analysis on smaller data set, with high-frequency measurements
Study authors proposed an analysis on restricted data set, which excluded some of the monitoring sites that provided only isolated and irregular analyses. Criteria set to retain the sampling sites in the smaller data set were:

- Period 2006-2013
- At least 4 annual GLY or AMPA measurement including the 4 seasons (January-March, April-June, July-September, October-december).

The resulting set is drastically reduced (for AMPA and GLY, respectively 4.8 and 4.3% of the samples, and 1.5 and 1.4% of sites from the original set corresponds to the criteria).

In term of seasonality of quantification of the smaller data set, author indicated there was clear relationship between quantifications and spring and summer periods, as shown in Figure 8.5-77 and Figure 8.5-78.

Also comparison of the % of quantification >0.1µg/L for "higher-frequency measurements" data set and original whole data set indicates the evolution of the % of exceedance through the period follow the same trend in the 2 sets, with sensibly lower proportion of exceedance in the reduced data set.
However, although analysing a reduced data set provides robustness on the temporal issue (since based on continuous and regular sampling period), it does not provide further confidence on the relation between results and pressure of use. Relevant sites (*i.e.* that could be related to glyphosate containing products) might have been excluded while false negative might still be included in the set. Since no further information on the pressure of use is available for the reduced data set, no straightforward conclusions can be drawn from this analysis.

The study (surface water part) is considered acceptable.

Data point:	CA 7.5/010
Report author	[redacted]
Report year	2016
Report title	Survey of glyphosate and AMPA in groundwaters and surface waters in Europe - 2015/16 update review – final report
Report No	MSL0027535
Document No	-
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

The study is relevant for multiple subchapters. The summary provided here includes only data from surface water monitoring. Data from groundwater monitoring are summarized in the relevant section.

Executive Summary

The report represents a review of glyphosate and AMPA monitoring results for surface (fresh) waters and groundwater across Europe, i.e. all 28 Member States of the European Union, as well as Norway and Switzerland, where information was available. The review is based on an earlier review carried out in 2012, which has been updated to include the latest available information.

Information has been obtained from professional contacts across Europe (government departments and research organisations). In addition, some data provided by Monsanto Europe, as well as from web and literature searches, and on-line databases are included. Some data from the previous review has been omitted where more up-to-date information has become available.

Additional data were collected for 13 countries, i.e. Belgium, the Czech Republic, Denmark, Finland, France, Germany, Italy, Norway, the Slovak Republic, Spain, Sweden, the Netherlands and the UK, as well as the Danube River Basin. In total, there is data for 17 countries, 16 countries plus the Danube River Basin for surface water, and 15 countries for groundwater, with most countries including both.

Surface water

Glyphosate and AMPA have been frequently detected in surface waters, AMPA usually at higher concentrations and in a larger proportion of samples. Glyphosate has been analysed in over 143,000 samples from over 4,400 sites (from 1993-2015) and detected in 31% of samples, with 21% above 0.1 µg/L. AMPA has been analysed in over 115,000 samples from over 3,500 sites (1997-2015) and detected in 50% of samples, with 39% above 0.1 µg/L. Concentrations vary widely, with maximum concentrations for glyphosate in the range 0.07-3400 µg/L and AMPA from 0.07-393 µg/L. The more persistent presence of AMPA in surface waters throughout the year may be mainly derived from aminophosphonate containing complexing agents in detergents and cooling waters, entering surface waters via wastewater treatment effluents, rather than from the degradation of glyphosate.

Generally, results are rather variable and not suggesting an increase in detection frequency or concentration observed over the years. However, a trend analysis from the Netherlands over the years 1997-2014 indicates a slight upward trend for glyphosate and a slight downward trend for AMPA.

I. MATERIAL AND METHODS

Information has been obtained from professional contacts across Europe (government departments and research organisations). In addition, some data provided by Monsanto Europe, as well as from web and literature searches, and on-line databases are included. Some data from the previous review has been omitted where more up-to-date information has become available.

Additional data were collected for 13 countries, i.e. Belgium, the Czech Republic, Denmark, Finland, France, Germany, Italy, Norway, the Slovak Republic, Spain, Sweden, the Netherlands and the UK, as well as the Danube River Basin.

In total, there is data for 17 countries, 16 countries plus the Danube River Basin for surface water, and 15 countries for groundwater, with most countries including both. However, the Czech and Slovak Republics monitor only surface water, whereas for Malta only groundwater was monitored in a special investigation. Data was mainly collated at national level, but in some cases at regional level, e.g. for Belgium (two regions) and Germany (surface water data Rhine and some individual Länder). 11 countries have confirmed that there is no monitoring of glyphosate and AMPA (Bulgaria, Croatia, Cyprus, Greece, Hungary, Latvia, Lithuania, Luxembourg, Poland, Portugal and Romania).Although it has been confirmed that glyphosate and AMPA are monitored in Slovenia, it has not been possible to obtain any data to date, nor has any information been received from Estonia. Although overall most data are considered reasonably reliable, it was not possible to fully assess their reliability, notably the French database which provides a comprehensive source of data for surface water and groundwater, includes several extremely high values, which were considered ‘outliers’ and excluded from this analysis.

II. RESULTS AND DISCUSSION

Table 8.5-138 provides an overview of the main data for surface water and groundwater, respectively. The summarised data is not precise but presents a best estimate, mainly because of the various forms in which the data was obtained, e.g. some results in terms of samples, others in terms of sites, and other information gaps.

Surface water

Table 8.5-138 Summary of glyphosate and AMPA data in surface water in Europe

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples ≥ 0.1 µg/L		Max. Conc.	LoQ (LoD)
				No.	%	No.	%	µg/L	µg/L
Austria									
AMPA	2001-2002	?	345	≥90	≥26	90	26	3.4	?
Belgium (Flanders-F and Wallonia-W)									
Glyphosate F	2007-2015	≥131	6802	5510	81.0	1628	23.9	139	0.02-0.4
AMPA F	2007-2015	≥132	6801	6256	92.0	3844	56.5	47	0.02-0.4
Glyphosate W	2001-2014	≥171	6118	≥961	≥15.7	961	15.7	15.5	(0.05)
AMPA W	2007-2014	≥171	5891	≥148(s)	≥86.6(s)	≥148	≥86.6(s)	35.8	(0.025-0.1)
Czech Republic									
Glyphosate	2010-2014	≥290	6358	2547	40.0	≤2476	≤38.9	52	0.025-1.0
AMPA	2010-2014	≥236	4845	3185	65.7	≤3020	≤62.3	83	0.05-10
Denmark									
Glyphosate	2004-2013	≥20	370	281	76	<281	<76	2.7[1]	0.01-0.1
AMPA	2010-2014	≥20	363	296	81	<269	<81	0.28[1]	0.01-0.2
Finland									
Glyphosate	2007-2011	4	82	5	6.1	5	6.1	0.9	0.1
AMPA	2007-2011	4	84	14	16.7	≤13	≤15.5	0.22	0.05
France									
Glyphosate	1997-2012	≥2003	91044	27999	30.7	19505	21.4	88	0.01-2.5
AMPA	1998-2012	≥2001	80817	42855	53	36053	44.6	106	0.01-0.25
Germany									
Glyphosate	1997-2013	>204	≥2018	831	41	≤712	≤35	4.7	0.02-1.5
AMPA	1997-2013	≥71	≥1362	≤837	61.4	≤719	52.8	1.4	0.05-0.5
Ireland									

Table 8.5-138 Summary of glyphosate and AMPA data in surface water in Europe

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples ≥ 0.1 µg/L		Max. Conc.	LoQ (LoD)
				No.	%	No.	%	µg/L	µg/L
Glyphosate	2005-2012	≥256	≥2544	142	5.6	≤142	≤5.6	186	0.08-0.1/20
AMPA	2010-2012	≥70	870	2	0.2	≥2	≥0.2	>200	20
Italy (Lombardia Region)									
Glyphosate	2005-2012	≥274	2851	754	26.4	673	23.6	37.6	0.1
AMPA	2008-2012	≥274	2229	1386	62.2	1386	62.2	393	0.1
Norway									
Glyphosate	1997-2015	12	98	88	89.8	≤71	≤72	0.93	0.01-0.05
AMPA	1997-2015	12	98	90	91.8	≤59	≤60	0.54	0.01-0.05
Slovak Republic									
Glyphosate	2006-2014	≥142	5018	835	16.6	775	15.4	4.2	0.05-0.5
Spain [2]									
Glyphosate	2009-2014	≥343	5418	1847	34	1218	22	3400	0.03-30
AMPA	2012-2014	≥ 84	830	543	65	534	64	9.2	0.05-0.2
Sweden									
Glyphosate	2000-2014	≥ 21	1439	442	30.7	≤433	≤30	370	<0.06-<1
AMPA	2000-2014	≥ 21	1418	320	22.6	≤312	≤22	36.0	<0.07-<1
Switzerland									
Glyphosate	2006	5	≥10	≥8	80	1	≤10	0.1	0.0007
AMPA	2006	5	≥11	≥11	100	≥3	27	0.29	0.0008
The Netherlands									
Glyphosate	2006-2014	≥373	9316	≥1223	≥13	≤1223	≤13	0.142)	?
AMPA	2006-2014	≥373	9270	≥1358	≥15	≤1358	≤15	0.07 2)	?
UK									
Glyphosate	1993-2015	≥102	3916	754	19.2	754	19.2	8.2	0.1-1
Danube									
Glyphosate	2013	68	68	5	7.3	0	-	0.07	0.03
AMPA	2013	68	68	66	97	≤66	≤97	0.96	0.03
Total									
Glyphosate	1993-2015	≥4419	≥143470	444232	31	30858	21	0.07-3400	Mainly 0.01-2.5
AMPA	1997-2015	≥3543	≥115302	≥57457	50	≥47876	41	0.07-393	Mainly 0.01-0.5

LoQ = limit of quantification (LoD = limit of detection)
(s) sites (number of samples not known, but assumed ≥1 per site)
[1] maximum 90 percentile value [2] maximum annual average concentration

Glyphosate has been analysed in over 143,000 surface water samples from over 4,400 sites (from 1993-2015) and detected in 31% of samples, with 21% above 0.1 µg/L. AMPA has been analysed in over 115,000 samples from over 3,500 sites (1997-2015) and detected in 50% of samples, with 39% above 0.1 µg/L. Concentrations vary widely, with maximum concentrations for glyphosate in the range 0.07-3400 µg/L and AMPA from 0.07-393 µg/L.

Glyphosate has a high usage rate and has been rated among the most frequently detected herbicides in some countries, notably in the Netherlands. It has been suggested that urban run-off can be a significant source of glyphosate in surface waters (France and the Netherlands). Where data allowed interpretation, glyphosate was linked to application periods (from spring through to autumn) and run-off events and does not seem to persist. The more persistent presence of AMPA in surface waters throughout the year may be mainly derived from aminophosphonate containing complexing agents in detergents and cooling waters, entering surface waters *via* wastewater treatment effluents, rather than from the degradation of glyphosate.

Generally, results are rather variable and not suggesting an increase in detection frequency or concentrations observed over the years. However, a trend analysis from the Netherlands over the years 1997-2014 indicates a slight upward trend for glyphosate from an annual average concentration of 0.102 µg/L in 1997 to 0.138 µg/L in 2014, and a slight downward trend for AMPA from 0.209 µg/L to 0.188 µg/L over the same period.

Some countries have proposed (or implemented) various environmental quality standards (EQS) or objectives for glyphosate in surface water, ranging from an EQS of 60 µg/L in Ireland, to a Proposed No Effect Concentration (PNEC) of 10 µg/L and a Maximum Admissible Concentration (MAC) of 100 µg/L in Belgium (Flanders), and in the Netherlands a Maximum Tolerable Risk (MTR) standard at 77 µg/L, and a pesticide authorisation standard of 64 µg/L. Some professionals (Belgium-Wallonia and Rheinland-Pfalz in Germany) suggested that an EQS should be set. However, none of these (proposed) standards have been exceeded on regular basis. Perhaps more importantly, the Netherlands apply the drinking water standard of 0.1 µg/L for pesticides to surface water intakes at waterworks, and LAWA in Germany has set a target value of 0.1 µg/L for the same purpose.

III. CONCLUSION

Ground and surface water monitoring data were gathered from 17 European countries, 16 countries plus the Danube River Basin for surface water, and 15 countries for groundwater, with most countries including both.

Glyphosate and AMPA have been extensively monitored and frequently detected in surface water above the 0.1 µg/L drinking water standard (21% of the samples for glyphosate and 39% for AMPA), but typically below the proposed environmental quality standards or objectives (ecotoxicologically relevant concentration).

Assessment and conclusion by applicant:
The study provides an overview on monitoring data (up to 2015) for groundwater and surface water from 15 and 17 European countries, respectively. No specific guideline is applicable to this data point.
The study is therefore considered valid.

Assessment and conclusion by RMS:
This study is an update of the study of [redacted], 2012 assessed in the RAR, 2015. It includes data from 1997-2015. Only data from surfacewater results were left here. Data from the groundwater monitoring are summarized in the relevant section.

Data collected from surface survey in this study overlaps the one collected in [redacted] 2020. Results are included in the summary of the study of [redacted], 2020.

However, it is noted that maximum concentration reported in this study are higher than those retained in [redacted], 2020, probably as considered outlier in [redacted]s, 2020. As no details are given on the procedure for determining outliers in [redacted], 2020, a data gap is set to applicant to clarifiy this point, and check wether a higher concentration that the one reported in [redacted], 2020 shall be retained.

Existing studies/assessment

Data point:	CA 7.5/013
Report author	[redacted]
Report year	2012
Report title	Survey of glyphosate and AMPA in groundwaters and surface waters in Europe
Report No	-
Document No	BVL No. 2310291
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	Yes, accepted in RAR (2015)
GLP/Officially recognised testing facilities	No (no experimental work performed)
Acceptability/Reliability:	Acceptable

The study is relevant for multiple subchapters. Only data results related to surface water have been left in the following summary.

Executive Summary

This review is based on an earlier review carried out in 2009, which has been updated to include the latest available information. The review covers glyphosate and AMPA monitoring results for surface (fresh) waters and groundwater across Europe, *i.e.* all 27 Member States of the European Union, as well as Norway and Switzerland, where available.

Information has been obtained from professional contacts across Europe (government departments and research organisations), and including some data provided by Monsanto Europe, as well as from web and literature searches, and by querying on line databases. Some data from the previous review has been omitted where more up to date information has become available.

Additional data has been obtained for twelve countries, *i.e.* Belgium, the Czech Republic, Denmark, France, Ireland, Italy, the Slovak Republic, Spain, Sweden, the Netherlands and the UK. In total, there is data for 17 countries, 14 each for surface water and groundwater, with most countries including both.

Surface water

Glyphosate and AMPA have been frequently detected in surface waters, AMPA usually at higher concentrations and in a larger proportion of samples. Glyphosate has been analysed in almost 75 000 samples from about 4 000 sites (from 1993-2011) and detected in 33% of samples, with 23% above 0.1 µg/L; AMPA has been analysed in about 56 700 samples from nearly 3 000 sites (1997-2011) and detected in 54% of samples, with 46% above 0.1 µg/L. The more persistent presence of AMPA in surface waters throughout the year may be mainly derived from aminophosphonate containing complexing agents in industrial and household detergents and in cooling waters, entering surface waters via wastewater treatment effluents, rather than from the degradation of glyphosate.

There have been some indications of an upward trend detections and concentrations found in recent years, e.g. in Belgium – Flanders and the Netherlands (not confirmed in recent years, and the opposite in NL - Flevoland), but the data may not be adequate to conclude on trends and coincides with higher numbers of sites and samples analysed.

Where data allowed interpretation, glyphosate has been linked to application periods (from spring through to autumn) and run-off events and does not seem to persist.

I. MATERIAL AND METHODS

This investigation is a desk study, and the information was obtained from professional contacts across Europe (government departments and research organisations in each of the countries), and including some data provided by Monsanto Europe, as well as from web and literature searches, and by querying on line databases.

II. RESULTS AND DISCUSSION

Table 8.5-139 provide an overview of the main data for surface water. The summarised data is not precise but presents a best estimate, mainly because of the various forms in which the data were obtained, *e.g.* some results in terms of samples, others in terms of sites, and other gaps in information.

In total, there is data for 17 countries, 14 each for surface water and groundwater, with most countries including both. However, the Czech and Slovak Republics monitor only surface water, and data for Spain was available for surface water only; for Malta and Switzerland only groundwater data was obtained. Data were mainly collated at national level, but in some cases regional, as for Belgium (two regions), Italy (one region), and Germany (surface water data for several Länder). Seven countries have confirmed that there is no monitoring of glyphosate and AMPA (Bulgaria, Cyprus, Hungary, Latvia, Lithuania, Luxembourg, Romania), no information was obtained from the remaining five countries (Estonia, Greece, Poland, Portugal and Slovenia).

Surface water

Table 8.5-139: Summary of glyphosate and AMPA data in surface water in Europe

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples ≥ 0.1 µg/L		Max. Conc.	LoQ (LoD)
				No.	%	No.	%	µg/L	µg/L
Austria									
AMPA	2001-02	-1)	345	≥90	≥26	90	26	3.4	-[1]
Belgium (Flanders - F and Wallonia - W)									
Glyphosate F	2007-11	198	5350	4450	83.2	1387	25.9	139	0.05-0.4
AMPA F	2007-11	198	5351	4967	92.8	3215	60.1	47	0.05-0.4
Glyphosate W	2001-06	26	531	≥ 429	≥ 81	429	81	1.3	≤ 0.1
Czech Republic									
Glyphosate	2010-11	41	359	168	47.8	96	28.7	5.3	0.025-0.05
AMPA	2010-11	9	165	165	100	138	83.6	1.37	0.05
Finland									
Glyphosate	2002-09	3	26	3	11.5	2	7.7	0.46	0.1
AMPA	2002-09	3	26	3	11.5	1	3.8	0.22	0.05
France									
Glyphosate	97-2009	≥2493	57171	17251	30.2	13655	23.9	50	0.03-0.2
AMPA	98-2009	≥2217	46969	24325	51.8	22062	47.0	48.9	0.02-0.5
Germany (Baden-Württemberg, Hessen, Rheinland-Pfalz, Thüringen & River Rhine combined)									
Glyphosate	97-2011	105	1298	386	29.7	96	7.4	4.7	0.02-1.5
AMPA	97-2011	66	782	571	57.5	514	65.7	3.6	0.05-0.5
Ireland									
Glyphosate	2005-11	256	2483	139	5.6	≥42	≥1.7	186	0.08-0.1/ 20
AMPA	2010-11	-1)	496	1	0.2	1	0.2	>200	20
Italy (Lombardia Region)									
Glyphosate	2005-08	150	919	224	24.3	224	24.3	37.6	0.1
AMPA	2008	59	239	208	87.0	208	87.0	37	0.1
Norway									
Glyphosate	97-06	11	80	74	92.5	≤ 57	≤ 71	0.93	(0.01)
AMPA	97-06	11	80	74	92.5	≤ 48	≤ 60	0.54	(0.01)
Slovak Republic									
Glyphosate	2006-10	142	2092	321	15.3	261	12.6	3.6	(0.05)
Spain [2]									
Glyphosate	2006-08	115	748	96	7.4	80	11	15.3	0.003-0.1
Sweden									
Glyphosate	2000-10	≥ 21	1306	360	27.6	≥15	≥1.1	370	<0.1
AMPA	2000-10	≥ 21	1285	244	19.0	≥14	≥1.1	4.0	<0.1
The Netherlands									
Glyphosate	2010	293	1349	254 (s)	87 (s)	198 (s)	68 (s)	>1.0	<0.1
AMPA	2010	293	1374	293 (s)	100 (s)	≥ 40 (s)	≥14 (s)	>8.0	-[1]
UK									
Glyphosate	93-2011	≥105	3730	759	20.3	759	20.3	8.2	0.1
Total									
Glyphosate	93-2011	≥3959	75350	≥24914	≥33	≥17301	≥23	1.3-370	0.003-1.5 (20)
AMPA	97-2011	≥2879	57112	≥30941	≥54	≥26331	≥46	0.22->200	0.02-0.5 (20)

LoQ = Limit of Quantification, LoD = Limit of Detection

[1] No information

[2] Data from sites with known quality problems

(s) sites (number of samples not known)

Glyphosate has been analysed in almost 75 000 surface water samples from about 4 000 sites (from 1993-2011) and detected in 33% of samples, with 23% above 0.1 µg/L; AMPA has been analysed in about 56 700 samples from nearly 3 000 sites (1997-2011) and detected in 54% of samples, with 46% above 0.1 µg/L .

Glyphosate has a high usage rate and has been rated among the most frequently detected herbicides in some countries, notably in the Netherlands. It has been suggested that urban run-off can be a significant source of glyphosate in surface waters (France and the Netherlands). There have been some indications of an upward trend detections and concentrations found in recent years, e.g. in Belgium – Flanders and the Netherlands (not confirmed in recent years, and the opposite in NL - Flevoland), but the data may not be adequate to conclude on trends and coincides with higher numbers of sites and samples analysed.

Some countries have proposed various environmental quality standards (EQS) or objectives for glyphosate in surface water, ranging from a proposed EQS of 28 µg/L in Mecklenburg-Vorpommern (Germany) and 60 µg/L in Ireland (now accepted), to a proposed no effect concentration (PNEC) of 10 µg/L and a maximum admissible concentration (MAC) of 100 µg/L in Belgium - Flanders, and a Maximum Tolerable Risk (MTR) standard at 77 µg/L, and a pesticide authorisation standard of 64 µg/L in the Netherlands, whilst some professionals (Belgium – Wallonia and Rheinland-Pfalz (Germany) suggested that an EQS should be set. However, none of these standards have been exceeded on a regular basis. Perhaps more importantly, the Netherlands apply the drinking water standard of 0.1 µg/L for pesticides to surface water intakes at waterworks, and LAWA in Germany has set a target value of 0.1 µg/L for the same purpose.

Where data allowed interpretation, glyphosate has been linked to application periods (from spring through to autumn) and run-off events and does not seem to persist. The more persistent presence of AMPA in surface waters throughout the year may be mainly derived from aminophosphonate containing complexing agents in detergents and cooling waters, entering surface waters via wastewater treatment effluents, rather than from the degradation of glyphosate. This seems to be a fairly widely accepted view now, with more evidence having become available, and might explain why AMPA is not always found at higher concentrations, as for example in Sweden, where the population density is low.

III. CONCLUSION

Ground and surface water monitoring data were gathered from 17 European countries, 14 each for surface and groundwater, with most countries including both. Glyphosate and AMPA have been extensively monitored and frequently detected in surface water above the 0.1 µg/L drinking water standard (23% of the samples for glyphosate and 46% for AMPA), but typically below the proposed environmental quality standards or objectives (ecotoxicologically relevant concentration).

Assessment and conclusion by applicant:
The study compiles drinking water quality data (up to 2012) for glyphosate and AMPA from national authorities in Europe. The methods and results are sufficiently described.
The study is considered valid.

Assessment and conclusion by RMS:
This study had already been evaluated in the DAR, 2015. However, data from this study have been updated in [redacted], 2016 which is summarized and assessed above.

Data point:	CA 7.5/035
Report author	[redacted]
Report year	1972
Report title	Run-off of MON-0573 from Inclined Soil Beds
Report No	AgRR 275
Document No	
Guidelines followed in study	US EPA Guidelines for Registering Pesticides, 2nd draft, 5-1-72, part XI
GLP	No
Previous evaluation	Not accepted in RAR (2015)
Short description of study design and observations:	Study type: run-off from inclined soil beds Test item: [^{14}C] glyphosate, phosphonomethyl-label (97 % radiochemical purity) Test soil (type): Ray (silt loam), Norfolk (sandy loam), Drummer (silt clay loam) pH: 6.5, 5.7, 7.0 (medium not stated) Organic matter: 0.6 %, 0.6 %, 3.5 % Application rate: 1.12 kg a.s./ha; application was made to the upper third of the soil surface with a laboratory sprayer Test design: steel trays (91 x 30 x 15 cm), filled to 11-13 cm; inclined (7.5°) after application, watering of the soil led to unwanted leaching out of the test vessels; for each sampling, artificial rainfall equivalent to 19.05 mm/h was applied until collection of 2 x 50 mL samples of run-off water Sampling: 1, 3 and 7 days after treatment Workup: centrifugation, decantation Analysis of radioactivity: Runoff-water: LSC Runoff-sediment: combustion/LSC
Short description of results:	Radioactivity in run-off samples at day 1 / 3 / 7 (% AR, mean of 2 replicate samples): Ray soil Supernatant: 0.0045 / 0.0010 / 0.0003 Sediment: 0.0019 / 0.0016 / 0.0008 Total: 0.0064 / 0.0026 / 0.0011 Sum after 7 days: 0.0101 Drummer soil Supernatant: 0.0002 / 0.0013 / 0.0008 Sediment: 0.00004 / 0.0001 / 0.00001 Total: 0.0002 / 0.0014 / 0.0008 Sum after 7 days: 0.0042 Norfolk soil Supernatant: 0.0064 / 0.0007 / 0.0002 Sediment: 0.0031 / 0.0002 / 0.0002 Total: 0.0095 / 0.0009 / 0.0004 Sum after 7 days: 0.0108

	The results show a maximum total run-off amount of about 0.01 % AR.
Reasons for why the study is not considered relevant/reliable or not considered as key study:	The study is considered invalid due to the following deficiencies: - Study type is not relevant to the data requirement - No substance-specific analysis performed - Experimental conditions cannot be transferred to field scale and are therefore not relevant for risk assessment - Uncontrolled leaching out of the test vessels

Assessment and conclusion by RMS:
Based on the reasons mentioned above, the study is not considered acceptable.

Relevant literature articles

Articles from the literature have been provided by applicant, considered relevant or partially relevant for the surface water compartment, and are summarized below. The following table lists all the references provided.

RELEVANT LITERATURE ARTICLES					
Data point	**Study (Author, year)**	**Study type**	**Substance(s)**	**Type of measured data**	**Status**
CA 7.5	Boye K. et al., 2019	Long-term data from the swedish national environmental monitoring program of pesticides in surface waters	Glyphosate AMPA	Surface water – from 4 small watershed)	Reliable with restrictions
CA 7.5/036	Di Guardo, A., Finizio, A., 2018	Identifying surface waters at risk using pesticide monitoring data	Glyphosate	Surface water, (large regional scale monitoring)	Reliable with restrictions
CA 7.5/037	Huntscha, S. *et al.*, 2018	Seasonal dynamics in Lake Greifensee, Switzerland	Glyphosate AMPA	Surface water – Lake and tributaries	Reliable
CA 7.5/038	Masiol, M. *et al.*, 2018	Herbicides in river water across north eastern Italy	Glyphosate AMPA	Surface water	Reliable
CA 7.5/039	Dairon, R. *et al.*, 2017	Long term impact of reduced tillage on water and pesticide flow in a drained context	Glyphosate AMPA	Drainflow before entering SW	Reliable with restrictions
CA 7.5/040	Lefrancq, M. *et al.*, 2017	High frequency monitoring of pesticides in runoff water	Glyphosate AMPA	Surface runoff before entering SW	Reliable
CA 7.5/041	Lerch, R.N. *et al.*, 2017	Vegetative buffer strips for reducing herbicide transport in runoff	Glyphosate	Surface runoff from field, before entering SW	Reliable with restrictions

CA 7.5/042	Mottes, C. *et al.*, 2017	Monitoring of glyphosate in a horticultural catchment in Martinique, French West India (part of the EU).	Glyphosate AMPA	Surface water, ravine catchment	Reliable
CA 7.5/017	Poiger T. *et al.*, 2017	Simplified procedure for determination in water samples	Glyphosate AMPA	Surface water from various region	Reliable
CA 7.5/043	Reoyo-Prats, B. *et al.*, 2017	Multicontamination phenomena in Mediterranean coastal watercourses (Têt River, France)	Glyphosate AMPA	Surface water	Reliable with restrictions
CA 7.5/044	Desmet, N. *et al.*, 2016	A hybrid monitoring and modelling approach in large river catchments	Glyphosate AMPA	Surface water (Meuse river moniroting)	Reliable with restrictions
CA 7.5/045	Larsbo, M. *et al.*, 2016	Surface runoff of pesticides from a clay loam field in Sweden	Glyphosate AMPA	Surface runoff from field, before entering a SW	Reliable
CA 7.5/005	Napoli, M. *et al.*, 2016	A runoff experiment in a vineyard in Italy	Glyphosate AMPA	Surface runoff from field, before entering SW	Reliable
CA 7.5/046	Schreiner, V. *et al.*, 2016	Monitoring results of pesticides in some EU Member States and the USA	Glyphosate	Surface water	Reliable with restriction
CA 7.5/047	Stenrød, M., 2015	Long-term trends of pesticides in Norwegian agricultural streams and potential future challenges in northern climate	Glyphosate	Surface water, small agricultural catchments	Reliable with restrictions
CA 7.5/048	Székács, A. *et al.*, 2015	Monitoring results for pesticide residues in surface and groundwater in Hungary	Glyphosate	Surface water (large scale monitoring)	Reliable with restrictions
CA 7.5/049	Tang, T. *et al.*, 2015	Quantification and characterization of glyphosate use and loss in a residential area	Glyphosate AMPA	Urban runoff before entry into SW	Reliable
CA 7.5/050	Gasperi, J. *et al.*, 2014	Micropollutants in urban stormwater in three French sites	Glyphosate AMPA	Urban stormwater before entry into SW	Reliable with restrictions
CA 7.5/051	Maillard, E., Imfeld, G., 2014	Pesticide loss and input in a stormwater wetland	Glyphosate AMPA	Surface runoff, before entering wetland for vineyard catchment	Reliable with restrictions
CA 7.5/021	Norgaard, T. *et al.*, 2014	Leaching from an agricultural field	Glyphosate AMPA	Drainflow before entry into SW, PLAP site	Reliable with restrictions

CA 7.5/052	Ramwell, C. *et al.*, 2014	Contribution of household herbicide usage in surface water drains	Glyphosate AMPA	Urban runoff (storm drain, drain flow from domestic usage) before entering SW	Reliable
CA 7.5/006	Székács, A. *et al.*, 2014	Monitoring and biological evaluation of surface water and soil micropollutants in Hungary	Glyphosate	Surface water (large scale monitoring)	Reliable with restrictions
CA 7.5/007	Daouk, S. *et al*, 2013a	Validation of an analytical method in different water matrices	Glyphosate AMPA	Surface water associated with vineyards – River and lake	Reliable
CA 7.5/053	Daouk, S. *et al.*, 2013b	The role of infiltration and surface runoff	Glyphosate AMPA	Surface runoff from vineyard, before entry into SW	Reliable
CA 7.5/054	Houtman, C. *et al.*, 2013	Monitoring in the river Meuse in the Netherlands	Glyphosate AMPA	River Meuse	Reliable with restrictions
CA 7.5/055	Imfeld, G. *et al.*, 2013	Transport and attenuation of dissolved glyphosate and AMPA in a stormwater wetland	Glyphosate AMPA	Surface runoff, before entering wetland for vineyard catchment	Reliable
CA 7.5/022	Martin, J. *et al.*, 2013	Review of 10 year monitoring of herbicides and water pollution in Reunion Island	Glyphosate AMPA	Surface water	Reliable with restrictions
CA 7.5/024	Mörtl, M. *et al.*, 2013	A monitoring study with an immunoassay analytical method	Glyphosate	Surface water	Reliable with restrictions
CA 7.5/056	Vialle, C. *et al.*, 2013	Pesticides in roof runoff in rural and suburban sites	Glyphosate AMPA	Roof runoff	Reliable with restrictions
CA 7.5/057	Botta, F. *et al.*, 2012	Application and validation of a programme to reduce surface water contamination	Glyphosate AMPA	Surface water, urban dominated catchment	Reliable with restrictions
CA 7.5/058	Coupe, R. *et al.*, 2012	Fate and transport in agricultural surface waters	Glyphosate AMPA	Surface runoff, before entering wetland for vineyard catchment	Reliable with restrictions
CA 7.5/059	Petersen, J. *et al.*, 2012	Sampling of herbicides in streams during flood events	Glyphosate AMPA	Surface water, runoff event sampling in 3 catchments	Reliable
CA 7.5/060	Zgheib, S. *et al.*, 2012	Priority pollutants in urban stormwater	Glyphosate AMPA	Storm water from urban area of Paris, before entering SW	Reliable with restrictions

CA 7.5/061	Birch, H. *et al.*, 2011	Micropollutants in stormwater runoff and combined sewer overflow in Denmark	Glyphosate AMPA	Storm water from urban area of Copenhagen, before entering SW	Reliable with restrictions
CA 7.5/027	Bruchet A. *et al.*, 2011	Monitoring experiment in France	Glyphosate AMPA	Surface water - river and bank filtration	Reliable
CA 7.5/062	Lamprea, K., Ruban, V., 2011	Pollutant concentrations in stormwater and wastewater in France	Glyphosate AMPA	Storm/wastewater, before entry in SW, urban area	Reliable with restrictions
CA 7.5/063	Litz, N.T. *et al.*, 2011	Comparative studies on retardation and reduction during subsurface passage	Glyphosate AMPA	Surface water, River Havel, Berlin. Slow sand filter	Reliable with restrictions
CA 7.5/064	Maillard, E. *et al.*, 2011	Removal of pesticide mixtures in a stormwater wetland	Glyphosate AMPA	Surface runoff, before entering wetland for vineyard catchment	Reliable
CA 7.5/065	Meyer, B. *et al.*, 2011	Concentrations of dissolved herbicides and pharmaceuticals in a small river in Luxembourg	Glyphosate AMPA	Surface water (stream), small catchment runoff events	Reliable
CA 7.5/066	Busetto, M. *et al.*, 2010	Survey in waterways from the Lombardy region	Glyphosate AMPA	Surface water, Lombardy	Reliable
CA 7.5/067	Busetto, M. *et al.*, 2010	Translation of CA 7.5/066	See above		See above
CA 7.5/068	Gregoire, C. *et al.*, 2010	Use and fate of 17 pesticides applied on a vineyard catchment	Glyphosate AMPA	Concentration in wetland for vineyard catchment	Reliable
CA 7.5/069	Hanke, I. *et al.*, 2010	Relevance of urban glyphosate use for surface water quality	Glyphosate AMPA	Surface water, Urban dominated catchments	Reliable
CA 7.5/070	Botta, F. *et al.*, 2009	Transfer to surface waters through sewerage systems	Glyphosate AMPA	Surface water, Urban dominated catchments	Reliable with restrictions
CA 7.5/071	Ghanem, A., *et al.*, 2007	Concentrations and specific loads in French urban sewage sludge	Glyphosate	Sludge concentration	Not relevant (concentration in sewage sludges)
CA 7.5/072	Peschka, M. *et al.*, 2006	Trends in pesticide transport into the River Rhine	Glyphosate AMPA	Surface water (Rhine and 2 tributaries), waste water.	Reliable with restrictions
CA 7.5/073	Augustin, B., 2003	Urban sources of pesticide contamination of surface water	Glyphosate	Surface water, (Selz river)	Reliable with restrictions

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Data point:	CA7.5 - Submitted within litterature review
Report author	Boye, K.; Lindström, B.; Boström, G.; Kreuger, J.
Report year	2019
Report title	Long-term Data from the Swedish National Environmental
Document No	*Journal of Environmental Quality - vol 48 (2019) 1109-119*
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Environmental monitoring is essential for assessing the impact of human activities on the environment. Monitoring data are used to ascertain that environmental standards are met, to inform policy making, to determine trends, and to provide parameterization data for prediction models. The design of monitoring programs depends on what is being monitored, for what purpose, and available resources. Here we describe the strategy and design of the Swedish environmental monitoring program for chemical pesticides in surface waters and provide data generated within this program since 2002 (www.slu.se/en/pesticide_monitoring). We include examples of how the data can be used for toxicity assessments, trend analyses, and comparison between sampling strategies. Our goal is to increase awareness of this dataset and provide detailed information about the data so that it may be incorporated into meta-analytical research, comparison studies, model validation, and other scientific efforts.

Introduction

Chemical pesticides are used in conventional agriculture to maintain high yields and improve crop quality. Rigorous testing and continuous product development are undertaken to ensure that pesticides harm only targeted pests and then disappear quickly from the environment without further effects. The European Union (EU) has a harmonized procedure for pesticide approval to ensure that environmental effects from pesticides are avoided (Regulation EC 1107/2009) (EU, 2009b). However, reports from environmental monitoring programs and targeted sampling efforts reveal that pesticide residues reach surface waters and groundwater, frequently in concentrations that may harm aquatic organisms and exceed drinking water standards (Smith et al., 2012; Stone et al., 2014; Allinson et al., 2015; Morrissey et al., 2015; Silva et al., 2015; Stehle and Schulz, 2015; Stenrød, 2015; Székács et al., 2015; Teklu et al., 2015; Yadav et al., 2015; Bradley et al., 2017; Szöcs et al., 2017). With the implementation of the European Water Framework Directive (2000/60/EC) (EU, 2000) and the Directive for Sustainable Use of Pesticides (2009/128/EC) (EU, 2009a), the legal demands for preventing such occurrences have increased, and there is greater incentive for implementing mitigating measures. National environmental monitoring programs have a vital role to play in achieving the goals set by the directives, as well as to ensure that the general public is informed about the current environmental status and has confidence in the effectiveness of regulated prevention and mitigation efforts. Long-term, continuous sampling programs provide the trend data needed for predicting goal trajectories and assessing effects of mitigating efforts. Further, the data collected can help locate sources and identify management practices, crops, or pesticides that are problematic in terms of off-target pesticide effects and occurrences. This is crucial information for increasing the efficiency of targeted research and development efforts. The continuous monitoring of a multitude of substances together with ecological indicators will also be important for understanding the combined effects of pesticides and other chemical stressors, which are increasingly being emphasized as the prioritized focus for water quality assessments (Chèvre et al., 2006; Schuler and Rand, 2008; McKnight et al., 2012; Rasmussen et al., 2013; Malaj et al., 2014; Altenburger et al., 2015; Stenrød, 2015; Brack et al., 2017). Finally, environmental monitoring data are the basis for developing and testing models used for predicting pesticide behavior in the environment.

Broad-scale pesticide screening is associated with high analytical costs imposed by multimethod requirements to reliably detect and quantify organic compounds with a wide range of properties at low concentrations. This generally requires making compromises on spatial and/or temporal resolution, often in addition to narrowing the targeted substances to priority-listed chemicals or other subsets of substances depending on the aim, particularly within long-term monitoring programs. As a result, water quality assessment programs around the world vary widely in their design, depending on the longevity and extent of funding, the targeted aspects of water quality, and if the priority of the assessment is to capture the spatial distribution or temporal resolution or to provide comprehensive analyses of all occurring substances. Studies covering a wide spatial range have generally relied on grab sampling at relatively low frequency (Stone et al., 2014; Szöcs et al., 2017); others have sampled at higher frequency with smaller spatial coverage and over a limited time period (Papadakis et al., 2015). Studies combining different sampling methods have shown that grab sampling generally detects fewer substances than do time-integrated or event-triggered auto-samplers (McKnight et al., 2012; Rasmussen et al., 2013; Bundschuh et al., 2014; McKnight et al., 2015; Poulier et al., 2015). Passive samplers can detect pesticides at lower concentrations than other methods (e.g., Mazzella et al., 2007; Smith et al., 2012; Emelogu et al., 2013; Poulier et al., 2015), but monitoring is limited to substances conducive to the sampler and is associated with intrinsic uncertainties regarding the quantification of concentrations (Ahrens et al., 2015). Regardless of the sampling approach, most monitoring programs have narrowed the screened substances to a subset of relatively easy-to-analyze, commonly used, and/or priority-listed substances. While this approach lowers the cost per sample, it inevitably results in an underestimation of pesticide occurrences and associated toxicological and environmental risks (Moschet et al., 2014). However, a recent study indicated that it is possible to adequately assess risks with a reduced number of analyzed substances, as long as the appropriate substances are targeted and the sampling is conducted at a high temporal resolution and through composite samples (Spycher et al., 2018).

The Swedish monitoring program for chemical pesticides (Swedish University of Agricultural Sciences, 2019) was designed to capture the worst-case risks related to agricultural pesticide usage. Therefore, the monitoring is performed in four small catchments with predominantly arable land that are representative of, and located in, Sweden's major agricultural regions. The program is unique in its long-term (>15 yr), continuous (weekly or every other week), time-integrated, comprehensive analyses of all EU-listed priority substances and almost all active ingredients (and a number of metabolites) registered for use in Sweden, including glyphosate, which is often omitted from monitoring programs due to analytical complications. Additionally, the detection and quantification limits for the analytical methods used are low and allow for detection of substances, such as pyrethroids and neonicotinoids, that are highly toxic and otherwise often have a detection limit above the environmental quality standard or water quality objectives (WQOs). Thus, the dataset generated to date provides a uniquely comprehensive, long-term representation of how Swedish agricultural pesticide use affects surface water quality. In this publication, we aim to disseminate knowledge about this extensive and unique dataset so that others may contribute to expanding the use and informational gain from the data to their full potential.

Methods

Monitoring Locations

The Swedish monitoring program for chemical pesticides in surface waters in its current geographical extent began in 2002, through expanding a project initiated in 1990 (Kreuger, 1998). The program is performed in four small catchments (E21, M42, N34, and O18), referred to as *model catchments*, and two rivers, Skivarpsån and Vegeå, within separate, dominant agricultural regions in southern Sweden (Table 1, Fig. 1). The catchments are also included in the environmental monitoring program for nutrient losses from agriculture, which has been described elsewhere (Kyllmar et al., 2014). The focus of the two programs is to monitor agricultural contributions to pesticide occurrence and nutrient loads in surface waters. Note that the choice of model catchments and rivers was not based on randomized selection. Instead, informed decisions were made to target catchments and rivers that would be representative of the main agricultural regions in terms of soil types, agricultural practices, and major crops grown.

Table 1. Catchment overview.

Catchment	Total area	Farmland	Mean temperature†	Mean precipitation†	Dominant soil type‡	Main crops
	km²	%	°C	mm		
O18	7.66	92	7.2	628	Clay loam, silty clay loam	Cereals, oil seed
E21	16.32	89	7.2	567	Loam, clay loam	Cereals, oil seed, potato
N34	13.93	85	8.0	741	Sandy loam, loam	Cereals, forage, potato
M42	8.24	92	8.5	710	Sandy loam, loam	Cereals, sugar beet, oil seed
Skivarpsån	102.00	86	8.4	705		Cereals, forage, oil seed, sugar beet
Vegeå	488.00	66	8.7	700		Cereals, forage, oil seed, sugar beet

† Values represent averages for the period 2002–2016, using data from the closest operational weather station to each sampling location for each year (exact locations for nearest weather stations have varied over the period).

‡ Data from the Swedish Environmental Protection Agency arable land inventory (Eriksson et al., 2010), adapted to international particle-size standards according to Tranter et al. (2011) and Moeys (2014).

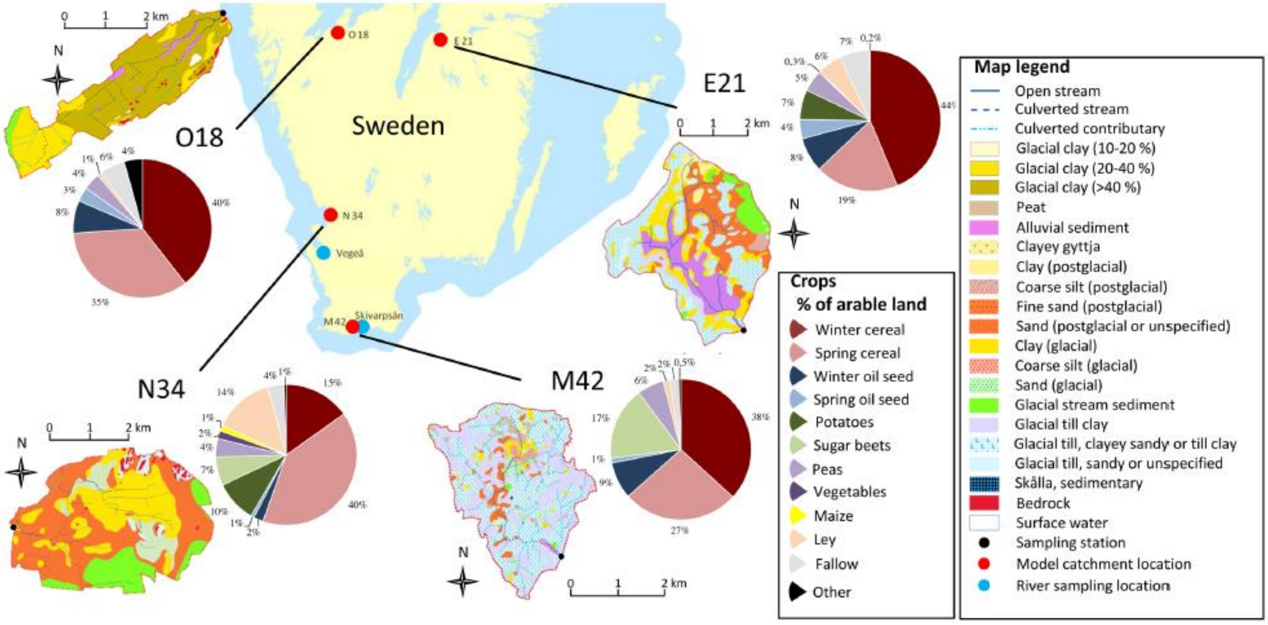


Fig. 1. Locations, soil maps, and dominant crops (average crop distribution during 2002–2012) within each of the four model catchments included in the Swedish monitoring program for pesticides in surface water: E21, M42, N34, and O18.

The catchments are small (8–16 km2), with 85 to 92% of the area under farmland, which minimizes contributions from nonagricultural practices, such as pesticide and fertilizer use in parks, gardens, greenhouses, and turf. Another reason for choosing intensely farmed catchments was to provide worst-case assessments of the impact on surface water quality from agriculture. The pesticide usage within each catchment (Table 2) is higher than average for the corresponding region (data available through Statistics Sweden [SCB, 2018]).

Table 2. Average pesticide use in the catchments for the period 2002–2016.

Catchment	Average dose				Portion of farmland treated			
	Herbicides	Fungicides	Insecticides	Total†	Herbicides	Fungicides	Insecticides	Total†
	kg ha⁻¹				%			
O18	0.50	0.17	0.07	0.58	85	43	17	87
E21	0.44	0.53	0.05	0.80	78	48	30	84
N34‡	0.93	1.18	0.04	1.57	62	39	24	65
M42	1.50	0.30	0.04	1.72	93	71	69	96

† Totals include growth regulators and substances used against slugs.

‡ Low percentages for treated farmland in N34 could be due to lower farmer participation in the questionnaires about management practices during the latter part of the period.

The two rivers included in the monitoring program, Skivarpsån and Vegeå, were selected to represent medium-sized catchments (102 and 488 km2 with 86 and 66% of the area under farmland) in Skåne, the most intensely farmed region in Sweden. The purpose of sampling the rivers is to provide large-scale comparison of data from the intensely monitored streams. Sampling in the rivers is less frequent and follows a different protocol, and less-detailed information is available regarding soil types, farming practices, pesticide usage, and so on. The median total concentration of pesticides is quite similar between the model catchments and the rivers, which supports the use of the model catchments to represent intensely farmed regions in Sweden (Fig. 2).

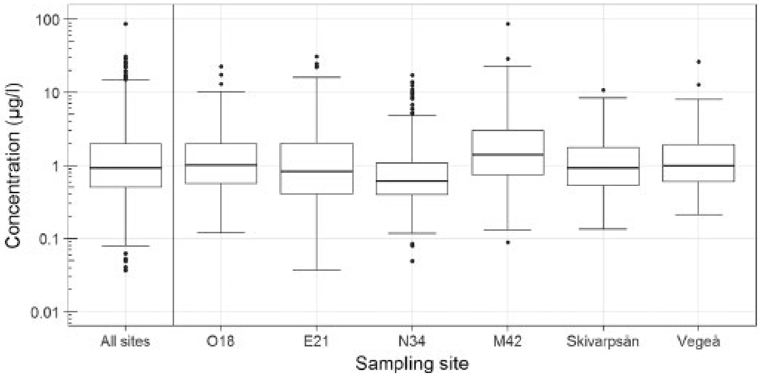
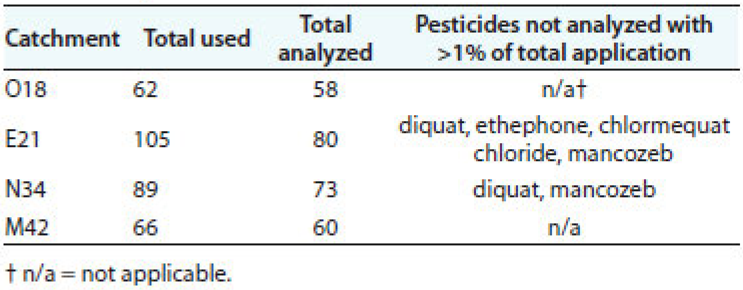


Fig. 2. Total concentration ($\mu g\ L^{-1}$) of pesticides per sample for all samples taken during the growing season (May–October). Note the logarithmic scale.

Data Collection for Agricultural Practices

Within the model catchments, all farmers are contacted yearly and asked to provide logs of their farming practices (crops, sowing and harvest dates, time and amount of pesticide applications) for each individual field within the catchment. Much effort has been made to inform the farmers of the importance of participation, accuracy, and completeness in providing the logs. They are asked specifically to proceed with their management practices as they would if they were not within the monitoring catchments. Nevertheless, as always when relying on voluntary participation, it cannot be guaranteed that the reported data are complete or fully accurate. The data from the questionnaires are shared with the monitoring program for nutrient losses. For privacy reasons, we can only report these data in aggregated form (tabulated data for the entire period 2002 to 2016 is available for download at www.slu.se/en/pesticide_ monitoring [Swedish University of Agricultural Sciences, 2019]). A summary of the agricultural practices within each model catchment since the start of the monitoring program is provided herein (Fig. 1, Tables 1, 2, and 3) as background information for the pesticide occurrence data in the publicly available dataset. For the river catchments, no data regarding farming practices are collected through the monitoring program, but regional data are available through the Swedish Agricultural Board (SCB, 2018).

Table 3. Number of pesticides used and number of pesticides included in the analyses. The right column lists pesticides that have not been included in the analyses and which constitute >1% of applied quantities over the period 2002–2016 within each catchment.



Catchment	Total used	Total analyzed	Pesticides not analyzed with >1% of total application
O18	62	58	n/a†
E21	105	80	diquat, ethephone, chlormequat chloride, mancozeb
N34	89	73	diquat, mancozeb
M42	66	60	n/a

† n/a = not applicable.

Water Sampling Procedures

Pesticide monitoring covers the agricultural cropping season, with weekly composite samples from the beginning of May until the end of October in catchments O18 and E21 and until the end of November in N34 and M42. This sampling period is referred to as the growing season. In catchments N34 and M42, the monitoring continues throughout the winter, but with longer sampling intervals (14 d) in the period December to April (winter season). The stream outlet from each catchment is equipped with an automatic

ISCO sampler (initially 3700FR, now 6712FR since 2008 in M42, 2011 in O18, and 2013 in E21 and N34) including a +4°C refrigerator with one glass bottle and one plastic (high-density polyethylene) bottle for storing samples for different types of analyses (described below). Samples are collected every 90 min through Teflon tubing extending into the stream according to the following procedure: (i) air cleaning (air is pumped out to remove any material around the tube), (ii) water rinse (water is pumped into a detector and then back out to the stream), and (iii) sampling (20 mL water is divided between the two bottles). The bottles are changed weekly and shipped on ice to the laboratory for analysis. Thus, each analyzed sample is a composite of the water samples taken during 1 wk. The winter samples from N34 and M42 follow the same protocol, but with 180-min sampling intervals and bottles changed every 2 wk.

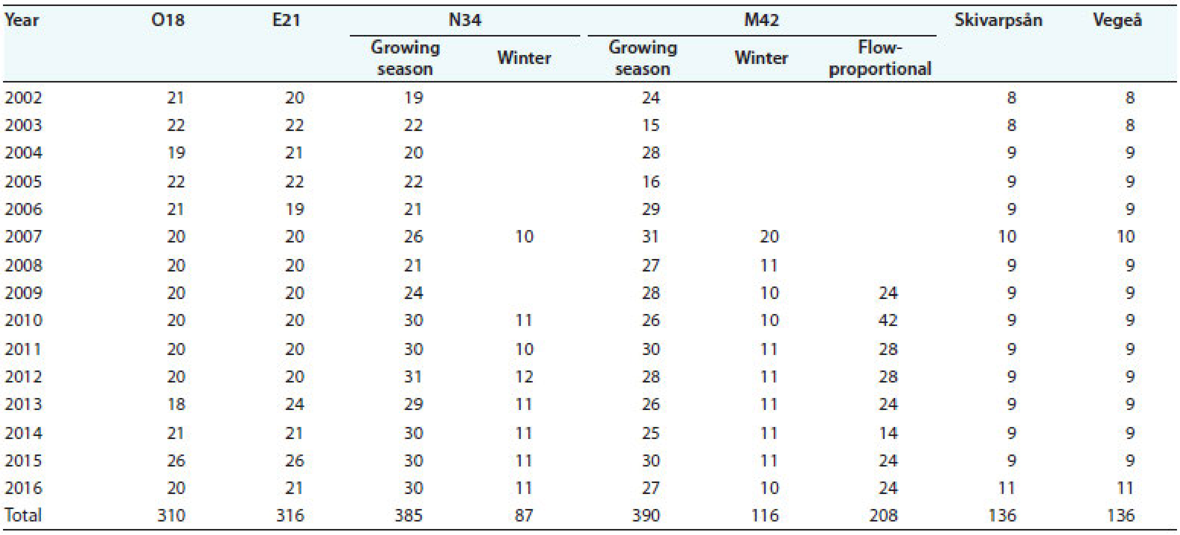
In catchment M42, a second ISCO 6712 sampler unit was installed to take flow-proportional samples during the growing season to capture peak-flow specific patterns in pesticide concentrations. This unit has eight bottles and collects samples when a set volume of water has passed. The set water volume is manually adjusted to increase sampling at high flow events (i.e., shortly after precipitation). Between 2009 and 2011, one sample was taken per bottle. From 2012 onward, the sampling program changed to three subsamples per bottle to better cover the peaks. The bottles are changed weekly and kept frozen (−18°C) until the end of the growing season, when a fixed number of samples are selected for analysis based on the relative change in flow during a week (to compare with the composite weekly sample). For economic reasons, all flow-proportional samples cannot be analyzed; hence, it is possible that some concentration peaks at high flow are missed.

The rivers are sampled by manual grab samples twice per month in May to June and once per month in July to November. Sampling is conducted by attaching bottles to a rod that is extended into the river; thereafter, bottles are submerged and filled. One plastic (high-density polyethylene) and one glass bottle (each 1 L) are filled on each sampling occasion. The bottles are shipped on ice to the laboratory (normally arriving within 24 h from the time of sampling).

A blank sample is obtained every other year from each catchment and every year from the rivers to discover contamination risks during the handling of bottles and ensure that no contamination of the sampling equipment has occurred. The blank bottles are handled like the sampling bottles, but filled with deionized water. Filled blank bottles are placed among the other sample bottles in the ISCO refrigerator for a week, and river blanks are filled with deionized water at the sampling site. Blank samples have never indicated contamination from the sampling procedure.

A summary of the types and total number of samples taken in the period 2002 to 2016 is given in Table 4. A few gaps exist in the time series of weekly composite samples, either due to sampling being prevented by low flow or to mechanical failures of the ISCO samplers, with the latter usually being replaced by grab samples.

Table 4. Total number and types of samples collected in catchment streams during the monitoring period 2002–2016.



Year	O18	E21	N34		M42			Skivarpsån	Vegeå
			Growing season	Winter	Growing season	Winter	Flow-proportional		
2002	21	20	19		24			8	8
2003	22	22	22		15			8	8
2004	19	21	20		28			9	9
2005	22	22	22		16			9	9
2006	21	19	21		29			9	9
2007	20	20	26	10	31	20		10	10
2008	20	20	21		27	11		9	9
2009	20	20	24		28	10	24	9	9
2010	20	20	30	11	26	10	42	9	9
2011	20	20	30	10	30	11	28	9	9
2012	20	20	31	12	28	11	28	9	9
2013	18	24	29	11	26	11	24	9	9
2014	21	21	30	11	25	11	14	9	9
2015	26	26	30	11	30	11	24	9	9
2016	20	21	30	11	27	10	24	11	11
Total	310	316	385	87	390	116	208	136	136

Pesticide Occurrence and Concentration Data— Analytical Procedures

All analyses during the entire period follow ISO/IEC 17025-accredited methods (ISO, 2017) conducted at the laboratory for organic environmental chemistry (OMK) at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences in Uppsala, Sweden. The laboratory routinely participates in international intercalibrations and conducts rigorous internal quality control to ensure that a high data quality standard is maintained.

The ambition of the program is to analyze all pesticides permitted for use within Sweden plus all pesticides listed as priority substances by the EU (Annex II of Directive 2008/105/EC [EU, 2008]), including those that have never been permitted for use in Sweden. New substances that are introduced into the market are normally added to the list of analytes the following year, as long as they are being used in the model catchments and there is an existing analytical procedure to detect them. Banned substances remain on the list of analytes until the concentrations are consistently below the analytical detection limit. Thus, the pesticides included in the analyses are reevaluated before each monitoring season in response to pesticide sales and usage regulations, but in general, the list is expanded yearly. In total, 148 different substances were analyzed in water samples during the period 2002 to 2016. The substances included in the analysis for each individual sample is noted in the dataset.

Despite extensive efforts to include all permitted and priority-listed substances, some substances used within the monitored catchments are too ephemeral to trace, some are too costly to analyze, or an analytical method for detection in natural waters has not yet been developed. The substances most commonly used but not analyzed within each model catchment are listed in Table 3. The OMK laboratory constantly refines and expands the ability to detect relevant substances using multi-residue methods, to meet the demands of introduced substances and the environmental quality standards. Since 2009, a combined liquid chromatography and tandem mass spectrometry method (OMK 57/OMK 58) (Jansson and Kreuger, 2010) has been used for the majority of substances. However, nonpolar substances require a separate method (OMK 51), as do glyphosate and its metabolite aminomethylphosphonic acid (AMPA) (OMK 59). A full list with short descriptions of the various methods used during the period 2002 to 2016 is provided in Table 5.

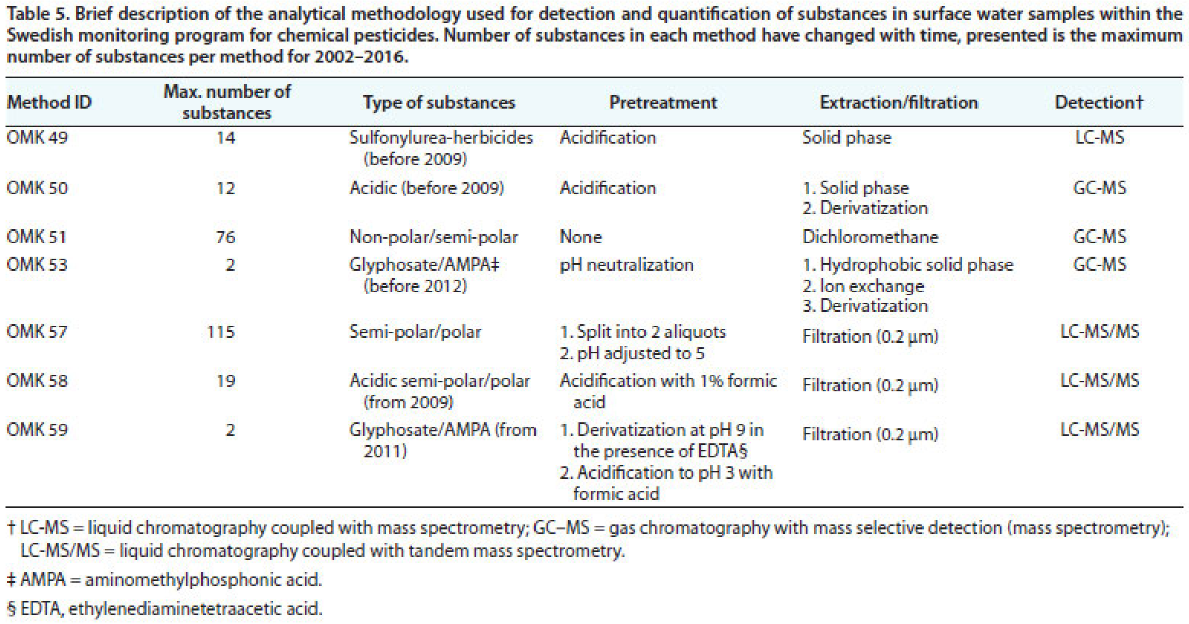


Table 5. Brief description of the analytical methodology used for detection and quantification of substances in surface water samples within the Swedish monitoring program for chemical pesticides. Number of substances in each method have changed with time, presented is the maximum number of substances per method for 2002–2016.

Method ID	Max. number of substances	Type of substances	Pretreatment	Extraction/filtration	Detection†
OMK 49	14	Sulfonylurea-herbicides (before 2009)	Acidification	Solid phase	LC-MS
OMK 50	12	Acidic (before 2009)	Acidification	1. Solid phase 2. Derivatization	GC-MS
OMK 51	76	Non-polar/semi-polar	None	Dichloromethane	GC-MS
OMK 53	2	Glyphosate/AMPA‡ (before 2012)	pH neutralization	1. Hydrophobic solid phase 2. Ion exchange 3. Derivatization	GC-MS
OMK 57	115	Semi-polar/polar	1. Split into 2 aliquots 2. pH adjusted to 5	Filtration (0.2 µm)	LC-MS/MS
OMK 58	19	Acidic semi-polar/polar (from 2009)	Acidification with 1% formic acid	Filtration (0.2 µm)	LC-MS/MS
OMK 59	2	Glyphosate/AMPA (from 2011)	1. Derivatization at pH 9 in the presence of EDTA§ 2. Acidification to pH 3 with formic acid	Filtration (0.2 µm)	LC-MS/MS

† LC-MS = liquid chromatography coupled with mass spectrometry; GC–MS = gas chromatography with mass selective detection (mass spectrometry); LC-MS/MS = liquid chromatography coupled with tandem mass spectrometry.

‡ AMPA = aminomethylphosphonic acid.

§ EDTA, ethylenediaminetetraacetic acid.

It should be noted that the introduction of OMK 57/OMK 58 increased the number of detectable substances and lowered the detection limit for substances formerly included in the analyses. As a consequence, increased pesticide occurrences logged in the dataset from 2009 onward, compared with before 2009, may not correspond to an actual increase in pesticide occurrence in the streams; instead, it could be an effect of an enhanced ability to detect pesticides that may have been present previously but not detected with the methods used before 2009. Hence, caution should be used when interpreting long-term trends related to the number of detected pesticides before and after 2009. However, it is still possible to conduct trend analyses over the entire period, for example, by excluding concentrations from 2009 to 2016 that are below the previous detection limits and/or limiting the trend analyses to a subset of substances that have consistently been included in all analyses and with robust detections above the detection limits over time.

When the concentration of a substance falls between the limit of detection (LOD) and the limit of quantification (LOQ), the exact concentration is less precise, as indicated by the annotation “trace value” in the dataset. Trace values recorded in the period 2002 to 2008 represent averages of the LOD and LOQ for each substance and analysis; trace values from 2009 onward are the actual measured concentrations. Although trace concentrations are less precise and, hence, should probably be omitted from long-term trend analyses, they are important to record to examine the contribution of high-flow events during the winter period to pesticide loads to surface water. Trace values are also crucial for recording the occurrence of highly toxic substances that have environmental standards below LOQ, such as some pyrethroids. Trace values recorded for the model catchments are included in total transport estimates.

Key Characteristics of the Dataset

The dataset from the Swedish environmental monitoring program for chemical pesticides is publicly available for download (www.slu.se/en/pesticide_monitoring [Swedish University of Agricultural Sciences, 2019]). The dataset contains the following information (recorded for each individual sample): sampling location, date collected, all substances included in the analyses, concentrations (including trace concentrations), LOD, and LOQ for each individual substance. Daily average water flow in the sampled stream or river is also available for download. For flow-proportional samples, in addition to the date, the exact time of sampling is recorded, together with the water flow at the sampling time.

There are a multitude of potential uses for this dataset. Here, we provide three examples: ecological risk assessments, examination of trends of individual substances, and evaluation of different sampling strategies.

Example 1: Toxicity Index

One of the main objectives of environmental monitoring programs is to provide data for environmental risk assessments. For chemical substances, there are a multitude of approaches for evaluating the ecological risk, most of which rely on comparing measured concentrations to established toxicological threshold values for indicator organisms, expressed as, for example, toxicity units (Sprague, 1970), risk quotients (EFSA, 2014), chemical risk indices (Malaj et al., 2014), water quality criteria (Chèvre et al., 2006), and water quality objectives (WQOs) (Gustavsson et al., 2017). In addition, a number of more sophisticated approaches have been proposed, such as species sensitivity distributions (Posthuma et al., 2002), multisubstance Potentially Affected Fraction (de Zwart and Posthuma, 2005), and effect-directed analysis of what drives the toxicological effects of chemical mixtures (Altenburger et al., 2015).

The dataset presented here constitutes by virtue of its extensiveness a valuable asset for evaluating ecological risks and different approaches for such evaluations. High temporal resolution, combined with almost complete inclusion of all substances being used within the monitored catchments, the low detection limits for highly toxic substances, and the extensive supporting data available for the catchments, provides the opportunity to combine this dataset with the ecotoxicological data and method of choice to calculate and/or model environmental risks associated with chemical pesticides. Within the monitoring program, we routinely calculate the Pesticide Toxicity Index (PTI) (Eq. [1]), which is equivalent to the sum of risk quotients calculated from the regulatory acceptable concentration (Szöcs et al., 2017):

$$\mathrm{PTI} = \sum_{i=1}^{n} \frac{C_i}{\mathrm{WQO}_i} \qquad [1]$$

where *Ci* is the measured concentration for the substance *i* and WQO*i* is the water quality objective for the same substance, as established by the Swedish Agency for Marine and Water Management (HaV, 2018) or the Swedish Chemical Inspection Agency (KemI, 2015). Many of the substances analyzed within the program do not have nationally established WQOs, in which case the WQO is replaced by a value calculated within the monitoring program (in the same manner as the national WQOs) (Andersson et al., 2009; Andersson and Kreuger, 2011). The most recent list of WQOs used in the monitoring program, with references for each substance, can be found with the data (www.slu.se/en/pesticide_monitoring [Swedish University of Agricultural Sciences, 2019]).

Due to the high toxicity at low concentrations of some substances, such as pyrethroids, the WQO is sometimes lower than the LOD. This is problematic, primarily because it means that these substances may be present at undetectable yet toxic levels in surface waters. Furthermore, a slight increase in concentration of such a substance (bringing it above LOD) can produce a tremendous jump in WQO-based summation toxicity indices. This can result in erroneous conclusions regarding toxicity trends and, as a consequence, substances with an LOD < WQO should be omitted from toxicity trend analyses, unless the probability of "false" nondetects of these substances can be calculated and accounted for in the trend analyses. To demonstrate this issue, we show the annual PTI calculated for each model catchment and the two rivers (summed for all samples from each sampling location each year), first with all detected substances (Fig. 3a–b) and then excluding substances with WQO below LOD (Fig. 3c–d). This example clearly shows how the detection of only one or a few single substances at concentrations close to LOD, but well above WQO, can generate a distinct peak in summed toxicity (note peaks present in Fig. 3a but not in Fig. 3c for N34 in 2003 and 2014, for M42 in 2005, and in Fig. 3b but not Fig. 3d for Skivarpsån in 2008). It further highlights the importance of improving the LODs for substances with a high toxicity at very low concentrations, as has been noted by others (Szöcs et al., 2017).

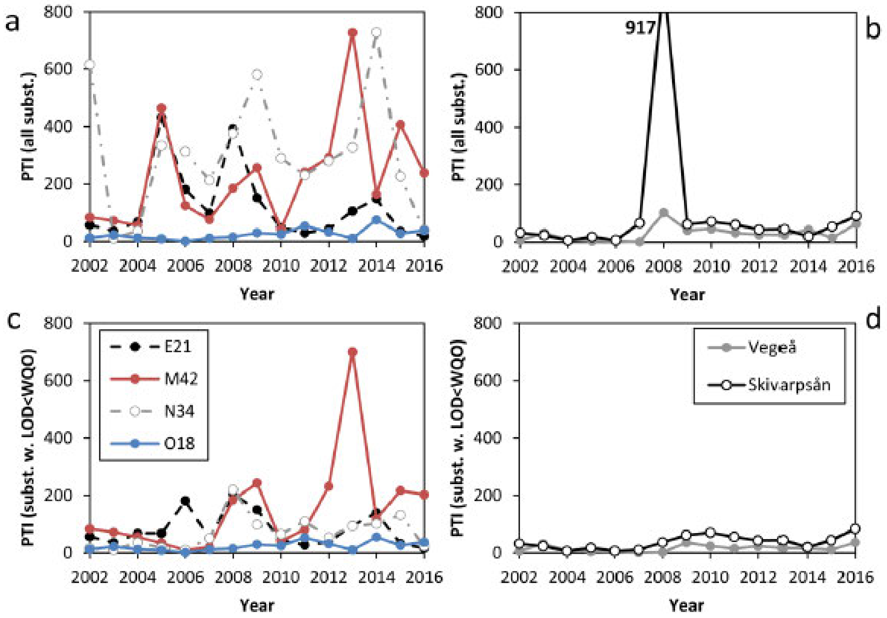


Fig. 3. Pesticide Toxicity Index (PTI) for the (a, c) model catchments and (b, d) rivers calculated for each growing season according to Eq. [1], with all detected substances (a, b) and without substances with a limit of detection (LOD) > water quality objective (WQO) (c, d). The PTI (917) for Skivarpsån in 2008 is noted numerically in (b) because it exceeded the *y* axis scale.

The PTI is just one example of how this dataset can be used for environmental assessments. We hope that publication of the dataset will encourage others to use it to test and develop alternative indices and methods of environmental assessment, such as those listed above, and to evaluate prioritized substances to include in monitoring programs. The data could also be used to guide the selection and concentrations of pesticides included in ecotoxicological tests of chemical mixtures, by providing long-term minimum, maximum, and average values of different substances in surface water within intensely farmed areas.

Example 2: Single Substance Trends

Another benefit of the Swedish monitoring program, and its long-term data with high temporal resolution, is that time series of individual substances can be evaluated. This can be of interest, for example, for substances that are newly introduced, recently banned, or subject to a dramatic change in demand, so that the environmental effect of such changes can be followed. Long-term data are also valuable for identifying substances of potential concern due to unexpectedly high concentrations or common occurrences compared with pre-approval testing and WQO values. To illustrate such changes for individual compounds, we present the long-term data for four substances (Fig. 4): (i) diflufenican, a commonly used herbicide in cereal crops, which is among the most frequently detected substances and the most frequently observed at concentrations above the WQO in the model catchments; (ii) glyphosate, another herbicide with a high detection frequency but that has never been detected in concentrations exceeding its WQO; (iii) imidacloprid, a neonicotinoid insecticide, for which a decrease of the LOD following the change in analytical method in 2009 led to a dramatic increase in the detection frequency; and (iv) terbuthylazine, an herbicide that has been prohibited from use in Sweden since 2003, with no sales registered since 1999. The slow decrease in detection frequencies and concentrations of terbuthylazine is an example of how substances can continue to affect the environment long after they have been banned (note occurrences above WQO on several occasions more than 10 yr after the last registered sale).

Figure 4 also illustrates how different substances vary in importance between different areas, depending on the crops that are grown and the climate. Overall, the differences in detection frequencies and concentrations between the model catchments are consistent with the application data for these substances. However, there is likely more information to be gained from in-depth statistical investigations of these variations and trend analyses.

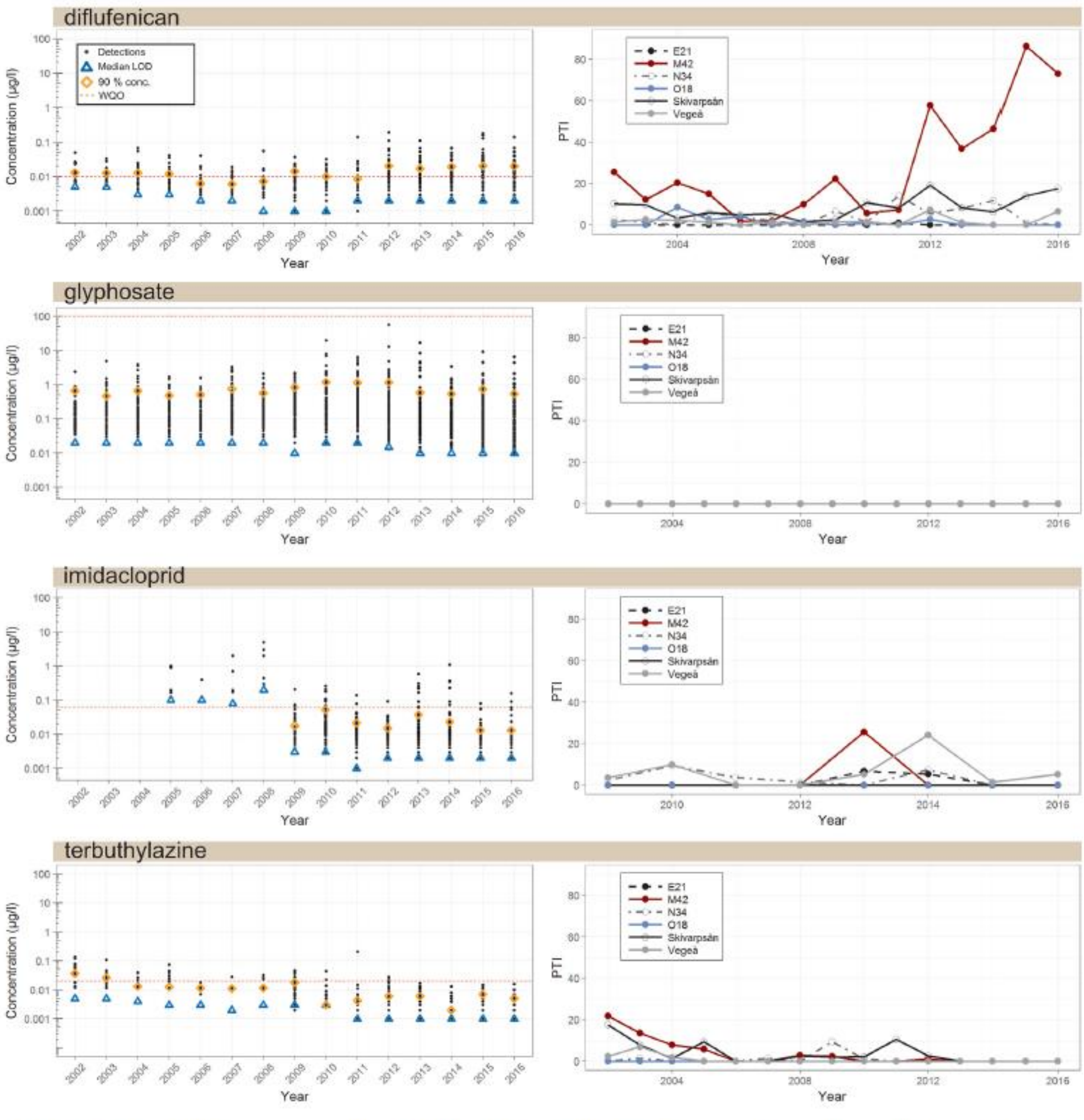


Fig. 4. Left-hand panels: All detected concentrations ($\mu g\ L^{-1}$) (black dots) of diflufenican, glyphosate, imidacloprid, and terbuthylazine plotted for each growing season (May–October, 2002–2016) together with the 90th percentile concentration for the same period (orange diamonds) and the median limit of detection (LOD) for each substance that year (blue triangles). The water quality objective (WQO) for each substance is indicated by a red dotted line within the respective panel. Right-hand panels: Corresponding Pesticide Toxicity Index (PTI) values for the same four substances within each sampling area for each growing season (2002–2016), calculated as the sum of C/WQO for samples with a concentration (C) exceeding the WQO.

Example 3: Peak Concentrations and Time-Averaged Evaluations

One of the concerns with time-integrated sampling is that peak concentrations resulting in acute toxicity effects can be missed. For this reason, flow-proportional samples have been analyzed in parallel with the time-integrated samples in model catchment M42 since 2009. In general, the highest concentrations and highest number of detected substances occur in flow-proportional samples compared with corresponding weekly composite samples (Table 6). This indicates that temporarily toxic concentrations of single substances or high summed concentrations may be missed by the time-integrated sampling approach.

Table 6. Total number of detected substances in flow-proportional samples compared to the time-integrated samples taken during the same week, per growing season in model catchment M42.

Total number of substances detected in ≥1 sample	2009	2010	2011	2012	2013	2014	2015	2016
Flow-proportional samples	36	37	68	63	67	51	63	63
Time-integrated samples	36	34	52	61	49	43	53	49
Detected in								
Both sample types	32	31	51	55	48	40	49	49
Flow-proportional samples only	4	6	17	8	19	11	14	14
Time-integrated samples only	4	3	1	6	1	3	4	0

However, plotting the ratios of concentration in flow-proportional and corresponding time-integrated samples shows that, in general, the concentrations are relatively consistent between the sampling methods and that concentration discrepancies between the two sampling strategies occur in both directions (Fig. 5). Further, the quotient between the concentrations is very rarely outside of the range 0.1 to 10 (i.e., most diverging concentrations are still within an order of magnitude of each other), suggesting that the risk of missing toxic concentrations with the weekly time-integrated approach is relatively low, at least in this catchment.

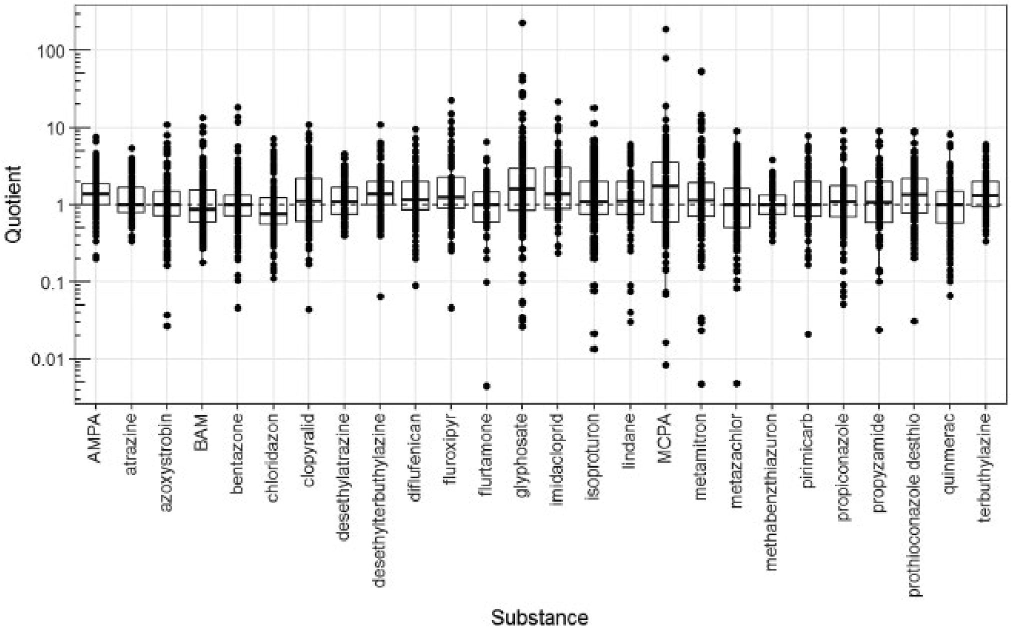


Fig. 5. Box-plot showing the quotient between concentrations in flow-proportional samples and time-integrated samples taken during the same week (2009–2016) in model catchment M42 for all substances with >80 detections in both types of samples. Only quotients where the flow-integrated samples were taken at a time of increased flow relative to the weekly average are included. AMPA, aminomethylphosphonic acid; BAM, 2,6-dichlorobenzamide; MCPA, (4-chloro-2-methylphenoxy)acetic acid.

Summary

Continuous monitoring for almost two decades of a large number of substances in four catchments characteristic of intensive Swedish agricultural regions makes the dataset of the Swedish national environmental monitoring program of pesticides in surface waters an exceptional resource for examining long-term trends in pesticide occurrences and environmental impact from agriculture. The dataset is unique in its high temporal resolution combined with the comprehensive screening of substances, including several that are normally omitted from monitoring programs (Moschet et al., 2014; Stone et al., 2014) due to analytical difficulties, e.g., glyphosate (which requires a separate method), neonicotinoids, and pyrethroids (which are toxic at concentrations below or around LOD for many analytical methods). Although the most intense monitoring activities are conducted in small catchments, the inclusion of the two rivers in the program links the observations from first-order streams to higher-order recipient rivers (Fig. 2), providing an important scaling feature of the dataset. The parallel flow-proportional sampling performed in one of the catchments provides the opportunity to examine the influence of sampling strategies, as well as the impact of high-flow events on the concentrations and number of detections and WQO exceedances. Additionally, continued time-integrated sampling through the winter season in two of the catchments provides insights into the off-season transport of pesticides and how this varies, depending on substance.

Because the monitoring program is performed in parallel with the program for environmental monitoring of nutrient losses from agriculture (Kyllmar et al., 2014), it offers unique opportunities for broad risk assessments of agricultural practices. Together, the two datasets provide a solid background for targeted studies, such as similarities and dissimilarities in pesticide substance and nutrient behaviors, overall ecological impacts of agriculture, or dominant transport processes related to soil type. Access to high-resolution, long-term data can, for example, help direct the timing or location of additional sample collection activities or the tailoring of questionnaires to obtain additional information from farmers. The extensive dataset is also a rich source of information for meta-analyses and efforts to validate models, and selected subsets of the dataset (depending on the question) can be included in international trend analyses or surveys of pesticide occurrences in surface waters.

It should be reemphasized that the aim of the program is to capture all pesticide occurrences in surface water within the model catchments, which together with the targeting of intensive agricultural catchments automatically puts the data in the "worst-case" scenario for current conventional agricultural management practices in these regions. Further, the program is designed to reflect reality in agricultural catchments, without manipulation or control over the management practices or natural processes. Thus, irregular events (e.g., unreported cleaning of equipment or preferential flow due to temporarily disturbed soil) that could lead to point-source leaching are not taken into account and may contribute to uncertainties in trend analyses and interpretations of causal mechanisms, as is often the case for environmental monitoring datasets. However, the no-interference design ensures that the data is representative of real-life agricultural impacts and not affected by experimental biases or manipulations.

Assessment and conclusion by RMS:

This study reference came out in the literature search performed by applicant and summarized under point B.8.6 of volume 3CA_B-8. The study has been considered relevant after detailed full-text assessment, but as supplementary information by applicant (cat B) and was not summarized and not included in its submission for monitoring data. After review of the full text, RMS eventually considered it provides reliable information (with restrictions) that should be presented in the present section B.8.5.

This study relies on results from the Swedish monitoring campaign and describes examples on how the data can be handled for different purposes: for toxicity assessments, trend analyses, and comparison between sampling strategies.

It therefore describes the strategy and design of the Swedish environmental monitoring program for chemical pesticides in surface waters and provide data generated within this program since 2002. The results however are not detailed and can only be read on graphical plots and therefore the study is considered reliable with restrictions.

Still, results plotted in fig 4 give indication of the profile of the measured concentration of glyphosate in all samplings over time. 90th percentile of all sampling seem stable over the years, being around 1 µg/L (note that log scale dos not allowe precise reading from the graphs). RMS indicates that the results from this campaign may be included in the review from [redacted], 2020 and [redacted], 2016. However, this could not be checked in detail by RMS (Note that the maximum glyphosate concentration of 370 µg/L reported in [redacted], 2020 for the period 1997-2018 in Swedish monitoring is not seen here).

The monitoring is performed in areas with predominantly arable land that are representative of, and located in, Sweden's major agricultural regions. The program is performed in four small catchments (E21, M42, N34, and O18), referred to as model catchments, and two rivers, Skivarpsån and Vegeå, within separate, dominant agricultural regions in southern Sweden. It is a long-term (>15 yr), continuous (weekly or every other week), time-integrated program.

Data point:	CA 7.5/036
Report author	Di Guardo, A., Finizio, A.
Report year	2018
Report title	A new methodology to identify surface water bodies at risk by using pesticide monitoring data: The glyphosate case study in Lombardy Region (Italy)
Document No	*Science of the Total Environment 610–611 (2018) 421–429*
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

In the last decades, several monitoring programs were established as an effect of EU Directives addressing the quality of water resources (drinking water, groundwater and surface water). Plant Protection Products (PPPs) are an obvious target of monitoring activities, since they are directly released into the environment. One of the challenges in managing the risk of pesticides at the territorial scale is identifying the locations in water bodies needing implementation of risk mitigation measures. In this, the national pesticides monitoring plans could be very helpful. However, monitoring of pesticides is a challenging task because of the high number of registered pesticides, cost of analyses, and the periodicity of sampling related to pesticide application and use. Extensive high-quality data-sets are consequently often missing. More in general, the information that can be obtained from monitoring studies are frequently undervalued by risk managers. In this study, we propose a new methodology providing indications about the need to implement mitigation measures in stretches of surface water bodies on a territory by combining historical series of monitoring data and GIS. The methodology is articulated in two distinct phases: a) acquisition of monitoring data and setting-up of informative layers of georeferenced data (phase 1) and b) statistical and expert analysis for the identification of areas where implementation of limitation or mitigation measures are suggested (phase 2). Our methodology identifies potentially vulnerable water bodies, considering temporal contamination trends and relative risk levels at selected monitoring stations. A case study is presented considering glyphosate monitoring data in Lombardy Region (Northern of Italy) for the 2008–2014 period.

Methods

This paper describes a methodology to address the environmental risk analysis for surface water bodies by using pesticide monitoring data as suggested by European regulations and in particular the National Action Plan drafted by Member States in the frame of the Sustainable Use of Pesticides Directive (European Commission, 2009). Its final target is to help risk assessors to identify waterbodies mainly at risk and to prioritise vulnerated areas on the territory. The methodology shall be applied for a single pesticide and foresees two distinct steps (Figure 8.5-79):

Phase 1: acquisition of the available monitoring data (MECs: Measured Environmental Concentrations) and calculation of statistical parameters (MEC_{mean}, MEC_{median} and $MEC_{95th\ percentile}$ for each monitoring station and available year). In addition, the ratios MEC/EQS or MEC/PNEC are calculated, where MEC is one of the above described statistical parameters and EQS and PNEC are the Environmental Quality Standard and the Predicted No Effect Concentration respectively.

Phase 2: expert analysis and rules for the identification of areas at risk (Table 8.5-140).

Figure 8.5-79: Flow diagram of the methodology

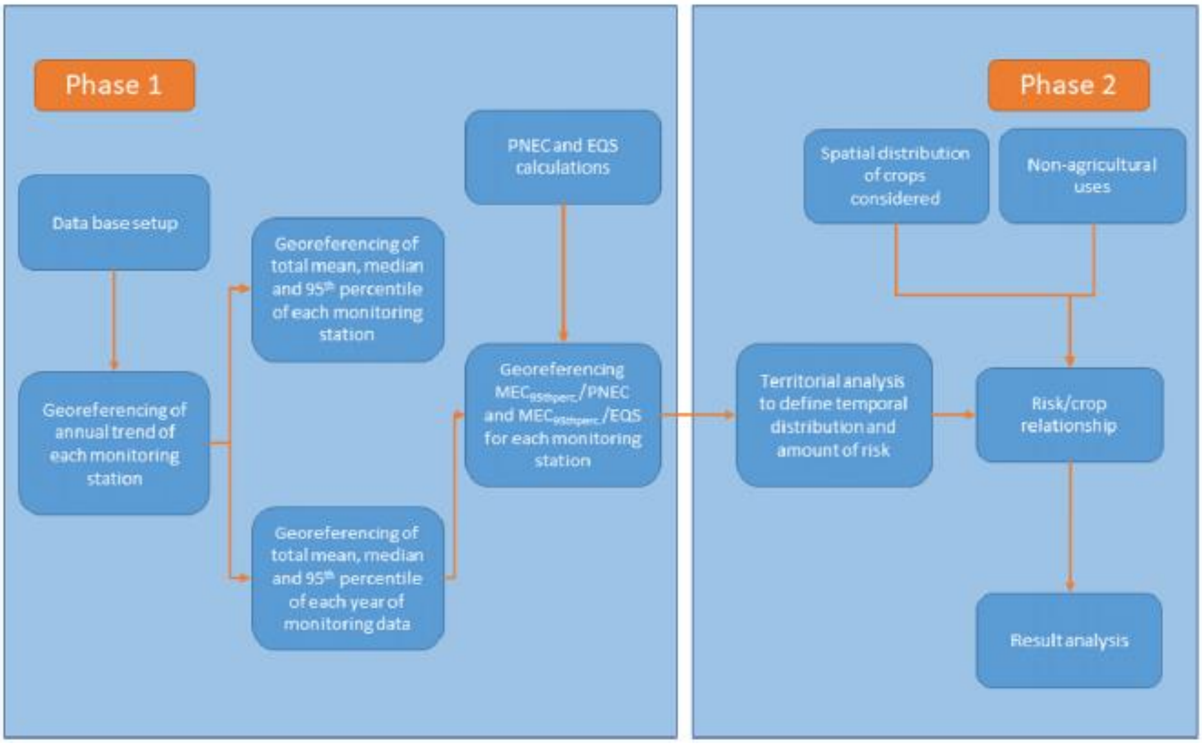
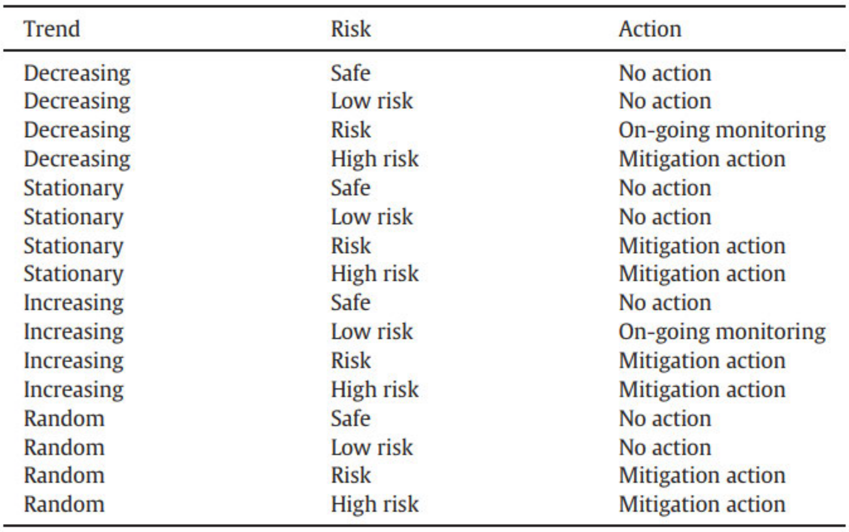


Table 8.5-140: **Scheme for the identification of mitigation actions based on temporal trend and risk analysis from surface water monitoring data of pesticides**



Trend	Risk	Action
Decreasing	Safe	No action
Decreasing	Low risk	No action
Decreasing	Risk	On-going monitoring
Decreasing	High risk	Mitigation action
Stationary	Safe	No action
Stationary	Low risk	No action
Stationary	Risk	Mitigation action
Stationary	High risk	Mitigation action
Increasing	Safe	No action
Increasing	Low risk	On-going monitoring
Increasing	Risk	Mitigation action
Increasing	High risk	Mitigation action
Random	Safe	No action
Random	Low risk	No action
Random	Risk	Mitigation action
Random	High risk	Mitigation action

Case study
In order to test the methodology, as a case study, we considered the already available historical series of monitoring data (2008–2014) of glyphosate residues in surface water bodies of Lombardy Region in Northern Italy. The data were gathered from the Environmental Protection Agency of the Lombardy Region (ARPA Lombardia).

Glyphosate (*N*-(phosphonomethyl)glycine) is a broad-spectrum systemic herbicide used to kill weeds, especially annual broadleaf weeds and grasses known to compete with commercial crops grown around the globe. In Italy, glyphosate has been authorized both for agricultural and non-agricultural uses. According to the most recent pesticide sales statistics, in 2014 usage of glyphosate in Lombardy Region reached a volume of about 585 Tonnes and because of this important figures we selected glyphosate as test case for our methodology.

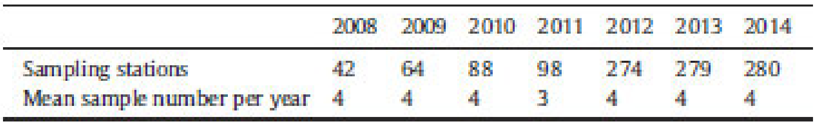
For glyphosate, at EU level, there is no an established EQS; since our elaborations are referred to an Italian scenario, we used a value of 0.1 µg/L. This value is suggested by the Italian regulation in absence of an EQS. In addition, for comparative purposes, we have also considered a PNEC value of 112 µg/L as suggested by Lombardy Region in the document implementing the National Action Plan (Giunta regionale della Regione Lombardia, 2015). Using both values (0.1 µg/L and 112 µg/L) allowed us to highlight the importance of setting appropriate EQS values for pesticides to help risk assessor in the decision-making process for risk mitigation measures on the territory.

Lombardy region has an extension of about 23.844 km^2 which almost a half of it is plain (47%) and the rest consists of hills (12%) and mountains (41%). Flat areas extend from West to East, while mountains are located at North (Alps) and in the South-West (Apennine). The last agriculture census reports that arable crops are cultivated in the 92.1% of the available crop area of the Lombardy plain, while the remaining part is dedicated to woody crops and grasslands; maize is the main crop of the Lombardy region, where it covers almost a half of the total arable area. In Lombardy, there are 669 rivers (520 natural rivers and 149 artificial channels) and 56 lakes (32 natural lakes and 24 artificial reservoirs).

The historical series (2008–2014) of monitoring data for surface water of Lombardy Region was provided by ARPA Lombardia, which oversees the official environmental monitoring for the entire Region. The analytical method utilized for determination of glyphosate was based on the derivatization with 9-fluorenylmethylchloroformate (FMOC-Cl), separation with high performance liquid chromatography (HPLC).

ARPA Lombardia positioned sampling stations considering the most important river courses and the density of the hydrographic network in Lombardy Region. The number of sampling stations of glyphosate increased during the considered period (Table 8.5-141) as more concern about this herbicide arose during last years, passing from an average value of 73 in the 2008–2011 period to 278 in the 2012–2014 period. On the contrary, the number of sampling per year has been fairly constant in all the considered period (4 sampling per year), as well as the Limit of Detection (LOD) which remained set at the value of 0.1 µg/L.

Table 8.5-141: Number of sampling stations in which glyphosate was included in the monitoring programme

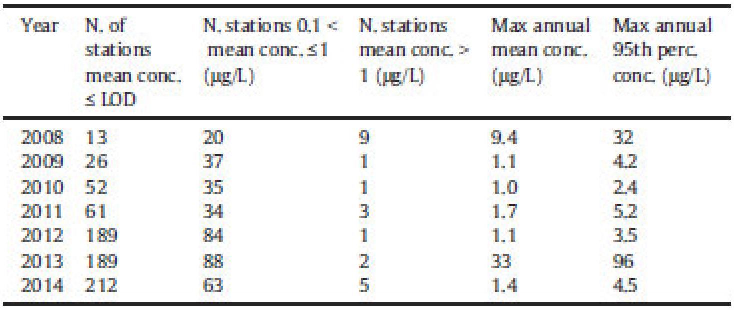


	2008	2009	2010	2011	2012	2013	2014
Sampling stations	42	64	88	98	274	279	280
Mean sample number per year	4	4	4	3	4	4	4

Results

Phase 1 of the proposed methodology foresee the development of a georeferenced statistical database. As an example, in our case study, means and 95th percentiles values of MECs for glyphosate were calculated for each sampling station and for all available years. In Table 8.5-142, the annual mean of the herbicide residues (µg/L) measured in surface water bodies of Lombardy Region are summarized. Particularly, the monitoring stations were divided in three different clusters (mean conc. ≤ 0.1; 0.1 b mean conc. ≤ 1; mean conc. >1). In the same Table, maximum annual means and maximum 95th percentiles of concentrations are also reported.

Table 8.5-142: **Monitoring stations subdivided for class membership of the annual mean and 95th percentile of glyphosate concentration (0.1 µg/L = LOD) and maximum annual mean and 95th percentile detected across all the stations**



Year	N. of stations mean conc. ≤ LOD	N. stations 0.1 < mean conc. ≤1 (µg/L)	N. stations mean conc. > 1 (µg/L)	Max annual mean conc. (µg/L)	Max annual 95th perc. conc. (µg/L)
2008	13	20	9	9.4	32
2009	26	37	1	1.1	4.2
2010	52	35	1	1.0	2.4
2011	61	34	3	1.7	5.2
2012	189	84	1	1.1	3.5
2013	189	88	2	33	96
2014	212	63	5	1.4	4.5

From Table 8.5-142 and plots of the spatial representation of the 95th percentile of concentrations of glyphosate for 2008, 2010, 2012 and 2014 years (not shown) the following considerations can be made:

- during the considered period, there has been an increase in the number of monitoring stations for glyphosate; however, this did not correspond to a linear increase in contaminated sites where glyphosate has been detected in concentrations above 0.1 µg/L. For example, in 2008 there was 29 contaminated sites and 42 monitoring stations for glyphosate (69% of contaminated sites) while in 2014 figures were 68 and 280 respectively (24% of contaminated sites);
- the presence of glyphosate in surface water bodies of Lombardy Region seems to be widespread. Even if the annual mean of MECs are less than the LOD, the residues of this herbicide were measured at least once a year in almost every monitoring stations;
- there is a large spatial and temporal variability of MECs; for example, during different years, even in the same monitoring station, concentrations range from values below the LOD up to tens of µg/L. The highest values of glyphosate concentrations were measured in the areas of Cremona and Mantova (South-Eastern part of the region) which reached annual mean concentrations of 33 µg/L (highest MEC = 108 µg/L) in 2013 and 9.4 µg/L (highest MEC = 38 µg/L) in 2008, respectively. However, in other years, MEC values were more evenly distributed. Consequently, these spike values could be then explained with occasional events such as improper uses of the pesticide.

As a further analysis, we calculated the I(95perc/EQS) index either considering the substance characteristics and in a worst-case perspective. For glyphosate, an EQS of 0.1 µg/L was considered; this represents the regulatory default value in Italy to be used in absence of an EQS at EU level. However, we also considered a PNEC value for glyphosate of 112 µg/L in order to evaluate the importance of EQS in the perception of risk on a territory. If the ratio I(95perc/EQS) (or in alternative I(95perc/PNEC)) is above 1 the water body is considered risk.

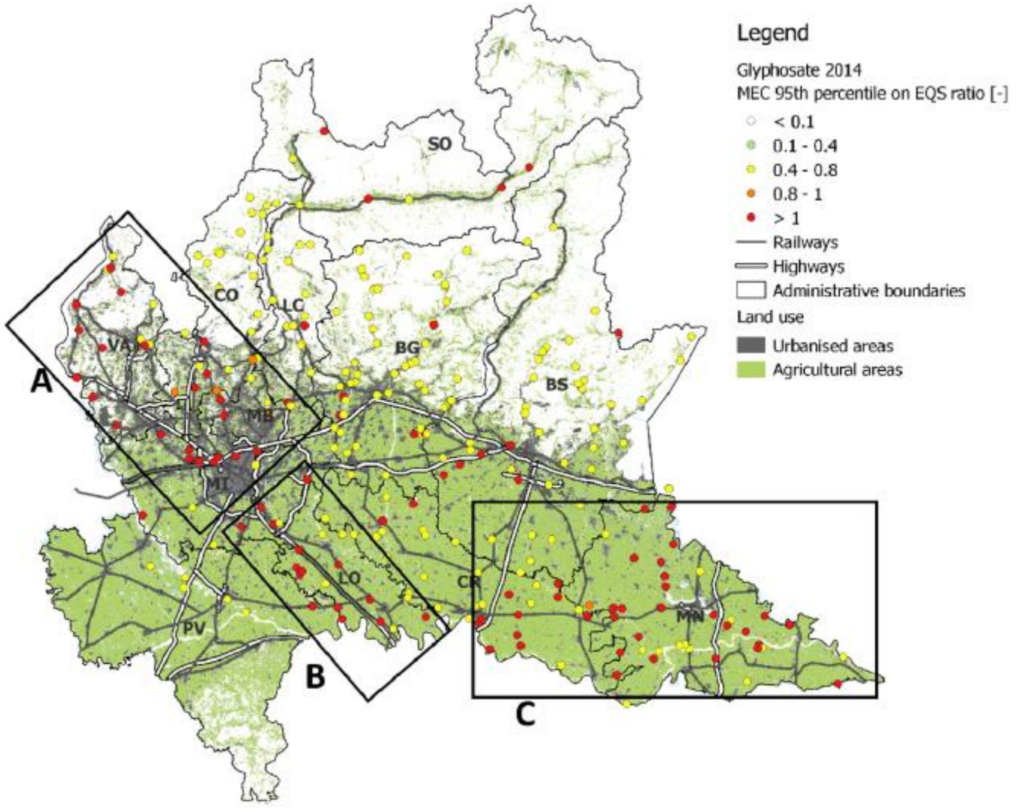
It is worth noting the differences when we take into consideration PNEC values instead of the regulatory EQS. The index I(95perc/PNEC) is always <0.1, which is at least an order of magnitude lower than a potential risk for aquatic organisms. In ANNEX VIII of the EU Water Framework Directive (WFD), glyphosate is listed among the so called “Specific Pollutants”. They are defined as substances that can have a harmful effect on ecological quality, and which may be identified by Member States as being discharged to water in “significant quantities”. Surface water bodies are assigned to one of the Directive's five ecological status classes – High, Good, Moderate, Poor or Bad. The EQS for Specific Pollutants contribute to ecological status classification; in fact, where a standard is failed the water body cannot be classed as Good. In a previous work (Finizio *et al.*, 2011) it was demonstrated that the use of a value of 0.1 µg/L, as a surrogate of EQS cannot be considered appropriate for the evaluation of the effects of pesticides on the aquatic communities, as each pesticide is characterised by its own inherent toxicity for different non-target organisms. In that study, this was clearly evident when the procedures for setting EQS (based on the calculation of PNECs) suggested by the WFD was considered. In fact, the differences in risk characterisation, depending on the approach used, were quite evident. In general, the risk for surface water seemed to be higher in the case of insecticides when the PNEC approach was used. On the contrary, the criterion of the 0.1 µg/L cut-off indicated herbicides as the major driver of risk for surface water. These considerations highlight the importance of the availability of well-defined EQS for pesticides both for an appropriate classification of the ecological status of surface water bodies and for a proper action of risk management of these substances.

The second phase of the methodology sets rules for the prioritization of areas where mitigation actions on the territory should be taken in place. It is articulated in three different steps.

Firstly (step 1), a territorial analysis is performed to get a picture of the spatial and temporal distribution of the water bodies at risk on the territory. In our case study, we identified 192 sites in which at least in one year the I(95perc/EQS) was above 1. Particularly, we identified 14 safe sites (I(95perc/EQS) < 0.8), 27 sites at low risk (0.8 < I(95perc/EQS) < 1) 54 sites at risk (1 < I(95perc/EQS) < 2) and 97 sites at high risk (I(95perc/EQS) > 2). Furthermore, the territorial analysis also allowed the identification of the temporal trend of risk for each of the available monitoring sites. Particularly, we identified 12, 34, 30, and 114 sampling sites with a random, decreasing, increasing or stationary temporal trends respectively (2 sites were not classified due to paucity of data).

The second step of phase II links the risk distribution for surface water bodies with the uses of pesticides on the territory. Consequently, it gives precious information about the identification of potential sources of contamination, which should be reduced through risk mitigation actions. In our case, we considered both the agricultural and non-agricultural uses of glyphosate. We used the GIS technique of overlaying the map of I(95perc/EQS) index with maps of major transportation infrastructures and agricultural land use (all crops). Results are reported in Figure 8.5-80.

Figure 8.5-80: **Analysis of areal clusters by overlying I_{EQS}^{95perc}, land use and infrastructural networks maps**

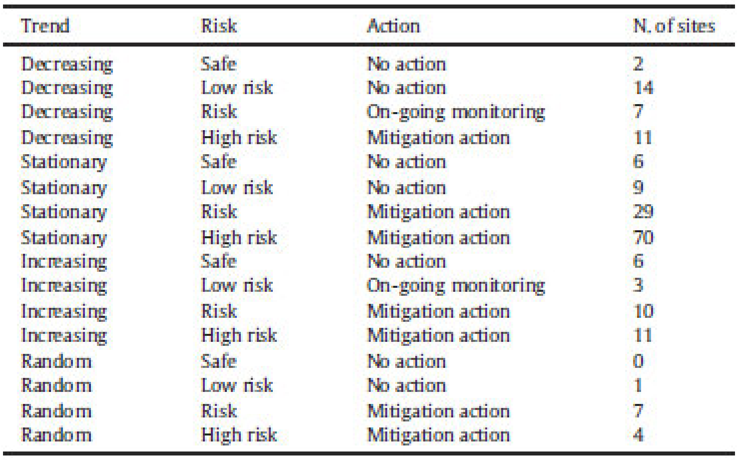


In Figure 8.5-80 we identified three main areal clusters where the exceeding of the index threshold is steady during the period (A = Monza-Brianza and North Milan provinces; B = Lodi and Pavia provinces; C = Mantua province). The map in this figure refers to the year 2014, but the same behaviour can be steadily observed in all the available years.

Cluster A is a highly-urbanised area with a strong presence of road infrastructures: in this area glyphosate residues in monitoring stations could be linked to non-agricultural uses. Cluster C is in an area with prevailingly rural activities and therefore the presence of glyphosate in surface water is linked to agricultural uses (particularly maize). The case of cluster B is in the middle of the other two: the area is typically rural, but it is crossed by some of the most important regional rail and road networks.

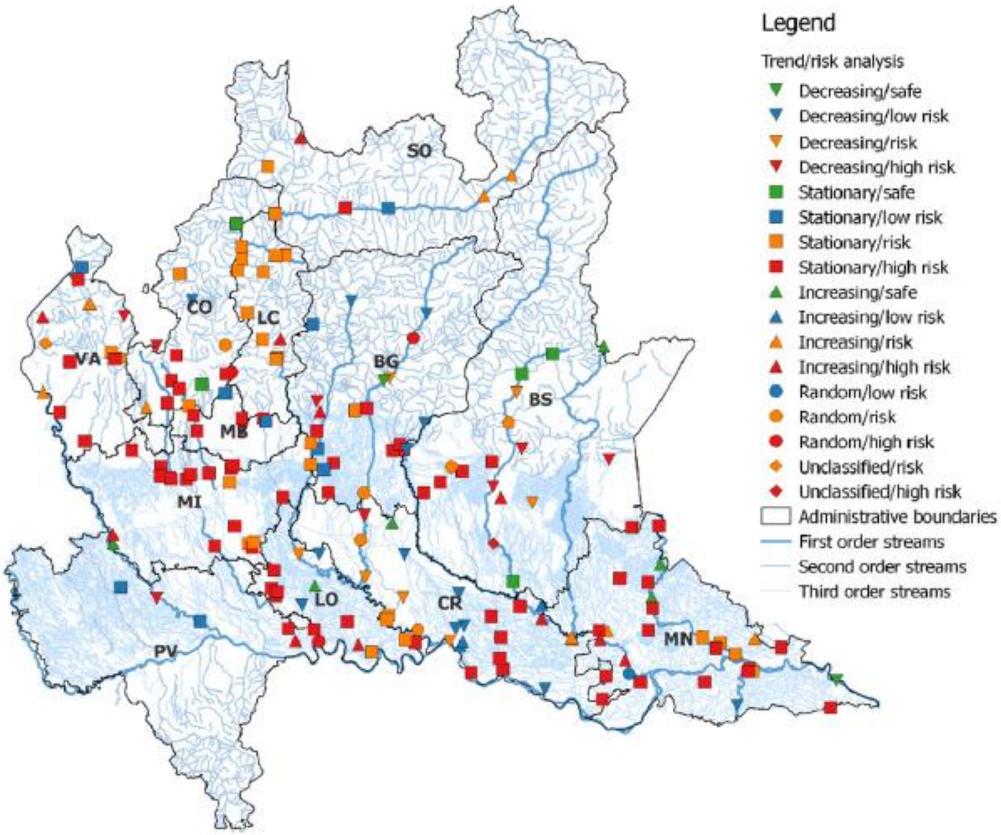
In the third step of phase II, and following the expert judgement schema reported in Table 8.5-140, risk managers can identify areas where mitigation actions should be undertaken. In Table 8.5-143, the combination of temporal trend and risk analyses (step 1 of phase II) together with the proposed actions for glyphosate are reported. They are also represented in Figure 8.5-81.

Table 8.5-143: **Number of sites categorised by trend and risk**



Trend	Risk	Action	N. of sites
Decreasing	Safe	No action	2
Decreasing	Low risk	No action	14
Decreasing	Risk	On-going monitoring	7
Decreasing	High risk	Mitigation action	11
Stationary	Safe	No action	6
Stationary	Low risk	No action	9
Stationary	Risk	Mitigation action	29
Stationary	High risk	Mitigation action	70
Increasing	Safe	No action	6
Increasing	Low risk	On-going monitoring	3
Increasing	Risk	Mitigation action	10
Increasing	High risk	Mitigation action	11
Random	Safe	No action	0
Random	Low risk	No action	1
Random	Risk	Mitigation action	7
Random	High risk	Mitigation action	4

Figure 8.5-81: **Map of trend and risk analysis on the selected monitoring stations of Lombardy region with details of places where mitigation actions are suggested (following Table 8.5-142)**



Conclusion

This study proposes a new methodology for risk managers to implement pesticide risk mitigation measures for surface water bodies at the territorial. The methodology combines GIS techniques and statistical analyses on historical series of monitoring data of PPPs. The latter are derived from national monitoring plans of pesticides residues in surface water. In order to show the proposed approach, the glyphosate in Lombardy region as a case study was proposed. In brief, the analysis highlighted a wide- spread presence of glyphosate in surface water bodies in Lombardy Region; almost the 50% of the monitoring stations considered in Phase II of the methodology shows a contamination level that should be deepened and seamlessly mitigation actions should be foreseen. In several cases the risk could be attributed to a non-agricultural use of glyphosate. In fact, many monitoring stations classified at risk or high risk are in highly urbanised areas or near railways or major roads. Finally, in this paper, we highlighted that the perception of which substances might present a risk for surface water can be completely different according to the cut-off criteria identified. In fact, the perception of risk posed by glyphosate (or other pesticides) completely changes if the regulatory value of 0.1 µg/L or a more scientifically sound PNEC value is used. This could have significant consequences in the classification of the ecological status of surface water bodies and for implementing appropriate risk mitigation actions on the territory.

Assessment and conclusion by applicant:

The article presents an approach for combining long-term surface water monitoring data from the Lombardy Region of Northern Italy with GIS analysis to identify contamination levels and implement pesticide risk mitigation measures for surface water bodies No experimental or monitoring data were generated. The measured maximum concentration of glyphosate was 108 µg/L in 2013.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

This article describes the developpement of a methodology to identify vulnerable water bodies, combining GIS techniques and statistical analyses on historical series of monitoring data of PPPs. As such, it is mainly aimed at developing risk management priorities and was not further assessed here.

However, it provides results from the Lombardia monitoring program from the period 2008-2014, that were apparently not included in the monitoring raw data review of [redacted], 2020 (CA 7.5/002) or [redacted], 2016 (CA 7.5/010). Maximum value reported for glyphosate is 108 µg/L in 2013.

The article is considered reliable with restrictions.

Data point:	CA 7.5/037
Report author	Huntscha, S. *et al.*
Report year	2018
Report title	Seasonal Dynamics of Glyphosate and AMPA in Lake Greifensee: Rapid Microbial Degradation in the Epilimnion During Summer
Document No	Environ. Sci. Technol. 2018, 52, 4641-4649
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

Occurrence and fate of glyphosate, a widely used herbicide, and its main metabolite AMPA was investigated in Lake Greifensee, Switzerland. Monthly vertical concentration profiles in the lake showed an increase of glyphosate concentrations in the epilimnion from 15 ng/L in March to 145 ng/L in July, followed by a sharp decline to <5 ng/L in August. A similar pattern was observed for AMPA. Concentrations of glyphosate and AMPA in the two main tributaries generally were much higher than in the lake. Simulations using a numerical lake model indicated that a substantial amount of glyphosate and AMPA dissipated in the epilimnion, mainly in July and August, with half-lives of only ≈2-4 days which is ≫100 times faster than in the preceding months. Fast dissipation coincided with high water temperatures and phytoplankton densities, and low phosphate concentrations. This indicates that glyphosate might have been used as an alternative phosphorus source by bacterio- and phytoplankton. Metagenomic analysis of lake water revealed the presence of organisms known to be capable of degrading glyphosate and AMPA.

Materials and methods

Field Site: Greifensee and its Catchment Area.

The field study was conducted in the catchment area of Lake Greifensee, a eutrophic lake located near Zurich, Switzerland (47°21′N, 8°41′E). The lake has a surface area of 8.46 km^2 (length: 6.5 km; width: 1.9 km), a maximum depth of 32 m, and is dimictic with vertical mixing from surface to bottom in autumn and spring. During the warmer season (April-November) the lake is stratified into a warmer epilimnion and a cold hypolimnion. Regular sequences of oxic (winter/spring) and anoxic conditions (summer/fall) are observed in the hypolimnion of the lake. It is fed by several tributaries of which the rivers Aa Uster and Aa Mönchaltorf contribute more than 60% of the total inflow. Its sole outflow is the river Glatt. More details on the hydrology and morphology of the lake are found elsewhere (Ulrich, M. M., 1994).

Lake Greifensee has a catchment area of 160 km^2 of which ≈50% are used as agricultural land (field crops, grassland, and some orchards). Forests (21 %), urban areas (19%), water bodies (7%), and unproductive land (3%) constitute the other 50% of the catchment area. Approximately 120 000 inhabitants are living in the catchment area, most of them in that of Aa Uster, which is more urbanized than the Aa Mönchaltorf. Eight wastewater treatment plants (WWTPs) are located in the catchment area, of which two discharge directly into the lake and one into Aa Mönchaltorf downstream of the gauging and sampling station (see Figure 8.5-82).

Figure 8.5-82: **Map of the catchment area of Lake Greifensee with sampling points. Weekly flow-proportional composite samples were obtained from the automatic sampling stations at the tributaries to the lake, Aa Uster (2) and Aa Mönchaltorf (3) as well as the outflow from the River Glatt (1). Monthly grab samples from several depths were taken at the deepest point of the lake (4). Daily flow-proportional composite samples of treated wastewater were obtained from WWTP Uster (5). The sub-catchments discharging at the sampling points 2 & 3 are marked in red and green, respectively.**

Water Sampling and Analysis

To establish a mass balance for glyphosate and its metabolite AMPA in the lake, monthly water samples were taken from 10 different depths (0, 1, 2.5, 5, 7.5, 10, 15, 20, 25, and 30 m) between March and November 2013 by regional authorities (Canton of Zurich), who also measured orthophosphate concentrations. During the same period, weekly flow-proportional composite samples of the rivers Aa Mönchaltorf, Aa Uster, and Glatt were analyzed, allowing determination of input and export loads of the two compounds, based on concentration measurements and river water discharge data. In rare cases (five incidents), when the automated sampling of the tributaries malfunctioned, concentrations were interpolated from values of adjacent weeks.

In WWTP Uster, the largest WWTP in the study area, flow-proportional, 24 h composite samples of treated wastewater were taken every 4-16 days (on average every 8.5 days). The installation operates with a mechanical, biological (activated sludge with an estimated sludge age of 17-20 days, with nitrification and denitrification), and chemical treatment (phosphate precipitation by iron salts, no chlorination), and subsequent sand filtration.

All samples were transferred to the lab in HDPE bottles, fortified with an internal standard solution ($^{13}C_2{}^{15}N$-glyphosate and $^{13}C^{15}ND_2$-AMPA), and kept at 4°C until analysis, typically within 1 week of arrival. Samples were analyzed with a method based on derivatization with fluorenylmethyloxycarbonyl chloride (FMOC-Cl), online-enrichment, reversed-phase liquid chromatography, and tandem mass spectrometry. This method does not include a filtration step so that measured concentrations comprise dissolved and sorbed glyphosate and AMPA. Limits of quantification were 5 ng/L for both compounds.

Lake Model

The software AQUASIM (Version 2.1 g, available from http://www.eawag.ch/en/department/siam/software/) was used to establish a mathematical model for simulation of vertical concentration profiles and mass balances for glyphosate and AMPA in Lake Greifensee with a temporal resolution of 1 day. It considers the morphology and hydrology of the lake as well as fate and vertical transport of chemical compounds. The lake is described by 128 horizontal boxes of 25 cm thickness, for which horizontal mixing within 1 day is assumed. Vertical mixing is described by time- and depth-dependent diffusion coefficients derived from fitting water temperatures to measured vertical temperature profiles.

A water balance was set up with discharge data from gauging stations of the three largest tributaries and the outflow of the lake, lake water levels, evaporation, and precipitation data. The discharge of the remaining nine minor tributaries was calculated by the difference of the above-mentioned. Subsurface water exchange can be neglected (<5%).

Chemical input of glyphosate and AMPA into the lake was modeled to occur exclusively through the tributaries into the epilimnion of the lake. For the unknown inputs from those tributaries that were not sampled, average concentrations of Aa Mönchaltorf and Aa Uster were used and multiplied with the estimated discharge (see above). Input through the three WWTPs was calculated from the sum of their discharge and the concentrations found in WWTP Uster, which accounts for >85% of the treated wastewater directly entering the lake.

The model comprises a degradation process in the lake's epilimnion which was implemented as a (pseudo) first-order degradation in the upper 0.5 m layer of the lake. Through the fast vertical diffusion within the epilimnion, this degradation process affects the concentrations in the whole epilimnion. The degradation rates reported in the Results and Discussion section were thus recalculated using the actual depth of the epilimnion (based on temperature profiles) to refer to the whole epilimnion.

Metagenomic Sequencing

Lake Greifensee water was sampled at three depths (0, 2.5, and 7.5 m) on 7 July 2014. 1 L of lake water per sample was then centrifuged at 5000 rcf for 10 min and the pellet was stored at -20°C until further processing. Total DNA was extracted using the PowerSoil DNA isolation kit (MO BIO, Carlsbad, CA). The integrity of the DNA was assessed on agarose gels and the quantity was measured by the Quant-iT PicoGreen kit (Invitrogen, Carlsbad, CA). Libraries were generated and indexed using the TruSeq DNA library preparation kit (Illumina, San Diego, CA) and sequenced on an Illumina MiSeq generating 300 bp paired end reads available under (https://www.mg-rast.org/linkin.cgi?project=mgp1139). All metagenomic data analyses were performed on the MG-RAST server.

Results

Major Inputs of Glyphosate and AMPA to the Lake from Tributaries and WWTP Uster

Glyphosate concentrations in the weekly composite samples from the two main tributaries ranged from <5 to 1430 ng/L (median, 145 ng/L in Aa Mönchaltorf and 175 ng/L in Aa Uster). The highest concentrations appeared in July and August in Aa Mönchaltorf and in March and July in Aa Uster, which is consistent with the main agricultural uses of glyphosate for treatment of sugar beet and maize fields prior to seeding in spring and postharvest treatment of cereal fields in summer. Urban use of glyphosate is not so well-defined, but is expected to have a higher impact on the concentrations in Aa Uster, which has a higher percentage of urban land use. Glyphosate concentrations in treated wastewater from WWTP Uster were between 18 and 350 ng/L (median, 106 ng/L) with maximum concentrations in June and September, when they exceeded those in the tributaries.

AMPA concentrations in the two main tributaries ranged from 24 to 415 ng/L (median, 150 ng/L in both rivers). Similar to glyphosate, the highest AMPA concentrations were found in July (Aa Uster) and August (Aa Mönchaltorf). Concentrations in treated wastewater from WWTP Uster reached up to 1680 ng/L (median, 516 ng/L), and were thus higher than those in the tributaries at all sampling times. Maximum concentrations in wastewater were found in August and September. AMPA is also a degradation product of various phosphonates used in industry and degradation of these compounds to AMPA in WWTPs likely is an important source of AMPA in Lake Greifensee.

Spearman's rank correlation analysis indicated fairly strong correlation of glyphosate and AMPA concentrations in the more rural tributary Aa Mönchaltorf ($\sigma = 0.70$, $p < 0.001$) suggesting that the occurrence of AMPA in this stream probably was related to the use of glyphosate in the catchment area. In contrast, in the more urban tributary Aa Uster, there was no apparent correlation ($\sigma = 0.31$, $p = 0.09$) indicating that AMPA may, at least in part, be derived from sources other than glyphosate in the catchment. Even in treated wastewater from WWTP Uster, the correlation between glyphosate and AMPA was higher ($\sigma = 0.62$, $p < 0.001$) than in Aa Uster. The best correlation, however, was found in the outflow of the lake ($\sigma = 0.83$, $p < 0.001$). This is most likely due to the similar fate of the two compounds (see below) rather than similar sources.

Weekly loads of glyphosate into Lake Greifensee (Figure 8.5-83b) were up to 0.97 and 0.63 kg in Aa Mönchaltorf and Aa Uster, respectively. Inputs from the more urbanized catchment area of Aa Uster were highest and quite uniform between March and June. From July on, these inputs decreased to lower levels. Inputs from the agriculturally dominated catchment area of Aa Mönchaltorf started later (mid-April) and fluctuated with a clear maximum during the rainiest week at the end of May. Glyphosate loads from WWTP Uster were generally low and lower than those in the tributaries at all times. Highest loads from WWTPs were found in June.

Weekly loads of AMPA into Lake Greifensee (Figure 8.5-83c) reached their maximum in the week with the highest precipitation, with values of 0.64 and 0.57 kg for Aa Mönchaltorf and Aa Uster, respectively. In other weeks, AMPA loads were generally below 0.3 kg. Median AMPA loads from treated wastewater of WWTP Uster were 0.08 kg/week with a maximum of 0.14 kg in September. Compared with glyphosate, wastewater delivered significant amounts of AMPA, which regularly reached levels similar to those in one of the tributaries and even exceeded the loads in both main tributaries in the first week of September.

Figure 8.5-83: Daily precipitation in 2013 at a nearby weather station and water discharges at the outflow of Lake Greifensee (Glatt River) and the two main tributaries, Aa Uster and Aa Mönchaltorf (a). Mass loads of glyphosate (b) and AMPA (c) which were transported to and eliminated from the lake, respectively. Concentrations of glyphosate and AMPA (symbols indicate measured values, lines modeled concentrations) as well as phosphate in the uppermost 5 m of Lake Greifensee (d). Chl a was measured either monthly at a depth of 1 m (symbols) or in situ over a depth of 1.5-16 m (the line indicates mean values from 1.5 to 8 m).

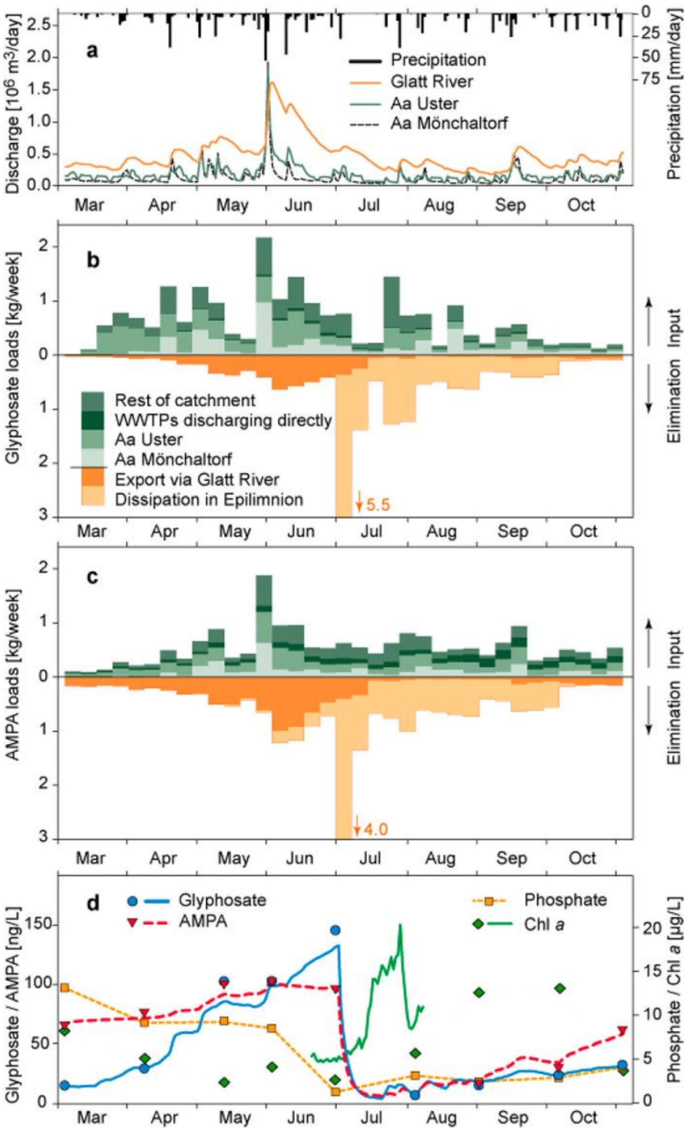
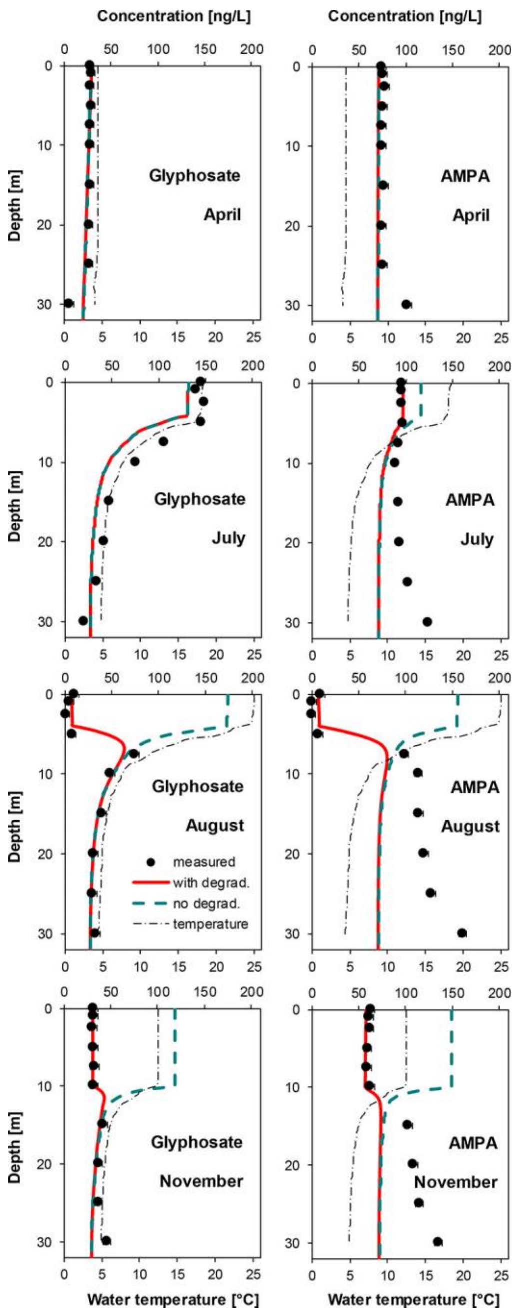


Figure 8.5-84: **Selected vertical concentration profiles of glyphosate (left) and AMPA (right) in Lake Greifensee, 2013. Measured values (circles) are compared to simulated concentrations assuming no degradation (blue dashed lines) or degradation in the epilimnion (red line). Also shown are the measured temperature profiles (dash dotted black lines).**



Concentrations of Glyphosate and AMPA in Lake Greifensee: Rapid Dissipation in the Epilimnion During Summer

Vertical concentration profiles of glyphosate and AMPA in Lake Greifensee were measured monthly between March and November 2013. Selected profiles are shown in Figure 8.5-84. In March and April, glyphosate concentrations were uniform at all depths except for the lowermost sample, which showed lower glyphosate concentrations. Concentrations (slowly) increased from ≈14 ng/L in March to 28 ng/L in April.

Between April and May, rising surface water temperatures initiated the stratification of the lake with the

formation of an epilimnion in the upper 4-6 m and a hypolimnion in the lowest 20 m. Both are divided by the metalimnion with a pronounced temperature (and thus density) gradient, which restricts water exchange between the epi- and the hypolimnion. Hence, beginning in May, glyphosate epilimnion concentrations increased steadily to values higher than 100 ng/L due to inputs from the tributaries, whereas hypolimnion concentrations remained constant (≈35 ng/L).
In July, epilimnion concentrations of glyphosate reached a maximum of 145 ng/L (Figure 8.5-84). However, between July and August, a sudden drop of glyphosate concentrations occurred in the epilimnion down to levels below the limit of quantification of 5 ng/L, despite further inputs through the tributaries. This is also illustrated in Figure 8.5-83d, where average epilimnion concentrations are plotted over time. These observations indicate a sudden, rapid dissipation in the epilimnion, which will be discussed in detail below.

From September onward, glyphosate concentrations again slowly increased due to further inputs, but also due to the fact that the depth of the epilimnion was increasing, causing mixing with water from deeper layers containing higher concentrations. Eventually epilimnion concentrations reached 30 ng/L in November (Figure 8.5-84).

For AMPA, a similar temporal pattern was observed as for glyphosate. Initial concentrations of AMPA were higher (70 ng/L) than those of glyphosate (14 ng/L), but they increased to only 100 ng/L until July. Between July and August, the same distinct concentration drop was observed in the epilimnion as for glyphosate, suggesting that the same dissipation process acted on both compounds. In the following months, AMPA epilimnion concentrations recovered to preseason levels of about 60 ng/L.

In contrast to glyphosate, AMPA concentrations in the hypolimnion increased, even after the stratification of the lake starting in April, up to concentrations of 130 ng/L in August (Figure 7.5-79). Since the metalimnion prevents water exchange between epilimnion and hypolimnion, this increase cannot originate from input by the tributaries. Furthermore, in all vertical profiles, AMPA concentrations near the bottom (30 m depth) were higher than in the rest of the hypolimnion. This coincides with slightly lower glyphosate concentrations between March and July in the same depth as mentioned above. Although further evidence is lacking, one could speculate that AMPA may be formed by degradation of phosphonates present in the hypolimnion and in or near the sediment by degradation of glyphosate and/or other phosphonates. Moreover, in analogy to phosphate, AMPA adsorbed to bottom sediment may be released due to reductive dissolution of iron oxides under anaerobic conditions. However, since the focus of this study was to investigate the fate of glyphosate and AMPA in the epilimnion and given the complexity of the matter (numerous possible AMPA precursors, such as nitrilotris-(methylenephosphonic acid) which is used as complexing agent in detergents), formation of AMPA in the hypolimnion was not further studied.

In a less extensive study in 2014, the same glyphosate and AMPA concentration trends were found between June and September.

Mass Balance

Between March and November, the cumulative input loads of both compounds were highest in the more urbanized Aa Uster (7.9 and 6.5 kg of glyphosate and AMPA, respectively, see Figure 8.5-83b, c), followed by the agricultural Aa Mönchaltorf (5.5 and 4.2 kg) and WWTP Uster (0.65 and 2.7 kg). Further input loads from two other WWTPs (0.13 and 0.5 kg) were calculated from the sum of their wastewater discharge and the concentrations found in WWTP Uster. Loads from the tributaries not included in the sampling (7.8 and 5.7 kg) were calculated based on average concentrations of Aa Mönchaltorf and Aa Uster and the estimated discharge from the water balance.

Cumulative glyphosate input loads of about 22 kg were in stark contrast to an export via the Glatt river of only 5.4 kg. In November, about 5.1 kg glyphosate were stored in the lake which was ≈3 kg more than in March (2.1 kg). This results in a dissipated load of 13.6 kg, which was accounted for in the model by the first-order degradation process with the dissipation rates discussed in the next section. Roughly 70 % of the dissipated load (9.5 kg) was disappearing within the 5 weeks between the measurements in July and August.

For AMPA, cumulative input loads of 19.6 kg were similarly contrasted by a relatively low export load of

8.7 kg. Measured storage of AMPA increased from 10.6 kg in March to 12.1 kg in November. However, this increase is largely due to formation of AMPA in the hypolimnion. According to the model calculations (see below), 55 % of the ≈11 kg AMPA which disappeared during the study period were eliminated between the measurements in July and August alone.

Application of the Lake Model: Indication for a Rapid Dissipation Process with a Half-Life of a Few Days
To describe the variation of concentrations over time and depth in the lake, a simple, one-dimensional model was set up including inputs from the various tributaries and WWTPs, export via the Glatt River, and vertical mixing, but, in a first step, excluding any degradation/dissipation processes. This model was able to describe the measured, vertical concentration profiles from March to July (dashed blue lines in Figure 8.5-84). However, in August, modeled concentrations in the epilimnion would have reached levels of 200 ng/L for glyphosate and 160 ng/L for AMPA. Consequently, all measured epilimnion concentrations after August were considerably overestimated by the model.

To account for the rapid elimination of glyphosate and AMPA, the model was refined by inclusion of a first-order dissipation process in the epilimnion (for details see methods section). Average dissipation rates were adjusted for every period between two lake samplings (21-35 days) until measured epilimnion concentrations were adequately represented by the model. Resulting concentration profiles are shown in Figure 8.5-84 (solid red lines).

For glyphosate, this dissipation process was negligible before July with first-order degradation rates <0.001/d, corresponding to half-lives (DT_{50}) >1000 days. In July and the first week of August, a considerably higher (≫100 x) dissipation rate of 0.38/d (DT_{50} = 1.8 days) was determined. Dissipation rates between the samplings in August and September remained high (0.19 d^{-1}; DT_{50} = 3.7 days) and decreased steadily from September (0.05/d; DT_{50} = 13 days) until October (0.002/d; DT_{50} >300 days).

Modeled dissipation rates for AMPA showed the same seasonal trend as those for glyphosate. As for glyphosate, the highest dissipation rate for AMPA was found in July and the first week of August. In general, dissipation rates were very similar to those of glyphosate.

Evaluation of Possible Elimination Processes for Glyphosate and AMPA in the Lake
The modeled dissipation rates represent all processes that may affect glyphosate and AMPA concentrations in the lake's epilimnion, including potential distribution processes between water and air or water and particles/sediment as well as different degradation processes such as hydrolysis, photodegradation, or biological degradation. The importance of these processes will be assessed in the following paragraphs.

Due to their zwitterionic speciation in lake water, glyphosate and AMPA have a very low vapor pressure and a high water solubility and, consequently, low air-water partition coefficients. Therefore, volatilization from the water surface can be ruled out as significant loss process.

Sorption to particles with subsequent sedimentation may lead to a certain loss of glyphosate and AMPA from the epilimnion. However, since the sedimentation of particles is a rather constant process and the sorption to these particles does not change rapidly, this process is unlikely to explain the observed, rapid loss of glyphosate and AMPA from the epilimnion in such a short period.

Both compounds are known to be hydrolytically stable, which excludes abiotic hydrolysis as elimination process.

From experience with other compounds in Lake Greifensee, experimental photolysis half-lives in summer sunlight of ≤1 h would be necessary to have a substantial impact on the concentrations in the epilimnion. Photolysis is thus not expected to contribute significantly to the observed, rapid removal of glyphosate and AMPA in the epilimnion.

This suggests that biodegradation is the most likely main elimination process to reasonably explain the distinct concentration drop of glyphosate and AMPA in Lake Greifensee between July and August. This conclusion is supported by the finding that phytoplankton growth was higher in July and the following months (with a short peak between the samplings in July and August; green line in Figure 8.5-83d) and that water temperatures were higher at the same time. Nevertheless, increasing phytoplankton density and water temperature alone would be expected to promote biodegradation, but still seem unlikely to be the sole cause of the sudden concentration drop, unless the conditions led to rapid growth of organisms, capable of degrading glyphosate and AMPA.

An additional factor enhancing biodegradation of glyphosate and AMPA may be the decreasing free phosphate (orthophosphate) concentration in the epilimnion, which fell below the limit of detection of 2 µg P/L in July (Figure 8.5-83d). As known from the literature, several bacteria, such as cyanobacteria or proteobacteria, are able to take up phosphonates and break the relatively stable C-P bond.

The degradation of glyphosate and AMPA by cyano- and/or proteobacteria is also supported by the observation that measured concentrations in August were lowest in the depths 1 and 2.5 m, where they fell below the limit of quantification of 5 ng/L, whereas in the depths 0 and 5 m, concentrations were between 8 and 11 ng/L despite the rather rapid mixing in the epilimnion. This suggests that degradation took place in a zone below the water surface around 1-2.5 m depth, which was also the zone of maximum primary production.

Metagenomic Sequencing to Identify Organisms Responsible for the Rapid Degradation of Glyphosate

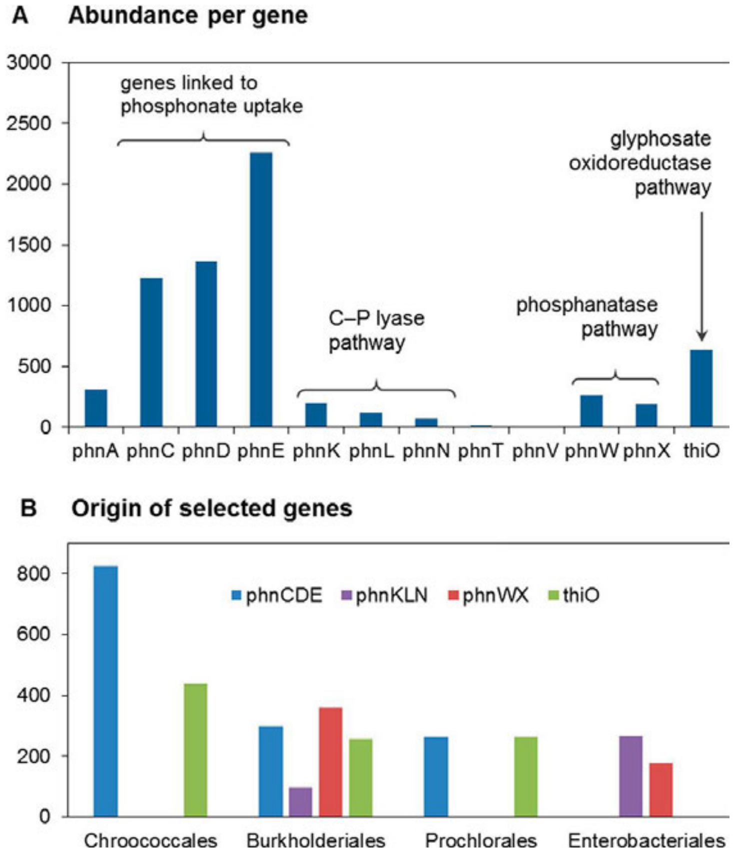
In July 2014, shortly after full depletion of glyphosate and AMPA, water samples for metagenomic analysis were taken from the epilimnion of Lake Greifensee. Sequencing yielded a total of 8.8 Gbp of sequence information. From these data, species abundance was estimated at multiple taxonomic levels. The most abundant phyla were cyanobacteria and proteobacteria. At the genus level, *Synechococcus* showed the highest abundance.

In order to further evaluate possible routes of phosphonate degradation in Lake Greifensee, the abundance of genes linked to phosphonate degradation and their respective species of origin was evaluated using MG-RAST. The *phnCDE* genes previously linked to phosphonate uptake were highly abundant in the sample and were assigned mainly to the genus *Synechococcus* (Chroococcales, Figure 8.5-85). Relatively few DNA reads mapped to selected C-P lyase pathway genes (*phnKLN*, Figure 8.5-85) and thus some evidence for a working C-P lyase pathway was found. These genes were assigned to proteobacteria (Burkholderiales and Enterobacteriales), as were the genes phn*WX* of the phosphonatase pathway. The gene *thiO*, previously reported to catalyze the oxidation reaction from glyphosate to AMPA, was associated with the families of Chroococcales, Burkholderiales and Prochlorales (Figure 8.5-85). No evidence of a glyphosate oxidoreductase gene (*gox*), previously linked to microbial glyphosate oxidation, was found within this study. All these data indicate that microorganisms of multiple genera may be involved in the biodegradation of glyphosate and that the compound is probably degraded via different pathways.

Evidence for Biodegradation from Batch Incubation Experiments

Batch incubation experiments were performed with two cyanobacterial species, *Microcystis aeruginosa* (isolated from Lake Greifensee) and *Synechococcus* (isolated from another Swiss lake). In summary, the experiments with *Microcystis aeruginosa* and *Synechococcus* showed that glyphosate is rapidly degraded and that degradation depends on the depletion of phosphate in the growth medium (no degradation or much slower degradation in the presence of P_i). Extrapolated to a biomass corresponding to 15 µg/L chlorophyll a, as measured in summer 2013 in Lake Greifensee (Figure 8.5-83d), the dissipation rates for P_i-starved *Microcystis aeruginosa* (0.07/d) and *Synechococcus* (0.18/d) were, however, somewhat lower than the rate obtained through modeling, indicating that microorganisms capable of degrading glyphosate and AMPA more efficiently than the two tested species must be present in the lake’s epilimnion.

Figure 8.5-85: **Functional abundance of selected genes in the Lake Greifensee metagenome (A) and assignment of some of these genes to families of bacteria (B)**



Conclusion

This study shows that under certain conditions, degradation of glyphosate and AMPA in large water bodies (i.e. lakes) is orders of magnitude faster than expected. The conditions leading to this phenomenon do not seem to be very specific as they were met in Lake Greifensee at least in the summers of 2006, 2013, and 2014 and in Lake Murten in 2006. Note that in 2006, only a single vertical concentration profile was measured in the two lakes in summer. Nevertheless, as the use pattern was very similar at the time (at least concerning application timing and consequent input to surface waters via surface runoff) it appears likely that the same seasonal changes caused the observed depletion of glyphosate and AMPA in the epilimnion.

A likely explanation for the rapid degradation is a combination of the bloom of cyanobacteria during summer and a depletion of inorganic phosphorus that probably caused increased uptake and metabolism of phosphonates in these organisms. The distinct seasonal dynamics as well as the specific conditions required for efficient degradation of glyphosate and AMPA probably are difficult to reproduce in laboratory degradation experiments as requested in official guidelines for pesticide testing such as the OECD tests for transformation in aquatic sediment systems or aerobic mineralization in surface water. However, this study provides strong evidence, at field scale, for the potential of (cyano)-bacteria in lakes for degradation of glyphosate and AMPA.

Assessment and conclusion by applicant:

The article describes the concentrations of glyphosate and AMPA in lake Greifensee in Switzerland representing a catchment with high portion of agricultural land use. The maximum concentration of glyphosate in samples from the two main tributaries of the lake was 1430 ng/L. Maximum glyphosate concentration in treated wastewater discharging into the lake was 350 ng/L. The maximum AMPA concentration in the two main tributaries was 415 ng/L. Concentrations in treated wastewater reached up to 1680 ng/L. For lake Greifensee, concentration of glyphosate reached a maximum of 145 ng/L in the epilimnion, and concentration of AMPA reached a maximum of 130 ng/L in the hypolimnion.

The article is considered reliable.

Assessment and conclusion by RMS:
This article is considered reliable.
Concentration of glyphosate and AMPA were monitored in a lake and its main tributaries, so as from treated waste water from water treatment plant between March and November 2013.

The analytical method used in the one described in Poiger, T. et al. (CA7.5/017). It is worth noting that "This method does not include a filtration step so that measured concentrations comprise dissolved and sorbed glyphosate and AMPA. Limits of quantification were 5 ng/L for both compounds".

The following main results and conclusions from the study can be retained. It is noted that detailed results of all sampling points are available as supporting information linked with the study.

Measured concentrations in the lake
Monthly vertical concentration profiles in the lake showed an increase of glyphosate concentrations in the epilimnion from 15 ng/L in March to 145 ng/L in July, followed by a sharp decline to <5 ng/L in August.
Initial concentrations of AMPA were higher (70 ng/L) than those of glyphosate. They increased to 100 ng/L until July.

Measured concentration in the tributaries
Glyphosate concentrations in the weekly composite samples from the two main tributaries ranged from <5 to 1430 ng/L (median, 145 ng/L in Aa Mönchaltorf and 175 ng/L in Aa Uster). The highest concentrations appeared in July and August in Aa Mönchaltorf and in March and July in Aa Uster, which is consistent with the main agricultural uses of glyphosate for treatment of sugar beet and maize fields prior to seeding in spring and postharvest treatment of cereal fields in summer.

AMPA concentrations in the two main tributaries ranged from 24 to 415 ng/L (median, 150 ng/L in both rivers). Similar to glyphosate, the highest AMPA concentrations were found in July (Aa Uster) and August (Aa Mönchaltorf).

Measured concentration from the WWTP
Glyphosate concentrations in treated wastewater from WWTP Uster were between 18 and 350 ng/L (median, 106 ng/L) with maximum concentrations in June and September, when they exceeded those in the tributaries.

AMPA concentrations in treated wastewater from WWTP Uster reached up to 1680 ng/L (median, 516 ng/L), and were thus higher than those in the tributaries at all sampling times.
Maximum concentrations in wastewater were found in August and September. AMPA is also a degradation product of various phosphonates used in industry and degradation of these compounds to AMPA in WWTPs likely is an important source of AMPA in Lake Greifensee.

Correlation of glyphosate and AMPA concentrations
Spearman's rank correlation analysis indicated fairly strong correlation of glyphosate and AMPA concentrations in the more rural tributary Aa Mönchaltorf ($\sigma = 0.70$, $p < 0.001$) suggesting that the occurrence of AMPA in this stream probably was related to the use of glyphosate in the catchment area.

In contrast, in the more urban tributary Aa Uster, there was no apparent correlation ($\sigma = 0.31$, $p = 0.09$) indicating that AMPA may, at least in part, be derived from sources other than glyphosate in the catchment.

Even in treated wastewater from WWTP Uster, the correlation between glyphosate and AMPA was higher ($\sigma = 0.62$, $p < 0.001$) than in Aa Uster. The best correlation, however, was found in the outflow of the lake ($\sigma = 0.83$, $p < 0.001$). This is most likely due to the similar fate of the two compounds rather than similar sources.

Data point:	CA 7.5/038
Report author	Masiol, M. *et al.*
Report year	2018
Report title	Herbicides in river water across the northeastern Italy: occurrence and spatial patterns of glyphosate, aminomethylphosphonic acid, and glufosinate ammonium
Document No	Environmental Science and Pollution Research (2018) 25:24368-24378
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

Glyphosate and glufosinate ammonium are the active ingredients of commonly used herbicides. Active agricultural lands extend over a large part of the Veneto region (Eastern Po Valley, Italy) and glyphosate and glufosinate ammonium are widely used. Consequently, surface waters can be potentially contaminated. This study investigates the occurrence of glyphosate and glufosinate ammonium as well as aminomethylphosphonic acid (AMPA, the degradation product of glyphosate) in river water of Veneto. Eighty-six samples were collected in 2015 at multiple sampling points across the region. Samples were analyzed for the two target herbicides, AMPA as well as for other variables, including water temperature, pH, dissolved oxygen, conductivity, hardness, BOD, COD, inorganic ions, total nitrogen, total phosphorus, total suspended solids, arsenic, and lead. The average concentrations (all samples) were 0.17, 0.18, and 0.10 µg/L for glyphosate, AMPA, and glufosinate ammonium, respectively. The European upper tolerable level for pesticides (annual average 0.1 µg/L) was often exceeded. Chemometric analysis was therefore applied to (i) investigate the relationships among water pollutants, (ii) detect the potential sources of water contamination, (iii) assess the effective water pollution of rivers by identifying river basins with anomalous pollution levels, and (iv) assess the spatial variability of detected sources. Factor analysis identified four factors interpreted as potential sources and processes (use of herbicides, leaching of fertilizers, urban/industrial discharges, and the biological activity on polluted or stagnant waters). A discriminant analysis revealed that the pollution from anthropogenic discharges is homogeneously present in surface water of Veneto, while biological activity and fertilizers present heterogeneous distributions. This study gives insights into the concentrations of herbicides in rivers flowing through a wide region that has heavy use of these chemicals in agriculture. The study also points out some hot-spots and suggests the future implementation of the current monitoring protocols and network.

Materials and methods

The Veneto region

The Veneto covers an area of ~ 18,000 km^2 and hosts a population of 4.9 million inhabitants. The northwestern part is mainly occupied by mountains (Alps), with a low population density mostly concentrated along narrow valleys. A wide southeastern alluvial plain accounts for most (56%) of the territory and is affected by heavy anthropogenic pressures due to the presence of major cities, industrial areas, and intensive farming. A belt of hilly environments is located between mountains and the lowland: it hosts rural environments and farming, mostly vineyards and orchards. The alluvial plain is composed of sandy to silty-clay materials deposited by major rivers: the northwestern plain is generally characterized by more permeable soils, while the central and southern plain host heavy soils and waterlogging with shallow groundwater levels (sometimes <2 m). The two areas are separated by a belt of springs called “risorgive”, which generate several streams.

The mountain chains (Alps and Prealps) are mainly composed of sequences of sedimentary rocks (mainly limestone and dolomite) on metamorphic basements with magmatic extrusions. Springs of major rivers (e.g., Piave, Brenta, Adige) are located in the Alps, while other rivers flow (Livenza) or join tributaries (e.g., Brenta) flowing from karstic systems. Other major rivers (e.g., Bacchiglione, Dese, Sile, Zero) born in the "risorgive" area from springs fed by aquifers catching water across the Prealps area. Soils in the plain areas are also characterized by low organic carbon content, especially where intensive agriculture is practiced. The low levels of soil organic matter limit the cation exchange capacity, lower the fertility, and increase the potential mobility of contaminants, including herbicides.

Table 8.5-144: Characteristics of the sampling sites and average (min-max) concentrations of target compounds. GLY glyphosate, GLU glufosinate ammonium, AMPA aminomethylphosphonic acid. Provinces are BL, Belluno; TV, Treviso; VE, Venice; PD, Padua; RO, Rovigo. LOQ limit of quantification

Main drainage basin	Secondary drainage basin	River name	Site no.	Province	No. samples	GLY		AMPA		GLU	
						µg L^{-1}		µg L^{-1}		µg L^{-1}	
						Mean	(min-max)	Mean	(min-max)	Mean	(min-max)
Adige		Adige	206	PD	4	0.04	(<LOQ–0.1)	0.17	(<LOQ–0.23)	0.07	(<LOQ–0.22)
Brenta		Brenta	436	VE	3	0.29	(<LOQ–0.83)	0.13	(<LOQ–0.35)	0.13	(<LOQ–0.33)
Brenta	Bacchiglione	Bacchiglione	181	PD	3	<LOQ	–	<LOQ	–	<LOQ	–
Brenta	Bacchiglione	Cagnola	175	PD	2	<LOQ	–	<LOQ	–	<LOQ	–
Brenta	Bacchiglione	Tesinella	112	PD	3	0.04	(<LOQ–0.06)	<LOQ	–	<LOQ	–
Brenta	Gorzone	Gorzone	437	VE	2	<LOQ	–	<LOQ	–	<LOQ	–
Canalbianco		N. Adigetto	223	RO	4	0.40	(<LOQ–1.4)	0.36	(<LOQ–0.75)	0.18	(<LOQ–0.55)
Livenza	Monticano	Monticano	620;1147	TV	5	0.04	(<LOQ–0.1)	0.31	(<LOQ–0.83)	0.08	(<LOQ–0.3)
Livenza	Monticano	Cervada	621	TV	4	0.49	(0.07–1.3)	0.28	(0.07–0.56)	0.11	(<LOQ–0.3)
Livenza	Monticano	Crevada	6008	TV	1	0.45	(0.45–0.45)	<LOQ	–	0.30	(0.3–0.3)
Livenza		Livenza	72;453	TV, VE	4	0.34	(<LOQ–0.55)	0.42	(<LOQ–1.4)	0.05	(<LOQ–0.11)
Livenza		Meschio	23;236	TV	2	0.11	(<LOQ–0.2)	<LOQ	–	0.11	(<LOQ–0.2)
Piave		Anfella	409	BL	4	0.06	(<LOQ–0.1)	0.04	(<LOQ–0.07)	0.07	(<LOQ–0.22)
Piave		Piave	65	VE	5	0.17	(<LOQ–0.66)	0.28	(<LOQ–1.2)	0.06	(<LOQ–0.12)
Piave		Teva	6013	TV	2	0.31	(0.11–0.51)	0.77	(0.72–0.82)	0.42	(<LOQ–0.82)
Piave		Val di Frari	420	BL	4	0.06	(<LOQ–0.17)	<LOQ	–	0.05	(<LOQ–0.12)
Po		Po	227	RO	4	0.05	(<LOQ–0.08)	0.22	(<LOQ–0.54)	<LOQ	–
Sile		Bigonzo	6033	TV	4	0.32	(<LOQ–0.7)	0.16	(0.09–0.27)	0.08	(<LOQ–0.14)
Sile		C.U.A.I.	351	VE	3	0.10	(<LOQ–0.26)	0.06	(<LOQ–0.14)	<LOQ	–
Sile		Melma	333	TV	4	0.13	(<LOQ–0.37)	0.12	(<LOQ–0.26)	0.10	(<LOQ–0.26)
Sile		Sile	238;329	TV, VE	5	0.07	(<LOQ–0.25)	0.10	(<LOQ–0.25)	0.09	(<LOQ–0.25)
Lagoon of Venice		Musoncello	1127	TV	3	0.72	(<LOQ–2.1)	0.48	(<LOQ–1.4)	0.72	(<LOQ–2.1)
Lagoon of Venice		Tergola	117	PD	3	<LOQ	–	<LOQ	–	<LOQ	–
Lagoon of Venice		Zero	488	TV	5	0.04	(<LOQ–0.06)	0.03	(<LOQ–0.05)	0.03	(<LOQ–0.05)
Extra samples		"Risorgive"	NA	TV	3	<LOQ	–	0.05	(<LOQ–0.1)	0.05	(<LOQ–0.1)

Sampling

Sites were selected along 24 major rivers or streams flowing across eight main drainage basins (Table 8.5-144), named Adige, Brenta, Canalbianco, Livenza, Piave, Po, Sile, and the drainage basin of the Lagoon of Venice (DBLV). This latter basin needs special care: it hosts several streams and small rivers flowing directly into a large (~ 500 km^2 wide) coastal lagoon affected by high nutrient and pollutant levels, such as dissolved nitrogen and phosphorous, heavy metals (As, Co, Cd, Cu, Fe, Pb, Zn, Ni, Cr), persistent organic pollutants (polychlorinated biphenyls, organochlorine pesticides), and polycyclic aromatic hydrocarbons in top sediments. Three more samples were collected close to springs in the "risorgive" area. Each site was sampled during 1 year with different frequency (1-5 samples per site). Water was collected near the center of the river or, wherever not possible, at points having flowing water stream (i.e., no samples were collected on stagnant water conditions). Samples were stored in pre-cleaned HDPE bottles and in the dark at + 4°C to prevent sample degradation and photochemical reactions and were analyzed within 6 days

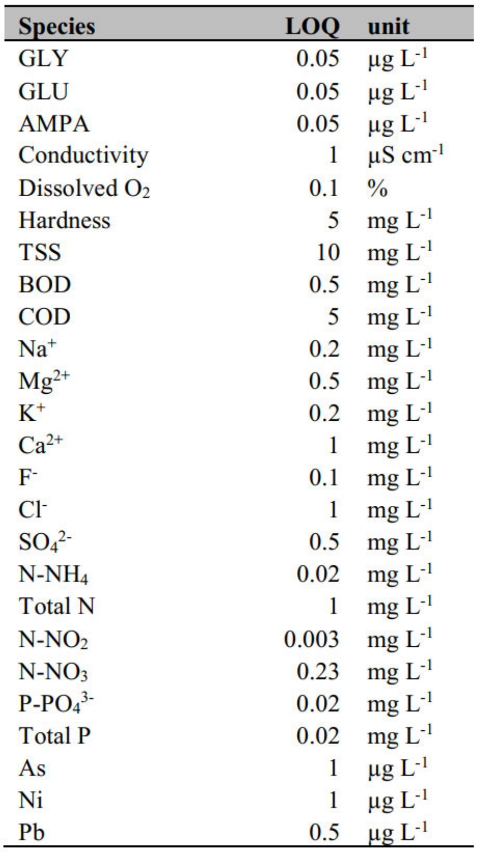
(ISO 2014). During the sampling, water temperature was also measured, as well as pH (method APAT-CNR-IRSA-2060) and dissolved oxygen (method APAT-CNR-IRSA-4120).

Experimental
Glyphosate, AMPA, and glufosinate ammonium were analyzed following the method ISO 16308:2014. Briefly, the compounds are derivatized using 9-fluorenylmethylchloroformate (FMOC-Cl) in order to lower their polarity and increase the retention of compound in a separation on a reverse phase column as well as to improve the mass spectrometric detection. The derivatized sample was then purified by liquid/liquid extraction and concentrated by solid phase extraction (SPE). Methanol (≥99.9%, Sigma Aldrich) was used in SPE extraction. For each sample extraction, ~ 13 mL methanol is used. The analysis is performed by high-performance liquid chromatography coupled with tandem mass spectrometry via an electrospray source (HPLC-ESI-MS/MS), using matrix-matched calibration. Calibration of the instrument was performed for every analytical batch; limit of quantification (LOQs, calculated according to the IUPAC Gold Book) was 0.05 µg/L.

Standards for spikes are dissolved in an aqueous matrix along with internal standards. Spikes are performed from these aqueous solutions. Once prepared, standards are kept at - 20°C for 6 months max (see ISO 5667-3:2012). Samples were spiked before the derivation step with labeled glyphosate (1,2 ^{13}C2, ^{15}N) and labeled AMPA (^{13}C, ^{15}N). The range of acceptability for recoveries adopted by ARPAV lab range from 75 to 125%. The mean recoveries (in the concentration range of analyzed samples) were 103, 103, and 109% for glyphosate, glufosinate ammonium, and AMPA, respectively. Physicochemical characteristics of water and chemical species were also analyzed using well established analytical protocols.

QA/QC and data handling
Method performance for glyphosate, AMPA, and glufosinate ammonium was tested by participation to LGC proficiency test AQ 492/2015 (LGC Aquacheck 2017) obtaining a satisfactory Z-score (Z <2) among laboratories of European countries and confirming a good accuracy of the adopted analytical protocol. At least two water samples for each batch were spiked with target compounds and then included in the analytical procedure: recoveries were in the range of 80-100%. Precision was evaluated through analysis of replicated spiked water samples: results showed relative standard deviations <30%. In this study, all the samples analyzed for herbicides were used for descriptive statistics, but only samples also analyzed for the remaining chemical and physical variables were further used for explorative analysis. Data below the LOQs (see Table 8.5-145) were set as LOQ/2.

Table 8.5-145: LOQs (limits of quantification) for the species/variables analyzed in this study



Species	LOQ	unit
GLY	0.05	µg L^{-1}
GLU	0.05	µg L^{-1}
AMPA	0.05	µg L^{-1}
Conductivity	1	µS cm^{-1}
Dissolved O_2	0.1	%
Hardness	5	mg L^{-1}
TSS	10	mg L^{-1}
BOD	0.5	mg L^{-1}
COD	5	mg L^{-1}
Na^+	0.2	mg L^{-1}
Mg^{2+}	0.5	mg L^{-1}
K^+	0.2	mg L^{-1}
Ca^{2+}	1	mg L^{-1}
F^-	0.1	mg L^{-1}
Cl^-	1	mg L^{-1}
SO_4^{2-}	0.5	mg L^{-1}
$N\text{-}NH_4$	0.02	mg L^{-1}
Total N	1	mg L^{-1}
$N\text{-}NO_2$	0.003	mg L^{-1}
$N\text{-}NO_3$	0.23	mg L^{-1}
$P\text{-}PO_4^{3-}$	0.02	mg L^{-1}
Total P	0.02	mg L^{-1}
As	1	µg L^{-1}
Ni	1	µg L^{-1}
Pb	0.5	µg L^{-1}

Chemometrics

The water samples were collected in rivers with different characteristics and/or affected by different anthropogenic pressures. Rivers also flow over different soil and rock types. This way, the chemical and physical characteristics of water may change according to the strength of natural/anthropogenic sources, the occurrence of biochemical processes in water, the soil characteristics, the flow rate, the closeness to point sources, the spatial distribution of diffuse sources, etc. A factor analysis (FA) was therefore performed to investigate the inter-variable relationships and to identify the most probable sources of water contamination or the ongoing biochemical processes. The principal aim of FA is to reduce the dimensionality of the dataset and to detect the main hidden processes/sources driving most of the variance of the original dataset.

Most of the species analyzed in this study are not normally distributed (Shapiro-Wilks test), with most of the variables exhibiting positive skewness. In addition, most variables have large differences in the units, i.e., the variables exhibits a striking difference in the amount of variability. For these reasons, non-parametric tests and correlations are used.

The Kruskal-Wallis analysis of variance by ranks was applied as a global non-parametric test for depicting statistically significant seasonal variations of analyzed variables. The null hypothesis is rejected for $p < 0.05$, meaning that concentrations are statistically different among seasons.

Since factor analysis is affected by data distribution and data scale, a series of data transformations were applied to obtaining a robust dataset. Firstly, a Box-Cox transformation was applied to approach normal distributions; thus, a standardization (mean zero and unit variance) was applied to scale the data and overcome differences in variation ranges.

In a second step, a discriminant analysis (DA) was applied to the factor score matrix to study the spatial distribution of identified factors, i.e., to verify whether the sites in a drainage basin are isolated or characterized by a general homogeneity of the sources/processes. DA is typically applied to detect variables which significantly explain differences between two or more groups (drainage basins, in this case). The results of the test of univariate equality of group means can classify variables (factors, in this case) as not discriminant or discriminant: highWilks' Λ (>0.9) and significance >0.3 identify not discriminant variables, i.e., homogeneously present in all drainage basins. On the contrary, significances below 0.05 identify discriminant variables, i.e., having a heterogeneous distribution over the study area.

Results

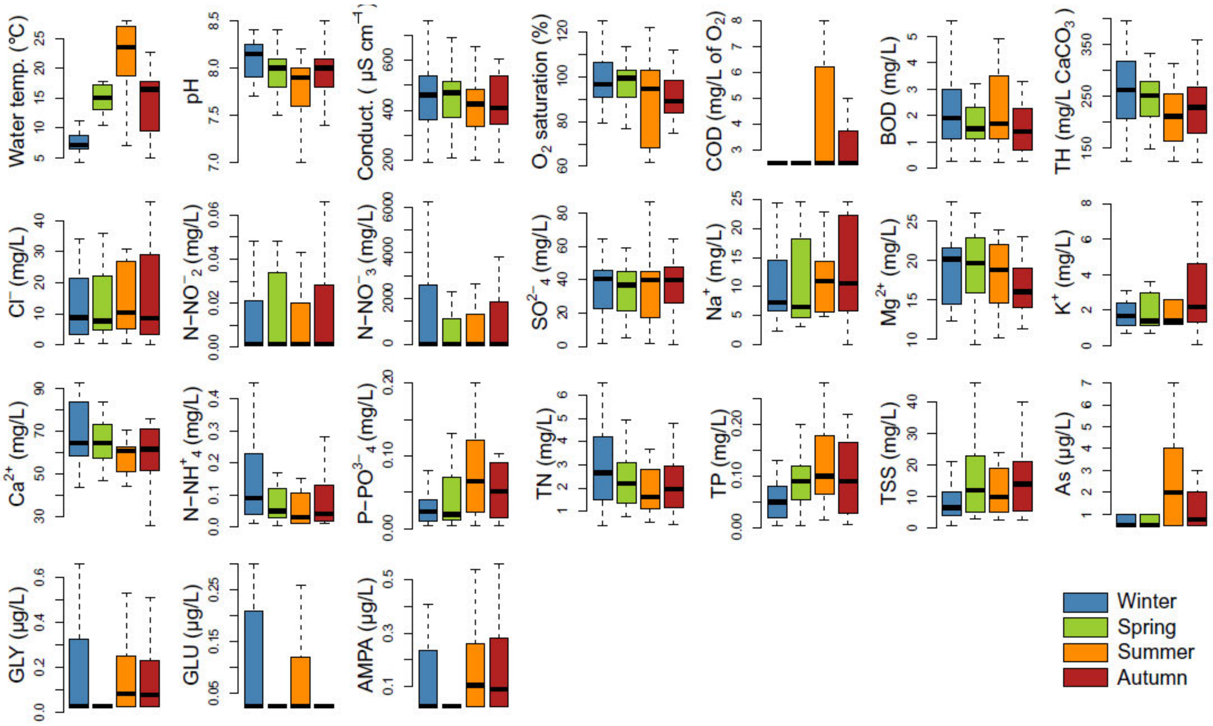
The average concentrations across the Veneto (all seasons, all sites) were 0.17, 0.18, and 0.10 µg/L for glyphosate, AMPA, and glufosinate ammonium, respectively (Table 8.5-144). The higher annual average concentrations of glyphosate were recorded on Musoncello (0.72 µg/L), followed by some sites along Livenza (Cervada, 0.49 µg/L; Livenza 0.45 µg/L) and Canalbianco (Nuovo Adigetto 0.4 µg/L), while AMPA was higher on Teva (0.77 µg/L), Musoncello (0.48 µg/L), and Livenza (0.55 µg/L). The river Musoncello was also affected by the higher annual concentrations of glufosinate ammonium (0.72 µg/L), followed by Teva (0.42 µg/L). Musoncello presents, therefore, the higher annual average concentrations of herbicides: it is affected by substantial loads from the urban sewer of Castelfranco Veneto (~ 33,000 inhabitants) and then flows through agricultural areas by also touching other towns (Resana). Finally, it joins the Dese River and, then, flows into the Lagoon of Venice. Therefore, further investigations and/or sampling campaigns are suggested for those polluted rivers in order to better monitor the sources of herbicides. In addition, more sites should be placed close to the outlets to quantify the load of herbicides flowing into the Lagoon of Venice.

In Europe, the upper tolerable level for all the pesticides in drinking water is administratively set to 0.1 µg/L. This regulatory limit is applied to annual average concentrations. The threshold of 0.1 µg/L was often exceeded in single samples (26, 37, and 22% of all analyzed samples, respectively); however, only 11, 14, and 7 sites breached the annual upper tolerable level computed over multiple samples for glyphosate, AMPA, and glufosinate ammonium, respectively.

The design of our sampling campaign is not sufficient to accurately represent seasonal concentrations or to identify peak concentrations at single rivers, which can be missed even with a weekly sampling interval. The analysis of seasonal differences was therefore assessed for the whole set of data (Figure 8.5-86): only water temperature, pH, and concentrations of glyphosate and AMPA were statistically different.

The herbicides were rarely detected during spring, while the higher median concentrations for glyphosate and AMPA were measured in summer, followed by autumn and winter. This pattern is likely related to the seasonality of crops. Glyphosate is typically applied after crops and weeds have emerged from the soil, but it can be applied more than once during the growing season: this way, in Northern Italy crops and orchards are mostly treated in late-spring and summer when unwanted plants grow faster. However, herbicides are also applied to vineyards until mid-autumn (grape harvest). In addition, residues of herbicides may remain in the soil for weeks (half-life for glyphosate and glufosinate ammonium are 2-91 and 3-42 days, respectively); therefore, surface runoff and draining to groundwater may continue for months after treatment.

Figure 8.5-86: **Seasonal distributions of the analyzed variables. Data are aggregated to show data collected at all sites during the four seasons. Boxplot lines = medians, boxes = 25th-75th percentile ranges, whiskers = ± 1.5*inter-quartile ranges. Outliers and extremes not shown. *COD* chemical oxygen demand, *BOD* biochemical oxygen demand, *TH* total hardness, *TN* total Kjeldahl nitrogen, *TP* total phosphorus, *TSS* total suspended solids, *GLY* glyphosate, *GLU* glufosinate ammonium, *AMPA* aminomethylphosphonic acid.**



Correlations among variables

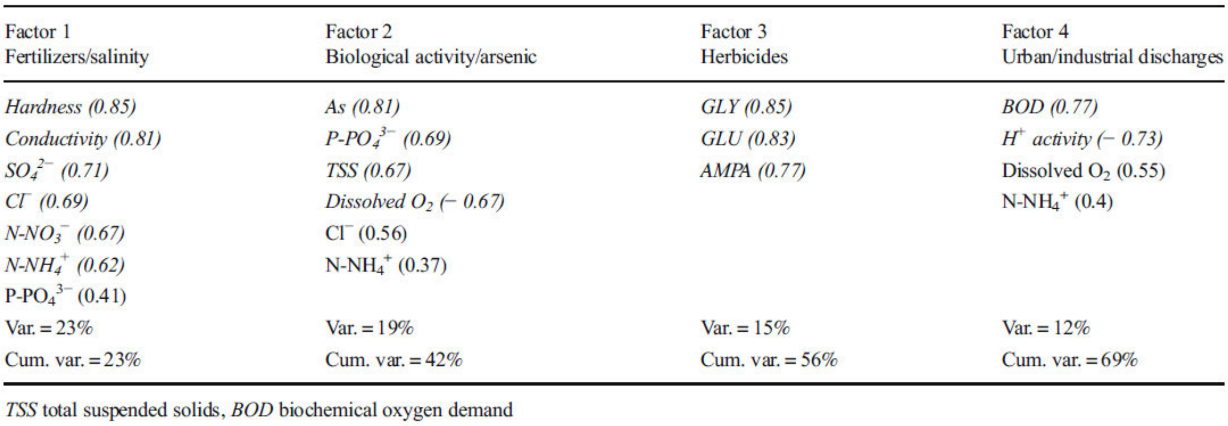
Glyphosate and glufosinate ammonium exhibit a moderate correlation (0.53) and are also well correlated with AMPA (0.64 and 0.44, respectively). However, they are not well correlated (ρ <0.4) with any other variable. AMPA exhibits a strong correlation with glyphosate (ρ = 0.64), a poor correlation with orthophosphate (ρ = 0.26) and it is uncorrelated to TP. This result suggests that glyphosate degradation is the dominant source of AMPA in river waters of Veneto. However, the lack of a clear correlation with P compounds may be masked by the strong input of P-containing species from other sources, e.g., fertilization and urban and industrial discharges.

Potential sources of river contamination

The transformed dataset (Box-Cox/standardized) was used as input for a Varimax-rotated FA. A first attempt was made by including all the species. However, a pre-selection of variables to be processed in FA was subsequently performed to ensure robust and reliable results and to exclude chemically redundant species: (i) some variables (chemical oxygen demand, Na^+, K^+, Pb)were excluded because their high percentage of missing data (>25%); (ii) missing data for other variables were substituted with the variable median; (iii) hardness was preferred to Mg^{2+} and Ca^{2+} because of their high correlation and the lower number of missing data; (iv) total phosphorous and total Kjeldahl nitrogen (TKN) were excluded because their strong correlations with orthophosphates and the sum of N-species, respectively; (v) nitrite was excluded because the high associated uncertainty due to its relatively unstable oxidation state; (vi) dissolved O_2 was converted from percent saturation to water concentration by considering the correction factors for water conductivity, water temperature and barometric pressure (USGS DOTABLES); (vii) hydrogen ion activity $[H^+]$ (mEq/L) was calculated from pH to obtain a linear variable. Four factors with eigenvalues >1 were extracted, accounting for ~ 70% of total variance.

Along with the factor loadings (Table 8.5-146), an $n \times m$ factor score matrix is also extracted: it is composed of n cases (samples collected) and m new variables proportional to the daily source impact.

Table 8.5-146: Results of factor analysis (Varimax rotated solution). Variables with factor loadings (> 0.6) are in italics; factor loadings less than 0.35 are not shown; variables are ordered for decreasing absolute loadings. Var (%): percentage of variance explained by each factor; Cum. var. (%): cumulative variance.



Factor 1 Fertilizers/salinity	Factor 2 Biological activity/arsenic	Factor 3 Herbicides	Factor 4 Urban/industrial discharges
Hardness (0.85)	*As (0.81)*	*GLY (0.85)*	*BOD (0.77)*
Conductivity (0.81)	*P-*PO_4^{3-} *(0.69)*	*GLU (0.83)*	H^+ *activity (− 0.73)*
SO_4^{2-} *(0.71)*	*TSS (0.67)*	*AMPA (0.77)*	Dissolved O_2 (0.55)
Cl^- *(0.69)*	*Dissolved* O_2 *(− 0.67)*		N-NH_4^+ (0.4)
N-NO_3^- *(0.67)*	Cl^- (0.56)		
N-NH_4^+ *(0.62)*	N-NH_4^+ (0.37)		
P-PO_4^{3-} (0.41)			
Var. = 23%	Var. = 19%	Var. = 15%	Var. = 12%
Cum. var. = 23%	Cum. var. = 42%	Cum. var. = 56%	Cum. var. = 69%

TSS total suspended solids, *BOD* biochemical oxygen demand

Factor 1 (23% of variance) mainly represents the analyzed ions and, in particular, all the nutrients. It is primarily composed (loading >0.6) of anions (chloride, sulfate, nitrate), ammonium and, secondarily (0.35 <loadings <0.6), orthophosphate (Table 8.5-146). Consequently, the factor also exhibits high loading of hardness (directly linked to Ca and Mg) and water conductivity (0.83), which reflects the ionic activity.

Factor 2 (19% of variance) is made up of arsenic, orthophosphate, total suspended solids and, secondarily, chloride and ammonium (Table 8.5-146). Under this view, it can be related to a pollution source and/or runoff. However, the temporal frequency of the sampling campaign has not allowed an analysis of the relation with rainfall depth or intensity. Consequently, the effect of runoff in this factor remains unclear.

Factor 2 also shows a strong negative loading with dissolved oxygen (− 0.67), which is indicative of an ongoing aerobic activity. The high loading of TSS further confirms this hypothesis, as the turbidity and the presence of colloids generally increase in more stagnant waters. The poor correlation of factor 2 with biochemical oxygen demand (BOD) (0.23) further suggests that the amount of biodegradable organic material is not a limiting factor for the aerobic activity or may indicate that the biological activity has depleted most of the organic material (i.e., the source does not represent a fresh input to the river).

Factor 3 (15%) only links glyphosate, AMPA, and glufosinate ammonium (Table 8.5-146). The absence of high loadings with any other analyzed species indicates that the contamination of herbicides is uncorrelated with other pollution sources. The higher scores are found in summer >autumn >winter, and sites in the province of Treviso generally show the higher factor scores throughout the year. Relatively high scores are also recorded during summer in the two more northern sites (Piave drainage basin), which generally show the lower scores for the remaining factors. These rivers (Anfella and Val di Frari) flow in mountain areas and, therefore, are not likely affected by a load of herbicides from agriculture or silviculture. These sites represent an anomaly that should be investigated in more detail.

Factor 4 (12%) links BOD, dissolved oxygen and, secondarily, ammonium; it also shows a negative correlation with the activity of H^+ (Table 8.5-146), i.e., it is linked to the more alkaline waters. No statistically significant inter-seasonal differences are found, i.e., it is almost constant all the year.

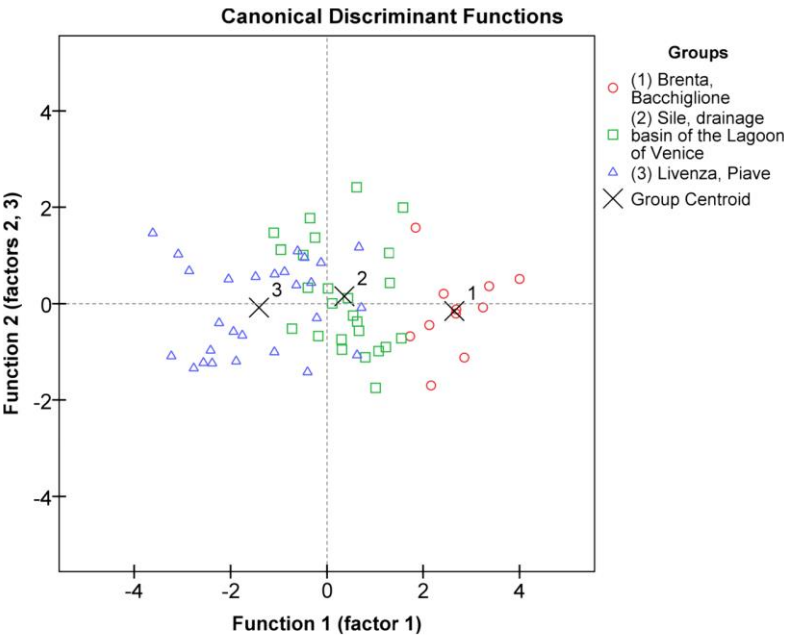
This factor depicts waters with high loads of organic matter (BOD), but it also represents waters with high primary production and/or affected by low aerobic activity (high loading of dissolved O_2). A possible interpretation is the fresh release of anthropogenic discharges of nutrients and effluents and the consequent increased photosynthetic activity.

Spatial distribution of sources

The factor scores were used in DA as independent variables; three areas including five drainage basins having similar characteristics were selected as grouping variable: (1) Brenta and Bacchiglione, i.e., rivers flowing in the center and southern part of Veneto; (2) DBLV and Sile, rivers mostly flowing from "risorgive" springs; (3) Piave and Livenza, rivers flowing in the northern part of Veneto with sources located in the Alps, but also having heavy contributions from "risorgive." Samples collected in Po, Canalbianco, and Adigewere excluded from DA due to the low number of sites and samples. The test of univariate equality of group means shows that only factor 4 is not discriminant, having the highest Wilks' Λ (0.98) and presenting a significance of 0.5. This result indicates that the pollution due to the fresh release of anthropogenic discharges (mostly attributable to urban or industrial sewage effluents) is homogeneously present in all the study area. Since the outputs from urban or industrial sewage effluents are expected to be constant through the year, this result confirms the interpretation of factor 4.

On the contrary, factors 1, 2, and 3 are highly discriminant (significance <0.05), i.e., they present heterogeneous distributions over the three groups of rivers. Two discriminating functions were also extracted and interpreted by analyzing their correlations with the input variables (factors): the first function only presents weak correlations with factor 1 (fertilizers/salinity) and 2 (biological activity and arsenic), while the second one presents the largest absolute correlation with the factors 2 and 3 (herbicides). Figure 8.5-87 shows the bi-dimensional scatterplot of sample scores into the planes defined by the discriminant functions. The plot shows that the samples in the three groups of rivers are generally well differentiated under the discriminant function 1 (weakly correlated with factors 1 and 2), with higher scores for samples collected in the southern area (Brenta-Bacchiglione) and lower for the samples collected to the north (Piave-Livenza). On the contrary, group centroids are not well separated along the discriminant function 2.

Figure 8.5-87: Discriminant scores scatterplot. Group centroids are shown as grey crosses



Conclusion

This study is the first one investigating the occurrence of glyphosate, glufosinate ammonium, and AMPA in river water of the NE Italy. The main findings of this study can be summarized as follows:

- The contamination of herbicides is a critical issue in Veneto: glyphosate, AMPA, and glufosinate ammonium frequently exceeded the European upper tolerable levels for pesticides (annual average

0.1 µg/L) during 2015. However, this tolerable level is based on political consensus, not ecotoxicological significance and it is very low if compared to the maximum level of glyphosate permitted in the USA (700 µg/L) based on toxicity tests;

- Glyphosate and AMPA showed statistically different seasonal concentrations, with higher medians in summer and autumn and lower in spring. This seasonal pattern agrees with the use of herbicides in agriculture and silviculture;

- The River Musoncello was affected by the higher annual average concentrations of glyphosate and glufosinate ammonium;

- The correlation and factor analyses pointed out the interspecies relationships. Four factors were extracted and interpreted as possible sources/processes affecting the water quality of rivers. Herbicides were identified by a single factor. Two more factors were linked to possible sources: the leaching of fertilizers and the urban/industrial discharges. Another factor was attributed to the biological activity on polluted or stagnant waters;

- A discriminant analysis was performed on the factor scores and over 3 areas representative of 5 drainage basins. Results revealed that the anthropogenic discharges (mostly attributable to urban or industrial sewage effluents) are homogeneously present over all the study area, while biological activity and fertilizers present heterogeneous distributions. However, a clear spatial gradient was not detected.

Assessment and conclusion by applicant:
The article reports measurements of glyphosate and AMPA in surface waters in Northern Italy. Maximum surface water glyphosate concentration measured at 0.72 µg/L, and maximum AMPA concentration at 0.77 µg/L.
The article is considered reliable.

Assessment and conclusion by RMS:
The article reports measurements of glyphosate and AMPA in surface waters in Northern Italy.
The analytical method is described and seems to be accurate, with recoveries in the range of 80-100%. The relative standard deviation may be rather high, based on indication of SD being <30% in analysis of replicated spiked water samples. The LOQ is 0.05 µg/L for glyphosate and AMPA.

24 sites were sampled 1 to 5 times within the year, which may not be sufficient to have a clear view of seasonal variation. Author indeed acknowledges that "The design of our sampling campaign is not sufficient to accurately represent seasonal concentrations or to identify peak concentrations at single rivers, which can be missed even with a weekly sampling interval".

Statistical analysis of the results indicated significant seasonal differences for glyphosate and AMPA. Authors indicates that "the herbicides were rarely detected during spring, while the higher median concentrations for glyphosate and AMPA were measured in summer, followed by autumn and winter". However, it is noticeable that the detailed number or sampling available per season is not given in the study.

Study indicates that this seasonal pattern is likely related to the seasonality of crops, although no data on the pressure of use of glyphosate is given within this study. Only general assumption of what is the typical use pattern of glyphosate is reported ("applied after crops and weeds have emerged from the soil, but it can be applied more than once during the growing season: this way, in Northern Italy crops and orchards are mostly treated in late-spring and summer when unwanted plants grow faster. However, herbicides are also applied to vineyards until mid-autumn (grape harvest)".

The study is considered reliable although cannot be related to use pressure of the active substance as herbicide.

Maximum surface water glyphosate concentration measured at 0.72 µg/L, and maximum AMPA concentration at 0.77 µg/L.

Data point:	CA 7.5/039
Report author	Dairon, R. *et al*.
Report year	2017
Report title	Long-term impact of reduced tillage on water and pesticide flow in a drained context
Document No	Environ Sci Pollut Res (2017) 24:6866-6877
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable (but concentration in drainflow and not in surface water)

Influence of more than 20 years (1988–2010) of reduced tillage (RT) practices on water and pesticide balances and dynamics is analyzed and compared to results from a conventional tillage plot (CT). The field study soils are described as silty clay stagnic luvisol, developed on a low permeable schist layer. A drainage network was set up according to French criteria (0.9 m deep, 10 m space) to avoid soil winter waterlogging. Climate is temperate oceanic and drainage generally occurs from November to March. Data were analyzed at yearly, weekly (pesticides) and hourly (water) time steps. Over the long term, cumulated drainage decreases significantly on RT (3999 mm) compared to CT (5100 mm). This differentiation becomes significant from 1999, 10 years after plowing was stopped. Strikingly, hourly drainage peak flows are higher under RT, especially during the second period (2000–2010), associated with low or no base flow. These results suggest a strong influence of the macropore network under RT practice. In particular, drainage peaks are higher at the beginning of the drainage season (mid-October to December). Consistently, pesticides applied in late autumn, which are the most quantified on this site, are often significantly more exported under RT. For atrazine, applied in spring, fluxes are linked to cumulative flow and are de facto higher under CT. For others pesticides, losses appear to be heterogeneous, with generally low or null export rates for spring application. Generally speaking, higher concentrations are measured on RT plot and explain observed exportation rate differences. Finally, there is no clear evidence of correlation between pesticide losses and long-term impacts of RT on hydrodynamics, pointing the importance of studying the short-term effect of tillage on water and especially solute flow.

Materials and methods

Site and plot description

The experimental station of La Jaillière is located in western France (47° 27′ N, 0° 57′ W). Soils, mainly stagnic luvisol are developed on a low permeable schist formation (saturated hydraulic conductivity Ks <0.2 mm/h). Clay content increases from surface layer (22%) to subsurface (>40%), where many hydromorphic features have been observed. Soil structure, fine and sub angular in surface becomes coarse and prismatic with depth. Climate is temperate oceanic, with a mean annual precipitation of 709 mm and a mean annual potential evaporation of 738 mm during the 1988–2011 period. To prevent soil waterlogging and improve crop growth during winter, tiled drainage was implemented in the 80s. The PVC tile drains (54 mm diameter) at this site are 0.9 m deep on average, with a spacing of 10 m, in order to respect French standard. Drain flow, surface runoff, and nitrate and pesticide fluxes have been monitored since 1987, 1989, and 1994, respectively. Historically, the “La Jaillière” site was set up for agronomical purposes to highlight the interest of subsurface drainage on crop yield (1980s). Then environmental issues of water quality in drained conditions rise in the 90s. Among the 11 plots, two were chosen in 1989 to compare RT and CT on the same soil context, climate, and agricultural practices. As previously enounced, this paper focuses on two plots, one conventionally tilled and the other one driven without plowing. Topsoiling and stubble cultivation operations are still performed on the RT plot (Table 8.5-147). These two plots, of 1 ha each, are located on the plateau and are only 200 m far one from the other. Both are hydraulically isolated from other neighbor plots. Slope is gentle on the site for both plots (<2%).

Soil texture, organic matter (O. M), pH, and C/N ratio were measured in 1987, 1994, 2004, and 2009 in order to investigate temporal modification of main soil characteristics. For soil texture, O.M and pH measurements were performed at 0–10, 10–25, and 25–50 cm for CT and 0–5, 5–10, 10–25, and 25–50 cm for RT. Bulk density was first measured in autumn 1994 (just after plowing). A new set of measurements was performed in 2013, during infiltration measurement campaign (data collected in April, 8 months after any previous tillage operation on CT plots).

Crop rotations and fertilization practices are identical on the two plots throughout the study period. However, pesticide applications slightly differ, because of a more regular use of herbicides on RT (glyphosate). Except for these applications, pesticides are applied at the same dates and rates on two plots.

Hourly precipitation, daily potential evaporation, net radiation, and temperature are recorded on-site. Tiled-drained flow is channeled towards a measurement chamber, where it is hourly recorded thanks to an ultrasound probe once flow has settled. Sampling strategy is based on flux quantification instead of flow event dynamic. Consequently, flow-weighted mean samples are composed of several subsample taken every 5 m^3/ha of drained water. The weekly samples are then stored at −18 °C for pesticide analysis in order to get representative mean concentrations and to calculate total pollutant export. Pesticides were analyzed on raw water, at INRA Versailles laboratory until 2000. Pesticides were extracted from the liquid phase by dichloromethane and/or by acetone/dichloromethane for pesticides adsorbed on suspended matter. Purifications were performed using solid-phase extraction (styrene divinyl benzene copolymer cartridges). Concentrations of pesticides were determined with gas chromatography equipped with an electron capture detector (GCECD) or with liquid chromatography equipped with a UV detector (HPLC-UV). Since 2000, analyses were performed at GIRPA Angers laboratory with the same extraction method(s). Concentrations were then measured by liquid or gas chromatography coupled with tandem mass spectrometry (MS/MS). For the determination of glyphosate and AMPA, water samples are first extracted with diethylether to remove organic matter then purified with ethylenediaminetetraacetic acid to prevent potential fixing of glyphosate and AMPA on calcium and divalent metals (iron, copper, zinc). The HPLC method used then, consists of sample derivatization, using 9-fluorenylmethylchloroformate (FMOC), followed by HPLC analysis with fluorescence detection (Using the ProStar 363 Fluorescence Detector).

Table 8.5-147: Main physico-chemical soil characteristics on conventional tilled plot

Horizon	Thickness	Clay (%)	Silt (%)	Sand (%)	O. M (%)	Bulk density (g.cm3)	pH (water)	CEC	C/N	Structure
Ap	25	22	46	32	2.2	1.48	6.3	8.7	9	Blocky
E	17	25.9	41.3	32.8	0.77	1.63	7	7.9	8.5	Blocky
Bt	18	49.2	35.3	15.5	0.46	1.7	5.6	9.5	8.5	Prismatic
Bt/C	45	42.7	35.8	21.5	0.36	1.7	4.9	9.5	8.5	Blocky

Results

Long-term evolution of soil physico-chemical characteristics

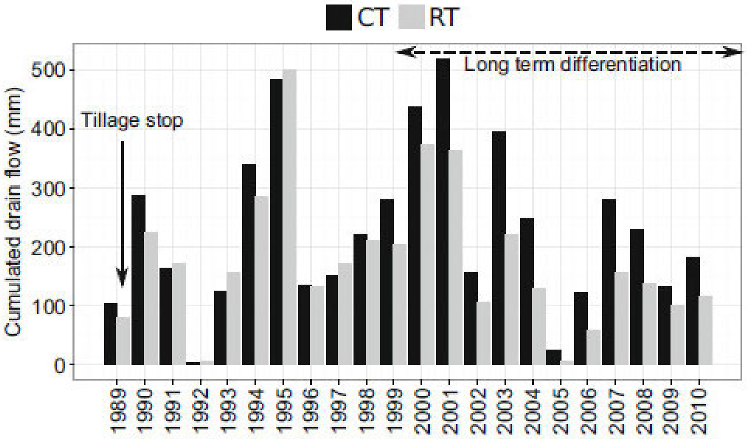
Changes induced by no tillage on the physico-chemical properties of soil are heterogeneous, for organic matter (O. M) has increased from 2.04 to 2.4% in the top layer (0–25 cm) of CT plot between 1987 and 2009. On RT plot, O. M content has risen in the top layer from 2.04 to 2.54%. However, in the first case (CT), the increase is uniform over the surface layer (0–25 cm) while for RT, the increase is located in the 0–10 cm with an O. M content of 3.4%. In the subsoil, O. M remains constant on both plots, around 0.8–0.9% from 25 to 37 cm and 0.4–0.5% from 37 to 65 cm. For bulk density, analyzed in 1994, result showed a higher value in the first layer for RT than in CT, with a mean value of 1.58 (±0.03) and 1.48 (±0.05) g/cm^3, respectively. Measurements performed in 2013 highlight bulk density stability on RT (1.59 g/cm^3)

while this characteristic has increased in CT plot (1.65 g/cm^3). Soil texture, pH, and C/N ratio show no significant variation during the study period in Ap horizon.

Water balance

Figure 8.5-88 shows annual drain flow for tilled and untilled plots from 1989 to 2010. Over the whole period, there is no significant difference between the two plots if annual data are used (p value 0.164). As illustrated, the two plots behave differently after 1999. So, drain flow becomes significantly lower on RT from 2000 to 2010 (p value 0.037). In the end, in 10 years, 1050 mm more water was drained in CT plot compared to RT plot, which is equivalent to 4 years of annual cumulated drainage (254 mm). We are therefore entitled to wonder how this difference impacts the dynamic of drainage and the consequence on pollutant transfer.

Figure 8.5-88: Annual drain water flow on CT and RT plots from 1989 to 2010



Hourly drainage dynamic

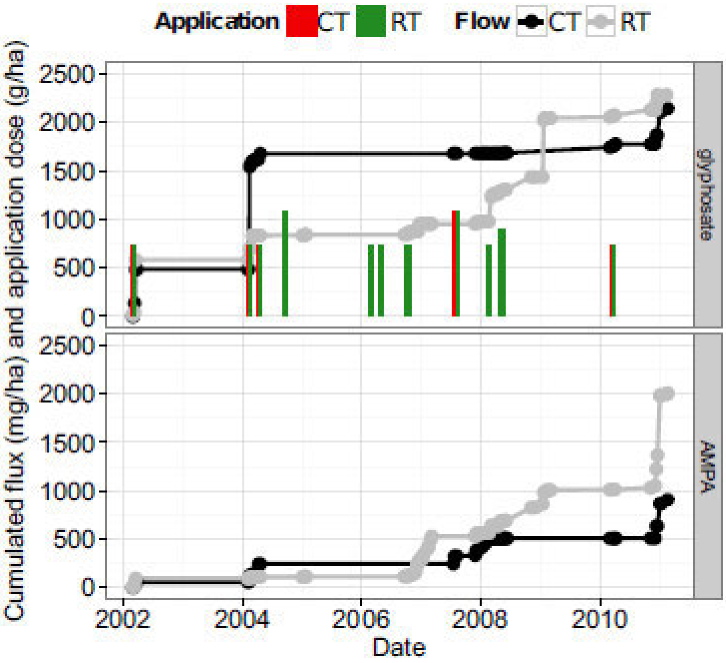
This section presents the results of hourly drainage flow analysis for the two study plots, based on flow duration curves. Analysis performed on the whole study period shows that for short duration events (1 to 6 h), flow values are higher on the untilled plot for most of the return periods. For intermediate duration events (6 to 18 h), both plots show similar flow values. For long duration events (24 to 48 h), flow values are lower on the untilled plot for a majority of the return periods. These two statements indicate that the two plots hydrodynamical behaviors are different. Thus, the unploughed plot, despite a large water deficit, shows higher peak flows than the tilled one.

We previously noticed a long-term differentiation of cumulated drained water between the two soil tillage practices. We will now study if this shift has influence on hourly drain flow dynamic. The goal is to assess how water balance variability affected the drainage hourly dynamic. Results show that for short duration events (1–6 h), ratio is decreasing from the first (1989–1999) to the second period (2000–2010) with values between 0.8–1.0 and 0.60–0.8, respectively. This means that despite a significant decline in the annual flow on RT, drain flow peak intensity has increased. Obviously, long duration events (1–2 days) exhibit higher ratio during the second period (>1.5) to offset water flow deficit. In fact, in most cases, no base flow is observed on RT (i.e, low flow values after rainy periods, corresponding to the drained water table recession). Consequently, drain peak flow on RT can be viewed as a Dirac delta distribution compared to peak flow on CT. Thus, stopping moldboard plow operation had a significant impact on water balance with a decrease of annual drained water on RT after 10 years. Surprisingly, this shift was accompanied by an increase of hourly peak flows. Difference in annual drainage is mainly caused by shorter drain flow recession and by the lack of drainage base flow as observed on the tilled plot.

Pesticides

As outlined previously, greatest applications of glyphosate on RT plot is part and parcel of this system. Thus, we choose to compare glyphosate and AMPA chronicles despite those differences. Quantification rates are higher under RT for glyphosate (58 vs 39%). Maximum glyphosate concentration and flow were observed on CT 2 days after winter application (11/02/2004) with a value of 12 µg/L and 1058 mg/ha, respectively. Accordingly, as observed in Figure 8.5-89, glyphosate exportations are link to first events following application. Over the long term, 0.052 and 0.025% of glyphosate applied dose were losses in drainage for CT and RT, respectively. There is no significant flow difference between both systems (p value 0.13) here compared on the overall period and not by application. In contrast, AMPA, which is also more quantified under RT than CT (67 vs 36%), is significantly more exported on RT plot (p value 0.006) as shown on Figure 8.5-89.

Figure 8.5-89: **Normalized cumulated solute flow (glyphosate or AMPA) versus normalized cumulated water flow from 2002 to 2009 for CT and RT plots. Date and dose of application (in g/ha) of glyphosate are also given.**



Conclusion

Despite a strong hydrodynamic differentiation (cumulated drainage, hourly dynamic) after 10 years of no-tillage practices, it is not clear if pesticide flow was or not influenced over the long term. Only periods following moldboard plow operations seem to significantly influence solute flow because tillage induces macropore network destruction, increase of water retention, and disturbance of earthworm activity. So, in this context, pesticides applied in autumn, just after tillage season, are more likely to be exported for no-tilled practices.

In conclusion, this study highlights the importance of very long term studies in tillage research (>10 years) and the interest of drained sites, in particular because of spatial integration and easy data sampling (water and solute). After 20 years without moldboard plow, a gradient of organic matter was observed in the first soil layer. Over the whole period, lower drained water on RT could be beneficial on an environmental point of view, in particular for nitrate (N–NO_3^-). In contrast, on RT plot, drainage events are more concentrated, especially during the beginning of the drainage season, leading to increased pollution risk for solute (pesticides, phosphorus) applied during this period. In addition, the absence of mechanical weeding involves an increased use of herbicide (glyphosate here). It therefore induces a possible additional risk to the diffuse pollution risk in agricultural areas, especially for soils where preferential flow are likely to happen. Finally, studying other aspects of farming systems are needed to conciliate economic, social and environmental objectives.

Assessment and conclusion by applicant:
The article describes the different long-term drainage behavior of glyphosate among other pesticides under reduced tillage and conventional tillage at the experimental station of La Jaillière located in western France. Influence of more than 20 years (1988–2010) of reduced tillage practices on water and pesticide balances and dynamics is analyzed and compared to results from a conventional tillage plot. The maximum glyphosate concentration in drainflow was observed on the conventional tillage plot 2 days after winter application with a value of 12 µg/L.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:
This articles describes a field study at experimental station of La Jaillière in western France.

It provides information on the concentrations of glyphosate and AMPA in drainflow samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

Drain flow from reduced tillage (RT) and conventional tillage (CV) plots are monitored. The influence of reduced tillage practices on water and pesticide balances and dynamics is analyzed and compared to results from a conventional tillage plot.

The applications of glyphosate are recorded, however the amounts applied are not identical on both plots and there is more regular use of pesticide on the reduced tillage plot.

The main results are reported here:
Quantification rates are higher under RT for glyphosate (58 vs 39%), but the maximum concentration in drainflow (12 µg/L, 2 days after winter application of 1058 g/ha of glyphosate) is recorded in the conventional tillage plot.

Over the long term, 0.052 and 0.025% of glyphosate applied dose were losses in drainage for CT and RT, respectively
In contrast, AMPA, which is also more quantified under RT than CT (67 vs 36%), is significantly more exported on RT plot (p value 0.006).

The article is considered reliable.

Data point:	CA 7.5/040
Report author	Lefrancq, M. *et al.*
Report year	2017
Report title	High frequency monitoring of pesticides in runoff water to improve understanding of their transport and environmental impacts
Document No	Science of the Total Environment 587-588 (2017) 75-86
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable (but concentration in surface runoff flow, and not insurface water).

Rainfall-induced peaks in pesticide concentrations can occur rapidly. Low frequency sampling may therefore largely underestimate maximum pesticide concentrations and fluxes. Detailed storm-based sampling of pesticide concentrations in runoff water to better predict pesticide sources, transport pathways and toxicity within the headwater catchments is lacking. High frequency monitoring (2 min) of seven pesticides (Dimetomorph, Fluopicolide, Glyphosate, Iprovalicarb, Tebuconazole, Tetraconazole and Triadimenol) and one degradation product (AMPA) were assessed for 20 runoff events from 2009 to 2012 at the outlet of a vineyard catchment in the Layon catchment in France. The maximum pesticide concentrations were 387 µg/L. Samples from all of the runoff events exceeded the legal limit of 0.1 µg/L for at least one pesticide (European directive 2013/39/EC). High resolution sampling used to detect the peak pesticide levels revealed that Toxic Units (TU) for algae, invertebrates and fish often exceeded the European Uniform principles (25%). The point and average (time or discharge-weighted) concentrations indicated up to a 30- or 4-fold underestimation of the TU obtained when measuring the maximum concentrations, respectively. This highlights the important role of sampling methods for assessing peak exposure. High resolution sampling combined with concentration-discharge hysteresis analyses revealed that clockwise responses were predominant (52%), indicating that Hortonian runoff is the prevailing surface runoff trigger mechanism in the study catchment. The hysteresis patterns for suspended solids and pesticides were highly dynamic and storm- and chemical-dependent. Intense rainfall events induced stronger C-Q hysteresis (magnitude). This study provides new insights into the complexity of pesticide dynamics in runoff water and highlights the ability of hysteresis analysis to improve understanding of pesticide supply and transport.

Materials and Methods

Description of the vineyard catchment

Soils overlay an impermeable Armorican substratum (Namurian Shale, Sandstone and Psammites). The catchment is characterized by three different gradients: (i) The upper catchment has 0-5% slopes (51% of the total catchment area); (ii) The middle catchment has 5-15% slopes (40%); and (iii) The lower catchment has >15% slopes (9%), including agricultural terraces. Soil depths vary from 30 cm in the lower zone to 120 cm in the upper zone. Spatial variability of the soil was characterized using 50 surface soil samples (0-20 cm) taken from across the three areas. Soil characteristics for the catchment are as follows (mean ± SE): sand: 42.3 ± 5.1%; silt: 36.1 ± 3.0%; clay: 19.5 ± 2.3%; OM: 2.1 ± 0.4%; pH: 7.1 ± 0.4; CEC: 10.4 ± 0.8 meq 100/g; $CaCO_3$: 0.1%. The structural stability of the soils was measured by immersing soil aggregates in water followed by the separation of the soil fraction using mechanical sieving. Fractions >250 µm were measured and constituted an index of soil stability. Grassed rows were comprised of 38 ± 12% stable aggregates while weeded rows were comprised of 18 ± 6% stable aggregates, which indicate a limited risk of soil sealing. Mean annual rainfall is 623 mm (±124 mm) (1985-2014, Beaulieu sur Layon, 3 km from the study site).

Pesticide properties and application

In the studied vineyard, 31 commercial products with 21 different active ingredients were applied in the following amounts: 3.1, 4.8, 2.1 and 3.0 kg in 2009, 2010, 2011 and 2012, respectively. Of those products used, 53, 28, 54 and 32% were fungicides, respectively. The study focused on 7 pesticides (Dimetomorph (DIM), Fluopicolide (FLU), Glyphosate (GLY), Iprovalicarbe (IPR), Tebuconazole (TEB), Tetraconazole (TET) and Triadimenol (TRI)) and one degradation product (AMPA) because of their detection frequency and their yearly applied mass within the study catchment (Table 8.5-148 and Table 8.5-149). The physical and chemical characteristics of these 8 compounds are provided in Table 8.5-148. The 7 pesticides were mostly applied between March and July. TEB and TRI were generally applied to the upstream section of plot A, while FLU, IPR and TET were only applied to plot B (Figure 8.5-90). The ability of high resolution sampling to improve our knowledge of the pesticide sources, transport pathways and ecological impacts in runoff was assessed using these 8 compounds.

Figure 8.5-90: **The study catchment with the experimental setup (Rochefort sur Loire, 47°19″ 19.47″N;0°38″21.39″W)**

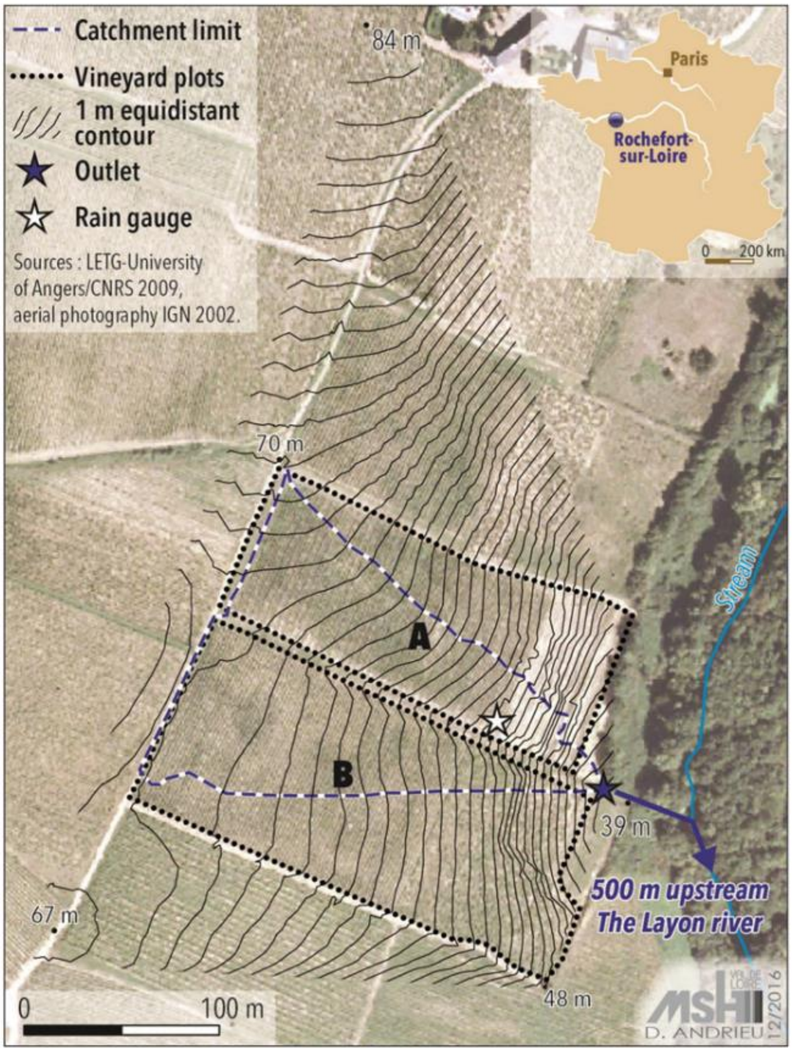


Table 8.5-148: **Family, type, commercial formulations, physicochemical properties, toxicity and detection frequency of the 7 pesticides (DIM, FLU, GLY, IPR, TEB, TET, TRI) and degradation product (AMPA)**

Compound	Abbrv.	Commercial formulation	Chemical family	Formula	Physico-chemical characteristics of active substances						
					Log K_{ow}[a] [–]	Log K_{oc}[d] [–]	Henry constant[a] (25 °C) [Pa m^3 mol^{-1}]	DT_{50} (aerobic-anaerobic soil)[b] [day]	DT_{50} field[d] [day]	EC50[a,c] [ppm]	Detection frequency (20 events) [%]
Dimethomorph	DIM	Panthéos/ Arco DTI/ Fastime/ Tulsa	Morpholine	$C_{21}H_{22}ClNO_4$	2.68	2.61	2.04×10^{-05}	75–26	10–61	> 10.6	90.9
Fluopicolide	FLU	Profiler	Benzamide	$C_{14}H_8Cl_3F_3N_2O$	2.90	2.50	4.15×10^{-05}	415–561	132	>1.8	100
Glyphosate	GLY	Roundup/ Vival/ Sirlene	Phosphonoglycine	$C_3H_8NO_5P$	−3.20	3.85	2.10×10^{-07}	96–22	5–21	40	100
AMPA	*AMPA*	–	Unclassified	CH_6NO_3P	−1.63	–	0.16	n.a.	76–240	n.a.	100
Iprovalicarbe	IPR	Ocarina	Carbamate	$C_{18}H_{28}N_2O_3$	3.20	–	1.40×10^{-06}	15.5–n.a	n.a.	n.a.	40.9
Tebuconazole	TEB	Abilis	Triazole	$C_{16}H_{22}ClN_3O$	3.7	3.00	1.00×10^{-05}	597–1260	20–92	2.79	22.7
Tetraconazole	TET	Greman	Triazole	$C_{13}H_{11}Cl_2F_4N_3O$	3.56	–	3.60×10^{-04}	364–180	136–1688	3.0	86.3
Triadimenol	TRI	Abilis	Triazole	$C_{14}H_{18}ClN_3O_2$	3.18	2.40	3.5×10^{-06}	250–n.a	110–375	51	31.8

[a] Obtained from the PPDB (2007, 2008, 2009), The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU) at the University of Hertfordshire.

[b] Obtained from the PAN (PAN, 2006) pesticide data base.

[c] *Daphnia magna* test, 48 h obtained from PPDB data base.

[d] Obtained from AGRITOX.

Table 8.5-149: **Application amount [g] and number of applications [-] (in brackets) of the 7 pesticides (DIM, FLU, GLY, IPR, TEB, TET, TRI) in 2009, 2010, 2011 and 2012**

	Applied total mass [g] (number of applications [−])				
Compound	2009	2010	2011	2012	Total
DIM	373.8 (2)	177.8 (1)	177.8 (1)	231.2 (2)	960.5 (6)
FLU			105.2 (1)		105.2 (1)
GLY	1087.2 (3)	2642.4 (3)	933.3 (2)	1999.8 (2)	6662.7 (10)
IPR	213.3 (1)			89.6 (1)	302.9 (2)
TEB	124.2 (3)	54.0 (1)	54.0 (1)		232.2 (5)
TET	40.3 (2)	39.5 (2)	39.5 (2)	39.5 (2)	158.8 (8)
TRI	41.4 (3)	18.0 (1)	18.0 (1)		77.4 (5)

Hydrological and sampling procedures

Rainfall intensity was recorded using a tipping bucket rain gauge. Water discharge was measured at the catchment outlet every 30 s using a bubbler flow module with a 5 mm precision combined with a Venturi channel. As soon as the water level increased above 2 cm, 500 mL of water were sampled every 2 min using an automatic sampler containing 24 polyethylene flasks of 500 mL. Automatic phone calls notified people on duty if the rainfall event exceeded the capacity of the sampler, enabling manual sampling of the rest of the event when necessary. Water samples were then collected and placed on ice for transportation to the laboratory.

Chemical analysis

Samples were filtered to measure the total suspended solid concentration (TSS). Raw and filtered samples were kept at -18°C in the dark prior to chemical analysis. GLY and AMPA samples were analysed after filtering (0.45 µm). Other compounds were analysed in raw water in order to not underestimate the runoff export via the particulate phase (>0.45 µm). However, for 22 arbitrarily selected samples from the measured runoff events, fungicides were analysed in both filtered and raw forms to investigate the partitioning of those fungicides in the “dissolved phase” (<0.45 µm) and in the particulate phase (>0.45 µm). DIM, FLU, IPR and TET concentrations in raw and filtered water did not differ significantly, indicating that fungicides were predominantly transported in the dissolved phase, which is supported by previous studies (Maillard and Imfeld, 2014). TEB and TRI were not quantifiable in the 22 samples but are hypothesized to behave similarly to TET because they belong to the same triazole family and have a similar log K_{ow} (Table 8.5-148). GLY and AMPA were analysed using HPLC separation with spectrofluorimetric detection after decomplexation of both analytes, followed by a derivatization using 9-fluorenylmethyl chloroformate (FMOC-Cl). The average recovery rates were 100 % and 105 % for glyphosate and AMPA, respectively. The detection and quantification limits were 0.03 µg/L and 0.09 µg/L for glyphosate and 0.04 µg/L and 0.1 µg/L for AMPA, respectively. Other pesticide analyses were performed as follows. After spiking with surrogate standards chlorpyriphos-d_{10} and diuron-d_6, water samples (500 mL) were successively liquid-liquid extracted at 3 pHs (<2, 7 and >12) using a mixture of dichloromethane: ethyl acetate 80:20. The extracts were combined, dehydrated and evaporated under vacuum. The concentrated extract was transferred into a vial and adjusted accurately to 1 mL with ethyl acetate. An aliquot of this extract was solvent exchanged with a mixture of water:methanol (50:50 with 0.1 % acetic acid). Analysis was performed by liquid chromatography/electrospray ionisation tandem mass spectrometry (LC/ESI-MSMS). The remainder of the ethyl acetate extract was analysed by gas chromatography/ion trap tandem mass spectrometry GC/IT-MS-MS. The pesticide quantification limit within the water samples was 0.05 µg/L. Recovery rates ranged between 86 and 96%.

Data analysis and calculation

Climatic and hydrological data

To compare the amount, intensity and duration of rainfall events, an event index (EVI) was calculated using the following ratio (Baartman *et al.*, 2013):

$$EVI = \frac{\mathrm{Imax} \times \mathrm{Rtot}}{\mathrm{D}} \quad (1)$$

where I_{max} is the maximum rainfall intensity [mm/h], R_{tot} is the rainfall amount [mm] and D is the rainfall duration [min]. A high EVI represents a short but intense rainfall event, whereas a low EVI indicates an event with a low intensity but long duration. The catchment response time is defined as the time between the gravity centre of the rain event and the peak outflow.

Pesticide export

The maximum pesticide concentration, which was measured, was supposed to be the maximum of the event and was labelled the pesticide peak. To calculate pesticide loads, linearity of the values between two successive concentration data points or flow measurements was assumed. When pesticides were not detected (336 analyses, i.e. 16%), concentrations were set to zero to calculate the mean concentrations, occurrences and loadings. When pesticide concentrations were detected but lower than the quantification limit (186 analyses, i.e. 9%), the sample concentration was set to half of the quantification limit. Pesticide export coefficients were estimated as the ratio of the exported loads from a runoff event compared to the cumulative application of the year preceding the studied runoff event. Hydrological characteristics and pesticide concentrations were compared using the paired nonparametric Wilcoxon signed rank test and the Spearman rank correlation test. Statistical tests were performed using the R software.

Ecotoxicological data

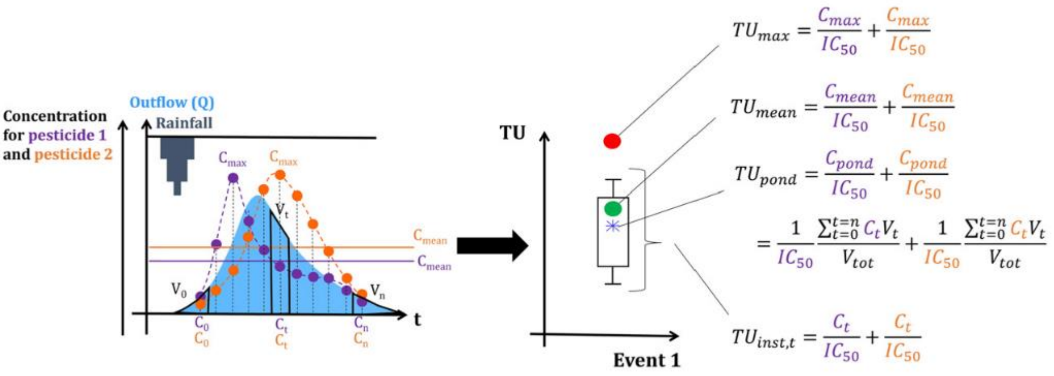
The impact of the pesticide mixture toxicity on the aquatic ecosystem was evaluated using the TU approach (Bundschuh *et al.*, 2014). TU was estimated as follows for each event:

$$TU = \sum_{i=1}^{n} \frac{C_i}{IC_{50i}} \quad (2)$$

where C_i is the concentration of pesticide i within a mixture of n pesticides [µg/L] and IC_{50i} is the concentration of pesticide i which induces a response halfway between the baseline and maximum after a specified exposure time [µg/L]. In our study, IC_{50} values were taken from the PPDB database (Lewis *et al.*, 2016) and were related to three trophic levels: algal growth inhibition (acute 72 h), invertebrate immobility (acute 48 h) and fish mortality (acute 96 h). Although other species may be more sensitive, for comparison purposes, Daphnia magna and Oncorhynchus mykiss were used to study the effects of all pesticides, except for TET, on invertebrate and fish species, respectively. TET effects on fish species were measured using Lepomis macrochirus. Pseudokirchneriella subcapitata and Scenedemus subspicatus were primarily used to study the effects of the 8 target compounds on green algae. If no data for these green algae species were available (i.e., for GLY, FLU, IPR and TET), IC_{50}-data for any other green algae species were used (Bundschuh *et al.*, 2014). Four different methods were used to estimate C_i to test the loss of ecotoxicological information associated with the different sampling methods. The formulas used are illustrated in Figure 8.5-91. Within these formulas, C_i represents: (i) the point concentration within each sample ($C_{inst,t}$ used to estimate $TU_{inst,t}$), (ii) the maximum concentration during the runoff event (C_{max} used to estimate TU_{max}), (iii) the average concentration during runoff event (C_{mean} used to estimate TU_{mean}) and (iv) the discharge-weighted average concentration (C_{pond} used to estimate TU_{pond}). C_{mean} represents the concentration of a pool of samples obtained at regular time intervals, whereas C_{pond} represents the concentration of a pool of samples obtained for a constant outflow volume. $C_{inst,t}$ represents the potential concentration that may occur for a random sample. Estimated TU values were compared to the European Union TU threshold of 0.1 for algae and 0.01 for invertebrates and fish, which are known as the European Uniform Principles (European Commission, 2011). Tus were estimated for all studied runoff events except

October, 20 2009 and October, 14 2012. Data for these two events were omitted because not all compounds were analysed.

Figure 8.5-91: **Representation of the four different TU_{max}, TU_{mean}, TU_{pond}, TU_{inst} calculations for an artificial runoff event with n samplings for two different compounds, called 1 (purple) and 2 (orange)**



First flush calculation

A first-flush effect is defined to occur when a disproportionately greater pesticide load is transported by a relatively small proportion of the runoff volume during the beginning of a runoff event. The first flush (FF [%]) is defined as follows:

$$FF_X = \frac{\int_0^{t_X} C(t)Q(t)dt}{\int_0^{T} C(t)Q(t)dt} \times 100 \qquad (3)$$

where X is the defined runoff volume of a sample as a percent of the total runoff [%], here, 10, 25, 50 and 75%; C(t) [µg/L] and Q(t) [L/s] are the pesticide concentration and the runoff outflow at time t, respectively; T is the duration of the runoff event [min]; and t_x is the time at which X% of runoff has been delivered [min]. A FF_X value significantly larger than X indicates a disproportionate phenomenon. Bertrand-Krajewski *et al*. (1998) assumed that a significant first flush occurred if at least 80% of the total pollutant mass was transported in the first 30% of runoff discharged during a rainfall event.

Hysteresis pattern

Runoff events for which at least 2 sample points were quantifiable have been taken along both the rising and falling limb were used in the present study to investigate the hysteresis patterns. To compare the hysteretic loops of different runoff events and solutes, two quantitative indices were used. First, the rotational parameter ΔR, which integrates information on the hysteresis area and direction, was estimated as follows:

$$\Delta R = R \times A_h \qquad (4)$$

where A_h is the normalized hysteresis area, calculated as the polygon area of the convex-hull of the C-Q hysteresis curve after standardizing discharges and concentrations to a unity scale; and R is the hysteresis direction (1 for clockwise, -1 for anticlockwise and 0 for no or an unclear hysteresis pattern). Therefore, ΔR varied between -1 to 1. The magnitude parameter, ΔC, represents the relative change in pesticide concentrations during the runoff event and is measured as follows:

$$\Delta C = \frac{C_{max} - C_{min}}{C_{max}} \quad (5)$$

where C_{max} and C_{min} are the maximum and minimum pesticide concentrations, respectively.

Results

Characteristics of selected rainfall-runoff events

Twenty rainfall-runoff events occurring between 2009 and 2012 were studied. Each event yielded >1 m^3 total discharge at the outlet of the catchment. These events represented a wide range of rainfall intensities and durations, runoff percentages and volumes (Figure 8.5-92 and Table 8.5-150). Selected rainfall events exhibited return periods ranging from 0 to 10 years (Data from MeteoFrance, Table 8.5-150). The runoff coefficient ranged from 0.3 to 47 %. The catchment response time ranged between 5 and 482 min, with an average of 88.5 min. For events with a high EVI, i.e., intense and short rainfall, discharge occurred rapidly (short response time) ($p < 0.001$) (Table 8.5-150). The concentration of TSS ranged between 11 and 6454 mg/L (Table 8.5-151) and was positively correlated with outflow ($p < 0.001$), suggesting that rill erosion occurred. Maximum pesticide concentrations reached 13, 8, 386.9, 47, 3, 81, 68 and 4.2 µg/L for DIM, FLU, GLY, AMPA, IPR, TEB, TET and TRI, respectively (Table 8.5-151). For each runoff event, maximum pesticide concentrations decreased with increasing time following the last application of the analysed pesticide ($p < 0.016$) (Table 8.5-151). This indicates the occurrence of a dissipation effect, as previously mentioned in literature (Arias-Estévez *et al*., 2008). The exported pesticide and AMPA loads for each of the events are represented in Figure 8.5-92. Maximum exported loads for a single event reached 154, 142, 2229, 660, 39, 185, 255 and 39 mg, for DIM, FLU, GLY, AMPA, IPR, TEB, TET and TRI respectively. This export corresponded to 0.04, 0.13, 0.21, 0.02, 0.23, 1.29 and 0.22% of the application loads during the preceding year of the runoff event, respectively (Table 8.5-151). Such high export for single event may lead to significant ecotoxicological impact on the surrounding ecosystem.

Figure 8.5-92: **Rainfall, outflow, total suspended solids (TSS) and pesticide and degradation product loads (GLY, AMPA, DIM, FLU, IPR, TEB, TET, TRI) for 20 runoff events in a vineyard catchment (Rochefort sur Loire, France)**

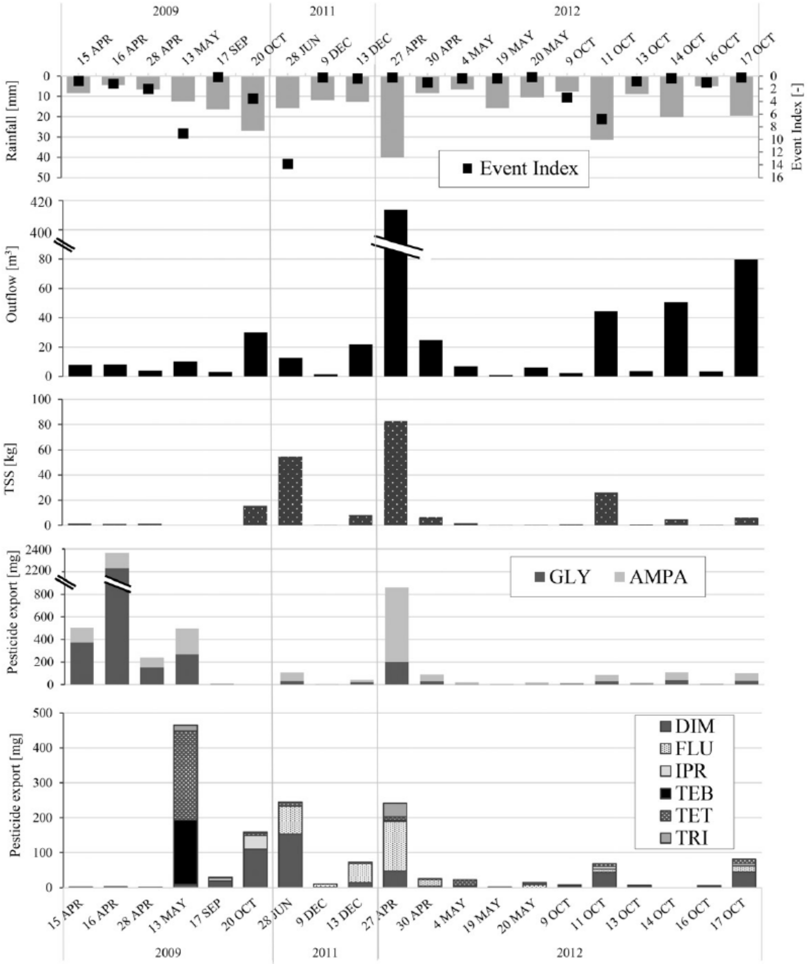
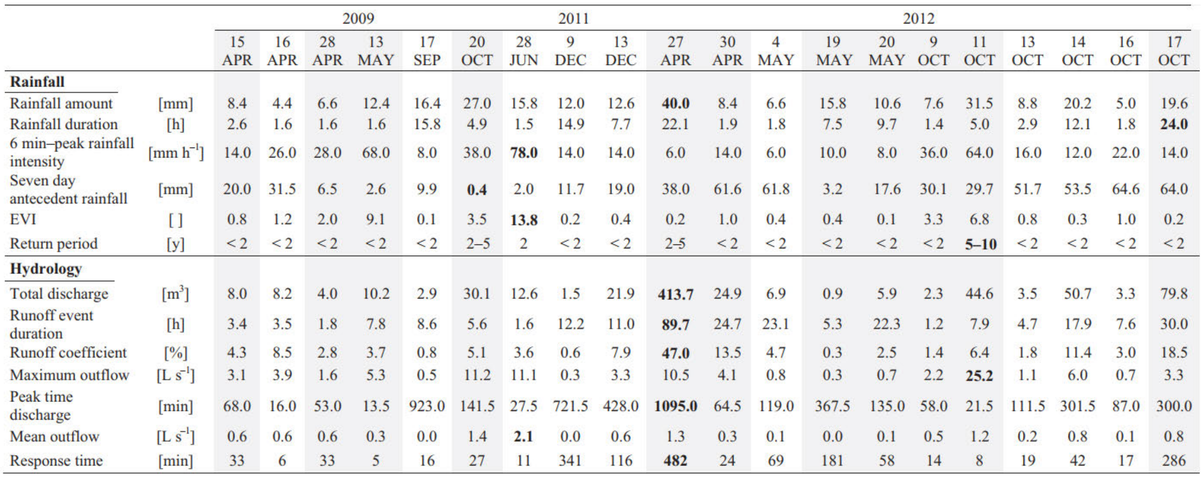


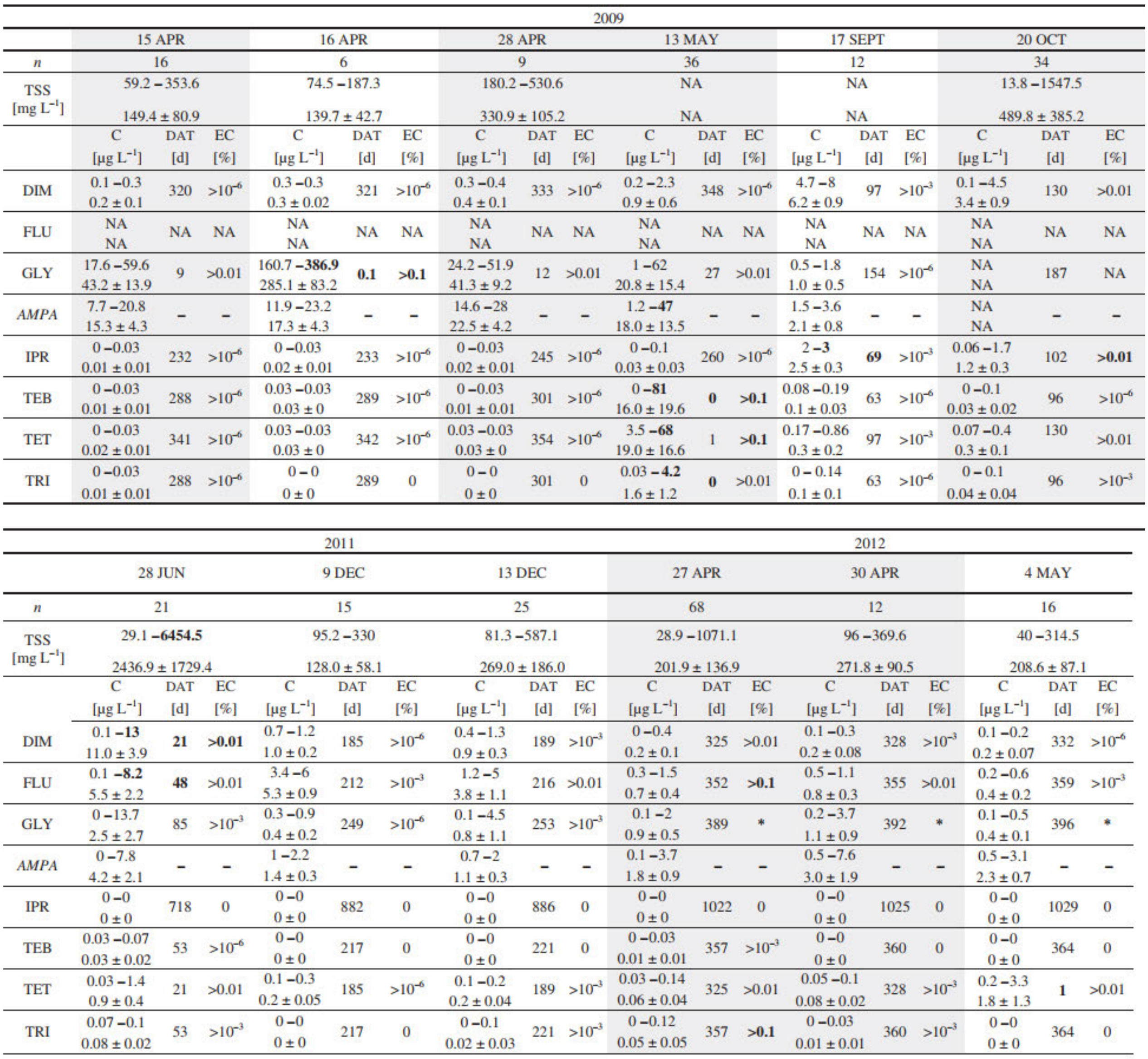
Table 8.5-150: **Climatic and hydrology characteristics of the 20 studied runoff events (Rochefort sur Loire, France). Values in bold are extremes. Grey cases represent hysteresis analysis events with at least two measured points along the rising and falling limbs**



		2009						2011			2012										
		15 APR	16 APR	28 APR	13 MAY	17 SEP	20 OCT	28 JUN	9 DEC	13 DEC	27 APR	30 APR	4 MAY	19 MAY	20 MAY	9 OCT	11 OCT	13 OCT	14 OCT	16 OCT	17 OCT
Rainfall																					
Rainfall amount	[mm]	8.4	4.4	6.6	12.4	16.4	27.0	15.8	12.0	12.6	**40.0**	8.4	6.6	15.8	10.6	7.6	31.5	8.8	20.2	5.0	19.6
Rainfall duration	[h]	2.6	1.6	1.6	1.6	15.8	4.9	1.5	14.9	7.7	22.1	1.9	1.8	7.5	9.7	1.4	5.0	2.9	12.1	1.8	**24.0**
6 min–peak rainfall intensity	[mm h^{-1}]	14.0	26.0	28.0	68.0	8.0	38.0	**78.0**	14.0	14.0	6.0	14.0	6.0	10.0	8.0	36.0	64.0	16.0	12.0	22.0	14.0
Seven day antecedent rainfall	[mm]	20.0	31.5	6.5	2.6	9.9	**0.4**	2.0	11.7	19.0	38.0	61.6	61.8	3.2	17.6	30.1	29.7	51.7	53.5	64.6	64.0
EVI	[ ]	0.8	1.2	2.0	9.1	0.1	3.5	**13.8**	0.2	0.4	0.2	1.0	0.4	0.4	0.1	3.3	6.8	0.8	0.3	1.0	0.2
Return period	[y]	< 2	< 2	< 2	< 2	< 2	2–5	2	< 2	< 2	2–5	< 2	< 2	< 2	< 2	< 2	**5–10**	< 2	< 2	< 2	< 2
Hydrology																					
Total discharge	[m^3]	8.0	8.2	4.0	10.2	2.9	30.1	12.6	1.5	21.9	**413.7**	24.9	6.9	0.9	5.9	2.3	44.6	3.5	50.7	3.3	79.8
Runoff event duration	[h]	3.4	3.5	1.8	7.8	8.6	5.6	1.6	12.2	11.0	**89.7**	24.7	23.1	5.3	22.3	1.2	7.9	4.7	17.9	7.6	30.0
Runoff coefficient	[%]	4.3	8.5	2.8	3.7	0.8	5.1	3.6	0.6	7.9	**47.0**	13.5	4.7	0.3	2.5	1.4	6.4	1.8	11.4	3.0	18.5
Maximum outflow	[L s^{-1}]	3.1	3.9	1.6	5.3	0.5	11.2	11.1	0.3	3.3	10.5	4.1	0.8	0.3	0.7	2.2	**25.2**	1.1	6.0	0.7	3.3
Peak time discharge	[min]	68.0	16.0	53.0	13.5	923.0	141.5	27.5	721.5	428.0	**1095.0**	64.5	119.0	367.5	135.0	58.0	21.5	111.5	301.5	87.0	300.0
Mean outflow	[L s^{-1}]	0.6	0.6	0.6	0.3	0.0	1.4	**2.1**	0.0	0.6	1.3	0.3	0.1	0.0	0.1	0.5	1.2	0.2	0.8	0.1	0.8
Response time	[min]	33	6	33	5	16	27	11	341	116	**482**	24	69	181	58	14	8	19	42	17	286

Table 8.5-151: Number of days after treatment (DAT) [d], export coefficient (EC) [%] and total suspended solids (TSS) [mg/L] and pesticide concentrations [µg/L] (C; provided as min - max and mean ± standard deviation) (DIM, FLU, GLY, AMPA, IPR, TEB, TET, TRI) in the study catchment (Rochefort sur Loire, France). Values in bold signify extremes for each lines. n is the number of samples for each event. Grey cases represent hysteresis analysis events with at least two measured points along the rising and falling limbs. EC are expressed in four classes: "≥0.1" for EC ≥0.1, "≥0.01" for 0.1 N EC ≥0.01, "≥10-3" for 0.01 N EC ≥0.001 and "≥10-6" for 0.001 N EC ≥10-6.

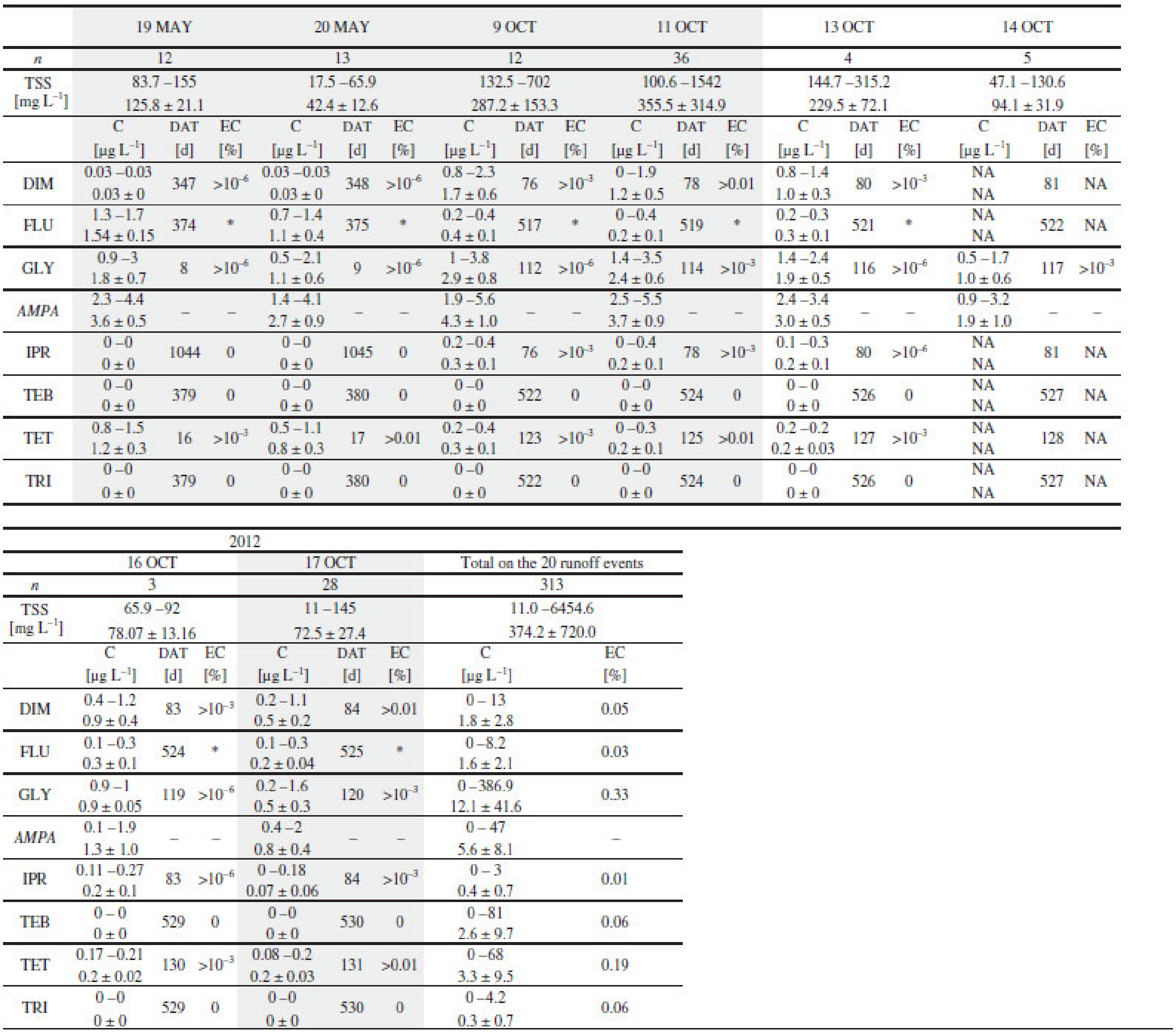
*** showed cases when positive exported loads of pesticide occurred while this pesticide was not applied during the previous year.**



	2009																	
	15 APR			16 APR			28 APR			13 MAY			17 SEPT			20 OCT		
n	16			6			9			36			12			34		
TSS [mg L^{-1}]	59.2 – 353.6 149.4 ± 80.9			74.5 – 187.3 139.7 ± 42.7			180.2 – 530.6 330.9 ± 105.2			NA NA			NA NA			13.8 – 1547.5 489.8 ± 385.2		
	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]
DIM	0.1 – 0.3 0.2 ± 0.1	320	$>10^{-6}$	0.3 – 0.3 0.3 ± 0.02	321	$>10^{-6}$	0.3 – 0.4 0.4 ± 0.1	333	$>10^{-6}$	0.2 – 2.3 0.9 ± 0.6	348	$>10^{-6}$	4.7 – 8 6.2 ± 0.9	97	$>10^{-3}$	0.1 – 4.5 3.4 ± 0.9	130	>0.01
FLU	NA NA	NA	NA	NA NA	NA	NA	NA NA	NA	NA	NA NA	NA	NA	NA NA	NA	NA	NA NA	NA	NA
GLY	17.6 – 59.6 43.2 ± 13.9	9	>0.01	160.7 – **386.9** 285.1 ± 83.2	**0.1**	**>0.1**	24.2 – 51.9 41.3 ± 9.2	12	>0.01	1 – 62 20.8 ± 15.4	27	>0.01	0.5 – 1.8 1.0 ± 0.5	154	$>10^{-6}$	NA NA	187	NA
AMPA	7.7 – 20.8 15.3 ± 4.3	–	–	11.9 – 23.2 17.3 ± 4.3	–	–	14.6 – 28 22.5 ± 4.2	–	–	1.2 – **47** 18.0 ± 13.5	–	–	1.5 – 3.6 2.1 ± 0.8	–	–	NA NA	–	–
IPR	0 – 0.03 0.01 ± 0.01	232	$>10^{-6}$	0 – 0.03 0.02 ± 0.01	233	$>10^{-6}$	0 – 0.03 0.02 ± 0.01	245	$>10^{-6}$	0 – 0.1 0.03 ± 0.03	260	$>10^{-6}$	2 – **3** 2.5 ± 0.3	**69**	$>10^{-3}$	0.06 – 1.7 1.2 ± 0.3	102	**>0.01**
TEB	0 – 0.03 0.01 ± 0.01	288	$>10^{-6}$	0.03 – 0.03 0.03 ± 0	289	$>10^{-6}$	0 – 0.03 0.01 ± 0.01	301	$>10^{-6}$	0 – **81** 16.0 ± 19.6	**0**	**>0.1**	0.08 – 0.19 0.1 ± 0.03	63	$>10^{-6}$	0 – 0.1 0.03 ± 0.02	96	$>10^{-6}$
TET	0 – 0.03 0.02 ± 0.01	341	$>10^{-6}$	0.03 – 0.03 0.03 ± 0	342	$>10^{-6}$	0.03 – 0.03 0.03 ± 0	354	$>10^{-6}$	3.5 – **68** 19.0 ± 16.6	1	**>0.1**	0.17 – 0.86 0.3 ± 0.2	97	$>10^{-3}$	0.07 – 0.4 0.3 ± 0.1	130	>0.01
TRI	0 – 0.03 0.01 ± 0.01	288	$>10^{-6}$	0 – 0 0 ± 0	289	0	0 – 0 0 ± 0	301	0	0.03 – **4.2** 1.6 ± 1.2	**0**	>0.01	0 – 0.14 0.1 ± 0.1	63	$>10^{-6}$	0 – 0.1 0.04 ± 0.04	96	$>10^{-3}$

	2011									2012								
	28 JUN			9 DEC			13 DEC			27 APR			30 APR			4 MAY		
n	21			15			25			68			12			16		
TSS [mg L^{-1}]	29.1 – **6454.5** 2436.9 ± 1729.4			95.2 – 330 128.0 ± 58.1			81.3 – 587.1 269.0 ± 186.0			28.9 – 1071.1 201.9 ± 136.9			96 – 369.6 271.8 ± 90.5			40 – 314.5 208.6 ± 87.1		
	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]
DIM	0.1 – **13** 11.0 ± 3.9	**21**	**>0.01**	0.7 – 1.2 1.0 ± 0.2	185	$>10^{-6}$	0.4 – 1.3 0.9 ± 0.3	189	$>10^{-3}$	0 – 0.4 0.2 ± 0.1	325	>0.01	0.1 – 0.3 0.2 ± 0.08	328	$>10^{-3}$	0.1 – 0.2 0.2 ± 0.07	332	$>10^{-6}$
FLU	0.1 – **8.2** 5.5 ± 2.2	**48**	>0.01	3.4 – 6 5.3 ± 0.9	212	$>10^{-3}$	1.2 – 5 3.8 ± 1.1	216	>0.01	0.3 – 1.5 0.7 ± 0.4	352	**>0.1**	0.5 – 1.1 0.8 ± 0.3	355	>0.01	0.2 – 0.6 0.4 ± 0.2	359	$>10^{-3}$
GLY	0 – 13.7 2.5 ± 2.7	85	$>10^{-3}$	0.3 – 0.9 0.4 ± 0.2	249	$>10^{-6}$	0.1 – 4.5 0.8 ± 1.1	253	$>10^{-3}$	0.1 – 2 0.9 ± 0.5	389	*	0.2 – 3.7 1.1 ± 0.9	392	*	0.1 – 0.5 0.4 ± 0.1	396	*
AMPA	0 – 7.8 4.2 ± 2.1	–	–	1 – 2.2 1.4 ± 0.3	–	–	0.7 – 2 1.1 ± 0.3	–	–	0.1 – 3.7 1.8 ± 0.9	–	–	0.5 – 7.6 3.0 ± 1.9	–	–	0.5 – 3.1 2.3 ± 0.7	–	–
IPR	0 – 0 0 ± 0	718	0	0 – 0 0 ± 0	882	0	0 – 0 0 ± 0	886	0	0 – 0 0 ± 0	1022	0	0 – 0 0 ± 0	1025	0	0 – 0 0 ± 0	1029	0
TEB	0.03 – 0.07 0.03 ± 0.02	53	$>10^{-6}$	0 – 0 0 ± 0	217	0	0 – 0 0 ± 0	221	0	0 – 0.03 0.01 ± 0.01	357	$>10^{-3}$	0 – 0 0 ± 0	360	0	0 – 0 0 ± 0	364	0
TET	0.03 – 1.4 0.9 ± 0.4	21	>0.01	0.1 – 0.3 0.2 ± 0.05	185	$>10^{-6}$	0.1 – 0.2 0.2 ± 0.04	189	$>10^{-3}$	0.03 – 0.14 0.06 ± 0.04	325	>0.01	0.05 – 0.1 0.08 ± 0.02	328	$>10^{-3}$	0.2 – 3.3 1.8 ± 1.3	**1**	>0.01
TRI	0.07 – 0.1 0.08 ± 0.02	53	$>10^{-3}$	0 – 0 0 ± 0	217	0	0 – 0.1 0.02 ± 0.03	221	$>10^{-3}$	0 – 0.12 0.05 ± 0.05	357	**>0.1**	0 – 0.03 0.01 ± 0.01	360	$>10^{-3}$	0 – 0 0 ± 0	364	0

Table 8.5-151 – continued



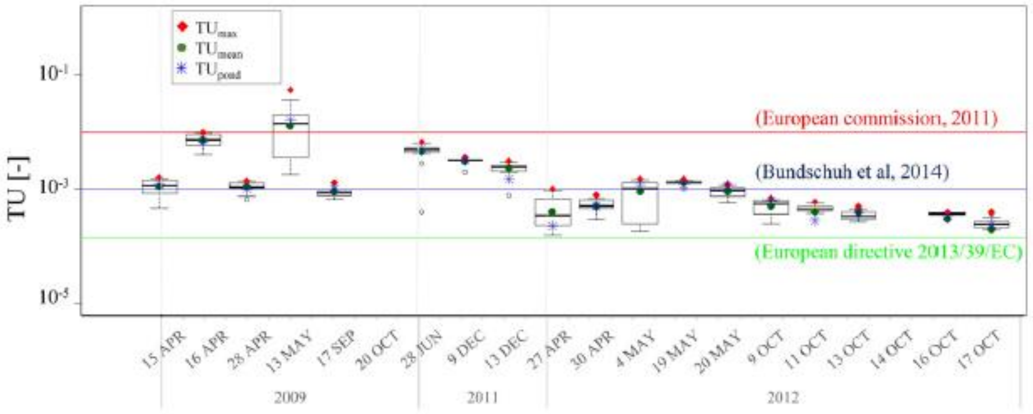
	19 MAY			20 MAY			9 OCT			11 OCT			13 OCT			14 OCT		
n	12			13			12			36			4			5		
TSS [mg L^{-1}]	83.7 –155 125.8 ± 21.1			17.5 –65.9 42.4 ± 12.6			132.5 –702 287.2 ± 153.3			100.6 –1542 355.5 ± 314.9			144.7 –315.2 229.5 ± 72.1			47.1 –130.6 94.1 ± 31.9		
	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]
DIM	0.03 –0.03 0.03 ± 0	347	>10^{-6}	0.03 –0.03 0.03 ± 0	348	>10^{-6}	0.8 –2.3 1.7 ± 0.6	76	>10^{-3}	0 –1.9 1.2 ± 0.5	78	>0.01	0.8 –1.4 1.0 ± 0.3	80	>10^{-3}	NA NA	81	NA
FLU	1.3 –1.7 1.54 ± 0.15	374	*	0.7 –1.4 1.1 ± 0.4	375	*	0.2 –0.4 0.4 ± 0.1	517	*	0 –0.4 0.2 ± 0.1	519	*	0.2 –0.3 0.3 ± 0.1	521	*	NA NA	522	NA
GLY	0.9 –3 1.8 ± 0.7	8	>10^{-6}	0.5 –2.1 1.1 ± 0.6	9	>10^{-6}	1 –3.8 2.9 ± 0.8	112	>10^{-6}	1.4 –3.5 2.4 ± 0.6	114	>10^{-3}	1.4 –2.4 1.9 ± 0.5	116	>10^{-6}	0.5 –1.7 1.0 ± 0.6	117	>10^{-3}
AMPA	2.3 –4.4 3.6 ± 0.5	–	–	1.4 –4.1 2.7 ± 0.9	–	–	1.9 –5.6 4.3 ± 1.0	–	–	2.5 –5.5 3.7 ± 0.9	–	–	2.4 –3.4 3.0 ± 0.5	–	–	0.9 –3.2 1.9 ± 1.0	–	–
IPR	0 –0 0 ± 0	1044	0	0 –0 0 ± 0	1045	0	0.2 –0.4 0.3 ± 0.1	76	>10^{-3}	0 –0.4 0.2 ± 0.1	78	>10^{-3}	0.1 –0.3 0.2 ± 0.1	80	>10^{-6}	NA NA	81	NA
TEB	0 –0 0 ± 0	379	0	0 –0 0 ± 0	380	0	0 –0 0 ± 0	522	0	0 –0 0 ± 0	524	0	0 – 0 0 ± 0	526	0	NA NA	527	NA
TET	0.8 –1.5 1.2 ± 0.3	16	>10^{-3}	0.5 –1.1 0.8 ± 0.3	17	>0.01	0.2 –0.4 0.3 ± 0.1	123	>10^{-3}	0 –0.3 0.2 ± 0.1	125	>0.01	0.2 –0.2 0.2 ± 0.03	127	>10^{-3}	NA NA	128	NA
TRI	0 –0 0 ± 0	379	0	0 –0 0 ± 0	380	0	0 –0 0 ± 0	522	0	0 –0 0 ± 0	524	0	0 –0 0 ± 0	526	0	NA NA	527	NA

	2012							
	16 OCT			17 OCT			Total on the 20 runoff events	
n	3			28			313	
TSS [mg L^{-1}]	65.9 –92 78.07 ± 13.16			11 –145 72.5 ± 27.4			11.0 –6454.6 374.2 ± 720.0	
	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	DAT [d]	EC [%]	C [µg L^{-1}]	EC [%]
DIM	0.4 –1.2 0.9 ± 0.4	83	>10^{-3}	0.2 –1.1 0.5 ± 0.2	84	>0.01	0 – 13 1.8 ± 2.8	0.05
FLU	0.1 –0.3 0.3 ± 0.1	524	*	0.1 –0.3 0.2 ± 0.04	525	*	0 –8.2 1.6 ± 2.1	0.03
GLY	0.9 –1 0.9 ± 0.05	119	>10^{-6}	0.2 –1.6 0.5 ± 0.3	120	>10^{-3}	0 –386.9 12.1 ± 41.6	0.33
AMPA	0.1 –1.9 1.3 ± 1.0	–	–	0.4 –2 0.8 ± 0.4	–	–	0 – 47 5.6 ± 8.1	–
IPR	0.11 –0.27 0.2 ± 0.1	83	>10^{-6}	0 –0.18 0.07 ± 0.06	84	>10^{-3}	0 – 3 0.4 ± 0.7	0.01
TEB	0 – 0 0 ± 0	529	0	0 –0 0 ± 0	530	0	0 –81 2.6 ± 9.7	0.06
TET	0.17 –0.21 0.2 ± 0.02	130	>10^{-3}	0.08 –0.2 0.2 ± 0.03	131	>0.01	0 –68 3.3 ± 9.5	0.19
TRI	0 –0 0 ± 0	529	0	0 –0 0 ± 0	530	0	0 –4.2 0.3 ± 0.7	0.06

Toxicity impact

All runoff water samples contained at least one pesticide with a concentration exceeding 0.1 µg/L (Table 8.5-151). Thus, pesticide levels in the studied catchment continuously exceed mandated acceptable concentrations (European directive 2013/39/EC). Toxic units based on maximum concentrations (TU_{max}) reached 0.29, 0.05 and 0.04 for algae, invertebrate and fish, respectively. The percentage of runoff events that exceeded the European Uniform Principles threshold for these species was 15, 5 and 25%, respectively. Several researchers questioned the relevance of the TU threshold set by the EU for invertebrates (red line in Figure 8.5-93). Instead, these researchers preferred to use a TU value of 0.001 for invertebrates (blue line in Figure 8.5-93). Based on this threshold, 55% of events analysed in the present study may represent a risk to the integrity of the aquatic ecosystem. Dilution occurs when these flows reach the Layon River 500 m downstream. However, approximately 182 km^2 of vineyards feed the Layon River, suggesting the potential combination of contaminated flows from >8000 small headwater catchments with features similar to our study site. TU (max and mean) for fish and invertebrates were negatively correlated with seven-day antecedent rainfall ($p < 0.001$), highlighting a dissipation effect with preceding rainfall (Olsson *et al*., 2013). The variations between the different TU estimations are represented for invertebrates in Figure 8.5-93. Surprisingly, very little variation was observed between TU_{mean} and TU_{pond}. There was, on average, 1.6 (and up to 4) times greater TU_{max} than TU_{mean} and 3.4 (up to 30) times greater than TU_{inst}. The method used to estimate TU results in significant differences in the values obtained, which is partly due to the variability of pesticide concentrations patterns throughout the hydrograph.

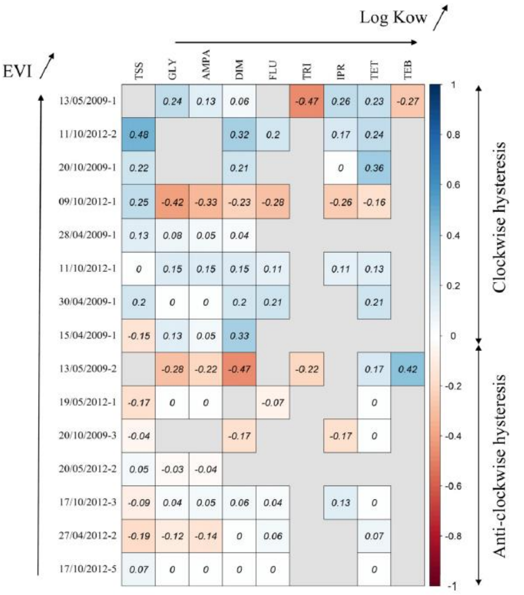
Figure 8.5-93: Toxic unit for Daphnia magna immobility (acute 48 h) based on observed point concentrations (boxplot), maximum concentrations (red) and mean concentrations (green) for the 20 runoff events (log scale).Horizontal lines represent the toxic unit threshold of the European commission for invertebrates (0.01 in red), based on ecotoxicological studies (Bundschuh *et al*., 2014) (0.001 in blue) and calculated using mandated acceptable concentrations of 0.1 µg/L for each pesticide (European directive 2013/39/EC) (0.00014 in green).



First flush and concentration-discharge patterns

The mean and range of the first flushes FF10, FF25, FF50 and FF75 for all chemicals across the 20 runoff events were 9.8 ± 5.2, 25.3 ± 10.2, 50.6 ± 13, 75.5 ± 11.6%, respectively. It suggests that no disproportionate event occurred. In other words, no “first flush effect” as defined by Bertrand-Krajewski *et al.* (1998) was observed, contrary to expectations. Nevertheless, this phenomenon may occur when pesticides are rapidly mobilized at the beginning of a runoff event if those pesticides are less-sorptive than those in the present study or if their source area is very near the catchment outlet. 15 runoff peaks allowed us to study the differences between the rising and falling limb of the hydrograph (at least two sample points for each rising and falling limb were taken during these events) (Figure 8.5-94). Between 57 and 99% of the water discharge volume occurred during the falling limb, which may be partly due to natural and artificial drainage features that delayed the flow. TSS and pesticide concentrations did not significantly differ between the rising and falling limb ($p > 0.05$) (except for AMPA and the triazole family: TEB, TET, TRI) and thus require a deeper analysis of concentration patterns. Based on previously determined hysteresis classifications (Bieroza and Heathwaite, 2015), 52% of the concentration versus discharge graph of quantified suspended solid or pesticide values exhibited clockwise patterns, 27% exhibited anticlockwise patterns and 21% had no or an unclear hysteresis pattern (Figure 8.5-94). ΔR ranged from -0.47 to 0.48, with an absolute average of 0.15 ± 0.11. ΔC ranged from 0.21 to 1, with an average of 0.64 ± 0.24. ΔR for TSS and EVI were correlated ($p < 0.01$), indicating that the clockwise hysteresis of TSS occurred for intense rainfall events, whereas an anti-clockwise hysteresis pattern was observed for mild rainfall events. The direction of the hysteresis loops for pesticides were not consistent between substances within an event, nor for one substance across all events. AMPA, DIM, FLU, IPR, TEB and TET presented predominantly clockwise hysteresis patterns (52%), while TRI exhibited anti-clockwise pattern (67%) and GLY exhibited unclear pattern (54%). Figure 8.5-94 shows that for intense events (high EVI), stronger hysteresis patterns (clockwise or anti-clockwise) were predominant, as indicated by a greater loop area. However, this tendency was significant only for GLY, FLU and TET ($p < 0.05$). ΔR for GLY, AMPA, DIM and FLU was significantly and positively correlated with maximum outflow and the runoff coefficient ($p < 0.05$). On the other hand, the number of days since the last application, air temperature and antecedent rainfall did not correlate with ΔR. No hysteresis trends were observed based on the pesticide affinity for water (K_{ow}), as might have been expected. That study found that pesticide molecules with low to moderate solubility resulted in clockwise hysteresis loops while soluble molecules resulted in anticlockwise loops in an 1110 km^2 groundwater-based catchment.

Figure 8.5-94: **Hysteresis rotational parameter ΔR (clockwise=positive (blue), anti-clockwise=negative (red) and no or unclear hysteresis pattern=null) for the 15 runoff peaks and TSS, GLY, AMPA, DIM, FLU, TRI, IPR, TET and TEB. Values represent the normalized area of the C-Q hysteresis. Grey cases represent undetected or unavailable data. Runoff peaks are named with the runoff date and a subscript which represents the number of the peak within the runoff event.**



	TSS	GLY	AMPA	DIM	FLU	TRI	IPR	TET	TEB
13/05/2009-1		0.24	0.13	0.06		-0.47	0.26	0.23	-0.27
11/10/2012-2	0.48			0.32	0.2		0.17	0.24	
20/10/2009-1	0.22			0.21			0	0.36	
09/10/2012-1	0.25	-0.42	-0.33	-0.23	-0.28		-0.26	-0.16	
28/04/2009-1	0.13	0.08	0.05	0.04					
11/10/2012-1	0	0.15	0.15	0.15	0.11		0.11	0.13	
30/04/2009-1	0.2	0	0	0.2	0.21			0.21	
15/04/2009-1	-0.15	0.13	0.05	0.33					
13/05/2009-2		-0.28	-0.22	-0.47		-0.22		0.17	0.42
19/05/2012-1	-0.17	0	0		-0.07			0	
20/10/2009-3	-0.04			-0.17			-0.17	0	
20/05/2012-2	0.05	-0.03	-0.04						
17/10/2012-3	-0.09	0.04	0.05	0.06	0.04		0.13	0	
27/04/2012-2	-0.19	-0.12	-0.14	0	0.06			0.07	
17/10/2012-5	0.07	0	0	0	0			0	

Discussion

High frequency sampling is costly but reveals important information about the ecotoxicity and underlying hydrological and hydrochemical processes governing pesticide transport in headwater catchments.

Hydrological functioning of catchments

Often, saturation excess runoff is related to low soil depth, good soil structure, high organic matter content, and low erosion potential. On the other hand, Hortonian runoff is associated with steep slopes, the absence of base flow, and crusted soils characterised by low clay and organic matter contents and low structural stability (Descroix *et al*., 2007; Tilahun *et al*., 2016). In this study, indicators of both types of possible runoff scenarios are present such as low soil depth (30-120 cm), 20% clay content and high structural stability indicating saturation excess runoff but also steep slopes and the absence of a base flow indicating Hortonian runoff. For all runoff events, pesticide concentrations correlated with flow rate (significant except for FLU and TET, $p < 0.05$), indicating a concentration effect and not a dilution effect. The concentrations of the 8 compounds correlated with TSS concentrations ($p < 0.0025$). This suggests that pesticide mobilisation and transport occurred along similar pathways as TSS, which was largely a function of Hortonian runoff associated with intense rainfall. In addition, maximum concentrations are positively correlated with EVIs (only significant for GLY and AMPA, $p < 0.01$). A clockwise hysteresis loop was the most observed pattern within the study site, as was expected for a small catchment (Hudson, 2003; Seeger *et al*., 2004). This suggests the direct and rapid mobilisation of TSS and pesticides via runoff and indicates that drainage had a minimal impact on pesticide and TSS export (Marttila and Kløve, 2010). In the present study, intense rainfall events caused stronger hysteresis patterns (whether clockwise or anti-clockwise) with greater loop areas (Figure 8.5-94). This is partly due to two different, chronological occurrences. For clockwise hysteresis patterns, intense rainfall events rapidly induced surface runoff and a higher runoff coefficient.

Rapid mobilisation of pesticides can thus occur as a flush of available pesticides prior to peak outflow. For anti-clockwise hysteresis patterns, intense rainfall events can activate pesticide sources further from the catchment outlet, less hydrologically connected or dryer (Doppler *et al*., 2014). On the contrary, mild rainfall events did not possess enough energy or power to rapidly mobilise pesticides nearby or to activate and transport pesticides from further away, resulting in diffuse pollution with a small or non-existent hysteresis area. The shift from a clockwise to anti-clockwise hysteresis pattern for different substances within an event or for one pesticide across runoff events was highly dynamic and dependent on the storm and substance rather than only on the catchment characteristics as previously suggested (Bieroza and Heathwaite, 2015; Thompson *et al.,* 2012) (Figure 8.5-94).

Ecotoxicological impact of runoff events
Maximum TU values were observed for runoff events that occurred very near the application date, for intense rainfall events and after a dry period; in other words, for the first significant rainfall event after application. There are only small differences in the TU_{mean} and TU_{pond} values (Figure 8.5-93) indicating that frequent sampling at short time intervals gives relatively the same value for TU regardless of the method of computation. The potential range of concentrations with random sampling are reflected with the point concentration (or TU_{inst} values). Random sampling, e.g., every month, as often performed by national monitoring programs (Botta *et al*., 2012; Bundschuh *et al*., 2014), may underestimate peak exposure.

This highlights the importance of the sampling method in assessing the ecotoxicological impact of contaminated runoff on nearby ecosystems. Where FLU represented 19% of the total pesticide load in all runoff in 2011 and 2012, this pesticide accounted for 59, 79 and 96% of the composite TU value for invertebrates, fish and algae. FLU was extremely persistent and was always detected (>525 days) after a single application of the pesticide on plot B.

Supply limitation vs transport limitation
Pesticides primarily enter agricultural streams during rainfall events *via* runoff; their movement is dependent on the presence of a sufficient amount of the given pesticide and its availability (supply), as well as its ability to be mobilized via runoff (transport). No first flush effect was observed in the present study and the contribution of pesticide exports was similar during almost all runoff events. Pesticide transport rather than pesticide sources appeared thus to be the limiting factor in pesticide exports from the catchment. The sequence of several runoff peaks, with the clockwise followed by anticlockwise runoff peaks was observed on both May 13, 2009 and October 20, 2009 (13/05/2009-1 followed by 13/05/2009-2 and 20/10/2009-1 followed by 20/10/2009-3 in Figure 8.5-94). This sequence supports the hypothesis that an exhaustion effect was present, i.e., the rapid mobilisation of pesticides or suspended solids occurred during the first peak (transport limitation), which limited the source during the second peak (supply limitation) (Bieroza and Heathwaite, 2015; Bowes *et al*., 2009). Degradation, and thus a supply limitation, can be evaluated for GLY in the presence of AMPA. The relationship between AMPA and glyphosate were evaluated by calculating % AMPA as a percentage of the molar load of AMPA compared to the total molar loads of GLY and AMPA (Imfeld *et al*., 2013). A gradual increase in % AMPA from the last application was observed, indicating degradation of glyphosate ($p < 0.05$). % AMPA generally exceeded 60%, except in April 2009, near the glyphosate application dates, and averaged 67.0 ± 19.3% across runoff events. AMPA and GLY always followed the same hysteresis patterns; however, % AMPA did not correlate significantly with ΔR or ΔC ($p > 0.05$). TEB and TRI exhibited similar concentration patterns ($p < 0.01$), with first flush calculations that differed significantly compared to the other studied chemicals ($p \leq 0.05$). These pesticides exhibited a predominantly anticlockwise hysteresis pattern. Given that their sorption characteristics fell within the same range as the other pesticides studied (Table 8.5-148), anti-clockwise patterns may be partly due to the application area, which was mainly on the upstream section of plot A. Further location of the application area may delay the pesticide arrival at the outlet of the catchment ([redacted], 2012). Hysteresis patterns for the different substances within an event or for an individual substance across events were highly dynamic and shifted between clockwise and anti-clockwise patterns. This may be partly due to (i) the complexity of the studied outflow discharge, which often had multiple peaks and indicated different flow pathways within the catchment (transport limitation) and (ii) the complex interplay between the temporal and spatial evolution of the pesticide stocks related to their application date, amount and mode (foliar or directly on soil), as well as their degradation or their availability via sorption (supply limitation). Few studies address surface dominated catchments or organic pesticides such as in the present study (Pietroń *et al*., 2015; Taghavi *et al.*, 2011), which limited our ability to make direct comparisons.

Conclusion

High frequency sampling is certainly costly but enables the reliable estimation of maximum pesticide concentration and fluxes. Furthermore, it reveals information about the underlying hydrological and hydrochemical processes governing pesticide transport. Altogether, the results highlight that (i) for all runoff events, the pesticide concentrations increased with outflow and significant pesticide export can occur during a single event; (ii) when the TU of the pesticide mixture was analysed, the European Uniform Principles for algae, invertebrates and fish were regularly exceeded (15%) and FLU was responsible for the majority of the toxicity (59-96%); (iii) random sampling may result in an up to 30-fold underestimation of the TU for invertebrates obtained using the maximum concentration, highlighting the important role of the sampling methods for assessing peak exposure; (iv) no first flush occurred, and the contribution of the pesticide loads from different section along the hydrograph was mostly homogeneous; and (v) hysteresis patterns were complex and highly dynamic. Individual events can be interpreted in a particular way but not consistently given the complex interactions between hydrology and reactive transport at the study site. The primary limitation of the study was the lack of knowledge about pesticide sources and availability in soils before each rainfall event. This knowledge would help to better interpret hysteresis patterns. Detailed off-site pesticide transport information may support the design and adaptation of mitigation strategies and crop management techniques. For example, here, the absence of an important first flush phenomenon for all of the studied pesticides questions the relevance of mitigation strategies based on the retention of the first part of the runoff volume, such as small storm water wetland. Further field studies that evaluate concentration-discharge patterns for pesticides are needed to better understand the hysteresis behaviour of pesticides and use it as a tool to predict the sources and pathways of pesticides within agricultural catchments. Such an internal signature for a catchment may help researchers to better understand pesticide source availability, mobilisation and transport in runoff water.

Assessment and conclusion by applicant:

The article reports the results from a runoff experiment in a French vineyard with different pesticides with a high-frequency setup. Data on glyphosate and AMPA were measured and reported.
The article is considered reliable.

Assessment and conclusion by RMS:

The article reports the results from a runoff experiment in a French vineyard with different pesticides with a high-frequency setup. Glyphosate concentration is recorded in flow based sampling of runoff events, monitored from 2009 to 2012.
It provides supportive information on the concentrations of glyphosate and AMPA in surface runoff flow samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

Water discharge was measured at the catchment outlet every 30 s using a bubbler flow module with a 5 mm precision combined with a Venturi channel. As soon as the water level increased above 2 cm, 500 mL of water were sampled every 2 min using an automatic sampler containing 24 polyethylene flasks of 500 mL.

Maximum concentration of 386.9 µg/L for glyphosate, less than one day after treatment, and of 47 µg/L for AMPA are reported in the article.

The article is considered reliable.

Data point:	CA 7.5/041
Report author	Lerch, R.N. *et al*.
Report year	2017
Report title	Vegetative Buffer Strips for Reducing Herbicide Transport in Runoff: Effects of Buffer Width, Vegetation, and Season
Document No	Journal of the American Water Resources Association (JAWRA) 53(3):667-683.
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

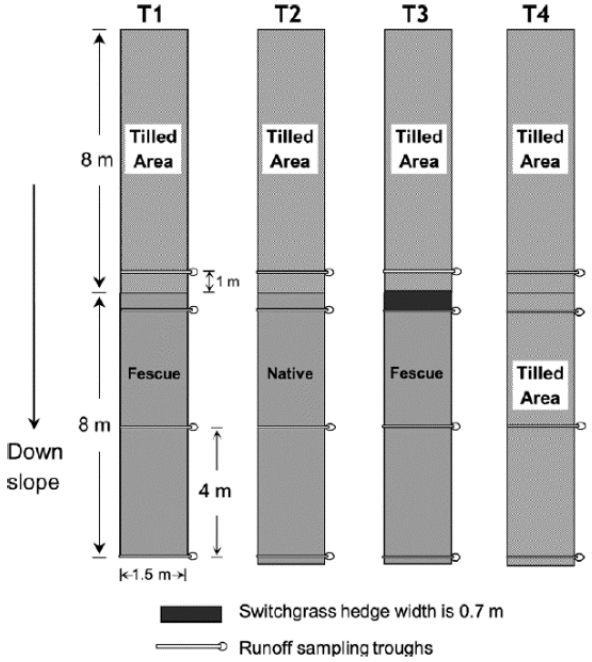
The effectiveness of vegetative buffer strips (VBS) for reducing herbicide transport has not been well documented for runoff prone soils. A multi-year plot-scale study was conducted on an eroded claypan soil with the following objectives: (1) assess the effects of buffer width, vegetation, and season on runoff transport of atrazine (ATR), metolachlor (MET), and glyphosate; (2) develop VBS design criteria for herbicides; and (3) compare differences in soil quality among vegetation treatments. Rainfall simulation was used to create uniform antecedent soil water content and to generate runoff. Vegetation treatment and buffer width impacted herbicide loads much more than season. Grass treatments reduced herbicide loads by 19-28% and sediment loads by 67% compared to the control. Grass treatments increased retention of dissolved-phase herbicides by both infiltration and adsorption, but adsorption accounted for the greatest proportion of retained herbicide load. This latter finding indicated VBS can be effective on poorly drained soils or when the source to buffer area ratio is high. Grass treatments modestly improved surface soil quality 8-13 years after establishment, with significant increases in organic C, total N, and ATR and MET sorption compared to continuously tilled control. Herbicide loads as a function of buffer width were well described by first-order decay models, which indicated VBS can provide significant load reductions under anticipated field conditions.

Materials and Methods

Experimental Design

Experiment was established in 2002 at the University of Missouri near Columbia, Missouri. Twelve 1.5 m x 16 m plots with four treatments replicated three times were arranged in a randomized complete block design (Figure 8.5-95). The upper half of each plot (1.5 m x 8 m) was managed under continuous cultivated fallow and served as the source area that received herbicide applications. The lower half of the plots included four vegetation treatments as one set of factors: (1) tall fescue (*F. arundinacea*) (TF); (2) TF with a 0.7-m wide switchgrass (*P. virgatum* L.) hedge at the upslope end of the VBS (Hedge + TF), (3) native warm-season grasses, mainly comprised of Indian grass (*Sorghastrum nutans* L.), eastern gamagrass (*T. dactyloides*), and switchgrass (Native); and (4) continuous cultivated control. Management of the source area under continuous cultivation was used to mimic pre-emergent herbicide application to tilled cropland, which is a common practice in the region. The control treatment represented a non-vegetative treatment for comparison to the grass treatments and tillage was a practical way to maintain consistent conditions. The study was conducted on an eroded Mexico silt loam with an average slope of 5%.

Figure 8.5-95: Schematic Diagram Showing One Set of Treatments with Plot Dimensions and Sampler Locations. Treatments were replicated three times. T1, tall fescue (TF); T2, native warm-season grass mixture (Native); T3, switchgrass hedge + tall fescue (Hedge + TF); and T4, Control.



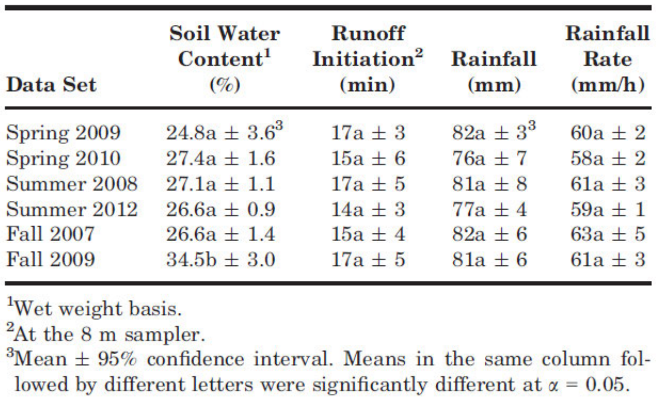
Runoff Event Simulations and Runoff Collection

A rotating-boom rainfall simulator was used to produce uniform antecedent soil water content in the plots before herbicide application and to generate runoff following application. To control antecedent soil water content, simulated rainfall was applied about 24 h before the runoff event until ponding occurred; typically 30-40 min of rainfall was required. Three soil samples were collected from the tilled portion of the plots immediately before the runoff events for determination of water content. Three herbicides, ATR (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine), S-metolachlor (MET) (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide), and glyphosate (GLY) (N-phosphonomethyl-glycine) were applied with a backpack sprayer to the upper 8 m of the plots approximately 16-20 h before simulated runoff was generated. Runoff samples were collected with the initiation of runoff at the 8-m sampler (i.e., runoff was generated over the entire plot area) for a given plot.

Laboratory Analyses

All samples were analyzed for suspended sediment concentration and dissolved and sediment-bound herbicide concentrations. Dissolved-phase herbicide concentrations were determined on filtered samples using magnetic particle enzyme-linked immunosorbent assays

Table 8.5-152: Summary of rainfall simulation and antecedent soil water content data



Data Set	Soil Water Content[1] (%)	Runoff Initiation[2] (min)	Rainfall (mm)	Rainfall Rate (mm/h)
Spring 2009	24.8a ± 3.6[3]	17a ± 3	82a ± 3[3]	60a ± 2
Spring 2010	27.4a ± 1.6	15a ± 6	76a ± 7	58a ± 2
Summer 2008	27.1a ± 1.1	17a ± 5	81a ± 8	61a ± 3
Summer 2012	26.6a ± 0.9	14a ± 3	77a ± 4	59a ± 1
Fall 2007	26.6a ± 1.4	15a ± 4	82a ± 6	63a ± 5
Fall 2009	34.5b ± 3.0	17a ± 5	81a ± 6	61a ± 3

[1] Wet weight basis.

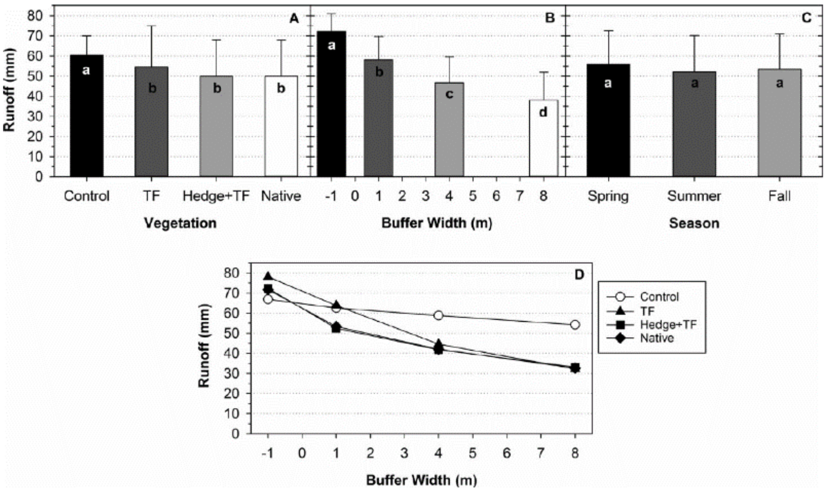
[2] At the 8 m sampler.

[3] Mean ± 95% confidence interval. Means in the same column followed by different letters were significantly different at $\alpha = 0.05$.

Statistical Analyses

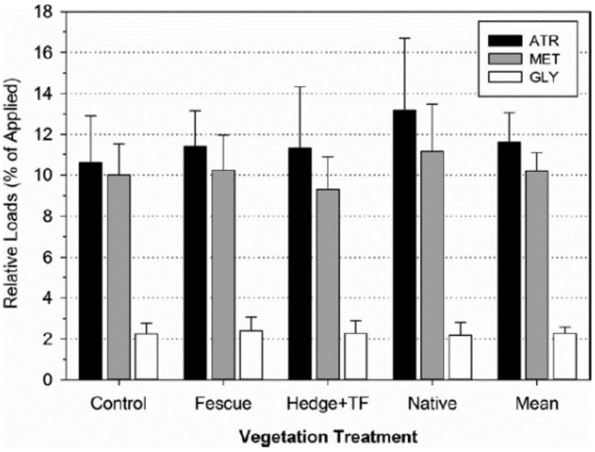
To assess consistency of the rainfall simulator, total applied rainfall, rainfall rate, time to runoff initiation (at the 8 m sampler), and antecedent soil water content were analyzed by one-way analysis of variance (ANOVA) grouped by the individual datasets (i.e., Spring 2009, Spring 2010, Summer 2008, Summer 2012, Fall 2007, Fall 2009) using the Excel add-in, Winstat. If the p value for the ANOVA was ≤0.05, then differences between treatment means were determined by the LSD method at p = 0.05.

Figure 8.5-96: Mean Runoff for the Following Factors: (A) Vegetation; (B) Buffer Width; (C) Season; and (D) Vegetation by Buffer Width Interaction. Error bars are 95% confidence intervals. Within a main effect, treatments with different letters were significantly different at α = 0.05. Control, unvegetated; TF, tall fescue; Hedge + TF, switchgrass hedge plus tall fescue; and Native, warm-season native grass mixture.



All other variables were analyzed as a three-way factorial using the mixed ANOVA procedure (PROC MIXED) in SAS 4.3 with year and plot as random effects. Differences between treatment means were determined by the PDIFF procedure. All main effects, interactions, and mean comparisons were considered significantly different at α = 0.05. Nonlinear regression was used to relate changes in INLs as a function of buffer width using a three-parameter first-order decay model.

Figure 8.5-97: Relative Herbicide Loads, as Percent of Applied, at the -1 m Sampler for Each Vegetation Treatment. Error bars are 95% confidence intervals. No significant differences between vegetation treatments for any of the herbicides. ATR, atrazine; MET, metolachlor; and GLY, glyphosate.



Soil Quality Assessments

General Soil Properties.
Soil samples were collected from 0 to 10 cm depth within the vegetative buffers by compositing at least 20 subsample cores of 1.3 cm diameter. Samples were collected in May 2010 in the Control, TF, and Native treatments and within the switchgrass hedge of the Hedge + TF treatment. For the Hedge + TF treatment, subsamples were collected in proportion to the area covered by switchgrass and TF and composited to achieve representative samples. Samples were stored field moist at 2-4°C until analyses could be completed. Soils were air-dried, mixed, and sieved to 2-mm before conducting basic chemical characterization analyses, including particle size analysis, cation exchange capacity, organic C, total N, and pH using methods reported by Nathan *et al.* (2012). These same treatments were also sampled for bulk density determination using 7.6 cm diameter by 7.6 cm long cores. In May 2011, a set of samples was collected in the same manner as described above for determination of microbial enzyme activities. Methods described by Lin *et al.* (2011b) were used to measure the activities of β-glucosidase (GLU), dehydrogenase (DHG), and fluorescein diacetate (FDA) hydrolysis. To determine saturated hydraulic conductivity (Ksat), two intact soil cores were collected from within the buffers of the four vegetation treatments at 0-10 and 10-20 cm depths in May 2012. The constant head method was used to measure Ksat for most samples while the falling head method was used on some samples with low Ksat values.

Herbicide Sorption.
Another set of soil samples was collected from the four vegetation treatments in December 2015 in the same manner as that described previously. These samples were assessed for herbicide sorption using a single concentration batch equilibration method as described by Chu *et al.* (2013). Prior to the sorption experiments, the field moist soils were sieved to 2-mm, root and plant material removed, and moisture content determined. For each herbicide, a stock solution of 1 mg/L in an electrolyte solution of 0.003 M $CaCl_2$ and 0.0015 M NaN_3 (antimicrobial agent) was prepared. Batch equilibration experiments were performed by adding 30 mL of herbicide stock solution to 15.0 g (dry weight) of soil in a 50 mL polypropylene co-polymer centrifuge tube, followed by agitation on an end-to-end shaker at 100 oscillations/min at room temperature (22-25°C). Preliminary experiments were performed to determine equilibration times for each herbicide: 16 h for ATR and MET; 24 h for GLY. After shaking, the samples were centrifuged for 5 min at 1,850 x g and the herbicide concentration remaining in solution was determined by ELISA using appropriate dilutions for each herbicide. Duplicate subsamples of each plot were analyzed along with soil-free herbicide samples and an electrolyte blank.

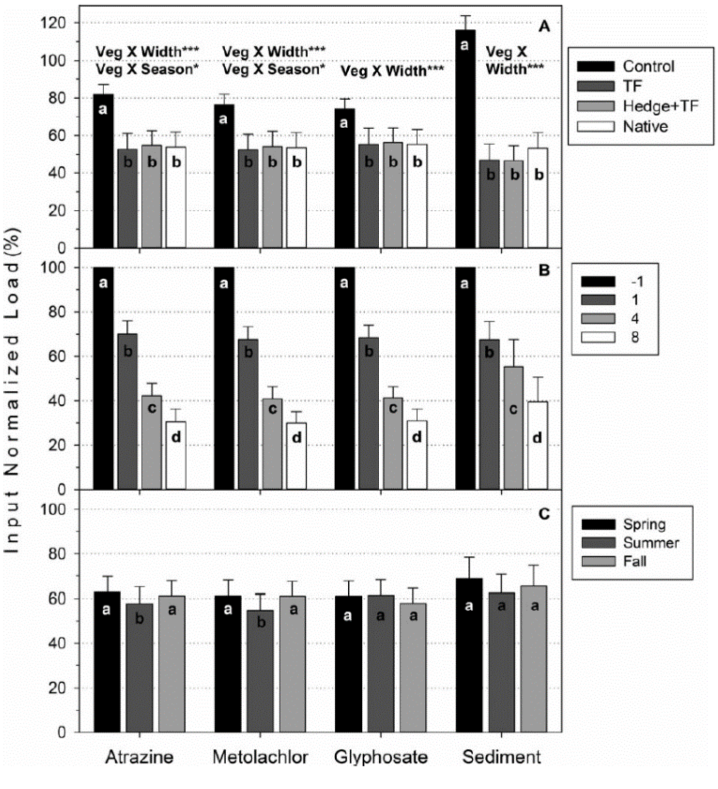
The solid-solution distribution coefficients, Kd (in L/kg), were computed as the ratio of the sorbed to solution concentrations at equilibrium. Statistical analyses to determine vegetation treatment differences in soil quality parameters were determined by either one-way or two-way ANOVA ($\alpha = 0.05$), and mean comparisons were made using the PDIFF procedure with Bonferroni adjustment.

Results and Discussion

Hydrologic Data

The rainfall simulator performed very consistently over the course of the experiment (Table 8.5-152). With the exception of Fall 2009, antecedent soil water content was similar among the datasets. The significantly greater soil water content in Fall 2009 resulted from a series of natural rainfall events within 24 h of all but one of the simulated events. However, the natural rainfall did not significantly affect the time to runoff initiation or the total rainfall applied compared to the other datasets. The average time to runoff initiation varied minimally, ranging from 14 to 17 min. Runoff was significantly affected by both vegetation and buffer width (Figure 8.5-96). The vegetation effect demonstrated that all the grass treatments were comparably effective at reducing runoff relative to the control. The significant vegetation by buffer width interaction occurred due to the greater reductions in runoff depth for the grass treatments as a function of buffer width compared to the control (Figure 8.5-96D). Compared to the runoff input at -1 m, the grass treatments decreased runoff depth by an average of 56% at 8 m, while the control only decreased runoff by 19%. TF had greater runoff depth at -1 m than the other vegetation treatments, but all grass treatments were significantly lower than the control at 4 m and 8 m.

Figure 8.5-98: **Mean Input Normalized Loads for atrazine, metolachlor, glyphosate, and sediment by Main Factors of: (A) Vegetation; (B) Buffer Width; and (C) Season. Error bars indicate 95% confidence intervals. Within a main effect, treatments with different letters were significantly different at a = 0.05. Significance of interactions: *p < 0.05; ***p < 0.001.**



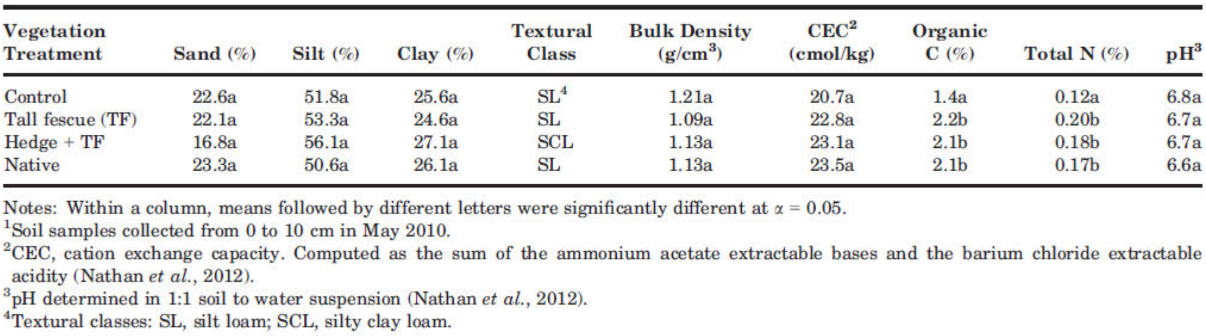
Herbicide and Sediment Loads

Relative herbicide loads at the -1 m sampler were consistent over the vegetation treatments (Figure 8.5-97) with no significant differences between treatments for any of the herbicides. Mean relative loads entering the VBS for ATR varied from 10.6% of applied for the control to 13.2% for the Native treatment. MET results were similar with relative loads ranging from 9.3% for the Hedge + TF to 11.2% for the Native treatments. In contrast, GLY loads were much lower, ranging from 2.2 to 2.4%, and also much less varied than those observed for ATR and MET. The relative load results indicated that the intense simulated storms represented robust scenarios for testing the ability of VBS to reduce herbicide transport. Dissolved-phase transport as a proportion of total herbicide load at the -1 m sampler was 99 ± 0.3% (95% CI) for ATR, 96 ± 0.6% for MET, and 64 ± 2.0% for GLY, results that are consistent with previous runoff studies (Wauchope, 1978; Lin *et al*., 2011a). These results demonstrated the much greater soil sorption of GLY compared to ATR and MET and the importance of both dissolved phase and sediment-bound transport to GLY losses in runoff.

The effect of the main factors on herbicide and sediment loss in runoff showed that vegetation treatment and buffer width had the greatest impact on loads while the effect of season was more limited (Figure 8.5-98). Analogous to the runoff results, the vegetation treatment effect showed that all grass treatments were similarly effective at reducing herbicide and sediment loads (Figure 8.5-98A). The three grass treatments significantly reduced herbicide and sediment INLs, and compared to the control, reduced average INLs by 28% for ATR, 23% for MET, 19% for GLY, and 67% for sediment. For ATR INLs, the grass treatments were less than the control by an average of 31% at 1 m, 38% at 4 m, and 43% at 8 m. Results for MET INLs were similar to those of ATR, but GLY INLs at 1 m showed limited decreases for the grass treatments, with only the Native treatment showing a significant reduction compared to the control. The grass treatments significantly reduced GLY INLs at 4 and 8 m, compared to the control, by an average of 24 and 36%, respectively. Overall, the results showed that grass treatments mitigated herbicide losses through a combination of reductions in runoff volume and sediment loads, demonstrating the ability of VBS to effectively decrease both dissolved-phase and sediment-bound herbicide transport. Averaged over vegetation treatment and season, INLs decreased with increasing buffer width for all three herbicides and sediment (Figure 8.5-98B), showing the strong influence of width on contaminant load. The effect of buffer width was very similar for all three herbicides. The effect of season was significant only for ATR and MET loads, but sediment INLs showed the same pattern (Figure 8.5-98C).

For both herbicides, summer INLs were significantly less than fall and spring, but the differences were relatively small compared to vegetation and buffer width effects. Compared to fall and spring, the summer INLs were 3-5% lower for ATR and 7% lower for MET. The season effect for ATR and MET was largely due to the significant decreases in summer and fall INLs for the Hedge + TF treatment as none of the other vegetation treatments showed any significant seasonal effects. The Hedge + TF treatment decreased ATR and MET summer INLs by 20-23% compared to spring. Despite no seasonal effect on runoff for the Hedge + TF treatment, these data indicated that increased switchgrass hedge growth and vigor in the summer and fall contributed to reductions in dissolved-phase herbicide loads.

Table 8.5-153: Basic Chemical and Physical Properties of Soil Samples Collected from Four Vegetation Treatments[1]



Vegetation Treatment	Sand (%)	Silt (%)	Clay (%)	Textural Class	Bulk Density (g/cm^3)	CEC[2] (cmol/kg)	Organic C (%)	Total N (%)	pH[3]
Control	22.6a	51.8a	25.6a	SL[4]	1.21a	20.7a	1.4a	0.12a	6.8a
Tall fescue (TF)	22.1a	53.3a	24.6a	SL	1.09a	22.8a	2.2b	0.20b	6.7a
Hedge + TF	16.8a	56.1a	27.1a	SCL	1.13a	23.1a	2.1b	0.18b	6.7a
Native	23.3a	50.6a	26.1a	SL	1.13a	23.5a	2.1b	0.17b	6.6a

Notes: Within a column, means followed by different letters were significantly different at $\alpha = 0.05$.

[1] Soil samples collected from 0 to 10 cm in May 2010.

[2] CEC, cation exchange capacity. Computed as the sum of the ammonium acetate extractable bases and the barium chloride extractable acidity (Nathan *et al.*, 2012).

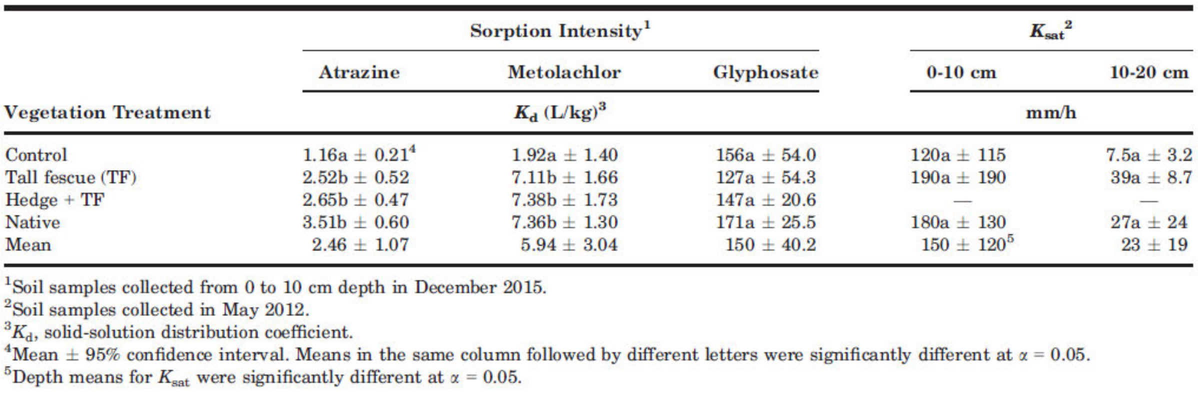
[3] pH determined in 1:1 soil to water suspension (Nathan *et al.*, 2012).

[4] Textural classes: SL, silt loam; SCL, silty clay loam.

Vegetative Buffer Width and Load Reduction

By measuring herbicide loads at four points along the buffer, the experimental design employed for this study provided the opportunity to relate reductions in herbicide INLs to buffer width and SBAR. Because of the modest seasonal effect on loads, regression equations were developed for each vegetation treatment with data pooled across seasons. The three parameter first-order decay models were significant for all vegetation treatments and herbicides (Figure 8.5-99). This relationship indicated that short VBS widths can be very effective at reducing herbicide loads, even for a high runoff potential claypan soil. Applying the regression equations to a range of buffer widths (from 0.16 to 8 m; SBAR = 50:1-1:1) resulted in predicted load reductions that were within 10% of each other for the grass treatments, indicating that all three of these VBS types would be similarly effective for reducing herbicide loads in runoff. The highly significant R^2 values (0.700-0.861) for the grass treatment models demonstrated that these models would be useful for predicting expected reductions in herbicide loads.

Table 8.5-154: Herbicide Solid-to-Solution Distribution Coefficients (Kd) and Saturated Hydraulic Conductivity (Ksat) of Soils Collected from Each Vegetation Treatment



	Sorption Intensity[1]			K_{sat}[2]	
	Atrazine	Metolachlor	Glyphosate	0-10 cm	10-20 cm
Vegetation Treatment	K_d (L/kg)[3]			mm/h	
Control	1.16a ± 0.21[4]	1.92a ± 1.40	156a ± 54.0	120a ± 115	7.5a ± 3.2
Tall fescue (TF)	2.52b ± 0.52	7.11b ± 1.66	127a ± 54.3	190a ± 190	39a ± 8.7
Hedge + TF	2.65b ± 0.47	7.38b ± 1.73	147a ± 20.6	—	—
Native	3.51b ± 0.60	7.36b ± 1.30	171a ± 25.5	180a ± 130	27a ± 24
Mean	2.46 ± 1.07	5.94 ± 3.04	150 ± 40.2	150 ± 120[5]	23 ± 19

[1] Soil samples collected from 0 to 10 cm depth in December 2015.

[2] Soil samples collected in May 2012.

[3] K_d, solid-solution distribution coefficient.

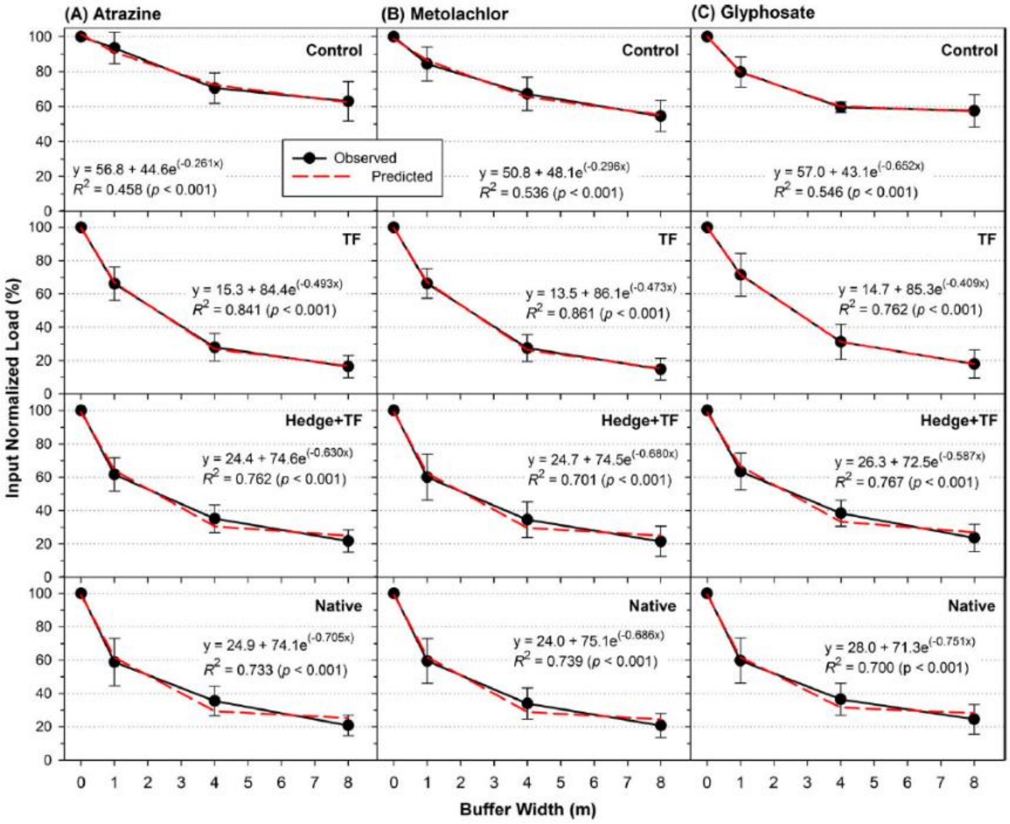
[4] Mean ± 95% confidence interval. Means in the same column followed by different letters were significantly different at $\alpha = 0.05$.

[5] Depth means for K_{sat} were significantly different at $\alpha = 0.05$.

Soil Quality Assessments

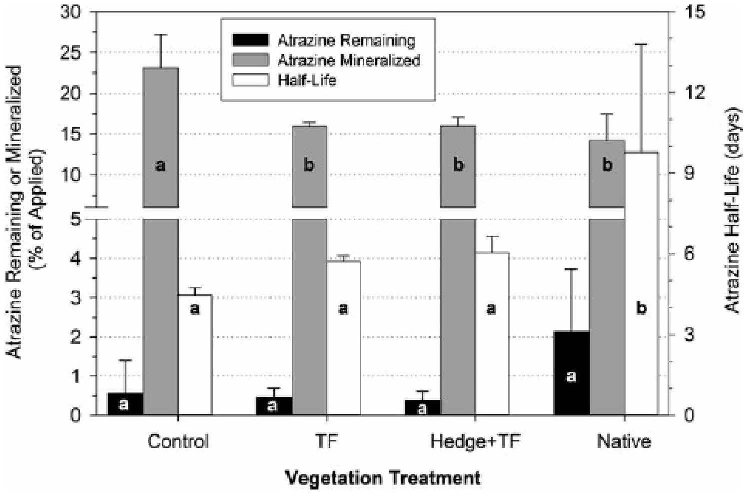
Organic C and total N concentrations of the surface soils were significantly increased in the grass treatments, by an average of 53%, compared to the control (Table 8.5-153). However, basic surface soil (0 - 10 cm) parameters such as texture, bulk density, cation exchange capacity, and pH were not significantly affected by vegetation treatment. The long term inputs and decomposition of plant and root biomass presumably led to the observed accumulation of soil C and N in the grass treatments. Measurement of K_{sat} in surface (0-10 cm) and shallow subsurface (10-20 cm) soils showed no statistical differences among the vegetation treatments, but the surface soils did have significantly greater K_{sat} rates than the subsoil (Table 8.5-154). Surface soils showed variable K_{sat} rates that ranged from 110 to 190 mm/h. A major source of variation was whether or not the claypan horizon was present within the 0-10 cm samples as the depth to the claypan was in the range of 8-12 cm below the surface.

Figure 8.5-99: Regression Equations Correlating Relative Load Reduction (y) as a Function of Buffer Width (x) for: (A) atrazine; (B) metolachlor; and (C) glyphosate. Error bars represent the 95% confidence interval.



Regardless, the profound impact of the claypan on K_{sat} rates could be seen as the subsoil rates were an average of 6.5 times lower than the surface soil. As previously noted, runoff depth was reduced by the grass treatments compared to the control, and the K_{sat} data indicated that the observed reductions were due to slower runoff velocity leading to the increased infiltration and not a function of improved percolation through the soil. Sorption experiments showed that all three grass treatments significantly and similarly increased sorption intensity of ATR and MET (Table 8.5-154). Compared to the control, grass treatments increased K_d values by an average of 2.5 times for ATR and 3.8 times for MET. GLY sorption was not affected by vegetation treatment, with K_d values ranging from 127 to 171 L/kg. The K_d values reported here were similar to those reported for these herbicides in a wide variety of soils. Other possible indicators of improved soil quality, such as herbicide degradation and enzyme activities, showed that VBS had only modest impacts on these biological processes. Results from the ATR degradation study showed that amount of ATR remaining in the soil after 56 days was not significantly different between treatments (Figure 8.5-100). However, the control treatment showed greater ATR mineralization and faster degradation rates than the grass treatments. Microbial enzyme activities were not greatly affected by vegetation treatment as neither DHG nor FDA activities were significantly different among treatments, but GLU activity did show significant increases in the grass treatments compared to the control (Figure 8.5-101). These results were not expected as most studies have reported that VBS enhanced pesticide degradation and increased microbial enzyme activities in soil. The plots used in this study have received ATR application to the source area eight times since 2004, and therefore, microbial adaptation seemed likely given the frequent applications. However, the results suggest greater activity of ATR-degrading genes in the control than the grass treatments. Possible explanations for the findings reported here include: (1) greater labile soil C and N in the grass treatments (Table 8.5-153) resulted in slower and less complete ATR degradation as more energetically favorable substrates were utilized for growth (Figure 8.5-101; greater GLU activity in grass treatments); (2) increased labile soil C and N led to decreased gene copy number and/or activity of ATR degrading genes in the grass treatments; and (3) greater ATR sorption in surface soil of the grass treatments reduced its bioavailability (Table 8.5-154).

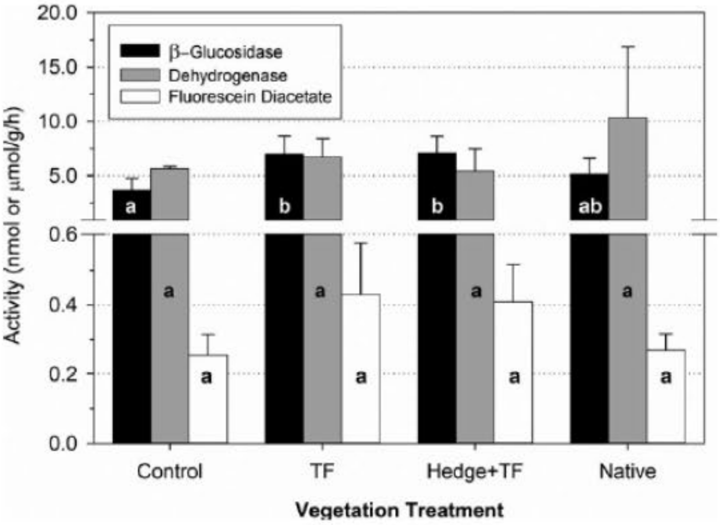
Figure 8.5-100: Atrazine Degradation in Surface Soil (0-10 cm) Collected from Each Vegetation Treatment. The left y-axis represents atrazine remaining and mineralized after 56 days of incubation. The right y-axis is the atrazine half-life estimated from first order kinetic models. Error bars represent the 95% confidence interval. Vegetation treatments with different letters were significantly different at α= 0.05.



Conclusions

This study showed that VBS can substantially reduce loads of ATR, MET, and GLY in runoff from a highly eroded claypan soil, a setting known to be the most vulnerable for herbicide losses within the Corn Belt. Thus, VBS were effective for reducing herbicides transported by dissolved-phase and sediment-bound modes. All grass treatments significantly reduced surface runoff via improved infiltration and showed significant reductions in sediment load compared to the unvegetated control. Of the three main factors studied, vegetation treatment and buffer width had much greater effect on herbicide loads than season. Compared to the control, grass treatments reduced herbicide INLs by 19-28% and sediment INLs by 67%. These data showed that C3 and C4 grasses used alone or in combination can achieve very similar herbicide and sediment load reductions. Therefore, the choice of VBS grass species appears to be flexible and can be made based on practical considerations such as the site condition, cost and availability of seed, and ease of establishment. Partitioning of dissolved phase herbicide loads retained within the VBS revealed that grasses increased infiltration and adsorption of herbicides compared to bare ground. The results demonstrated that VBS can effectively reduce herbicide loads for soils with limited infiltration or cases in which the SBAR is high (e.g.,>10:1) *via* enhanced herbicide adsorption to soil and vegetation. Grass treatments resulted in modest improvements to surface soil quality 8-13 years after establishment, with significant increases in soil organic C, total N, and ATR and MET sorption. Nonlinear regression analyses showed that herbicide INLs as a function of buffer width were well described by first-order decay models and that VBS can provide significant load reductions when implemented at realistic SBARs. These equations, in combination with existing simulation models that can account for changes in slope, rainfall intensity, and crop management, can be used as the basis for designing VBS that can achieve desired herbicide load reductions while minimizing land taken out of production. This approach provides conservation agencies and landowners a simple and applied tool for effectively implementing VBS to control herbicide losses from cropped fields.

Figure 8.5-101: **Microbial Enzyme Activities in Surface Soil (0-10 cm) Collected from the Vegetation Treatments. Error bars represent 95% confidence intervals. For each enzyme, treatments with different letters were significantly different at α= 0.05.**



Assessment and conclusion by applicant:
The article describes a runoff experiment to evaluate the effectiveness of vegetative buffer strips in USA.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:
The article describes a runoff experiment to evaluate the effectiveness of vegetative buffer strips in USA.

This article is considered reliable with restrictions. It does not give any measured concentration of glyphosate, but the resulting effect of VBS are expressed as "input normalised loads %".

Data point:	CA 7.5/042
Report author	Mottes, C. et al.
Report year	2017
Report title	Relationships between past and present pesticide applications and pollution at a watershed outlet: The case of a horticultural catchment in Martinique, French West Indies
Document No	Chemosphere (2017) 184:762-773
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities (Laboratoire Departemental d'Analyses de la Drome)
Acceptability/Reliability:	Reliable

The understanding of factors affecting pesticide transfers to catchment outlet is still at a very early stage in tropical context, and especially on tropical volcanic context. We performed on-farm pesticide use surveys during 87 weeks and monitored pesticides in water weekly during 67 weeks at the outlet of a small catchment in Martinique. We identified three types of pollution. First, we showed long-term chronic pollution by chlordecone, diuron and metolachlor resulting from horticultural practices applied 5-20 years ago (quantification frequency higher than 80%). Second, we showed peak pollution. High amounts of propiconazole and fosthiazate applied at low frequencies caused river pollution peaks for weeks following a single application. Low amounts of diquat and diazinon applied at low frequencies also caused pollution peaks. The high amounts of glyphosate applied at high frequency resulted into pollution peaks by glyphosate and aminomethylphosphonic acid (AMPA) in 6 and 20% of the weeks. Any intensification of their uses will result in higher pollution levels. Third, relatively low amounts of glufosinate-ammonium, difenoconazol, spinosad and metaldehyde were applied at high frequencies. Unexpectedly, such pesticides remained barely detected (<1.5%) or undetected in water samples. We showed that AMPA, fosthiazate and propiconazole have serious leaching potential. They might result in future chronic pollution of shallow aquifers alimenting surface water.

Methods

Our research analyses farmers' pesticide use practices and water contamination data acquired on an experimental catchment. Our complete dataset rely on different data acquired over different periods: Figure 8.5-102 summarizes data acquired from 2011 to 2013. We started acquiring farming practices before the water sampling campaign to take into account potential pesticide transfer lags. The 67 weeks period lasting from the 11/10/2011 to the 01/02/2013 is an overlapping period of pesticide practices and water quality samples (Figure 8.5-102). For past farming practices, Houdart provided us with the practices of the Ravine catchment farmers for years 2001-2002 (Houdart, 2005).

Study site

The experimental horticultural catchment studied is the Ravine catchment (Mottes *et al*., 2015). It is located on the Northeast side of the Martinique Island, French West Indies (140490200 N, 610701400 W). This catchment is part of the Capot catchment (57 km^2) that provides 20% of the drinking water in Martinique while being chronically contaminated by pesticides. In Martinique, the climate is tropical humid with a maritime influence. Rainfall pattern is characterized by two seasons: a dry season from January to March and a wet season from June to September. The average annual rainfall on the catchment is 3600 mm. The Ravine catchment covers 131 ha with elevation ranges varying from 312 m to 628 m. The mean slope of the catchment is 14% with the upper part slopes comprised between 15 and 30% while the lower part slopes ranges from 0 to 15%. The land use is agriculture, with more than 200 fields which belong to 20 farms (Figure 8.5-103): 18 % of agricultural lands are chayote (*Sechium edule*), 13% banana (*Musa* spp.), 6% pineapple (*Ananas comosus*), 17% are covered by other horticultural species, 6.5% by fallow (multiple species), and less than 2% are covered by roads and tracks roads. Forests, meadows and pastures cover the remaining surface (37.5%). The soils are andosol (Colmet-Daage and Lagache, 1965; Quantin, 1972), which are young volcanic ash soils with high infiltration rates (Cattan *et al*., 2007; Charlier *et al*., 2008). Drillings showed that subsoil is constituted by a 1-12 m pumice layer and multiple layers of pyroclastic block and ash flow deposits ("nuées ardentes") with different levels of alteration. The total height of block and ash flow deposits exceeds 70 m. Pumices and block and ash flow deposits are porous materials which contain aquifers drained by the volcanic streams (Charlier *et al*., 2008). An in-depth analysis of the hydrological functioning of this catchment is presented by Mottes *et al.* (2015). In particular, they showed that the hydrological functioning of the catchment is dominated by groundwater flows (50-60% of annual flows) and that aquifers are highly connected to surface water.

Pesticide use survey

Two types of survey among farmers were performed. In a first step, a global survey of the current pesticides used on various cropping systems in 2010 was performed. From this survey, a list of molecules that farmers applied on fields was compiled. This was completed by adding banned pesticides used in the past to the list, such as chlordecone (banned in 1993), paraquat (banned in 2007), lindane (banned in 1998) or diuron (banned in 2007) and other potential significant pesticides and metabolites that the French water office (ODE) found in water samples at a regional scale. Finally, a final list of 77 molecules (Table 8.5-155) was produced. After this consolidated pesticide list was compiled, Houdart provided a description of the practices of the farmers of the Ravine catchment for years 2001-2002 (Houdart, 2005). Several molecules were found to be applied on the catchment at that time that were not identified in the pesticide list: disulfoton, imidacloprid, methomyl, parathion-methyl, simazine, sulfosate, tebuconazole, terbufos and tridemorph (Table 8.5-155). As a result, these pesticides were not analyzed in water samples (Table 8.5-155). In a second step, all the farmers of the Ravine catchment were surveyed. First, farmers were asked to describe their cropping systems and their strategies to control pests on the different crops they grow. When it was available, the log or notebooks of the farmers were recorded. Second, practice follow up surveys were performed every month from July 2011 to April 2013. During these surveys and for each field, the farmers were asked to detail the field scale practices they performed every week during the previous month. Plantation, harvest, tillage operation, mowing, pruning as well as pesticide applications and other pest management practices were surveyed. The practice application dates were collected, as well as the modalities of application (equipment, localization of practices, dose and commercial product).

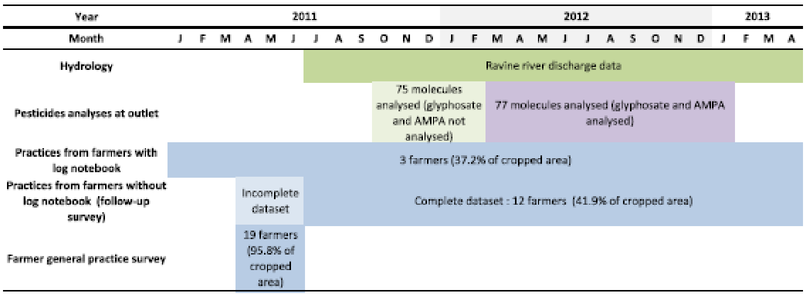
Water sampling

The water at the catchment outlet was sampled with an automatic sampler (ISCO 6712, ISCO Incorporation). Throughout each week, that lasted from Tuesday to the next Tuesday unless exception, the sampling frequency of the water in the river was proportional to the stream discharge calculated from the records of a pressure sensor PCDR 1830 (Campbell scientific). Depending on the period, the automatic sampler collected two 100 mL subsamples each time 300-1800 m^3 discharged at the outlet. To avoid pesticides bounding to container, each first subsample was stored in a plastic container while each second subsample was stored in a glass container (Amalric, 2009). During each week, the automatic sampler progressively built the composites samples by adding each new first subsample into the plastic container, and each new second subsample into the glass container. At the end of each week, the two containers containing the composite samples were collected and filled the bottles provided by the laboratory (3 glass bottles: 2 x 1 L + 100 mL and 2 plastic bottles: 150 mL + 100 mL totaling 2.35 L) with aliquots from the composite samples stored in the plastic and glass containers. The composite samples were collected every week from 11/10/2011 to 01/02/2013.

Laboratory analyses

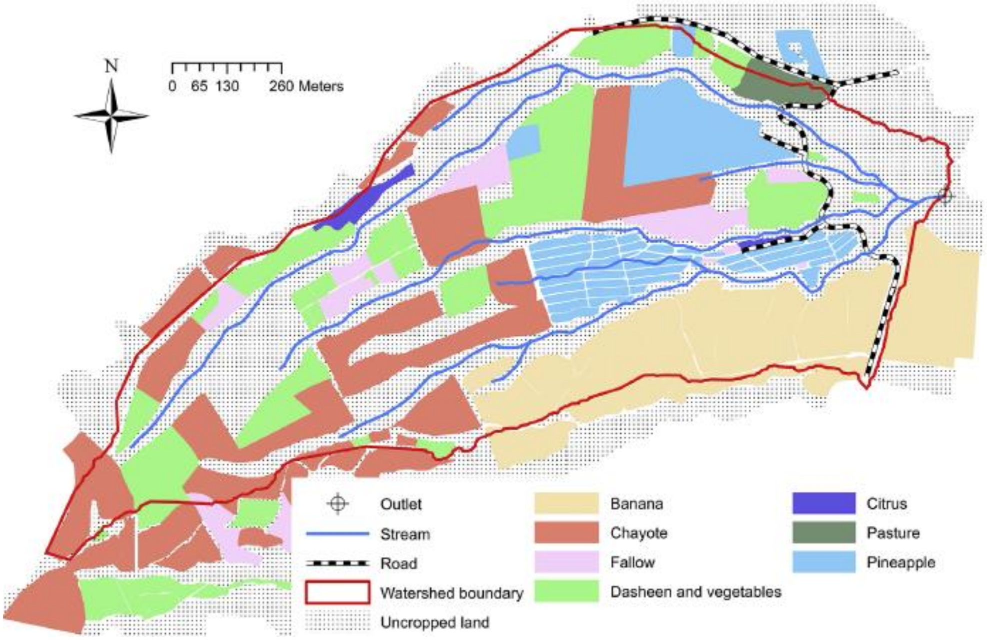
Pesticides concentrations in water samples for the 77 molecules were analyzed by the "Laboratoire Departemental d'Analyses de la Drome" (LDA26). The laboratory has been accredited by Cofrac, the French Accreditation Committee for pesticide analyzes providing guarantees for their technical skills and reliability as well as good management practices. LDA26 complies with ISO 17025 standards for testing and calibration. The methods mobilized for pesticides analysis rely on the EPA-methods 507, 508, 610 and 625. Results are given with a 30% confidence interval for the analytical error. Depending on pesticides, extraction and analysis methods, limits of quantification for organic molecules ranged from 0.01 to 0.2 $\mu g\ L^{-1}$.

Figure 8.5-102: Data acquired from 2011 to 2013 and associated time periods



Year	2011												2012												2013			
Month	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A
Hydrology							Ravine river discharge data																					
Pesticides analyses at outlet										75 molecules analysed (glyphosate and AMPA not analysed)			77 molecules analysed (glyphosate and AMPA analysed)															
Practices from farmers with log notebook	3 farmers (37.2% of cropped area)																											
Practices from farmers without log notebook (follow-up survey)					Incomplete dataset		Complete dataset : 12 farmers (41.9% of cropped area)																					
Farmer general practice survey					19 farmers (95.8% of cropped area)																							

Figure 8.5-103: Land uses of the Ravine catchment



Pesticide application patterns

In order to determine pesticide application patterns, two metrics for each pesticide were calculated: [1] $I_{frapplied}$, a metric of the temporal intensity of the application dynamics. It is defined by the fraction of weeks with applications of the pesticide on the catchment; [2] I_{amount}, a metric of the weekly average amount of pesticide applied on the catchment when it is applied:

$$I_{amount} = \frac{1}{A_{catch}} \times \frac{\sum_{week_{[Qpestapplied_{week}>0]}}^{Nweeks_{[Qpestapplied_{week}>0]}} Qpestapplied_{week} \times e^{-7 \times \left(\frac{\ln(2)}{DT_{50}soil}\right)}}{Nweeks_{[Qpestapplied_{week}>0]}}$$

where $Qpestapplied_{week}$ is the amount of pesticide applied on the catchment during the week "*week*" (g). $e^{-7 \times \left(\frac{\ln(2)}{DT_{50}soil}\right)}$ is a degradation factor derived from a first order degradation kinetics that accounts for potential degradation of the pesticide during 1 week (7 d) with half-life $DT_{50}soil$ (d). A_{catch} is the total area of the catchment (ha). $Nweeks_{[Qpestapplied_{week}>0]}$ is the number of weeks over the considered period with application of the pesticide. I_{amount} is set to 0 for pesticides that were not applied on the catchment in 2011–2013.

We analyzed pesticides application patterns during the practice-monitored period that last from the 1st of June 2011 to the 1st of February 2013 totaling 87 weeks.

Pesticide water pollution

Two metrics for each pesticide to characterize water pollution by pesticide were calculated. First, the frequency of quantification of each pesticide at concentrations higher than 0.1 µg L^{-1} in water samples was calculated. Second, an average concentration metric by taking into account weeks with concentrations over 0.1 µg L^{-1} was calculated.

$$IConc_{pest} = \frac{\sum_{week_{[Cpest_{week} \geq 0.1\ \mu g\ L^{-1}]}}^{Nweeks_{[Cpest_{week} \geq 0.1\ \mu g\ L^{-1}]}} Cpest_{week}}{Nweeks_{[Cpest_{week} \geq 0.1\ \mu g\ L^{-1}]}}$$

where $Cpest_{week}$ is the concentration of pesticide "*pest*" during the week "*week*" (µg L^{-1}). $Nweeks_{[Cpest_{week} \geq 0.1 \mu g\ L^{-1}]}$ is the number of weeks over the considered period with concentration of the pesticide "*pest*" over 0.1 µg L^{-1}.

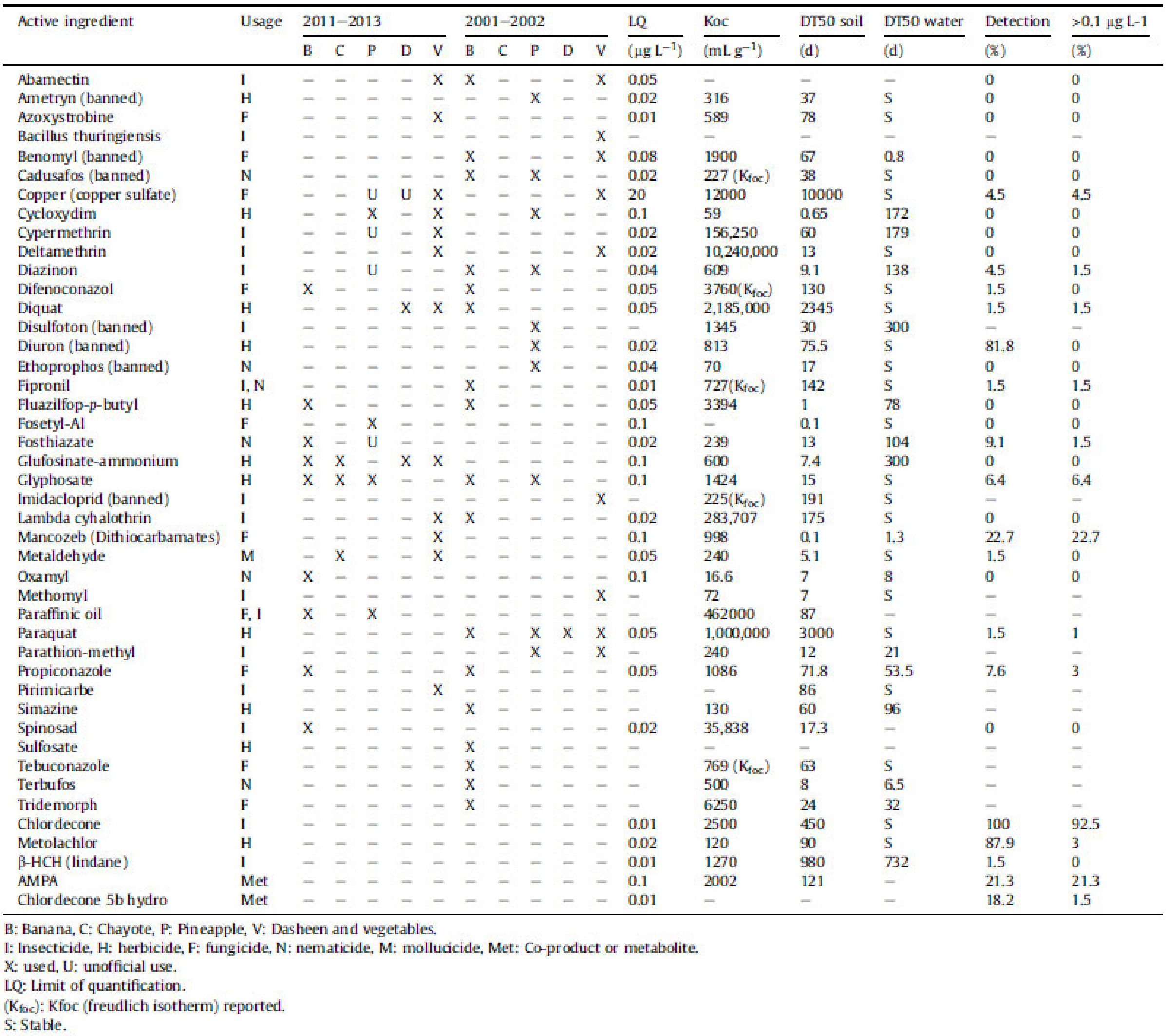
Results and Discussion

Table 8.5-155 summarizes pesticides applied on the Ravine catchment in 2001-2002 and in 2011-2013 and pesticides found in water samples in 2011-2013. Farmers applied 27 commercial products corresponding to 17 active ingredients during the 2011-2013 period. Table 8.5-155 indicates that weekly pesticide samples showed contamination of the water at the Ravine catchment outlet. 16 active ingredients at the catchment outlet (Table 8.5-155) were found and provided concentration dynamics for 9 (Figure 8.5-104). Among these, 4 are nowadays prohibited and unreported in the survey (diuron, paraquat, chlordecone and b-HCH), 2 are metabolites or co-products from respectively glyphosate and chlordecone (aminomethylphosphonic acid (AMPA) and chlordecone-5b-hydro) and 10 are still authorized (propiconazol, difenoconazol, dithiocarbamates, copper sulfate, diquat, fosthiazate, diazinon, glyphosate, metolachlor and metaldehyde). Except for banned pesticides, metabolites and metolachlor, farmers of the Ravine catchment declared the use of the measured pesticide in water.

5 pesticide application patterns were found according to the two application metrics calculated from April 2011 to April 2013 (Figure 8.5-105a): [A] high amounts of pesticide applied at high frequency, [B] low amounts of pesticide applied at high frequency, [C] low amounts of pesticide applied at low frequency, [D] high amounts of pesticide applied at low frequency and [E] historical currently unapplied pesticide (removed from Figure 8.5-105a for better readability).

According to Table 8.5-155 and Figure 8.5-104 three types of pesticide concentration dynamics were found: [1] undetected pesticides (all pesticides applied on the catchment but never found in water samples), [2] chronic pollution (pesticides showing pollution periods of several weeks such as chlordecone, diuron, metolachlor and di-thiocarbamates), and [3] peak pollution (pesticide with isolated pollution peaks such as glyphosate, AMPA, propiconazole, difenoconazol, copper sulfate, diquat, paraquat, chlordecone-5b-hydro, fosthiazate, diazinon, b-HCH and metaldehyde). Figure 8.5-105b shows that for the 0.1 µg L^{-1} threshold, chlordecone and dithiocarbamates are the two chronic pollutants. Metolachlor concentrations are barely higher than 0.1 µg L^{-1}. Figure 8.5-105b also shows that pollutants over the 0.1 µg L^{-1} threshold belong to all pesticide application patterns except pattern B (low amounts applied at high frequency).

Table 8.5-155: Characteristics of pesticide used on the catchment. Applications on different crops in 2001 – 2002 and 2011 – 2013, Environmental characteristics (Footprint, 2013): Koc:soil water – organic carbon coefficient, DT50 soil: pesticide half-life in soil, DT50 water: pesticide half-life in water. Detection and quantification ≥0.1 µgL-1 frequencies at the outlet of the Ravine catchment.



Active ingredient	Usage	2011–2013					2001–2002					LQ	Koc	DT50 soil	DT50 water	Detection	>0.1 µg L-1
		B	C	P	D	V	B	C	P	D	V	($\mu g\ L^{-1}$)	($mL\ g^{-1}$)	(d)	(d)	(%)	(%)
Abamectin	I	–	–	–	–	X	X	–	–	–	X	0.05	–	–	–	0	0
Ametryn (banned)	H	–	–	–	–	–	–	–	X	–	–	0.02	316	37	S	0	0
Azoxystrobine	F	–	–	–	–	X	–	–	–	–	–	0.01	589	78	S	0	0
Bacillus thuringiensis	I	–	–	–	–	–	–	–	–	–	X	–	–	–	–	–	–
Benomyl (banned)	F	–	–	–	–	–	X	–	–	–	X	0.08	1900	67	0.8	0	0
Cadusafos (banned)	N	–	–	–	–	–	X	–	X	–	–	0.02	227 (K_{foc})	38	S	0	0
Copper (copper sulfate)	F	–	–	U	U	X	–	–	–	–	X	20	12000	10000	S	4.5	4.5
Cycloxydim	H	–	–	X	–	X	–	–	X	–	–	0.1	59	0.65	172	0	0
Cypermethrin	I	–	–	U	–	X	–	–	–	–	–	0.02	156,250	60	179	0	0
Deltamethrin	I	–	–	–	–	X	–	–	–	–	X	0.02	10,240,000	13	S	0	0
Diazinon	I	–	–	U	–	–	X	–	X	–	–	0.04	609	9.1	138	4.5	1.5
Difenoconazol	F	X	–	–	–	–	X	–	–	–	–	0.05	3760(K_{foc})	130	S	1.5	0
Diquat	H	–	–	–	X	X	X	–	–	–	–	0.05	2,185,000	2345	S	1.5	1.5
Disulfoton (banned)	I	–	–	–	–	–	–	–	X	–	–	–	1345	30	300	–	–
Diuron (banned)	H	–	–	–	–	–	–	–	X	–	–	0.02	813	75.5	S	81.8	0
Ethoprophos (banned)	N	–	–	–	–	–	–	–	X	–	–	0.04	70	17	S	0	0
Fipronil	I, N	–	–	–	–	–	X	–	–	–	–	0.01	727(K_{foc})	142	S	1.5	1.5
Fluazilfop-p-butyl	H	X	–	–	–	–	X	–	–	–	–	0.05	3394	1	78	0	0
Fosetyl-Al	F	–	–	X	–	–	–	–	–	–	–	0.1	–	0.1	S	0	0
Fosthiazate	N	X	–	U	–	–	–	–	–	–	–	0.02	239	13	104	9.1	1.5
Glufosinate-ammonium	H	X	X	–	X	X	–	–	–	–	–	0.1	600	7.4	300	0	0
Glyphosate	H	X	X	X	–	–	X	–	X	–	–	0.1	1424	15	S	6.4	6.4
Imidacloprid (banned)	I	–	–	–	–	–	–	–	–	–	X	–	225(K_{foc})	191	S	–	–
Lambda cyhalothrin	I	–	–	–	–	X	X	–	–	–	–	0.02	283,707	175	S	0	0
Mancozeb (Dithiocarbamates)	F	–	–	–	–	X	–	–	–	–	–	0.1	998	0.1	1.3	22.7	22.7
Metaldehyde	M	–	X	–	–	X	–	–	–	–	–	0.05	240	5.1	S	1.5	0
Oxamyl	N	X	–	–	–	–	–	–	–	–	–	0.1	16.6	7	8	0	0
Methomyl	I	–	–	–	–	–	–	–	–	–	X	–	72	7	S	–	–
Paraffinic oil	F, I	X	–	X	–	–	–	–	–	–	–	–	462000	87	–	–	–
Paraquat	H	–	–	–	–	–	X	–	X	X	X	0.05	1,000,000	3000	S	1.5	1
Parathion-methyl	I	–	–	–	–	–	–	–	X	–	X	–	240	12	21	–	–
Propiconazole	F	X	–	–	–	–	X	–	–	–	–	0.05	1086	71.8	53.5	7.6	3
Pirimicarbe	I	–	–	–	–	X	–	–	–	–	–	–	–	86	S	–	–
Simazine	H	–	–	–	–	–	X	–	–	–	–	–	130	60	96	–	–
Spinosad	I	X	–	–	–	–	–	–	–	–	–	0.02	35,838	17.3	–	0	0
Sulfosate	H	–	–	–	–	–	X	–	–	–	–	–	–	–	–	–	–
Tebuconazole	F	–	–	–	–	–	X	–	–	–	–	–	769 (K_{foc})	63	S	–	–
Terbufos	N	–	–	–	–	–	X	–	–	–	–	–	500	8	6.5	–	–
Tridemorph	F	–	–	–	–	–	X	–	–	–	–	–	6250	24	32	–	–
Chlordecone	I	–	–	–	–	–	–	–	–	–	–	0.01	2500	450	S	100	92.5
Metolachlor	H	–	–	–	–	–	–	–	–	–	–	0.02	120	90	S	87.9	3
β-HCH (lindane)	I	–	–	–	–	–	–	–	–	–	–	0.01	1270	980	732	1.5	0
AMPA	Met	–	–	–	–	–	–	–	–	–	–	0.1	2002	121	–	21.3	21.3
Chlordecone 5b hydro	Met	–	–	–	–	–	–	–	–	–	–	0.01	–	–	–	18.2	1.5

B: Banana, C: Chayote, P: Pineapple, V: Dasheen and vegetables.
I: Insecticide, H: herbicide, F: fungicide, N: nematicide, M: mollucicide, Met: Co-product or metabolite.
X: used, U: unofficial use.
LQ: Limit of quantification.
(K_{foc}): Kfoc (freudlich isotherm) reported.
S: Stable.

Historically applied pesticides

The analysis first showed that water pollution is due to several pesticides, which farmers do not use anymore. Indeed, most of them are now prohibited (e-phy, 2010). This shows that even after 5 to more than 20 years after their ban, they still contaminate water at the catchment outlet. The historical pesticides show 3 types of detection patterns at the catchment outlet. First, chlordecone, diuron and metolachor were detected at a very high frequency throughout the sampling period (Figure 8.5-104, Table 8.5-155); second, Paraquat, b-HCH, chlordecone-5b-hydro are detected only anecdotally (Table 8.5-155), and finally some are not detected anymore such as ametryn, cadusaphos or ethoprophos. Our hypothesis for the first 2 types is that these pesticides are still stocked in soil (DT_{50soil}>75 d) so that they slowly leach into groundwater, soil behaving as pollution source.

Chlordecone, diuron and metolachlor were applied for a long time and on large areas of the catchment. These three pesticides still chronically contaminate water at the outlet. Their detection frequency is higher than 80 % at the catchment outlet and reaches 100 % for chlordecone. Such pollution are characterized by a weekly concentration varying within a narrow range (from 0.05 to 0.77 µg L^{-1} for chlordecone; from

<0.02 to 0.09 µg L^{-1} for diuron and from <0.02 to 0.14 µg L^{-1} for metolachlor (pollution peak removed)). We did not observe a strong relationship between water concentrations and rainfall. According to Dores *et al.* (2009), we found metolachlor and diuron to leach in tropical conditions. The three historical pollutants are characterized by long soil half-lives (>75 d). Because persistent and long-term pollution involve the contamination of soils and aquifers, such soil persistence favor permanent pollution of rivers (Cabidoche *et al.*, 2009; Mottes *et al.*, 2016). A persistent pollution of the stream by metolachlor was measured with water concentrations under 0.1 µg L^{-1} most of the time. The authors expected the ending of a chronic pollution as with diuron. Nevertheless, its use is still authorized on pineapple crop (S-metolachlor compound). The authors suspected an application on the catchment even if no surveyed farmer reported S-metolachlor application. Indeed, a pollution peak (0.39 µg L^{-1}) was observed in water samples (Figure 8.5-104e). This pollution peak is consistent with the high transfer rate with runoff found by Dores *et al*. (2009) that could follow applications. This is the reason why this specific use could maintain the long-term pollution of the river. The use of such persistent contaminant of the environment should therefore be stopped in tropical context to avoid any increase of the pollution.

Figure 8.5-104: **Meteorological, hydrological and pollution at outlet time series on the Ravine catchment from 11 October 2011 to (a) daily rainfall; (b) discharge at outlet, (c) chlordecone concentrations, (d) diuron concentrations, (e) metolachlor concentrations, (f) glyphosate concentrations (black), AMPA concentrations (green), (g) fosthiazate concentrations, (h) propoconazole concentrations (black), defenoconazol concentrations (green), (i) dithiocarbamates concentrations.** For detected but unquantified pesticides, we estimated concentrations to quantification limit divided by 3 as suggested by laboratory guidelines.

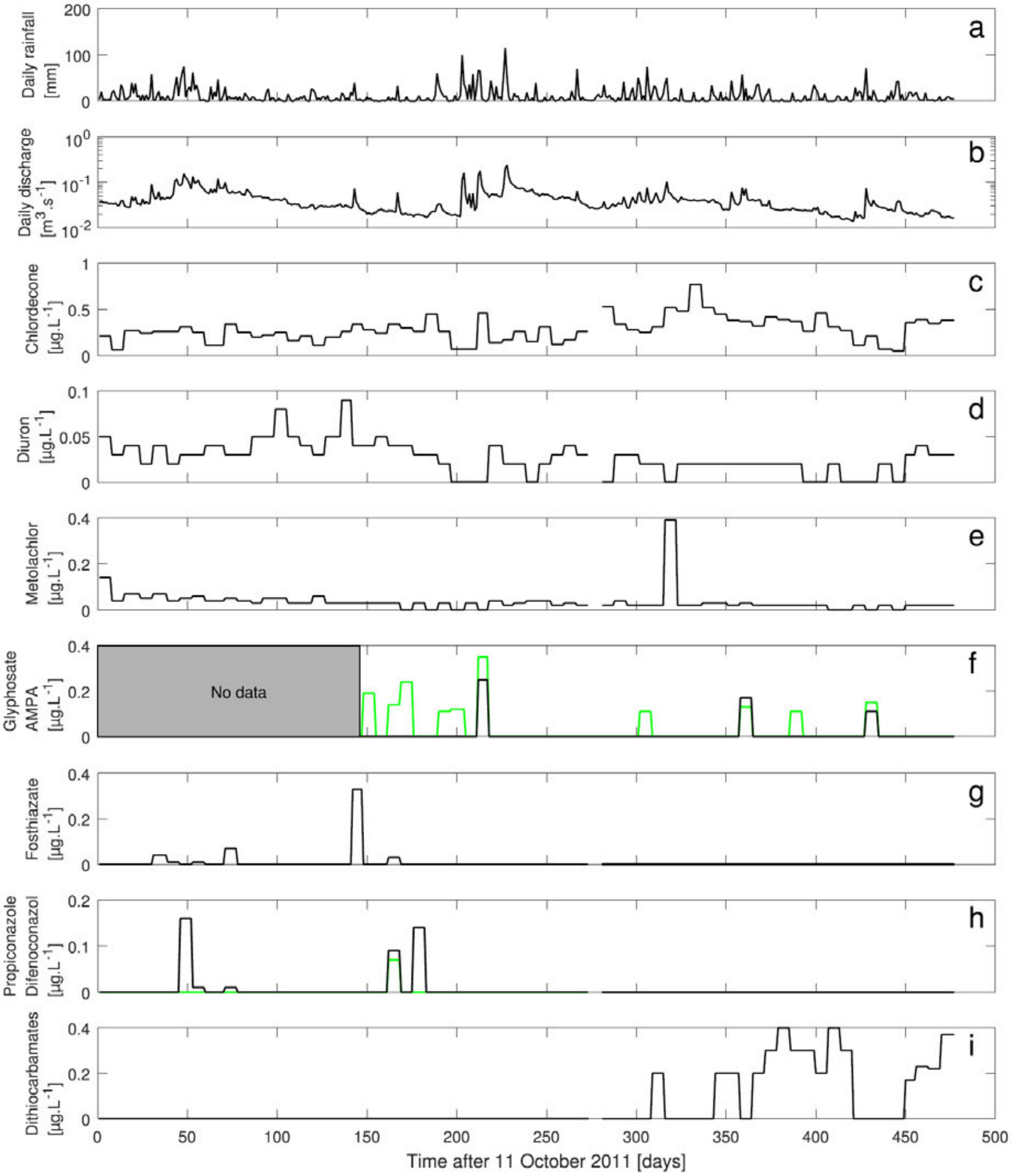


Figure 8.5-105: **Pesticide uses and pollution intensities on the Ravine catchment (a) Pesticide application intensities; (b) Pesticide pollution intensities ≥0.1 µg L^{-1}. Pesticide application pattern [-] undefined, [A] high amounts applied at high frequency, [B] low amounts applied at high intensities, [C] low amounts applied at low frequency, [D] high amounts at low frequency, [E] historical currently unapplied pesticides.**

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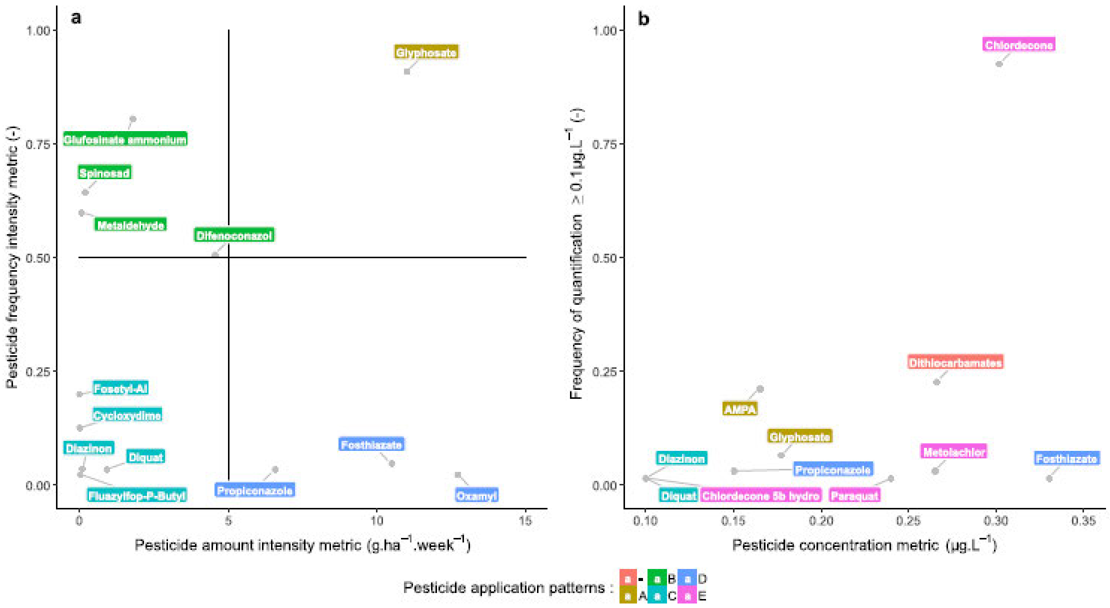


Paraquat and b-HCH were used in a less intensive manner or during shorter periods of time than chlordecone, diuron and metolachlor. Chlordecone-5b-hydro is a co-product of chlordecone production that corresponds to a very small fraction of the chlordecone amount applied. Chlordecone-5b-hydro and paraquat were unfrequently quantified at concentrations higher than 0.1 µg L^{-1} (Figure 8.5-105b) while b-HCH did not exceed this threshold. The low detection frequencies of these pesticides could be explained by the lower amounts of residues remaining in soil because smaller amounts of these pesticides or co-products were applied on the catchment. It is likely that specific environmental characteristics such as tillage, high water flows, or both led to their remobilization from soil to the catchment outlet. Nevertheless, the small number of detections and the lack of knowledge on the behavior or the spatial and temporal application patterns of these pesticides in the past harms the robustness of this conclusion.

Ametryn, cadusaphos or ethoprophos are pesticides with high dissipation potentials. Charlier *et al.* (2009) clearly demonstrated that cadusaphos quickly contaminated surface water during both high and low flows. Farmers used cadusaphos and ethroprophos as nematicides, they applied both onto the soil. Although these pesticides may have contaminated the environment when they were applied, they were apparently quickly transferred, diluted and/or degraded in the environment leading to no more detection nowadays. At the molecular composition level, we observed that chlordecone, diuron and metolachlor carry at least one chlorine radical, while ametryn, cadusafos and ethoprophos do not. According to our results, we are in the opinion that chlorine radicals could favor the stability and the persistence of molecules in the environment. This is confirmed by Calvet *et al.* (2005) who indicated that chlorine radical decreases the speed of the breaking of aromatic cycles in organic compounds. Henschler (1994) also support this hypothesis by indicating a frequently increased chemical stability of chlorinated organic compounds along with an easier enzymatic conversion. Consequently, the presence of chlorine radical in the molecule could favor the long-term potential pollution of the environment even if the molecule is classified under another organic compound family than organochlorine such as phenylurea, carbamate or triazole.

<u>Pesticides used on the catchment during the sampling period</u>

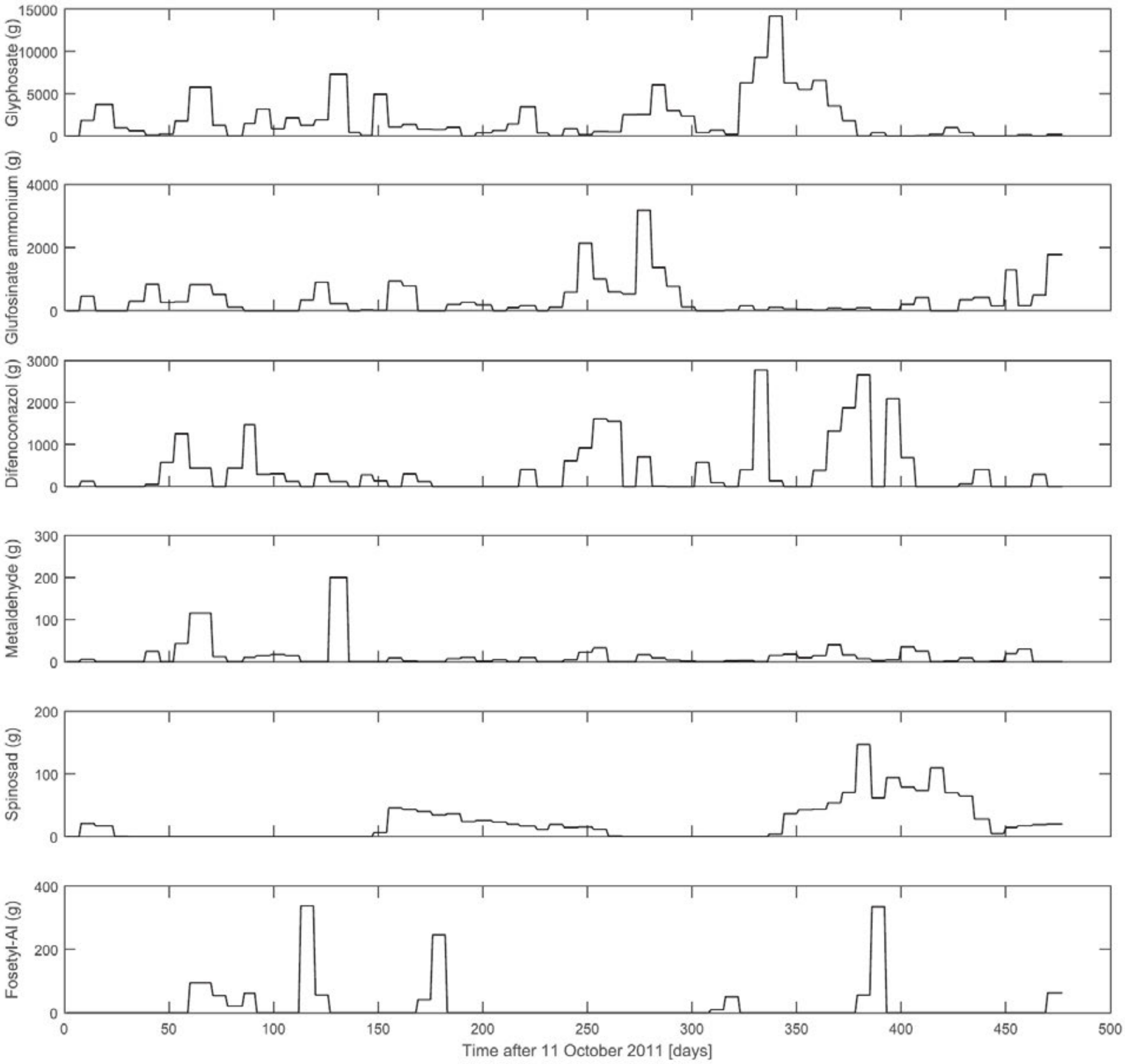
Pesticides regularly applied on the catchment

The survey showed that 5 pesticides were regularly applied on the catchment: glyphosate, glufosinate ammonium, difenoconazol, spinosad and metaldehyde (Figure 8.5-105a). These pesticides were applied on more than 50% of the weeks during the sampling period. Glyphosate was applied on 90% of the weeks at very high rates (Figure 8.5-105a and Figure 8.5-106). Glufosinate ammonium was applied 75% of the weeks at lower rates (Figure 8.5-105a and Figure 8.5-106). Difenoconazol was applied during half of the weeks of the sampling period at intermediate application rates while spinosad and metaldehyde were applied during more than half of the weeks but at low rates (Figure 8.5-105a and Figure 8.5-106). In the water samples, Glyphosate and its metabolite AMPA were quantified over 0.1 µg L^{-1} (Figure 8.5-104 and Figure 8.5-105b) which is consistent with its very intensive use at the catchment scale. In spite of their frequent uses, glufosinate ammonium and spinosad were never detected in water samples while difenoconazol and metaldehyde were both quantified only once at concentrations lower than 0.1 µg L^{-1}.

Glyphosate is widely used as a general systemic herbicide. Glyphosate and its major metabolite Aminomethylphosphonic acid (AMPA) were frequently quantified at concentrations higher than 0.1 µg L^{-1} in our water samples at the catchment outlet. AMPA is a major pollutant detected in 21.3% samples. Glyphosate was found to have concentrations higher than 0.1 µg L^{-1} in 6.4% samples. For glyphosate pollution peaks, the pollution corresponded to a stormflow event occurring right after the application of glyphosate (Figure 8.5-104f and Figure 8.5-106a). It indicates that glyphosate was quickly degraded or highly adsorbed onto soil particles forming irreversible bounding in agreement with the conclusions drawn by Vereecken (2005) and Borggaard and Gimsing (2008). The surveyed farmers applied glyphosate all year round because weeds are one of the strongest constraints in the humid tropics. Because of this constant application pattern, it is likely that rainfall generating pollution peaks occurred after applications, especially in the tropical climate characterized by heavy and intense rains. AMPA, one of the major glyphosate metabolites, was always present in water samples when we found glyphosate. Nevertheless, AMPA was found with no companion glyphosate during eight weeks over the sampled period. AMPA was found during weeks that are not characterized by significant runoff events. Similarly to chlordecone and diuron, two pesticides which led to permanent contamination at the outlet, AMPA shows a long half-life and a high K_{OC} (Table 8.5-155). In the literature, results from different studies do not agree on the leaching potential of AMPA but some studies showed that AMPA potentially leaches in structured soil conditions (Kjaer *et al*., 2005; Landry *et al.*, 2005; Bergstrom *et al*., 2011). In tropical volcanic catchment conditions, soils are structured with very high infiltration rates (Cattan *et al*., 2007; Charlier *et al.*, 2008). Because of the quantification of AMPA outside runoff periods, it is likely that AMPA contaminates at least shallow aquifers on a regular basis. It is likely that glyphosate quickly degrades into AMPA, which is stored in high organic soils, and is leaching to aquifers along with rainfalls. As a result, it was concluded that the widespread and quasi-permanent use of glyphosate on tropical volcanic catchments, such as the Ravine catchment, is likely to result in persistent stream pollution by AMPA within mid-to long-terms.

Glufosinate-ammonium is the second most used herbicide on the catchment. This pesticide was never detected during the weekly analyses, even when runoff events occurred during the same week when farmers applied glufosinate-ammonium. In the literature, glufosinate transfers have been found with that for glyphosate and other herbicides (Screpanti *et al.*, 2005; Shipitalo *et al*., 2008). Anionic retention capacity of andosol (Sansoulet *et al*., 2007) may cause glufosinate ammonium retention in the soils of the catchment. In spite of a high application frequency, the amount of glufosinate-ammonium applied at the catchment scale is lower than glyphosate (Figure 8.5-106) and even lower when considering the degradation rate (Figure 8.5-105a). It might be that pollution is not yet measurable now but could appear in the case of an increase of the amount of glufosinate-ammonium applied at the catchment scale. Glufosinate-ammonium has two identified metabolites that could contaminate the river (3-methyl-phosphinico-propionic acid and 2-methyl-phosphinico-acetic acid) (Footprint, 2013). Unfortunately, their quantifications were outside of the analytic capacity of the laboratory. In the light of this discussion, the authors recommend further investigation on the fate of this pesticide and its metabolites in andosol. They also recommend not to substitute glyphosate by glufosinate-ammonium but rather to find alternatives to exclusive chemical weeding with reduced uses of herbicides.

Figure 8.5-106: **Weekly amounts of pesticides applied on the Ravine catchment (g) for glyphosate, glufosinate-ammonium, difenoconazol, metaldehyde, spinosad and fosetyl-al**



Difenoconazol has been detected only once in water samples at a concentration below 0.1 µg L^{-1} (Figure 8.5-104h). Difenoconazol has an intermediate application pattern at catchment scale in term of frequency and amounts: it is applied on a relatively frequent manner (~50% of the weeks) at intermediate levels (Figure 8.5-105a). Because of its long soil half-life (85-130 d) reported in the Footprint database (Footprint, 2013) it was expected to detect more frequently difenoconazol in water samples. The only detection occurred on a week characterized by a runoff event the same day that application was performed. That event may have transported the pesticide directly to the outlet during application or right after its application bypassing the soil compartment. This is the reason why the authors are of the opinion that the half-lives of difenoconazol may be lower than the one reported in the Footprint database. This hypothesis is supported by Wang *et al.* (2012) who found short half-life of difenoconazol in water (0.30-2.71 d) and by Mukhopadhyay *et al*. (2011) and Wang *et al*. (2012) who found soil half-life ranging between 4 and 23 d. In the light of this discussion, it is very likely that difenoconazol degraded faster than expected and that such high degradation rates in water explain the single quantification of difenoconazol at the outlet of the Ravine catchment.

Spinosad was frequently used on the banana fields of the catchment. According to Figure 8.5-105a, the amount intensity metric of spinosad is low. The pesticide is applied on banana bunches which are protected by a plastic bag thus limiting washoff and environmental diffusion of that pesticide. The authors are of the opinion that such low application rates under protected conditions limited spinosad transfers to the environment.

Metaldehyde was frequently applied on the catchment but according to Figure 8.5-105a, the amount intensity metric of metaldehyde is very low. Because of such very low amount intensity metric metaldehyde was not expected to be detected in water samples. Nevertheless, it was quantified once below 0.1 µg L^{-1}. As for other frequently applied pesticides, the authors are of the opinion that the high application frequency of the pesticide increases the probability of incorrect application conditions on a rainy day that transferred pesticides directly to outlet towards runoff.

The uncertainty surrounding the dithiocarbamates

Dithiocarbamates represent a family of molecules they are mainly used for their fungicide effects. The analytical procedure of the laboratory did not make it possible to identify the specific dithiocarbamate molecules among them. Dithiocarbamates were started to be frequently quantified in the stream from day 309 at concentrations higher than 0.1 µg L^{-1} (Figure 8.5-104i). The pollution by dithiocarbamates is the second most intensive after chlordecone (Figure 8.5-105b). Farmers highlighted the intensive use of fungicides on horticultural crops such as tomato, cucumber or pepper but the authors did not have confident enough application dynamics on the catchment to classify the dithiocarbamates application pattern (Figure 8.5-105). Dithiocarbamates were not found any more during high flow periods (Figure 8.5-104). Different hypotheses can be drawn to explain this situation:

(1) The molecules contaminate aquifers but the pollution is diluted below detection limits during high flow periods. However, according to data from the Footprint database (Footprint, 2013), this is unlikely because of the very short reported half-lives of dithiocarbamates (Table 8.5-155). On the contrary, Wilmington (1983), the first manufacturer of mancozeb, the dithiocarbamate used on the catchment, reported soil half-life to range from 4 to 8 weeks. Such values seem to be more realistic and consistent when compared with degradation rates of other pesticides (e.g. Table 8.5-155). (2) The contamination comes from a point source due to inappropriate handling of the unsprayed pesticides fraction. (3) Applications are regularly performed on vegetable crops but no pesticide is sprayed during rainy weeks. (4) Dithiocarbamates were used to produce photodegradable plastic mulches that can be ploughed directly into the soil (Wolfe *et al*., 1990; Scott, 1997). Degradable plastic mulches are used under pineapple crops but farmers could not attest whether they used photodegradable or biodegradable mulches. In spite of the difficulty to interpret our results, this pollution that appeared at the end of our sampling period is alarming because the stream is polluted in a quasi-persistent manner at high levels. The verification of these different hypotheses would require specific studies on cropping systems using dithiocarbamates and associated transfers to water. In the meantime, improvements of the analysis methodologies are required. Nevertheless, according to the long soil half-life reported by Wilmington (1983) and the K_{OC} of mancozeb (998 mL g^{-1} - Table 8.5-155), we are in the opinion that mancozeb may have contaminated shallow aquifers in our conditions.

Pesticides barely applied on the catchment that generated pollution

Propiconazole and fosthiazate were barely used on the catchment but at high application rates (Figure 8.5-105a). The practice survey showed that both pesticides were applied before the sampling period in response to specific problems such as high sigatoka (*Mycosphaerella fijiensis*, *Mycosphaerella musicola*) pressures or high infestation by nematodes (*Radopholus similis, Pratylenchus coffeae*) on banana fields. Diquat and diazinon were also barely applied but at low rates (Figure 8.5-105a). The four pesticides were detected in water samples at concentrations higher than 0.1 µg L^{-1} (Figure 8.5-104 and Figure 8.5-105b) meaning that any intensification of the use of these pesticides will result in pollution at levels higher than the one already observed.

Fosthiazate is an organophosphate nematicide applied onto banana fields. The pesticide was detected during two periods. During the first period (days 30-77), fosthiazate was detected at concentrations lower than 0.1 µg L^{-1} (Figure 8.5-104g). During this high flow period the highest concentrations at the peak flow were not observed in spite of a high solubility and a low K_{OC} of the pesticide. This result supports the hypothesis of a fast transfer toward a shallow aquifer diluted by surface runoff barely occurring in tropical volcanic conditions (Charlier *et al*., 2008; Mottes *et al*., 2015). Later, fosthiazate was detected twice when high rainfall events occurred during a dry period (low average stream discharge). It is likely that the peaks observed during the second period resulted from an unofficial use of the pesticide on pineapple fields before high rainfall events occurred during the dry period (field observations). In the literature, fosthiazate persistence in soil is reported to increase under low pH (Qin *et al*., 2004; Pantelelis *et al*., 2006). Thus, in spite of a short reported soil half-life of 13 d (Footprint, 2013), its persistence in tropical andosols with low pH (Clermont-Dauphin *et al*., 2004) may reach the 47 d values obtained by Pantelelis *et al*. (2006). Its increased stability in tropical volcanic condition can enhance its leaching potential. The contamination of both overland flows and shallow aquifer flows has been observed in similar pedoclimatic conditions by Charlier *et al.* (2009) who studied the transfers of cadusaphos, a nematicide with close molecular characteristics. On the basis of the pollution observed with moderate high flows on the Ravine catchment and results from Charlier *et al*. (2009), there is every likelihood that fosthiazate transfers to catchment outlet toward both overland flows and shallow aquifers.

Propiconazole was detected during a peak flow that took place during the first high rainy event after the beginning of the sampling period (Figure 8.5-104h). The only reported use for propiconazole occurred 82 d before the beginning of the sampling period. The authors believe that the pollution peaks resulted from that particular pesticide application because a large proportion of the catchment (13%) was treated on that day by helicopter and because the reported half-life of propiconazole in soil is high 70-200 d (Bromilow *et al*., 1999; Footprint, 2013). Although, propiconazole was reported by several authors to have low leaching potentialities (Bromilow *et al.*, 1999; Kim *et al.*, 2002), Oliver *et al.* (2012) found that propiconazole was transported in a persistent manner from horticultural cropping systems in Australia. Battaglin *et al*. (2011) also observed its presence in United States streams and Toan *et al.* (2013) found that propiconazole significantly contaminated surface water in Vietnam. Propiconazole was frequently found (in 43% of samples) in a banana oriented catchment in Costa Rica where it was intensively applied (Castillo *et al.*, 2000). Propiconazole pollution dynamics is difficult to interpret because it did not appear systematically during all runoff events; it showed contamination tail during high flow period and a high concentration on weeks without high flow (Figure 8.5-104h). The high soil half-life of the pesticide reminds the ones from historical permanent pollutants (chlordecone, diuron and metolachlor). Propiconazole polluted surface waters in many places but on the Ravine catchment, it did not show clear transfers pathways. The authors suspected however propiconazole to have quickly reached shallow aquifers. Further research on the fate of this pesticide in the specific conditions is warranted, as well as reduction measures to avoid further contaminations of streams. In the French West Indies, application of propiconazole is authorized only once a year. In spite of this restriction, it keeps contaminating water for a long time after being applied. Because this pesticide was found to be a significant water contaminant over the world (Castillo *et al.*, 2000; Battaglin *et al*., 2011; Oliver *et al.*, 2012; Toan *et al.*, 2013) and in the Ravine catchment, we recommend restricting the usage of propiconazole in cases where farmers cannot use alternative techniques, or at least on very small areas of catchments.

Conclusion

The authors have shown that the current and past uses of pesticide in a tropical volcanic catchment resulted in pesticide pollution at catchment outlet and that the approach was relevant to identify potential sources of water pollution at different time scales. Pesticide pollution was not only dependent on the intrinsic characteristics of pesticides but also on the combination of application intensities in terms of frequencies and amounts and on the hydrological functioning of the catchment. Historical pesticides used in horticulture 10-20 years ago resulted in persistent pollution at catchment outlet due to soil and aquifer contaminations. This type of pollution raises the question of the management of the contaminated compartments (such as soils and aquifers) and of the potential implication of such long-term local conditions on larger scale pollution. Pesticides still in use in tropical conditions present serious risk of aquifers contamination. Metolachlor is still authorized while it chronically polluted the catchment outlet. The authors think that the use of glyphosate, fosthiazate and propiconazole could result in mid-to long-term persistent contamination of the stream, as some historical pesticides. In order to avoid the past errors and decrease the risk of long-term pollution of water resources, the only mean to protect them is to reduce or ban the use of these pesticides in horticultural systems. This conclusion raises the question of the design of cropping systems less dependent on pesticides and their appropriation by farmers. The classification also showed that several pesticides remain undetected in rivers in spite of intensive application patterns. These undetected pollution raise the questions of the underlying processes of the fate of such pesticides. First, the understanding of their fate will make it possible to better anticipate and avoid forthcoming pollution. Second, this will make it possible to assess the potential effect of their increased use in case of farmers shifting of pesticides (cropping system change or regulation evolutions). To assess the three questions raised, the authors recommend further research combining modeling and monitoring to assess the current and future effects of pesticides in tropical horticultural cropping systems on water resources. The combined approach of modeling and monitoring appears to be an interesting approach for co-designing and adjusting cropping systems with farmers.

Assessment and conclusion by applicant:
The article describes the monitoring of glyphosate among several pesticides in a horticultural catchment in Martinique, French West India (part of the EU). Methods and results are well described.
The article is considered reliable.

Assessment and conclusion by RMS:
The article is considered reliable. It however describes a particular tropical context and the mean slope of the catchment is 14%.

It describes an on farm pesticide survey performed during 87 weeks and associated pesticide monitoring (including Glyphosate and AMPA) performed during 67 weeks (11/10/2011 to 01/02/2013). It provides detailed information on soils and land cover and on the use of pesticide within the catchment area of the monitoring site (57 km^2).

The water at the catchment outlet was sampled with an automatic sampler. The sampling frequency of the water in the river was proportional to the stream discharge calculated from the records of a pressure sensor.

Regarding Glyphostate and AMPA, the following information can be retained from this article:

Glyphosate was applied on 90% of the weeks. The surveyed farmers applied glyphosate all year round because weeds are one of the strongest constraints in the humid tropics.

Glyphosate and its major metabolite AMPA were frequently quantified at concentrations higher than 0.1 µg L^{-1} in water samples at the catchment outlet. Glyphosate was found to have concentrations higher than 0.1 µg L^{-1} in 6.4% samples. AMPA is detected in 21.3% samples.

The high amounts of glyphosate applied at high frequency resulted into pollution peaks by glyphosate and aminomethylphosphonic acid (AMPA) in 6 and 20% of the weeks, respectively

The article also indicates that it is likely that rainfall generating pollution peaks occurred after applications, especially in the tropical climate characterized by heavy and intense rains. AMPA was always present in water samples together with glyphosate. Nevertheless, AMPA was found without glyphosate during eight weeks over the sampled period. AMPA was found during weeks that are not characterized by significant runoff events.

RMS notes that no detailed measured concentrations table results are given in the study. It can be read on Figure 8.5-107 that the maximum glyphosate and AMPA maximum concentration was < 0.4 µg/L.

Data point:	CA 7.5/017
Report author	Poiger, T. *et al.*
Report year	2017
Report title	Occurrence of the herbicide glyphosate and its metabolite AMPA in surface waters in Switzerland determined with on-line solid phase extraction LC-MS/MS
Document No	Environmental Science and Pollution Research (2017) 24:1588-1596
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (Agroscope)
Acceptability/Reliability:	Reliable

The article was found relevant for multiple subchapters. The summary is provided in the groundwater monitoring subchapter of this document.

Assessment and conclusion by RMS:

The article describes the derivation of a simplified procedure for the determination of glyphosate and AMPA in water samples

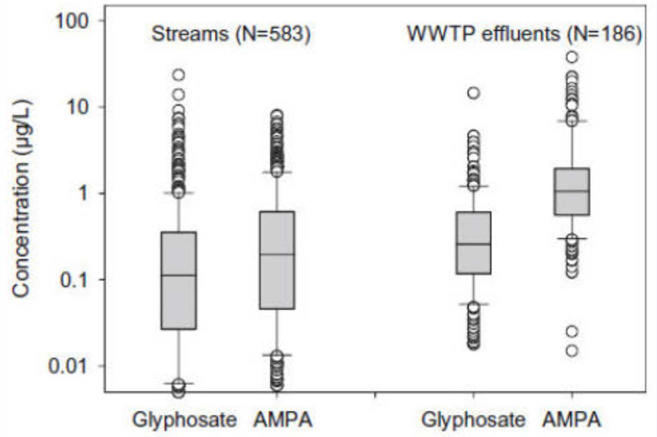
More than 1000 samples from ground and surface waters, and from treated wastewaters in Switzerland were tested with this method and the results are reported.

For surface water

- Grab samples from various streams in the area of Zurich, Switzerland, were collected during routine samplings by the Office for Waste, Water, Energy, and Air of the Canton of Zurich (AWEL) from 2006 to 2013
- Further grab samples from a small stream in the Canton of Vaud were provided by the water protection laboratory of the canton from 2011 to 2014
- Grab samples and 24-h flow proportional composite samples of treated wastewater from various WWTPs in Switzerland were obtained from the personnel of these plants.

Detailed raw data and analysis of the results is not given, concentration can be read from the following graph.

Distribution of glyphosate and AMPA concentrations in rivers and streams (*N* = 583) and WWTP effluents (*N* = 186), analyzed from 2006 to 2013. The boxes indicate median and 25th and 75th percentiles, the whiskers the 5th and 95th percentiles. Values outside this range are plotted individually.



40 out of 583 samples showed glyphosate concentrations below the LOQ of 0.005 µg/L (27 for AMPA).

The article is considered reliable.

Data point:	CA 7.5/043
Report author	Reoyo-Prats, B. *et al.*
Report year	2017
Report title	Multicontamination phenomena occur more often than expected in Mediterranean coastal watercourses: Study case of the Têt River (France)
Document No	Science of the Total Environment 579 (2017) 10–21
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

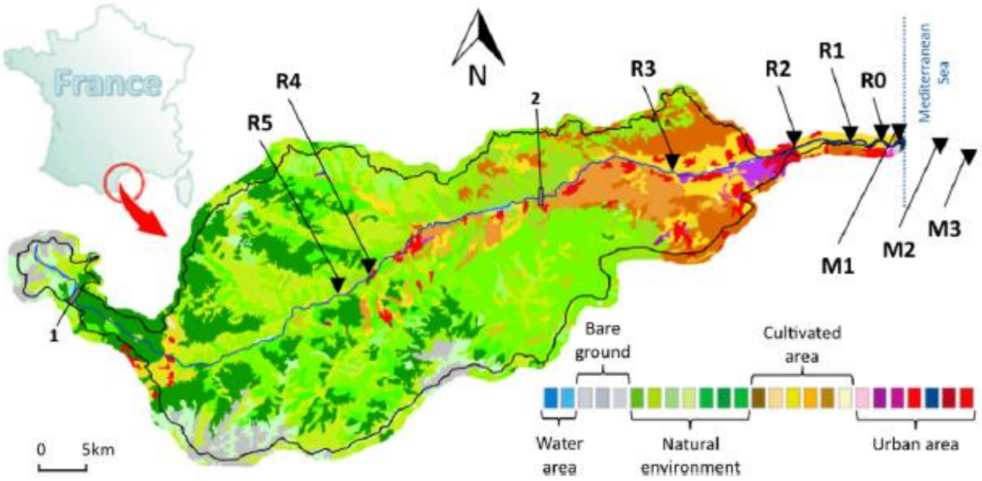
Contaminants found in watercourses are not only the result of anthropogenic activities but also depend on river's seasonal hydrodynamics. This is particularly true in Mediterranean climate regions where long dry periods are interrupted by strong rainfalls. Storm events remobilize particles from soils and sediments and, as a consequence, the load of particulate matter in rivers can be quite considerable, severely affecting water quality. Nevertheless, an absence of fieldwork studies exists concerning the simultaneous dynamics of mixtures of pollutants in river waters, particularly during strong rainfalls and floods. Our study assessed the concentrations of six families of pollutants, including pesticides, at these events, and compared them to those observed at drought sampling periods. We have used as model a typical Mediterranean coastal river from Southeast France, the Têt River, whose hydrodynamics and major elements fluxes have been fairly investigated. As expected, our results show that chemical mixtures due to human activities occur and that they are particularly relevant during storm events. But the results of our study argue that exceptional multi-contamination phenomena actually happen more often than expected because they are linked to recurrent sudden intense rainfall events in the Mediterranean. In particular, combined sewer overflows are responsible for this major issue in urbanized areas, whereas runoff and leaching will be the most important sources of pollutant mixtures occurring at flood flowpeak. After an overview of the sources responsible for chronic multiple stressors events in regions under a Mediterranean climate regime world-wide, we revisit best management measures to reduce risks from the presence of chemical mixtures in the environment.

Materials and Methods

Study site and sampling stations

The Têt River is the longest watercourse of the Pyrénées-Orientales department (Southeast France) with a total length of 115 km and a catchment area of 1417 km^2. Two dams partly control the river flow: the Bouillouses dam in the upstream section and the Vinça dam in the plain (see Figure 8.5-108). The Têt River has no major industrial or farm activities along its catchment but is impacted mainly by agriculture and urban activities (see below). It runs through the city of Perpignan, the main city of the department with 120,000 inhabitants. In this study sampling stations were chosen for their contrasted eco-systemic and anthropogenic characteristics along the river course (from R5 to R0 stations) and at the coastal area (from M1 to M3 stations) (Figure 8.5-108). Station R5 is the most upstream station, situated at Serdinya village, 30 km from the source. Upstream there are only little villages and no crop fields. R4 is located at Villefranche village, 4 km downstream R5, and is potentially impacted by fruit tree agriculture developed along the Rotja tributary. R3 is situated at Corneilla-la-Rivière village, 34 km after R4, and is a mildly impacted station with significant vegetable gardening activities and some bigger villages immediately upstream, such as Millas, with a WWTP of 6500 Population Equivalent (PE). R2 is situated 13 km after R3, in the city of Perpignan but upstream of its WWTP and downstream the Basse tributary, which is highly polluted by agriculture and urban activities. R1 is located 6 km downstream R2 at Villelongue-de-la-Salanque village and is downstream gardening and vineyards cultures as well as the sewage-overflow system and the WWTP of Perpignan city (350,000 PE). R0 is located 3 km downstream R1 station at the closest bridge downstream the WWTP of Perpignan, what allows sampling during flood events. But this station is also downstream of Sainte-Marie-la-Mer and Canet-en-Roussillon vacation resorts WWTPs (24,000 PE and 66,000 PE respectively). M1 is situated at the river mouth, 2 km after R0. M1 is the closest station downstream of vacation resorts WWTPs at drought sampling periods. M2 is approximately 1.5 km from the river mouth. M3 is 3 km offshore besides the CEFREM buoy. Water samples were collected in the summer drought on the 17 September 2013, in the autumn flood on the 17 November 2013 and in the winter drought on the 13 February 2014. M1, M2 and M3 samples from the summer were unfortunately lost for technical reasons. Moreover, to accurately define pollution dynamics during the flood, R0 was sampled a total of 13 times from 16 to 21 November 2013. During this flood, sampling was done from the top of bridges to avoid any danger from sudden water raise and because of the impossibility to access the river during high flow. Marine stations (M1, M2 and M3) were inaccessible as the flood went along with a major sea storm.

Figure 8.5-108: Land-use map from the Corine Land Cover dataset (European Environmental Agency) for the catchment basin of the Têt River. Sampling stations are indicated as black triangles and dams as grey rectangles (1) Bouillouses and (2) Vinça. See text for details on the main characteristics of sampling stations.



Chemicals analyses

Water sampling, total suspended solids (TSS) and total particulate organic carbon (POC) concentration determination
One (for flood) or two (for drought) 10 L capacity tanks were used for sampling. Tanks had previously been cleansed with 1.5 L of 1 M HCl and rinsed with 2 L of distilled water. Once in the field, tanks were rinsed three times with water from the sample station before being filled. Water samples were maintained refrigerated until processed. For each sample, glass filter columns were washed with distilled water. Sampled water was then filtered until clogging through 0.45 µm porosity GF/F filters using a vacuum pump. Three replicates were carried out per sample, but just two of them were averaged for reporting. The third replicate was kept in case the other two samples gave different results, which did not happen. After filtration, filters were dried at 40 °C for at least 24 h in a clean oven for TSS calculation from dry weight. Dried filters were decarbonized with repeated additions of H_3PO_4 (1 M) and HCl (2 M) and then dried again until no effervescence occurred. Remained sample was filtered in a pre-weighted and a pre-heated GF/F filter (0.7 µm in pore size) followed by repeated additions of HCl at 25% for inorganic carbon removal. Finally, POC contents were measured using a Leco CN 2000 elemental analyzer.

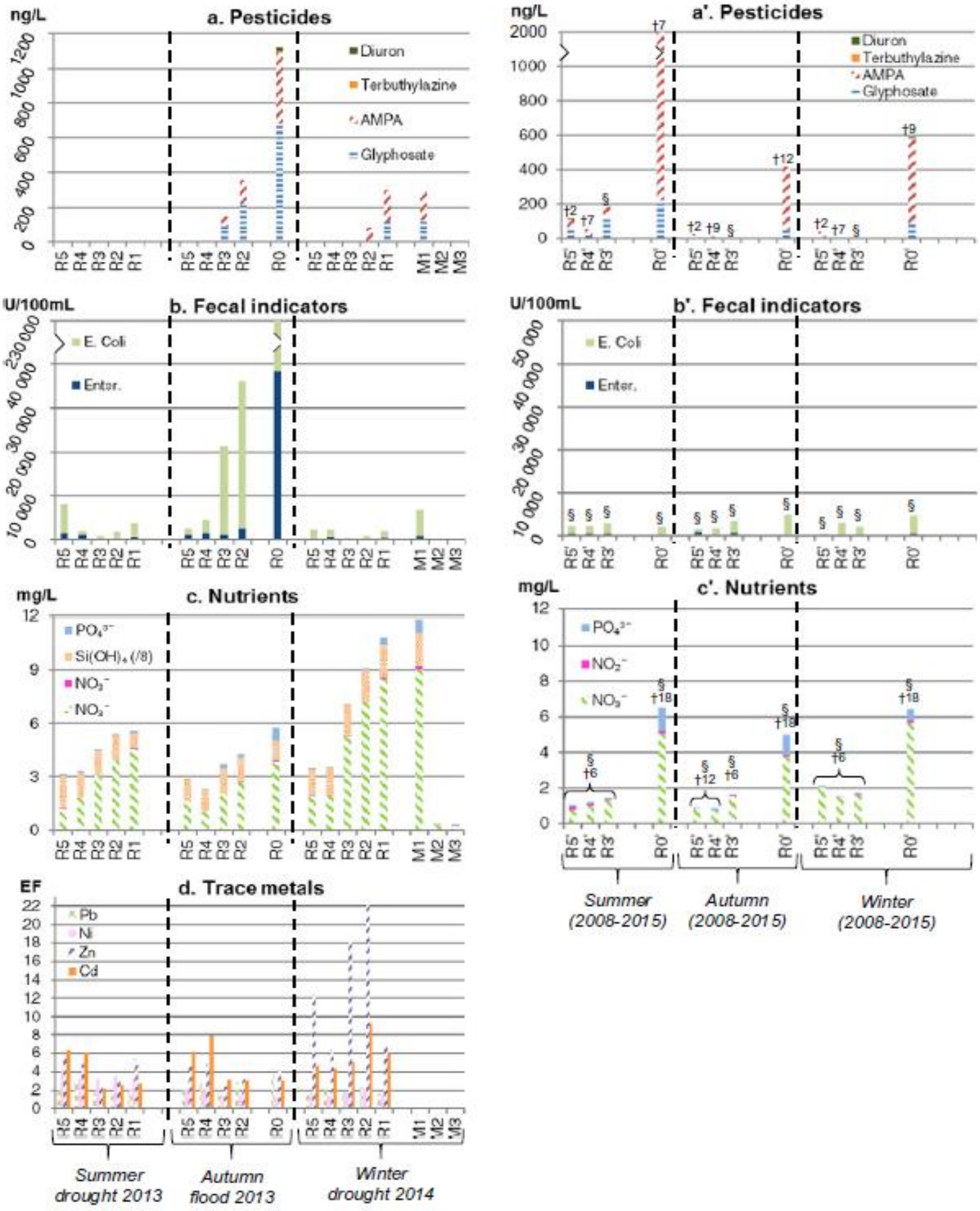
Pesticides analyses
ISO standards methods (International Organization for Standardization - www.iso.org, 2016) combined with three HPLC methods developed at the Centre d'Analyses Méditerranée Pyrénées (CAMP) were used in this study to detect up to 250 pesticide molecules. A first method started with a liquid-liquid extraction using dichloromethane and 1 L of water sample. Then the sample was evaporated under a dodecane stream (using a Turbovap II) and the residues dissolved in 1 mL of hexane. GC–MS analyses were carried out using a Varian 3800 gas chromatograph with a Saturn 4000 MS detector (ion trap) equipped with DB 5MS capillary column (30 m × 0.25 mm, 0.25 µm; IW Agilent). Helium was used as carrier gas at a flow rate of 1 mL/min. The injector temperature was set at 69 °C for 6 s, programmed to 290 °C at 150 °C/min where it was held for 5 min. The initial oven temperature was 69 °C held for 6 s, heated to 90 °C at 10 °C/min and held for 2 min, followed by 120 °C at 25 °C/min, then 190 °C at 15 °C/min and held for 5 min, followed by 220 °C at 10 °C/min and held for 10 min and finally followed by 320 °C at 5 °C/min and held for 5 min. Molecular ions were monitored for identification via electron ionization (EI) with a full mass range 70–500 *m/z*.

A second method consisted in LC-MS/MS analyses. The derivatization was done by mixing 100 mL water sample with 1.5 mL of FMOC-Cl (1 g/L), 10 mL of sodium tetraborate buffer (19 g/L, pH = 9.2), and 20 mL of acetonitrile (99.9%). After 24 h of reaction at 4 °C in the dark, reaction was stopped with the addition of 1 mL of orthophosphoric acid (99.9%). The derivation product was then analyzed by HPLC via an Agilent Bond Elut-PPL 50/PK 9 µm column (100 × 4.6 mm), a volume of 10 mL of methanol was added, the column was then rinsed with 20 mL mQ-water before passing the sample through; all those steps were conducted at a flow of 10 mL/min. The column was then dried for 15 min, before elution was conducted in 10 mL of acetonitrile/methanol (50/50 v/v). Evaporation was then performed with a Turbovap and the extract was obtained via acetonitrile/mQ-water (40/60 v/v) solvent. The LC analysis was conducted at a flow of 200 µL/min using a mixture of two solvents, E (99.9% acetonitrile/0.1% formic acid v/v) and F (99.9% mQ-water/0.1% formic acid v/v); elution steps were as follows: 0–2 min E at 5% and F at 95%, 2–13 min linear gradient from 5 to 100% for E and 95 to 0% for F, 13–17 min E holding at 100% and F at 0%, finally 17.01 min E and F went back to initial conditions (5% for E and 95% for F) until the end at 20 min. The TSQ Quantum ACCESS mass spectrometer used consisted of an HESI source operating with electrospray in the negative-ion mode set at 4 kV, 320 °C, and using collision energy from 16 to 56 eV for glyphosate and from 10 to 15 eV for AMPA. A third and last method started with mixing 100 mL water sample with 100 µL of MCCP D3 standard and 100 µL of formic acid (99%). Then, the mixture was filtered through a 0.45 µm PTFE membrane and 2 mL were recuperated for the online LC-MS/MS analysis. Sample preconcentration was performed on a Hypersil GOLD C18 5 µm column (2.1 × 50 mm), thanks to a LC pump performing at 0.5 mL/min using a mixture of two solvents, A (99.9% H_2O/0.1% formic acid v/v) and B (50% MeOH/50% hydrochloric acid CAN v/v); with a step for B solvent going from 5% to 100% at 5 min, held until 10 min before going back to 5%, while A solvent stayed at 95% except from 5 to 10 min where it was at 0%. Sample elution was performed on a Hypersil GOLD C18 3 µm (2.1 × 50 mm), via a MS pump at a flow of 300 µL/min using a mixture of two solvents, C (99.9% acetonitrile/methanol [50/50v]/0.1% formic acid v/v) and D (99.9% mQ-water/0.1% formic acid v/v); elution steps were as follows: 0–5 min C at 5% and D at 95%, 5–15 min linear gradient from 5 to 100% for C and 95 to 0% for D, 15–25 min C holding at 100% and D at 0%, finally 25.01 min C and D back to initial conditions (5% for C and 95% for D) until the end at 28 min. A TSQ Quantum ACCESS mass spectrometer was used in the same conditions as before, except for the collision energy, which was here from 17 to 28 eV.

Polycyclic aromatic hydrocarbons (PAHs) and PolyChlorinated biphenyls (PCBs)
PAHs and PCBs were analyzed on 1 L water sample using the ISO 17993 and ISO 6468 standard methods respectively. No PAHs or PCBs were found during the summer drought and the autumn flood, as a consequence they were not further analyzed.

Nutrients
Two replicates samples for nitrate (NO_3^- ± 0.02 µM), nitrite (NO_2^- ± 0.01 µM), phosphate (PO_4^{3-} ± 0.01 µM) and silicate ($Si(OH)_4$ ± 0.05 µM) were collected and stored in 15 mL acid washed polyethylene vials at − 20 °C until used. Samples were analyzed on a Seal-Bran - Luebbe auto-analyzer III according to the colorimetric method of Tréguer and Le Corre (1975) and modified by Aminot and Kérouel (2007).

Figure 8.5-109: **Simultaneous variations in contaminants concentrations at the Têt River from our study (a–d) and from government studies averaged per season over years (a'–c'). Variations are reported through space (from upstream to downstream stations) and time (seasonal variations). Notice division correction factor for silicates in c. § stands for CG66 studies of 2008 and 2012, and †x stands for water agency monitoring studies from 2010 to 2015 at x number of samplings.**



Results

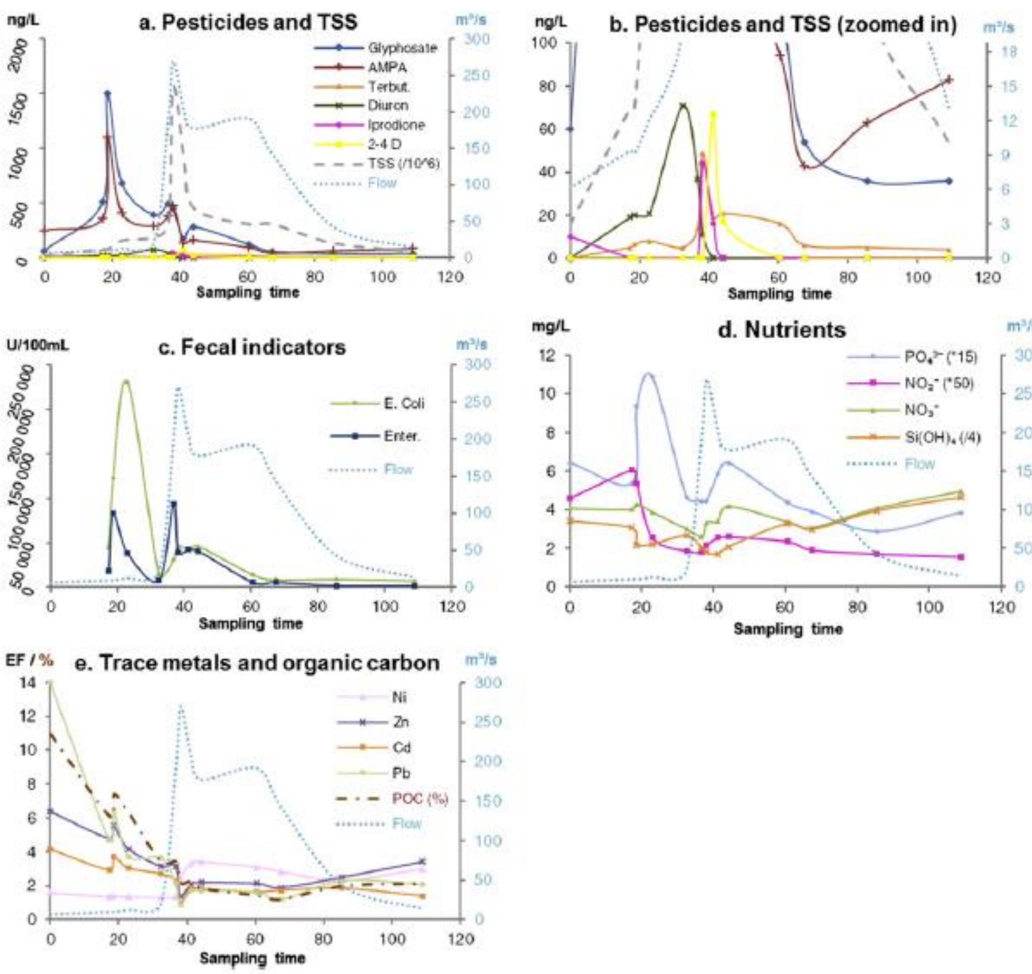
Variation in pesticides concentrations in the Têt River through space and time

The most abundant pesticides found in our study were by far the herbicide N-phosphonomethyl glycine (glyphosate) followed by its microbial degradation product aminomethylphosphonic acid (AMPA), which was present at a much lower concentration. Their highest concentrations were observed in the autumn flood 2013 with a total accumulation of 1119 ng/L at R0 (Figure 8.5-109a). But notice this is not the sample with the highest amount of pesticides in our study (see Figure 8.5-110a and next section for details). Indeed, because we sampled along the whole flood at R0, we chose to represent this station in Figure 8.5-109 by the closest sample in time to that immediately upstream station (R2). Glyphosate and AMPA were also observed at cumulated concentrations of respectively 360 ng/L and 148 ng/L at R2 and R3 stations in autumn, and lower than 300 ng/L at R2, R1 and M1 in the winter drought 2014. However, no pesticides were found at the three most upstream stations (R5, R4 and R3) at any season and neither at the two marine stations (M2 and M3) when measured in winter. Previous government studies (Figure 8.5-109a') found the highest concentrations of pesticides at R0' in summer, with an average total cumulated concentration of 1927 ng/L. In this case, AMPA (1702 ng/L) largely dominated over glyphosate (223 ng/L). Much lower concentrations were found on upstream R3', R4' and R5' during this season. On the contrary, no pesticides were found at any stations in the summer drought 2013 in our study (Figure 8.5-109a). High concentrations of AMPA were also found by government studies at R0' station during autumn (364 ng/L) and winter (496 ng/L) while in the upstream stations comparatively negligible concentrations were found (Figure 8.5-109a'). Regarding the presence of other pesticides, two other herbicides, diuron and terbuthylazine, were also found in our study, but only at the R0 station in autumn, with respective concentrations of 21 and 8 ng/L (but again, see next section). In government monitoring studies, terbuthylazine was only found during autumn at R0' (2 ng/L) while diuron was found at an average concentration of 5 ng/L at R5' and 2 ng/L at R0' during summer, in addition to 4 ng/L at R4' and 9 ng/L at R0' during winter.

Variations through space and time of other pollutants: Fecal indicators, nutrients and trace metals
Although *E. coli* and *enterococci* were always detected in river waters through the different seasons in all studies (Figure 8.5-109b&b'), much more of these fecal indicators were found in our study during the 2013 autumn flood at the downstream stations. Indeed, concentrations of 20,500, 33,500 and 230,000 U/100 mL of *E. coli* were measured at R3, R2 and R0, respectively, whereas 1670 and 3000 U/100 mL were measured at R5 and R4 during this flood. Thus, at R0, the amount of *E. coli* observed represents > 70 times the values found in summer and winter droughts in all studies. The same highly disproportional values were found during the flood 2013 for *enterococci*, even if they were much less encountered than coliforms (e.g. 38,300 U/100 mL for R1.3 at autumn flood). Exceptional concentrations of fecal pollutants were observed in M1 and R0' in winter (with 5950 U/100 mL and 4380 U/100 mL respectively) and in R5 in summer (6700 U/100 mL). In the two government samplings, however, an average level of only 1755 U/100 mL was found at R5'.

The dynamics of nutrients along the seasons followed a different pattern from fecal bacteria and pesticides. Silicates had the biggest concentrations (Figure 8.5-109c) but, as expected, they did not vary along space and time because they are not directly related to anthropogenic activities, as a consequence they will not be further discussed. Nitrates dominated over nitrites and phosphates and these nutrients progressively enriched along the watercourse (Figure 8.5-109c&c') with no significant differences in their concentrations at the same stations, and this for all seasons with the exception of the winter drought in our study. Indeed, statistically significant higher concentrations of nitrate were observed at this season in our study at downstream stations, from R3 to M1 (Wilcoxon-rank test $P = 0.0312$), with values approximately two times higher than those observed at the two other seasons. For instance, 4.58 mg/L of NO_3^- was measured at R1 in summer and 3.88 mg/L at R0 in autumn, compared to the 8.50 mg/L found at R1 in winter. Only anthropogenic trace metals, i.e. those with EF values higher than 2, are reported in Figure 8.5-109d. Nevertheless, trace metals with EF < 2 values did not show any significant spatial or temporal changes. Zn dominated the other anthropogenic metals during the winter drought with an average EF of 13.2 and a top EF of 22.4 at R2. Contrarily, Zn had an equivalent EF (4.1 in average) in summer and autumn. Furthermore, among all metals, Zn always had the highest EF value on R1 for the three campaigns. In the winter drought, Cd is the second most important anthropogenic metal with an average EF of 5.5 and also a top EF at R2 (9.3). However, Cd had the highest EFs in autumn and in summer, especially at R5 (6.2 and 6.3 respectively) and R4 (7.9 and 6.1 respectively), while the EF of R1 was only respectively 3 and 2.7. Ni and Pb had equivalent rather low EFs in the three seasons, even if a notable difference exists between these two metals, Ni had higher EFs in summer (average of 3.5 vs 2.0) while Pb had higher EFs in autumn (average of 2.7 vs 1.7).

Figure 8.5-110: **Flow variations and dynamics of pollutants during the autumn flood 2013 at the Têt River. Concentrations of pesticides and total suspended solids (TSS) (a and zoom-in b), fecal indicators (c), and nutrients (d), enrichment factors of trace metals and percentage of particulate organic carbon (POC) (e). "Terbut". stands for terbuthylazine. Notice correction factors for nutrients.**



Dynamics of pesticides during the flood at the Têt River
As opposed to government monitoring studies, which do not systematically sample during rainy events, in this study we have followed the 2013 autumn flood at R0 for a total of thirteen times (110 h). Figure 8.5-110a represents concentrations of pesticides encountered in the Têt River along this flood. Glyphosate and AMPA dominated in terms of concentrations, with averages of 367 and 300 ng/L, and major peaks of 1500 and 1100 ng/L respectively. These higher concentrations of pesticides occurred approximately at 20 h after the first rains, i.e. at the very beginning of the flood event. Second minor peaks of 490 ng/L of glyphosate and 480 ng/L of AMPA happened 20 h after, coinciding with major combined flow and TSS peaks for this flood event (Figure 8.5-110a). Figure 8.5-110b zooms over the dynamics of other pesticides, in particular the herbicides terbuthylazine, diuron and 2-4D and the fungicide-nematicide iprodione. They were much less important than glyphosate and AMPA, with a maximum average concentration of 13 ng/L and a maximum peak concentration of 71 ng/L for diuron. These pesticides peaked all at the same time, at around 40 h after the first rains, i.e. at the highest flood flow.

Flood dynamic comparison with other contaminants
Regarding fecal contamination, Figure 8.5-110c shows a top peak concentration for *E. coli* of 230,000 U/100 mL at around 20 h and a second lower peak of 45,900 U/100 mL at around 40 h after the first rains. For the *enterococci*, two peaks of approximately 88,000 U/100 mL occurred at the same lapses of time. With respect to nutrients, phosphates had the same concentration dynamics as *E. coli* and pesticides, with a first top peak concentration of 724 µg/L followed by a second smaller peak of 427 µg/L at the same ranges of time (Figure 8.5-110d). Nitrites had a top concentration of 121 µg/L at around 20 h followed by a rapid decrease until 40 h, where it slightly increased to stabilize progressively afterwards. Nitrates and silicates decreased until 40 h, but nitrates behaved as enterococci, they slightly peaked at 20 h and 40 h after the first rains. Phosphates, nitrates and silicates finally tended to increase at the end of the flood event,

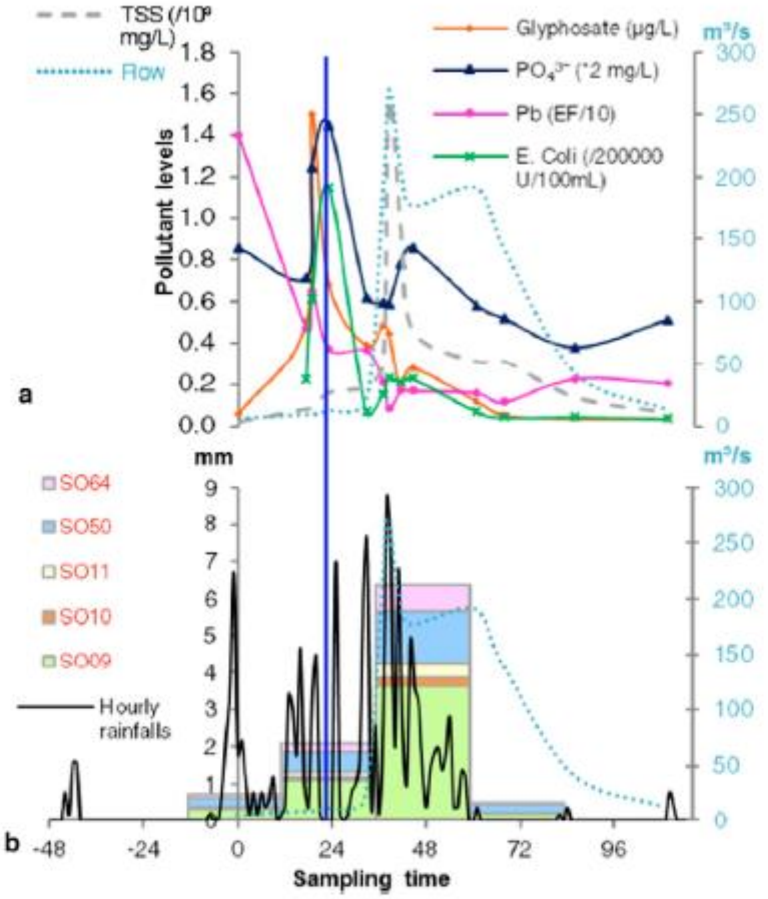
after 85 h. Anthropogenic trace metals and POC showed different dynamics from the other contaminants (Figure 8.5-110e). They peaked at our first flood sampling point (0 h). Then, they rapidly decreased during the first 17 h of the flood. POC levels decreased from 10.9 to 6.1 while EFs decreased for Pb from 14.0 to 6.5, for Zn from 6.4 to 4.8 and for Cd from 4.1 to 2.9. Ni is the exception here, with stable EFs under 2 during the first 40 h, which then suddenly went up to an average EF of 3, concomitant to the TSS maximum (Figure 8.5-110a), and remained at this value for the rest of the flood. Pb, Zn and Cd had two notable EF peaks, all together, at 20 h and 40 h. After that, their EFs remained stable at around 2 for the rest of the flood.

Discussion

Anthropogenic activities drive changes in multiple pollutants concentrations along space and time
At the Têt River, remarkable concentrations of AMPA and some glyphosate were found during summer at very high values at R0’ (Figure 8.5-109a’). The absence of these pollutants at R1, and the comparatively lower presence at R0’ during the other seasons, indicates these molecules are the result of a punctual pollution source, particularly from under-dimensioned activated sludge WWTPs of the summer resorts of Sainte-Marie-la-Mer and/or Canet located immediately upstream R0’. Indeed, this kind of WWTPs cannot be dimensioned for punctual summer-resorts tourism outbreaks but for average annual inputs. In fact, AMPA can be derived from both, detergents and the microbial metabolism of glyphosate, so most likely both wastewater effluents and vegetable or flower gardens leachates arriving to WWTPs are responsible for the presence of this contaminant in the environment. WWTPs are indeed known to be an important source of pesticides to the environment because pesticides are only partially eliminated at WWTPs. The presence not only of pesticides but also of fecal indicators at M1 and R0’ in winter, R0 and R0’ in autumn and the lower levels of fecal pollution in R1 in winter, corroborate this origin. As a matter of fact, the highest amounts of glyphosate and AMPA in our study (Figure 8.5-109a and 7.5-104a) were observed at R0 in the autumn flood 2013, but the impossibility of sampling at R1 during the flood impedes us to rule out the WWTP of Perpignan as responsible of this discharge during storm events (see also next section). The high levels of fecal indicators demonstrate that wastewater is responsible for the presence not only of pesticides but also of the higher concentrations of Pb and phosphates at R0, R2 and R3 during the flood (Figure 8.5-109). Similarly, wastewater inputs to the river can only be responsible for the abnormal fecal indicators levels in our most upstream river station, R5, in summer. Significant levels of other contaminants were not detected in R5, what is not surprising, as this station is surrounded by forests (Figure 8.5-108). Although federal local government studies did not detect this abnormal level of fecal indicators at the same station, poor wastewater treatments at villages upstream R5, which lack WWTPs, must be imputed because our results have been confirmed in successive samplings by our laboratory after 2014 (data not shown).

On the contrary, a diffuse contamination from agricultural seasonal treatments is certainly responsible for the presence of both glyphosate and AMPA in the watercourse in all other cases from all studies during droughts in the Têt River. This pollution is the result of leaching (subsurface flow) and runoff (surface flow) from occasional light rainfalls that occur during summer and winter, as well as, from crops irrigation during these seasons. This is confirmed in our study by the larger presence of nitrates, which are used as fertilizers in crops, and zinc and cadmium, which are known to be naturally present in phosphate minerals used as fertilizers. Furthermore, Zn carbamates are used as fungicides particularly in fruit crops and vineyards. Fruit crops are a major agriculture activity upstream R3 at the Têt River and vineyards are typical upstream R2. High levels of nitrites in this season confirm the origin of these contaminants in winter, at least for R1 and R2, what indicates heavy fertilization nearby these downstream stations. This origin is also confirmed by the absence of abnormal levels of fecal contamination upstream M1. Notice that, in winter, Zn is less important on R1 than on R2 and R3 upstream stations, but its EF is nevertheless still higher than the other three metals. Indeed, at R1, Zn is the metal with the highest EF in the three seasons, which traduces Zn base contamination level due to urban contamination and atmospheric deposition. Nickel does not vary much among stations (Figure 8.5-109d) indicating a non-anthropogenic origin of this metal in the Têt River in spite of an EF N 2. But this element might get concentrated at low water summer levels, explaining higher EFs during this season. High EFs values of Cd and Zn at R4 and R5 in summer and autumn can be attributed to both their higher than expected presence in mountain mother rocks compared to the minimal background values of downstream R1 used to calculate EFs (see Materials and methods section), and also to an atmospheric origin of these trace metals. In fact, as rainfalls are rather frequent in the mountain compare to the plain, atmospheric deposits may be washed more often at up-stream stations.

Figure 8.5-111: **(a) Contaminants dynamics as compared to hydrological variations of different compartments along the 2013 autumn flood of the Têt River. Each pollutant family studied is represented by one contaminant. Notice correction factors used to represent all contaminants together. (b) Rainfalls, volumes discharged by Sewer-Overflows (SO) and river flow along sampling time. Rainfalls are registered every hour while volumes discharged by the sewer-overflows (SO) are registered only every 24 h. Vertical blue line shows the major multicontamination phenomenon imputed to combined sewers overflows.**



Pollutants sources in coastal rivers under a Mediterranean climate regime

A thorough study of multiple pollutants dynamics has allowed us to build a complete picture of pollution sources in Med rivers. These sources are largely dependent on two different seasonal periods that characterize Med climate: drought and rainfall. During drought, main sources of pollution are not exceptionally different from other climates, with leaching and comparatively small runoff from crops, farms and urbanized areas (B) contributing to most pollutants found in watercourses. In urbanized areas, leachates are collected into the sewer system (A' and B') and will end up in the WWTP. If not treated, pollutants from leachates and from residences and industrial wastewaters will eventually end up in the watercourse (C). Exceptionally, poorly dimensioned WWTP can contribute to, much greater, punctual pollutions during droughts (C) that can be easily detected via fecal indicators analyses in river water from urbanized areas. During rainy periods, storm events transform leaching into runoff, which brings pollutants to watercourses from all surfaces (a and b). But according to our results, runoff during storm events in Med climate regions produces significant multicontamination phenomena. These phenomena happen for two main reasons: (i) high flow peaks during floods and (ii) Combined Sewer Overflows (CSO) due to sudden and intense rainfalls. Floods will remobilize river sediment-stocked pollutants (d) while CSO will bring both stormwater and wastewater directly into the river (e) without passing through the WWTP, as well as flush sewer pipe sediment-stocked pollutants (d').

Water multicontamination phenomena risk management in Mediterranean climate regions

Water management is recognized as inevitably linked to land. Urbanization, agricultural intensification, afforestation and wetlands removal are reducing the permeability of natural soils along with removing natural catchment areas. As a consequence, drainage intensifies contributing to the increased risk of flooding, at least as much as climate change. Our results show that an exceptionally important multicontamination phenomenon occurs at downstream urbanized areas during intense rainfall events, but still at rather small river water flows compared to typical autumn and spring floods (Figure 8.5-111a). This multiple stressors event was mainly due to CSO, as is the case in other regions when rapid snowmelt or heavy rainfalls occur. Nevertheless, snowmelts and floods are annual or bi-annual events, whereas sudden and intense rainfalls happen many times per year under a Med climate regime, and are actually increasing in frequency due to climate change. Given so, tackling constantly recurring CSOs in Med regions is particularly urgent. One first measure for doing so is to modernize the combined sewer network by transforming it, little by little, into a separate sewer. This way, raw wastewater will be carried into the WWTP even when overflow of the separate stormwater sewer will occur. This solution is, however, very expensive and cannot have much effect on pollutants such as pesticides coming from runoff, which would still be released directly into the river in case of overflow. Nevertheless, as demonstrated upon our results, runoff will contribute to a significant part of the pollution coming into watercourses from CSOs. Therefore, a better solution to cope with this issue is to increase the sewer network capacity by building constructions to temporarily stock combined waters during intense rainfalls before sending them to the WWTP at a smaller pace. In Perpignan city, a storage tank of 13,000 m^3 capacity is operative since October 2015. Comparing chemical mixtures levels before and after these types of constructions will be very interesting as predicted by Llopart-Mascaró *et al*. (2014). Alternative more economic methods consist in tackling the drainage problem at its source, by arranging permeable surfaces and/ or wetlands in urban and peri-urban agricultural areas, which will not only limit runoff from intense rainfalls but also improve the water quality and offer a bigger biodiversity. For instance, in the urbanized areas surrounding coastal rivers, creating public gardens that can be used as storm basins, and settling planted ditches designed to provide hydrological benefits can help to cope with CSO issues. Taking peri-urban crops into account is also essential since natural permeable plots arranged in buffer strips around cultivated crops can limit runoff and take up nutrients and pesticides, thus decreasing storm events consequences from runoff.

Natural permeable plots also provide ecosystem services such as pollinating insects and pest control which would result in a smaller use of pesticides and fertilizers. Indeed, previous solutions cope with the multicontamination peak during heavy rainfalls but we have seen that chemical mixtures can also contribute to the degradation of the water quality along dry periods. They enter the watercourse via leaching and runoff and, in the Têt River, they are due to agriculture only, but industrial and cattle or poultry breeding could also be a source of diffuse pollution in other rivers. In this case, management strategies are going to be dependent on the human activities along the watercourse. The presence of nutrients in our study indicates nearby abuse of fertilizers, so they should be dosed according to agriculture parcels size. This way only the necessary amounts for plant growing would be added to crops. In any case, solutions to reduce the use and abuse of pesticides would be advising farmers of good practices that take into account environmental toxicity effects of pesticides mixtures through indicators such as the EPRIP 2 (Environmental Potential Risk Indicator for Pesticide 2) or informing them of the benefits of alternative kinds of agriculture. Global management strategies are necessary to assess the environmental risk of chemical mixtures. Monitoring the surface water quality is one of the strategies implemented by federal and local governments for managing watercourses in developed countries. It consists in characterizing water quality not only through the analyses of several contaminants (nutrients, fecal indicators and sometimes also pesticides) as shown in our study, but also by using biomarkers in several river stations. Monitoring can then be complemented with environmental modelling for a better understanding of the managed system. In our case, we have chosen an alternative option, a carefully planned fieldwork study on multiple contaminants along a watercourse. This study can be considered as a step forward for currently undertaken measures for surface waters risk assessment. As a matter of fact, we are now capable of anticipating sources of chronic multiple stressors events in areas under a Med climate regime and, therefore, guiding sustainable management to deal with these sources. Indeed, contrarily to what is currently being implemented (Figure 8.5-109’), government monitoring protocols of Med surface waters should include samplings at pertinent stations during intense rainfalls and floods to better estimate chemical mixtures trends over time and evaluate if undertaken management measures are working. For instance, in order to determine if the storage tank built at Perpignan is useful to minimize CSO, an analysis of multiple contaminants will only make sense when intense sudden rainfalls occur. A next step would be to use environmental fate models in order to better predict long-term impacts of undergoing managed actions.

Conclusion

This study of several families of contaminants concentrations on a relatively well-studied river has allowed a fine understanding of chronic contamination sources, punctual and diffuse, in coastal Mediterranean water courses. We have corroborated that concentrations of pesticides, but also nutrients and fecal bacteria indicators, increased from upstream to down stream stations due to the increase of human activities, and that seasons played a role in these contaminants levels and their sources. Indeed, nutrients and trace metals are found concomitantly with pesticides during winter droughts at all downstream stations, indicating the diffuse origin from agriculture treatments of all these contaminants.

We demonstrated that the high concentrations of pesticides found by monitoring government studies at the most downstream station in summer are due to a punctual source of contamination, i.e. under-dimensioned WWTPs of upstream summer resorts, because immediately further up there are not such high levels of pesticides or even fecal indicators. On the other hand, we found that the highest concentrations of not only pesticides but also all other contaminants studied occur during strong rainfall events and we demonstrate they are mainly due to Combined Sewer Overflows (CSO) in urban areas. Given the current trend of intensification of extreme events, reduction of this chronic multi-contamination phenomenon should be a priority for risk management in Med climate regions worldwide. Solutions include better urban planning and land use as well as monitoring during intense rainfalls to carefully evaluate undertaken management measures. Since we worked on the results here presented, a new storage tank has been built at the city of Perpignan so a study to evaluate if this construction actually helps to improve river's water quality is underway. We also plan to follow the next storm events at high sampling frequency not only at R0 but also at R2 in order to discriminate the contribution of the sewer system upstream this station to CSO. Regarding the second multicontamination phenomenon, which is due to the flood highest flow peak, it would be interesting to model pollutants flow rate along the year. Indeed, during Med floods, these fluxes can represent up to 25% of the annual total suspended solids. Finally, no studies have yet assessed the ecotoxicology of river water samples impacted by multiple stressors at environmental concentrations. We plan to test the toxicity of water samples from this study that have contrasted levels of chemical mixtures.

Assessment and conclusion by applicant:
The article reports the contamination scheme of a Mediterranean river with different pollutant, among others glyphosate and AMPA. The considered approach identified that high concentrations peaks are caused by specific weather conditions, e.g. heavy rainfall after a dry period with consecutive overflow of WWTP, and other sources. The experiment does not focus explicitly on agricultural conditions. Maximum glyphosate and AMPA concentrations measured at 1.500 µg/L and 1.702 µg/L, respectively. The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions. The article is considered reliable with restrictions, since does not explicitly focuses on agricultural use of glyphosate.

Moreover the results and conclusions from the authors are not easy to read for glyphosate and AMPA. Concentration results presented in figure 8.5-108 are from the study and from what the study authors call "previous governmental studies". Authors reported "major peaks of 1500 and 1100 ng/L respectively for Glyphosate and AMPA" while the maximum cumulated glyphosate and AMPA concentrations reported in figure 8.5-108a is 1119 ng/L in their own study in autumn flood. The study also reports a maximum cumulated glyphosate and AMPA concentrations measured at 1927 ng/L in "previous governmental study" (including 1702 ng/L for AMPA).
The authors indicate that their study followed the 2013 autumn flood at R0 for a total of thirteen times (110 h). They also indicate that the peak concentrations were "found during summer at very high values at R0'" although figure 8.5-104 shows the peak concentrations for glyphosate and AMPA are reported in autumn 2013.

These peak concentrations of Glyphosate and AMPA are explained by authors to be linked with anthropogenic activities and punctual pollution source from "under-dimensioned activated sludge WWTPs of the summer resorts of Sainte-Marie-la-Mer and/or Canet located immediately upstream".

Data point:	CA 7.5/044
Report author	Desmet, N. *et al.*
Report year	2016
Report title	A hybrid monitoring and modelling approach to assess the contribution of sources of glyphosate and AMPA in large river catchments
Document No	Science of the Total Environment 573 (2016) 1580–1588
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Large river catchments with mixed land use capture pesticides from many sources, and degradable pesticides are converted during downstream transport. Unravelling the contribution of pesticide source and the effect of degradation processes is a challenge in such areas. However, insight and understanding of the sources is important for targeted management, especially when water is abstracted from the river for drinking water production. The river Meuse is such a case. A long-term monitoring data set was applied in a modelling approach for assessing the contribution of waste water treatment plants (WWTPs) and tributaries (sub-basins) to surface water contamination, and to evaluate the effect of decay on the downstream concentrations of glyphosate and AMPA at the point of drinking water abstraction. The results show that WWTPs are important contributors for glyphosate and AMPA in large river catchments with mixed land uses. In the studied area, the river Meuse in the Netherlands, the relative contribution of WWTP effluents is above 29% for glyphosate and around 12% for AMPA. Local industries are found to be potentially big contributors of AMPA. Glyphosate entering the river system is gradually converted to AMPA and other degradation productions, which results in downstream loads that are considerably lower than the sum of all influxes. In summer when the travel time is longer due to lower discharge, the first order decay of glyphosate in the river Meuse is estimated to result in about 50% reduction of the downstream glyphosate.

Materials & Methods

The case study in this paper is the river Meuse which is an important surface water source for drinking water production in the Netherlands. Drinking water standards for glyphosate are frequently exceeded in the river Meuse and high concentrations of the daughter product AMPA are also measured.

Glyphosate and AMPA
Glyphosate (*N*-phosphonomethylglycine) is a broad-spectrum, non-selective herbicide that controls most annual and perennial weeds by inhibiting the amino acid synthesis. Amino- methylphosphonic acid (AMPA) is the primary degradation product of glyphosate but it is also a degradation product of phosphonates which occur in domestic and industrial wastewaters. Phosphonates are used in detergent products and scaling inhibitors in hot water and cooling circuits. Minor applications include bleaching of paper/textile, stabilization of cement and cleaning/polishing of metals.

Study area and available monitoring data
The study area is the downstream part of the Meuse catchment where the river flows through Dutch territory. The Meuse catchment covers 36,000 km^2 and from source to mouth, the main river has a total length of N 900 km. The surface water from the river Meuse is used for drinking water production. The European drinking water standard for individual pesticides is 0.1 µg/L and the Dutch government imposes this limit for surface waters at points of drinking water abstraction. In the river Meuse the threshold of 0.1 µg/L is frequently exceeded for glyphosate and high concentrations of the daughter product AMPA are also measured. The investigated area is a 250 km river stretch between the Belgian- Dutch border (at Eijsden) and the point of drinking water intake “Biesbosch” (at Keizersveer). The land use in the Dutch part of the Meuse catchment is mixed and fragmented with 54–60% agriculture, 11–34% urban and 12–28% nature/forest/water. Glyphosate can originate from both agricultural and urban use. The runoff from agricultural land is mainly a diffuse source of pollution. The runoff in urban areas is generally collected in the sewage system and reaches the river as a point source through a drain, or in the effluent of waste water treatment plants (WWTPs) or due to sewer overflow. The urban areas in the river Meuse basin are mostly clustered around city centers surrounded by densely populated neighborhoods and industrial zones. There are over 50 WWTPs in the Dutch part of the Meuse catchment that discharge their effluent into the surface water. Industrial effluents are the second important point source for pollution in the river Meuse. AMPA can originate from all of these sources, either as a degradation product of glyphosate or as a decay product of phosphonates which occur in domestic and industrial wastewaters.

Monitoring data on glyphosate and AMPA concentrations were obtained from RIWA-Maas (international association of drinking water companies that use the river Meuse as a source). Historical monthly or biweekly monitoring data of glyphosate and AMPA concentrations in the river Meuse were available for the period 1995–2011. The monitoring dataset includes the two bordering locations of the study area: Eijsden (upstream) and Keizersveer (downstream). Furthermore, an extended monitoring dataset was available for 2006, 2008 and 2010. This dataset also includes AMPA and glyphosate concentrations in the main tributaries and in the effluent of WWTPs discharging into the river Meuse along the 250 km stretch considered in this case study. During these extended monitoring campaigns samples were collected on a monthly basis. The tributaries were sampled at downstream locations near the confluence with the river

Meuse and the WWTPs were samples at the outflow of the treatment plant (effluent). More details are given in the corresponding RIWA-reports.

Long term series of daily discharge data are available for the river Meuse in Eijsden (since 1950) and in Keizersveer (since 1994). Daily dis- charge data of the main tributaries are available for at least two years be- tween 2006 and 2010. For the WWTPs discharging into the river Meuse, daily effluent discharge data are available in the period 2006–2010, al- though for some WWTPs only one year of data is available. The discharge data were obtained from Rijkswaterstaat (Ministry of infrastructure and the environment of the Netherlands) and RIWA-Maas.

Modelling approach

The River Water Quality Model N°1 (RWQM1) was used to build a model for the downstream Dutch part of the river Meuse, starting at Eijsden (Dutch-Belgian border) and extending to the drinking water intake in Keizersveer. The total length of the modelled river stretch is about 250 km and the required information about geometry and roughness was derived from the hydraulic SOBEK-Maas model which encloses a large database of cross-section characteristics (about 460 sections for the considered stretch of the river Meuse).

The model includes the main course of the river Meuse between Eijsden and Keizersveer, the influx from seven main tributaries (Jeker, Geul, Geleenbeek, Roer, Neerbeek, Niers and Dieze), the influx from two smaller tributaries (Ur and Thornerbeek) and the influx from eight WWTPs discharging effluent into the river Meuse (Heugem, Limmer, Bosscherveld, Stein, Panheel, Roermond, Venlo and Cuijk). Transport of AMPA and glyphosate, as well as the conversion of glyphosate to AMPA and the degradation of AMPA (reaction product not defined and not quantified) are modelled. The conversion of glyphosate to AMPA is considered to be a first-order degradation process. Calculations are performed for a range of kinetic (degradation rate) parameter values. Half-life values (DT_{50}) for glyphosate in water reported in literature range from 1 day to 51 days. The stoichiometric maximum yield is 0.67 g AMPA per g glyphosate, but experimentally measured yields are often lower. Yield values reported for aerobic degradation in water-sediment studies range from 2% to 16% (water phase) and up to 27% (total system) of the total glyphosate applied. The reported yield values are apparent yields calculated as the ratio of AMPA retrieved over glyphosate applied. However, the final amount of AMPA retrieved in the system is not only resulting from glyphosate degradation but is also affected by adsorption, dissipation and further degradation of AMPA itself. These processes result in a decrease of the amount of AMPA retrieved and therefore the apparent yield generally is lower than the stoichiometric yield of 0.67 g AMPA per g of glyphosate. The stoichiometric yield ratio of 0.67 is applied in our model.

Map of the Meuse catchment on Dutch territory, showing the spatial distribution of land use. Study area of the model is the 250 km river stretch between the Belgian-Dutch border (Eijsden, grey diamond) and the downstream drinking water intake (Keizersveer, grey triangle).

The model only takes into account the water column. As a result, all glyphosate and AMPA that enters the river system is assumed to stay in the water column. Sorption and desorption on sediments is not taken into account. Given the gravelly nature of the sediment, this is considered to be a valid assumption. The river Meuse is characterised by a gravel-bed with bed material diameter D50 of about 16 mm in the upstream part of the study area and a transition towards a more sandy-bed downstream Roermond. Modelled dissipation routes are limited to dilution and degradation. In the model, AMPA is assumed to be the only degradation product of glyphosate. Although AMPA is the major daughter product of glyphosate, other degradation products are known to exist as well, but these are not taken into account here. The model only considers degradation of glyphosate to AMPA and degradation of AMPA without further specification of degradation products.

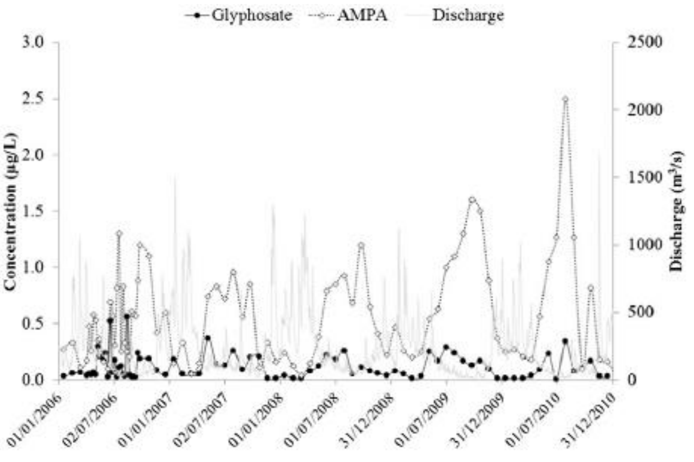
Model input data, boundary conditions and model output

The model requires discharge and concentration data at the boundaries, i.e. the upstream boundary at Eijsden, the tributary boundaries, and WWTPs effluents. These boundary conditions are defined based on available discharge (daily) and concentration data (biweekly or monthly) for the river, its main tributaries and WWTPs discharging into the river. The data were obtained from RIWA-Maas and Rijkswaterstaat.

Starting from 2006, daily discharge data and monthly or biweekly concentration data are available for the upstream boundary and for the main tributaries. The daily discharge data are directly used as input for the model. The concentration monitoring data, on the other hand, are used to generate, at each boundary, a single set of representative concentration levels (glyphosate and AMPA) based on the monthly mean concentration obtained for the available dataset with measured concentrations in the period 1995–2011. This dataset contained 15–22 observations per calendar month at the upstream boundary and 18– 29 observations per calendar month at the downstream drinking water intake. There are less observations in winter months than in spring and summer months due to lower frequency of monitoring and focus on the application period in the monitoring before 2002 (i.e. lower frequency monitoring in winter). The monthly mean value (based on the available monthly and biweekly data) is assigned to the 15th day of the month and in-between the concentration level is interpolated to generate a set of daily concentration values. This represents the average pattern of concentration time series throughout a year.

For some tributaries and WWTPs the available dataset lacks measurements in one or two months (in winter). The missing monthly concentration level in tributaries is estimated taking into account the relative seasonal variation of the concentrations in the river. While for WWTPs the missing effluent concentration of a missing month is assumed to be equal to the concentration level in the previous month because WWTPs with concentrations measurements for each month do not indicate any clear seasonal or other pattern in the effluent concentrations. There were no more than two successive months with missing data in the WWTP effluent data series. Simulated concentrations are compared with measured values at the drinking water intake. At the downstream end of the modelled river stretch (drinking water intake at Keizersveer), the monitoring data are resampled and represented in the same way as described above for the boundary input data. Model results are compared with this generated set of representative concentration levels based on the average concentration measured in a particular month over several years.

Figure 8.5-112: Glyphosate and AMPA concentrations and discharge measured in the river Meuse near the upstream boundary at Eijsden



Results & Discussion

Measured concentrations in the river Meuse

Figure 8.5-112 and Figure 8.5-113 show the measured time series of river water AMPA and glyphosate concentrations for the period 2006–2010 at the upstream boundary and at the drinking water intake, respectively. In that period, maximum glyphosate concentrations were 0.7 µg/L at the upstream border and 0.3 µg/L at the downstream drinking water abstraction. Maximum AMPA concentrations were 2.5 µg/L at the upstream border and 3 µg/L at the downstream drinking water abstraction. In general, higher concentrations of both glyphosate and AMPA were measured at low discharge of the river (summer) and lower concentrations were measured at high discharge (winter). Plotting concentrations versus discharge showed an inverse relation between AMPA concentration and river discharge, although correlation coefficients were rather small ($R^2 = 0.64$ at the upstream boundary and $R^2 = 0.46$ at the down- stream water intake). For glyphosate, however, the relation with dis- charge was less pronounced with considerably lower correlation coefficients (R^2 = 0.19 at the upstream boundary and R^2 = 0.11 at the downstream water intake). The better correlation of AMPA concentrations with discharge points to a more constant load of AMPA and thus more constant source influxes. The differences between glyphosate and AMPA in concentration pattern and correlation with discharge, indicates that different sources are involved. The temporal variation of glyphosate and AMPA shows a similar pattern at first glance that seems to be related to seasonal dynamics. There is large seasonal variation of the discharge in the river Meuse. If the load is constant, the concentrations will be inversely related to the river discharge when dilution is the main cause of temporal variation. The correlations analysis be- tween concentration and discharge, shows that for AMPA dilution is a likely possible reason for the observed temporal variation with high concentrations in summer (at low discharge) and low concentrations in winter (at high discharge). For glyphosate, however, the seasonal variation of the concentrations has poor correlation with the discharge. The likely possible reason for the observed temporal dynamics in glyphosate concentrations is the seasonal pattern of the use of glyphosate as pesticide. The application period ranges from March till October. The load increases when more glyphosate is applied and therefore also the concentrations increase.

At the upstream boundary the median glyphosate concentration was 0.08 µg/L and the 90th percentile value reached 0.27 µg/L (monitoring dataset 1995–2011). The median AMPA concentration was 0.50 µg/L (monitoring dataset 1995–2011). About 45% of the glyphosate concentrations exceeded the drinking water standard of 0.1 µg/L and 21% of the concentrations exceeded the standard by at least a factor of 2. About 20% of the AMPA concentrations exceeded the threshold of 1 µg/L. At the drinking water intake, the median glyphosate concentration was 0.07 µg/L and the 90th percentile value was 0.15 µg/L. The median AMPA concentration was 1.10 µg/L. About 32% of the glyphosate concentrations exceeded the drinking water standard of 0.1 µg/L, but only 2% of the concentrations doubled the standard. About 52% of the AMPA concentrations exceeded the threshold of 1 µg/L and 5% exceeded the level of 2 µg/L. From the concentration ranges and the time series (Figure 8.5-112 and Figure 8.5-113) it is clear that glyphosate concentrations in the river decreased along the 250 km river stretch between the upstream boundary and the drinking water intake. This is contrary to the AMPA concentrations which show considerable increase along the trajectory. Due to the increase of AMPA concentrations and the decrease of glyphosate concentrations along the river stretch the ratio of AMPA to glyphosate increases accordingly. At the upstream boundary, the median ratio is 5.9 while at the drinking water intake the median ratio is 12.7.

Measured concentrations in tributaries and WWTP effluents

In several tributaries concentrations were higher than in the river Meuse. Highest concentrations of glyphosate were found in the tributary Jeker and in WWTP effluents (highest concentrations measured at WWTPs Panheel and Roermond). The highest concentrations of AMPA were found in the tributaries Ur and Geleenbeek and in the WWTP effluents (with the highest concentrations measured at WWTPs Gennep and Panheel). Extremely high AMPA concentrations were found in the river Ur (average 28 µg/L, maximum 130 µg/L), while glyphosate concentrations were only moderate (average 0.7 µg/L, maximum 3.8 µg/L). This small tributary is mainly discharging effluent from an industrial waste water treatment plant. In 2005 and 2006, RIZA (Rijkswaterstaat, department of water) measured very high AMPA concentrations (up to 69 µg/L) in this effluent and concluded that this originated from the application of zinc phosphonates in the industrial cooling circuit. In 2008 and 2010, RIWA included the tributary Ur in its monitoring campaign for the river Meuse. In 2010 very high concentrations of AMPA (up to 130 µg/L) were found in the Ur but in 2008 the highest concentration measured in the Ur was only 4.1 µg/L.

Figure 8.5-113: **Glyphosate and AMPA concentrations and discharge measured in the river Meuse near the drinking water intake at Keizersveer**

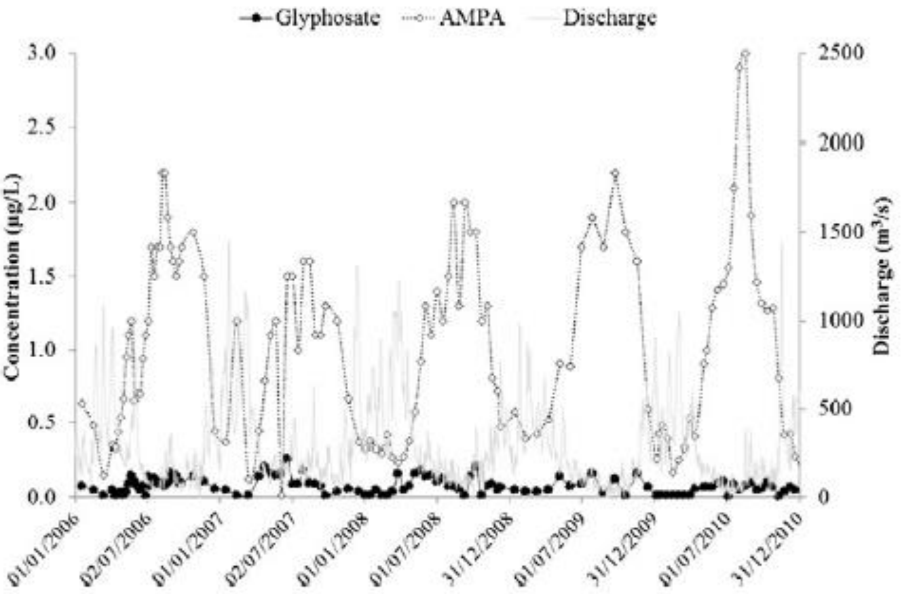


Table 8.5-156: **Percentile values for the AMPA/Glyphosate ratio at the upstream boundary (Eijsden) and at the downstream drinking water intake (Keizersveer), based on measurements in the period 2006–2010**

	AMPA/glyphosate ratio				
	P10	P25	P50	P75	P90
Upstream	1.67	3.52	5.93	9.33	16.38
Intake (downstream)	6.57	9.00	12.73	20.77	34.18

Table 8.5-157: **Range of glyphosate and AMPA concentrations measured in the period 2006–2010 in the river Meuse (upstream at Eijsden and downstream at Keizersveer), in the main tributaries and in the effluent of WWTPs discharging into the river Meuse**

	Glyphosate (µg/L)			AMPA (µg/L)		
	Mean	Min.	Max.	Mean	Min.	Max.
Meuse - upstream	0.13	<0.02	0.66	0.62	0.04	2.50
Meuse - downstream	0.08	<0.02	0.26	1.06	0.02	3.00
Jeker	2.18	0.26	12.00	1.62	0.05	4.50
Geul	0.41	<0.05	3.20	0.98	0.05	3.10
Ur	0.67	<0.05	3.80	27.79	0.20	130.00
Geleenbeek	1.33	0.05	4.60	3.14	0.05	10.00
Thornerbeek	0.46	<0.05	2.23	2.38	0.70	6.20
Roer	0.10	<0.05	0.80	0.56	0.05	1.50
Neerbeek	0.06	<0.05	0.20	0.37	0.05	0.98
Niers	0.25	<0.05	4.80	1.61	0.20	4.80
Dieze	0.23	<0.03	0.71	1.45	0.23	4.30
WWTPs	1.70	<0.05	6.63	3.06	0.25	7.06

Figure 8.5-114: **Measured and simulated discharge in the river Meuse at the downstream drinking water intake**

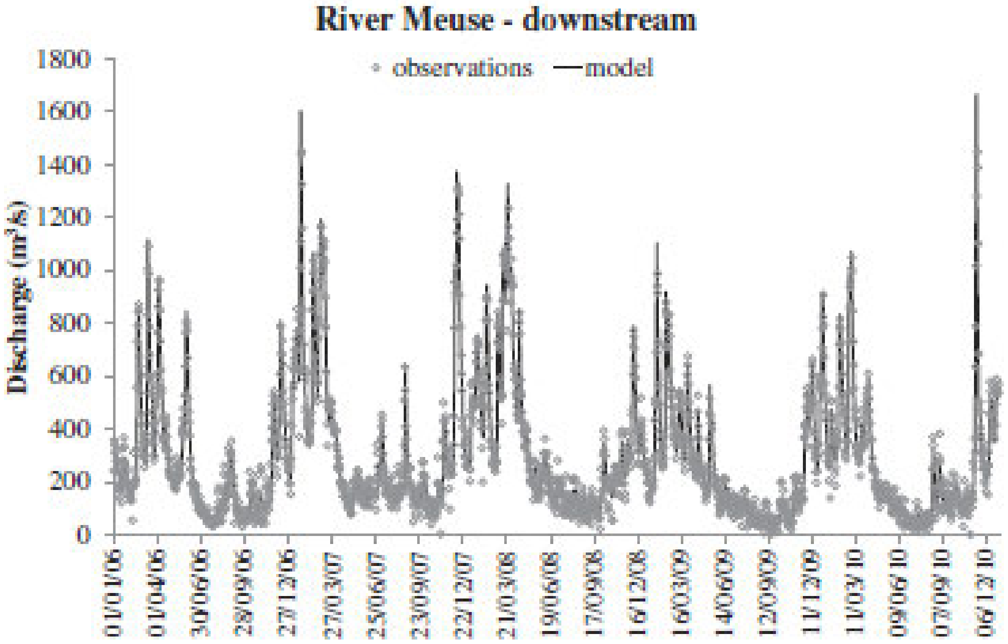
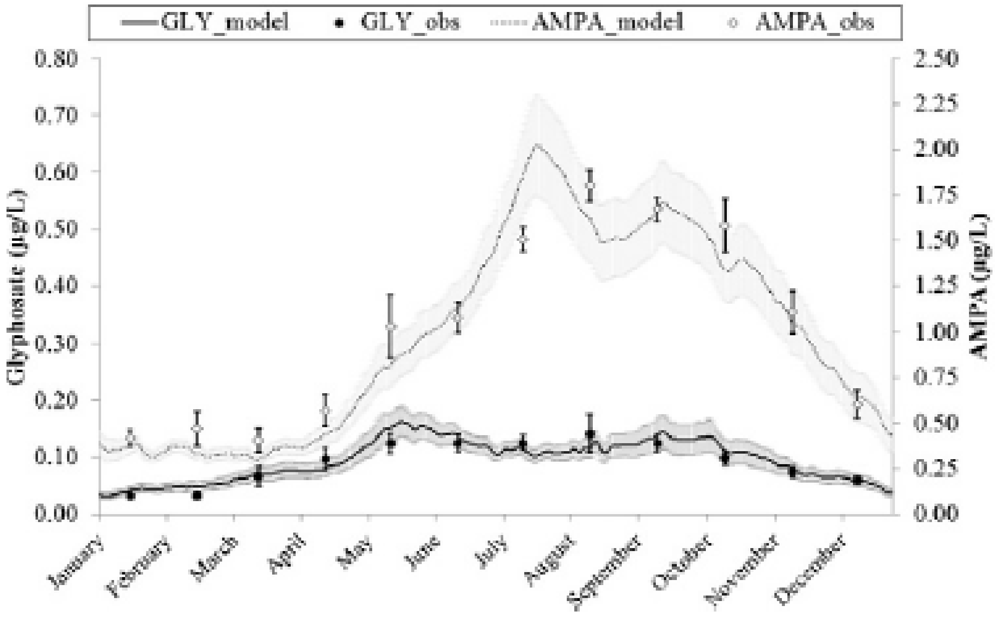


Figure 8.5-115: **Simulated and measured monthly mean concentrations of AMPA and glyphosate at the drinking water intake for an average year based on data from 1995 to 2011. Best fit obtained using the degradation parameter settings: glyphosate DT_{50} = 3.6 d, AMPA DT_{50} = 52.5 d. The shaded area represents the model uncertainty.**



Hydraulics

Observed and simulated daily-averaged discharges in the river at the downstream point of the modelled river stretch are presented in Figure 8.5-114. The hydraulic routing of the Meuse river is very well reproduced by the model (R^2 = 0.94, NRMSE = 4%, CV(RMSE) = 21%). Up to discharges of 1000 m^3/s

the river hydraulics are very well simulated. At peak discharges, the model sometimes overestimates and sometimes underestimates the maximum level, but it is not a systematic deviation. The increase in deviation between observed and simulated values at higher discharges is partially related to the temporal resolution of the flow input data. More accurate simulation of peak discharges requires sub daily input data. However, daily averaged values are sufficient for this study because the focus of the analysis is not on peak flow events.

Degradation of glyphosate to AMPA

The key parameter for the degradation process is the substance half- life value (DT_{50}). In order to estimate glyphosate half-life time and AMPA half-life time in the modelled part of the river Meuse, DT_{50} parameter values were varied within a given range (Table 8.5-159) and the model results were compared with the glyphosate and AMPA concentrations measured at the drinking water intake (Figure 8.5-115). The root mean squared error (RMSE) and sum of squared errors (SSE) were used as calibration statistics. Best fit results were obtained with glyphosate half- life time of 3.6 days and AMPA half-life time of 52.5 days (Figure 8.5-115, $R^2 = 0.86$). With these parameter settings both AMPA and glyphosate concentrations in the Meuse at the drinking water intake were well simulated by the model. The resulting correlation between observed and simulated values was $R^2 = 0.92$ for AMPA and $R^2 = 0.86$ for glyphosate. Since only the water phase is considered in the current modelling approach, the simulated degradation may in reality partly reflect dissipation to the sediment (eventually followed by degradation in the sediment). Water-sediment studies show that dissipation to the sediment can be an important pathway for glyphosate and AMPA losses from the water column. However, water to sediment ratios applied in these studies are quite low and merely representative for ditches and small water courses. In our case water to sediment ratios are generally much higher and therefore it can be assumed that dissipation to the sediment will be more limited compared to the aforementioned water-sediment studies.

In the current model AMPA was considered to be the only degradation product of glyphosate and the stoichiometric yield of 0.67 g AMPA per g glyphosate was applied. However, the apparent yield was b 0.67 g/g, because degradation of AMPA was also considered in the model. The apparent yield is the actual amount of AMPA originating from glyphosate measured or simulated divided by the amount of glyphosate de- graded. The apparent yield is less than the stoichiometric yield when the daughter product is further degraded. Due to further degradation of AMPA, the apparent yield of AMPA over glyphosate varies with the residence time in the river system. The smaller the flow velocity in the river, the larger the residence time, and the more degradation of AMPA occurs. So, the apparent yield of AMPA from glyphosate degradation was lower at low discharges in the river. At low discharges (in summer), the calculated hydraulic residence time between the upstream boundary and the drinking water intake is about 10 days. Using the best fit degradation parameter estimates (glyphosate DT_{50} = 3.6 d, AMPA DT_{50} = 52.5 d) the corresponding apparent yield of AMPA was about 0.58 g per g glyphosate.

The simulated apparent yield of AMPA in the river at the drinking water intake was higher than the apparent yield reported in several water-sediment studies, ranging between 0.05 and 0.27. However, the duration of these water-sediment studies is about 100 days or more. Applying the degradation parameters of the best fit model (glyphosate DT_{50} = 3.6 d, AMPA DT_{50} = 52.5 d) for a residence time of 100 days resulted in an apparent yield of about 0.18 g AMPA per g glyphosate, which is comparable to the yield observed in the water-sediment studies.

Contribution of sources

In order to distinguish the contribution of glyphosate degradation to the AMPA concentrations in the river, the calibrated model results (glyphosate DT_{50} = 3.6 d, AMPA DT_{50} = 52.5 d) were evaluated against the results of a reference run without glyphosate and AMPA degradation. The percentage of AMPA originating from glyphosate degradation is calculated as the relative difference between simulated AMPA concentrations with (best fit run) and without degradation (reference run). The effect of glyphosate decay on the downstream glyphosate and AMPA concentrations in the river varies with discharge because discharge affects the residence time of the water and thus the time available for degradation to occur. The conversion of glyphosate to AMPA and other degradation products during transport, results in a reduction of the glyphosate concentrations. The half-life for glyphosate in the river Meuse is estimated at 3.6 days. Since the travel time over the 250 km river stretch can reach up to 10 days, the effect of decay on glyphosate concentrations can be considerable. In summer when the travel time is longer due to lower discharge, the first order decay of glyphosate in the river Meuse is estimated to result in about 50% reduction of the downstream glyphosate concentrations (Figure 8.5-115 versus Figure 8.5-116).

According to our model results, the contribution of glyphosate decay to the observed AMPA concentrations at the drinking water intake ranged between 2% and 10%, and was highest in summer, at low discharge (Figure 8.5-117). In absolute concentration levels glyphosate degradation resulted in an average increase of the AMPA concentrations by 0.06 µg/L. At high discharge and limited residence time, the concentration increase due to glyphosate decay was b 0.01 µg/L. At low discharge, however, the contribution of glyphosate to AMPA concentration levels increased up to 0.15 µg/L. The percentage of AMPA originating from glyphosate is maximal in spring and does not coincide with the highest concentration levels in the river which are observed in summer.

In order to estimate the contribution of AMPA and glyphosate inflow from tributaries and WWTPs, scenario runs were performed with the calibrated model including and excluding each of the tributaries and the WWTPs. The scenario results are used to calculate the contribution of the tributaries and the WWTPs to the load of AMPA and glyphosate at the drinking water intake. In our approach only WWTPs discharging directly into the river Meuse were regarded as contributions from WWTP effluents because WWTPs discharging into a tributary of the Meuse were accounted for in the contribution of the tributary. As described before, note that the tributary Ur is mainly discharging effluent from an industrial waste water treatment plant (Volz, 2009). The relative contribution of upstream influx, tributaries and WWTP effluents to the concentrations in the river at the drinking water intake is shown in Figure 8.5-118 for glyphosate and in Figure 8.5-119 for AMPA, and is summarized in Table 8.5-158. The model scenario analysis shows that influx at the upstream border had a contribution of 56% in the load of both AMPA and glyphosate. The WWTPs accounted for 12.6% of the glyphosate load and 5.3% of the AMPA load. Considering only the influxes on Dutch territory (so excluding the upstream influx at the upstream border) the relative contribution of WWTP effluents was 29% for glyphosate and 12% for AMPA. This includes only the WWTPs that discharged directly into the river. The tributary influxes of glyphosate and AMPA also originated partly from WWTP effluents that are discharged upstream on the tributaries. So the total contribution of WWTPs is expected to be larger. Several studies already pointed out the importance of WWTPs as a source of glyphosate and AMPA inputs to surface water. However, assessments quantifying the contribution of the WWTP effluent loads are rarely made. For a small catchment (25 km^2) with mixed land use in Switzerland, the contribution of glyphosate originating from urban areas to the load during selected rain events was estimated at N 50% based on targeted monitoring of stream surface water, urban drainage water and WWTP effluents. Blanchoud *et al.* (2007) estimated the urban contribution to pesticides (among which glyphosate) in the Marne catchment (12,762 km^2) at about 50%.

Based on the average concentration levels measured in the Ur (which are used as input for the model), this tributary accounted for 12% of the AMPA load. But, one should note that the concentrations measured in the river Ur vary over a large range (see Table 8.5-157). So the contribution of the Ur to the AMPA load is probably quite variable in time and depends on the concentrations in the industrial effluent. The influxes from the tributary Dieze accounted for 10% of both AMPA and glyphosate loads at the drinking water intake. The influxes from the tributary Jeker contributed considerably more to the glyphosate load (7%) than to the AMPA load (2%). The monthly variation in the relative contribution of upstream influx, WWTP effluents, tributary Ur (discharging mainly industrial effluent) and other tributaries to the concentrations in the river at the drinking water intake is shown in Figure 8.5-118 for glyphosate and in Figure 8.5-119 for AMPA. The model scenario results also indicate that the relative contribution of different sources is quite variable throughout the year. The seasonal variation is larger for glyphosate than for AMPA. The contribution of AMPA influx at the upstream border ranged from 38% to 68%, while the contribution of glyphosate upstream influx ranged from 25% to 75%. The WWTP effluents accounted for 3% to 9% of the AMPA load and 13% to 21% of the glyphosate load. For both glyphosate and AMPA, the highest contributions from WWTPs occurred in summer. Main WWTP contributions for glyphosate occur from May until October. Main WWTP contributions for AMPA occur from June until September.

Figure 8.5-116: **Simulated and measured monthly mean concentrations of AMPA and glyphosate in the river Meuse at the drinking water intake for an average year based on data from 1995 to 2011. Reference run: without any degradation of glyphosate and AMPA. The shaded area represents the model uncertainty.**

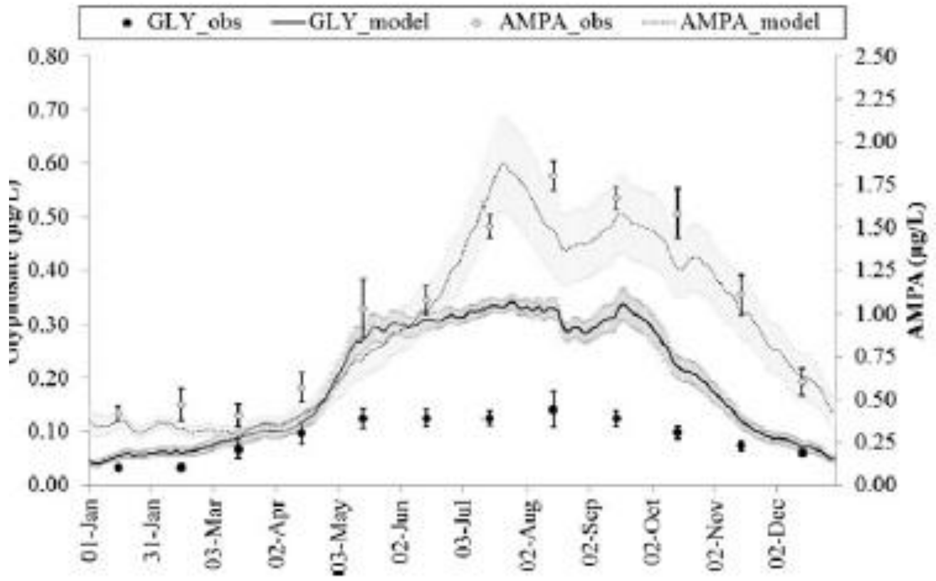


Figure 8.5-117: **Simulated relative contribution of glyphosate degradation to AMPA concentrations in the river at the drinking water intake. AMPA concentrations and river discharges.**

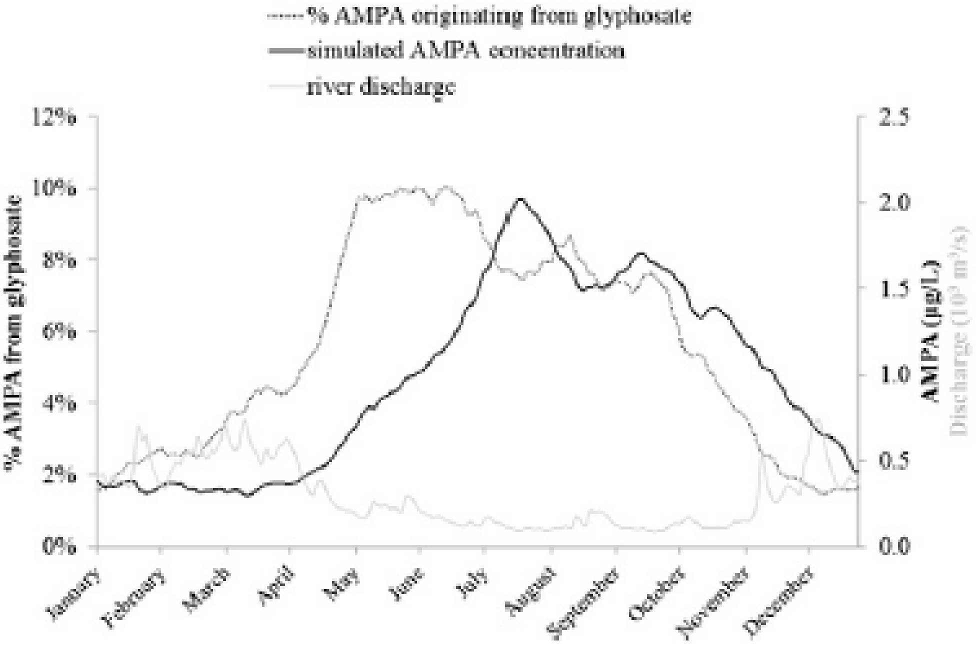


Figure 8.5-118: **Monthly variation in the relative contribution of upstream influx, WWTP effluents, tributary Ur (discharging mainly industrial effluent) and other tributaries to the glyphosate concentrations in the river Meuse at the drinking water intake.**

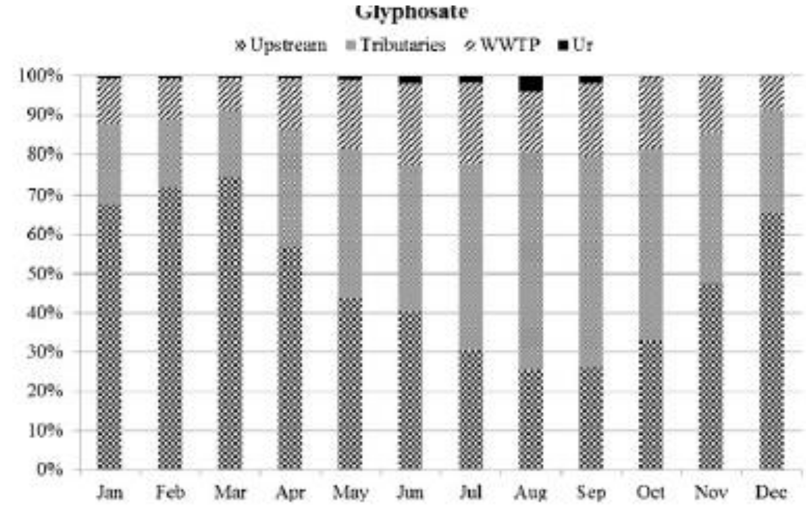


Figure 8.5-119: **Monthly variation in the relative contribution of upstream influx, WWTP effluents, tributary Ur (discharging mainly industrial effluent) and other tributaries to the AMPA concentrations in the river Meuse at the drinking water intake.**

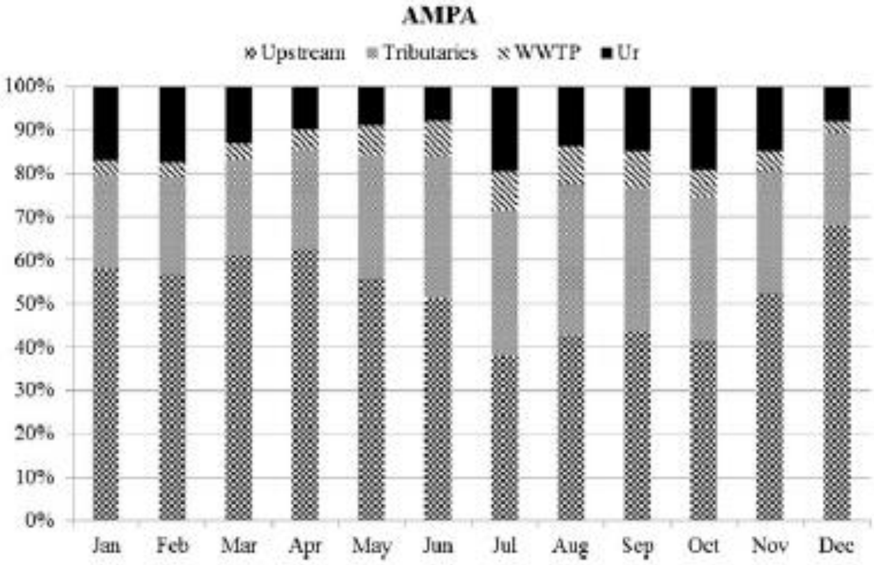
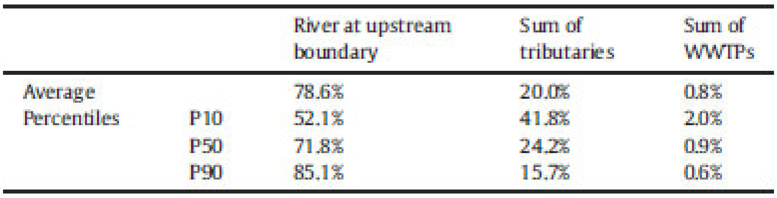
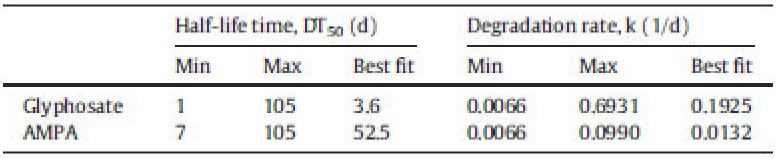


Table 8.5-158: Statistics on the contribution of upstream influx, tributaries and WWTP effluents to the discharge of the river at the drinking water intake



		River at upstream boundary	Sum of tributaries	Sum of WWTPs
Average		78.6%	20.0%	0.8%
Percentiles	P10	52.1%	41.8%	2.0%
	P50	71.8%	24.2%	0.9%
	P90	85.1%	15.7%	0.6%

Table 8.5-159: Range of DT50 values (min-max) used for calibration of the glyphosate and AMPA degradation rate and obtained best fit values



	Half-life time, DT_{50} (d)			Degradation rate, k (1/d)		
	Min	Max	Best fit	Min	Max	Best fit
Glyphosate	1	105	3.6	0.0066	0.6931	0.1925
AMPA	7	105	52.5	0.0066	0.0990	0.0132

Conclusion

Our results show that the application of a river model facilitates the assessment of pesticide loads and source contributions in dynamic downstream areas of a river catchment based on low-frequency (monthly) concentration data and high-frequency (daily) hydraulic data. The variability of pesticide concentrations and discharge in the study area impedes such assessments based on monitoring data soley. Our study illustrates how to overcome the limitations of low-frequency pesticide concentration data by means of modelling. The results further indicate that the effect of local measures to reduce the exposure concentration at the point of drinking water abstraction, is limited by dominant transboundary loads. In order to apply the model for decision making on pesticide use at specified locations, a dynamic coupling to detailed landscape information (urban areas, agriculture, land use, soil type, etc.) is needed. The application of a model- ling approach as proposed in this study in river management and decision making requires modelling expertise and sufficient information of the river system to develop an adequate water quality model. The results obtained for the modelling approach can be used as such in management to target measures sources with the largest load contribution. In the future the modelling approach can be re-used to assess the effect of taken measures on the loads and concentrations based on additional simulations updated with the recent monitoring data.

In large river basins, insight in the spatial distribution of pesticide in- fluxes along the main river course is important for policy makers in prioritizing certain areas for specific management actions. Local reduction programmes clearly affecting local concentrations might fail to show the expected impact on the larger scale due to fluxes coming from other (transnational) sub basins, hydrological variations, limited spatial and temporal resolution of monitoring data, and other larger scale is- sues. Recommendations to improve river basin management are targeted monitoring in sub basins and at the outlets of waste water treatment plants (WWTPs) and modelling the whole catchment to distinguish between sources and to derive cost-effective programme of measures. The model scenario results also indicated that the relative contribution of different sources varies throughout the year. The seasonal variation is larger for glyphosate than for AMPA.

Assessment and conclusion by applicant:

The article reports a hybrid monitoring and modelling approach to evaluate different sources of glyphosate and AMPA in the Meuse River in the Netherlands and their decay in the waterbody. Waste-water treatment plants and tributaries were considered as entry routes of the substances. The experiment does not consider or model explicitly the contribution of agricultural application of the substances. The measured maximum concentrations of glyphosate in the river Meuse was 0.7 µg/L and in its tributaries was 12 µg/L. Also, the measured maximum concentrations of AMPA in the river Meuse was 3 µg/L and in its tributaries was 130 µg/L.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant conclusions. The article is considered reliable with restrictions. The analytical method used for glyphosate and AMPA is not decribed within the study as it relies on monitoring data. Also, no precise relation to glyphosate use amount can be done.

Although not generating monitoring data itself, it relies on measured concentrations for glyphosate and AMPA from monitoring program of RIVA-Maas (Historical international association of drinking water companies that use the river Meuse as a source).

This study aimed at calibrating a river model to evaluate the contribution of different sources of glyphosate and AMPA in the river Meuse taking into account the measured concentrations in the river Meuse, measured concentration in the tributaries and WWTP effluents, the hydraulic (daily discharge). The model takes account of the degradation time for glyphosate and AMPA, but not the dissipation through adsorption.

The investigated area is a 250 km river stretch between the Belgian- Dutch border (at Eijsden) and the point of drinking water intake "Biesbosch" (at Keizersveer).

The land use in the Dutch part of the Meuse catchment is mixed and fragmented with 54–60% agriculture, 11–34% urban and 12–28% nature/forest/water. However the runoff from agricultural area does not seem to be accounted for in the model.

Monitoring data on glyphosate and AMPA concentrations were obtained from RIWA-Maas. Monthly or biweekly monitoring data of glyphosate and AMPA concentrations in the river Meuse were available for the period 1995–2011. This dataset also includes AMPA and glyphosate concentrations in the main tributaries and in the effluent of WWTPs discharging into the river Meuse along the 250 km stretch considered in this case study.

The measured maximum concentrations of glyphosate in the river Meuse was 0.7 µg/L and in its tributaries was 12 µg/L. Also, the measured maximum concentrations of AMPA in the river Meuse was 3 µg/L and in its tributaries was 130 µg/L.

Based on the modelling results, study concluded that the relative contribution of WWTP effluents is above 29% for glyphosate and around 12% for AMPA.

Data point:	CA 7.5/045
Report author	Larsbo, M. *et al.*
Report year	2016
Report title	Surface Runoff of Pesticides from a Clay Loam Field in Sweden
Document No	Journal of Environmental Quality 45:1367-1374
Guidelines followed in study	None

Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable (but concentration in surface runoff from field, and not in surface water)

Pesticides stored at or close to the soil surface after field application can be mobilized and transported off the field when surface runoff occurs. The objective of our study was to quantify the potential pesticide losses in surface runoff from a conventionally managed agricultural field in a Swedish climate. This was achieved by measuring surface runoff volumes and concentrations in runoff of six spring-applied pesticides and autumn-applied glyphosate and its metabolite aminomethylphosphonic acid (AMPA). Measurements were performed for 3 yr both during the growing seasons and during intervening winter snowmelt periods on a clay loam field close to Uppsala. During growing seasons, surface runoff was generated on only five occasions during one 25-d period in 2012 when the infiltration capacity of the soil may have been reduced by structural degradation due to large cumulative rainfall amounts after harrowing. Concentrations in surface runoff exceeded Swedish water quality standards in all samples during this growing season for diflufenican and pirimicarb. Surface runoff was generated during three snowmelt periods during the winter of 2012-2013. All of the applied pesticides were found in snowmelt samples despite incorporation of residues by autumn plowing, degradation, and leaching into the soil profile during the period between spraying and sampling. Concentrations of glyphosate ranged from 0.12 to 7.4 µg/L, and concentrations of AMPA ranged from 0 to 2.7 µg/L. Our results indicate that temporal changes in hydraulic properties during the growing season and when the soil freezes during winter affect pesticide losses through surface runoff.

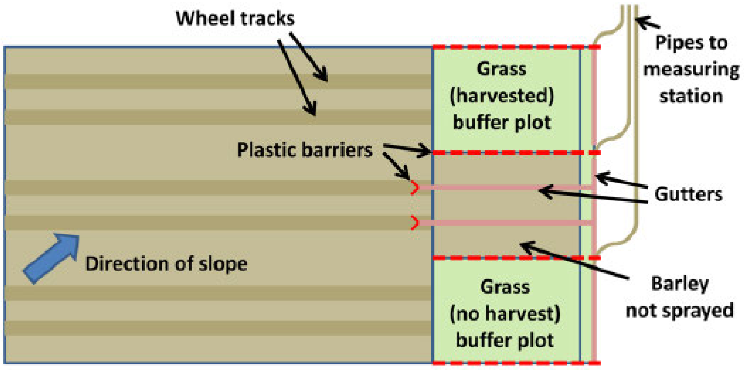
Materials and Methods

Site Description and Experimental Set-up

The field site is located close to Alsike church about 15 km south of Uppsala in eastern Sweden. The experimental field is about 0.42 ha (72 × 50 m), with a slope in the north-south direction of about 1%. The soil is a clay loam (32.3% clay, 33.1% silt, 34. % sand) and has an organic carbon content of 13 g/kg. The field was conventionally managed (i.e., autumn plowed to a depth of about 20 cm, harrowed to a depth of about 6 cm before sowing) and sown with spring barley during the years when measurements were made (2012-2014). Before the start of the project during the years 2007 to 2010, the field was under ley, and no pesticides were applied. In autumn 2010, glyphosate (1440 g/ha) was applied to the field, and the field was plowed. Oat was sown and treated with 2-methyl-4-chloro-phenoxyacetic acid (MCPA) (500 g/ha) and tribenuron methyl (5.6 g/ha) in spring 2011. In 2010, a 6-m-wide grassed buffer strip was established along the south side of the field. The buffer strip was divided into four blocks, each containing three plots (6 by 6 m). The plots within a block were randomly assigned one of three treatments: permanent grass with no harvest, permanent grass harvested once a year, or no buffer zone (i.e., the plot was sown with the same crop as the rest of the field). Each buffer zone plot is drained with a central 6-m long drain pipe at 1 m depth. The rest of the field is not drained.

Surface runoff was collected in an open permanent gutter at the bottom edge of each plot. During the growing season, surface runoff was only monitored from the plots sown with barley (i.e., with no grassed buffer zone) because preliminary experiments with a rainfall simulator showed that the infiltration capacity of the grassed plots was so large that it would be highly unlikely that any surface runoff would pass across the plots without infiltrating. In the plots sown with barley, temporary collection gutters were installed after spraying, which led the water directly from wheel tracks that were created during pesticide spraying to the permanent gutters (Figure 8.5-120). Surface runoff was monitored from all 12 plots during winter and spring snowmelt periods because the infiltration capacity at such times is limited by frozen soil.

Figure 8.5-120: Schematic illustration of one block with gutters collecting water from the wheel tracks during the growing season



Gutters were open and, hence, could collect rain falling directly on them. To calculate surface runoff collected from the wheel tracks in summer, this volume was subtracted from the total collected volume. The volume that fell directly on the gutters was estimated by the average volume collected from plots without temporary collection gutters. We assumed that surface runoff during winter and spring was dominated by snowmelt, so no corrections were made for precipitation falling directly on the gutters.

The surface runoff water was led to an automated measuring station where water volumes were measured using a tipping bucket system. Flow proportional subsamples were taken every 2 L (0.006 mm) of surface runoff. Pesticide concentrations (see below) were measured in bulk samples collected on an ad hoc basis after periods with surface runoff. Relative losses of pesticides from each of the four plots monitored during growing seasons and 12 plots during snowmelt were estimated by dividing the pesticide mass in surface runoff collected from a plot by the mass applied to one twelfth of the field area (0.035 ha). Pesticide losses from the field through surface runoff not captured by the collection gutters may have occurred because the direction of the slope of the field was not perpendicular to the gutters (Figure 8.5-120). During the growing season, wheel tracks directed surface runoff toward the collection gutters.

Precipitation was measured automatically at an hourly resolution at the site using a professional rain gauge (MJK automation AB). The rain gauge was not heated, which means that the amount of precipitation falling as snow was uncertain because it was only registered on melting. Therefore, for winter seasons we used daily precipitation data from Ultuna climate station located about 7 km north of the field site. Measurements of air temperature were also taken from Ultuna. The whole field except the buffer zone was sprayed each year in spring during 2012-2014 with the herbicides MCPA, clopyralid, fluroxypyr, and diflufenican; the fungicide prothioconazole; and the insecticide pirimicarb. In the autumns of 2012 and 2013, the field was sprayed with the herbicide glyphosate. All applications were performed at doses commonly used in Sweden using commercial products. Spring applications of pesticides were done perpendicular to the buffer zone starting outside each plot (Figure 8.5-120), whereas glyphosate applications were done parallel to the buffer zone. The permanent gutters were cleaned after spraying to remove any pesticide contamination caused by spray drift. Because degradation of prothioconazole is very fast (<1 d), the major metabolite formed in soil, prothioconazoledesthio (maximum formation in soil 49.4%) (PPDB, 2016), was analyzed instead of the parent compound. The major metabolite of glyphosate, aminomethylphosphonic acid (AMPA) (maximum formation in soil, 29.0%) (PPDB, 2016), which is more persistent in soil than the parent compound, was also analyzed. In addition to the applied pesticides and two metabolites, the fungicide carbendazim, which was not applied at the site during the experiment, was also detected in most surface runoff samples.

Analytical Methods

Spring-applied pesticides were analyzed using an automated on-line, solid-phase, extraction-liquid chromatography- tandem mass spectrometry procedure as described by Jansson and Kreuger (2010). About 95 pesticides are simultaneously measured with this method, which is why pesticides that were not applied during the course of the experiment, such as carbendazim, could be detected. Before analysis the samples were spiked with internal standard followed by filtration through a 0.2-µm regenerated cellulose filter. Limits of detection were in the 0.001 to 0.010 µg/L range, and limits of quantification were in the 0.002 to 0.050 µg/L range. Glyphosate and AMPA were analyzed in aqueous phase and bound to particles because both forms are known to contribute to leaching. The method used to separate the two phases is described in detail in Ulén *et al*. (2012). Limits of detection and limits of quantification for the aqueous phase were 0.010 and 0.025 µg/L, respectively, for glyphosate and 0.020 and 0.050 µg/L, respectively, for AMPA. Limits of detection and limits of quantification for the particle-bound fraction were and 0.035 and 0.050 µg/L, respectively, for glyphosate and 0.050 and 0.10 µg/L, respectively, for AMPA.

Infiltrometer Measurements

Four to five replicate tension infiltrometer measurements were performed on one, four, and three occasions during the growing seasons of 2012, 2013, and 2014, respectively. Measurements were done on uncompacted soil and, when present, in wheel tracks. We used two identical tension infiltrometers with 20-cm-diameter infiltration discs. A layer of fine sand was first placed on the soil surface to ensure good contact between the soil and the porous disc. Measurements were performed in a sequence from low to high pressure potentials at -6, -4.5, -2, and -1 cm in 2012 and at -6, -3, and -1 cm in 2013 and 2014. Near-saturated hydraulic conductivities were calculated from steady-state infiltration rates using the approach outlined in Ankeny *et al*. (1991). The hydraulic conductivities at -1 cm pressure potential give a good estimate of the saturated hydraulic conductivity providing there are no vertically oriented continuous pores with a diameter larger than 3 mm.

Statistics

Effects of the different buffer zone treatments on surface runoff volumes, pesticide concentrations, and losses during spring snowmelt periods when all 12 plots were used were analyzed accounting for the randomized block structure of the experimental field with the ANOVA tool implemented in CoStat. Differences between mean pesticide concentrations and losses between sampling events and between substances as well as differences in near-saturated hydraulic conductivities between measurement dates and between uncompacted areas and wheel tracks were analyzed using *t* tests assuming equal variances. Differences were considered significant for *p* values <0.05. Statistical significance should be interpreted with caution because the limited number of replicate samples did not allow us to test the underlying assumptions of normality and equal variances. Hydraulic conductivities were log-transformed before statistical analysis.

Results and Discussion

Tension Infiltrometer Measurements

The results from the tension infiltrometer measurements are presented in Figure 8.5-121 and Supplemental Figure 8.5-122. Generally, the variation in hydraulic conductivities between replicate measurements was large both for undisturbed soil and wheel tracks at all supply pressure potentials (average coefficient of variation was 62%). The hydraulic conductivities in August 2012 were significantly higher in the uncompacted soil than in the wheel tracks at supply pressure potentials of -1 and -2 cm, which is in line with the results presented by Ankeny *et al*. (1995). In the growing season of 2013, the hydraulic conductivity for the uncompacted soil was significantly higher in May than in the subsequent measurements at the -1 and -6 cm supply pressure potentials (Figure 8.5-121).

Figure 8.5-121: Temporal development in hydraulic conductivity rates at the supply pressure potentials of -1 cm (left) and -6 cm (right) during the growing seasons 2013 (top) and 2014 (bottom)

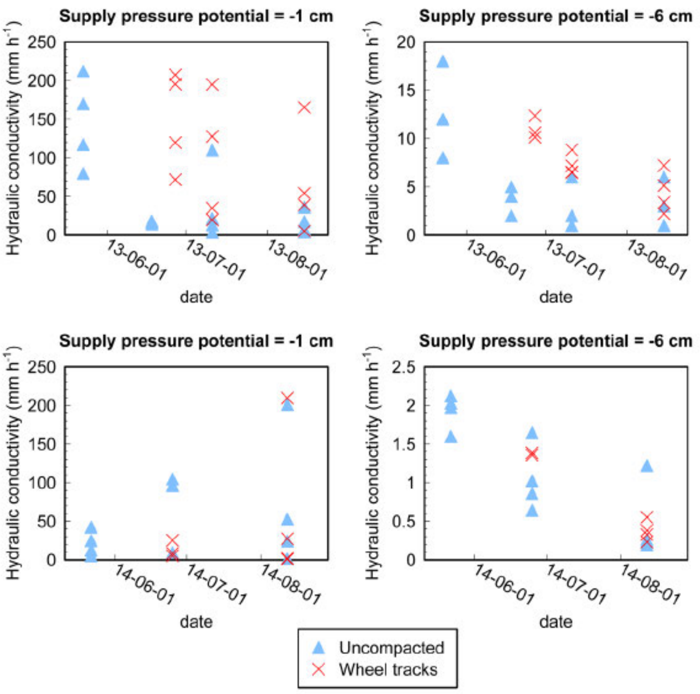
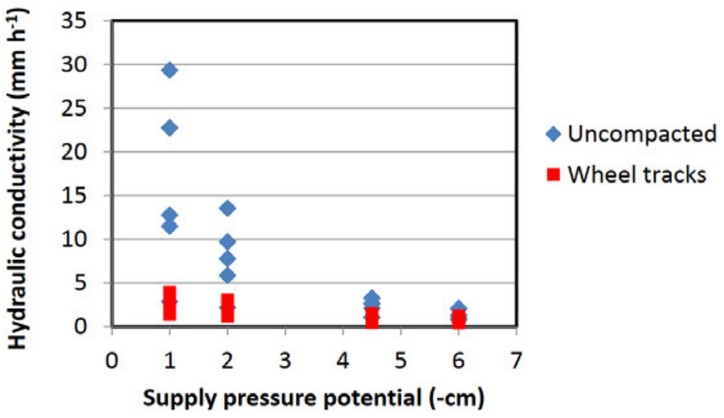


Figure 8.5-122: **Hydraulic conductivities measured in August 2012 at supply pressure potentials between -1 cm and -6 cm**



A significant decrease in the hydraulic conductivity was also apparent in the wheel tracks at -6 cm supply pressure potential. Hydraulic conductivities were significantly higher in the wheel tracks than in the uncompacted soil at -6 cm supply pressure potential in June and July 2013 and at -1 cm supply pressure potential in June 2013. These unexpected results can be explained by the formation of a surface crust before the pesticide application in 2013. This crust was destroyed at pesticide application in the tracked areas by the pressure exerted by the tractor tires, which recreated a fine aggregated structure at the soil surface. These results show that under certain conditions a surface crust may have a stronger influence on near-saturated hydraulic conductivity than traffic-induced compaction. In 2014 the hydraulic conductivities at a supply pressure potential of -6 cm were significantly lower in August than in the preceding measurements for the uncompacted soil and significantly lower in August than in June for the wheel tracks. There were no significant changes with time at -1 cm supply pressure potential. There were no significant differences in hydraulic conductivity between uncompacted soil and wheel tracks in 2014.

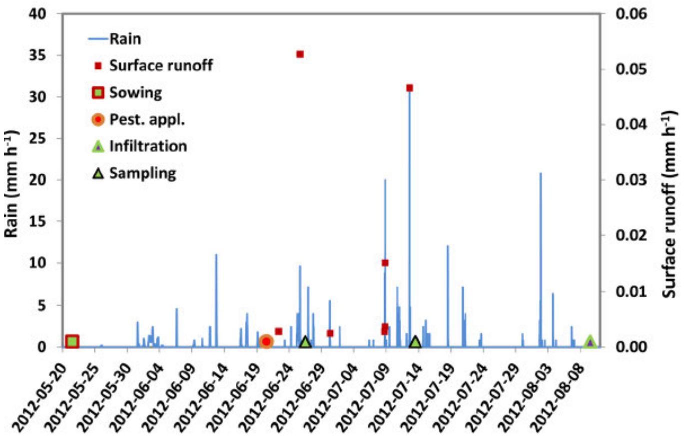
Our results show a complex behavior, but some general trends are apparent. The hydraulic conductivity during the growing season decreases with time from harrowing. The decrease in hydraulic conductivity is most apparent at the -6-cm supply pressure potential. A possible explanation is that the natural processes acting to regenerate structure during the growing season (e.g., shrinkage crack formation and burrowing animals) create pores that are too large to conduct water at -6 cm pressure potential. There were large differences in the measured hydraulic conductivities at -6 cm pressure potential between the years 2013 and 2014 (note the different scales in Figure 8.5-121 [top right vs. bottom right panels]). The first measurements in 2013 were made directly after sowing before any rain had affected the structure in the harrowed layer. The hydraulic conductivity on this occasion (average, 14 mm/h) was more than 7-fold higher than on the first measurement occasion in 2014 (average, 1.9 mm/h), which was made almost a month after sowing, by which time 50.2 mm rain had fallen on the soil. The hydraulic conductivity at -6 cm supply pressure potential in 2013 remained significantly higher than in 2014 throughout the growing season. These results indicate that the amount of rain that falls early in the growing season when the soil surface is unprotected by crops has a strong effect on hydraulic conductivities.

Runoff Events during the Growing Season

During the three monitored growing seasons, surface runoff was only generated on five occasions during a 25-d period in 2012. On these occasions cumulative runoff volumes from the plots were between 23 and 64 L (0.065-0.18 mm). This corresponds to an average runoff coefficient for the five events of 0.17%, which is small compared with those measured in comparable studies (Riise *et al*., 2004; Siimes *et al*., 2006). The limited number of times when runoff was generated during these three growing seasons suggests that this soil has a small potential for surface runoff under conventional management in this climate. The near-saturated hydraulic conductivity in wheel tracks was smallest (between 1.4 and 4.0 mm/h) in August 2012 (significantly smaller than all other occasions except August 2013 and August 2014). Unfortunately, we did not measure near-saturated hydraulic conductivity at the time when surface runoff was generated. However, rainfall intensities were much larger than the hydraulic conductivity at -1 cm pressure potential measured in August 2012 on a number of occasions during the growing season (Figure 8.5-123). Near-saturated hydraulic conductivities were generally larger than rainfall intensities during the growing seasons of 2013 and 2014 when no surface runoff was generated. A likely explanation for the smaller near-saturated hydraulic conductivity and the generation of surface runoff during the growing season of 2012 is the formation of a well-developed surface seal due to the larger cumulative rainfall amounts in the period after soil tillage when the soil was unprotected by crops (Fiener *et al*., 2011; Le Bissonnais *et al*., 2005). The cumulative rainfall amounts during the 30-d period after sowing were 85.6, 35.2, and 50.2 mm for the years 2012, 2013, and 2014, respectively. The differences in near-saturated hydraulic conductivities may also have been influenced by differences in soil water contents at pesticide spraying when the wheel tracks were created, which affects susceptibility to compaction (Batey, 2009; Strudley *et al*., 2008). The cumulative rainfall amounts during the week preceding pesticide application were 26.8, 14.2, and 6 mm for 2012, 2013, and 2014, respectively, which suggest wetter soil conditions during 2012. The infiltration capacity of the soil is not only dependent on the saturated hydraulic conductivity but also, among other things, on the antecedent soil water content, which determines the hydraulic gradient driving infiltration. Because both properties vary with time and space, it is difficult to relate runoff events to specific measurements of the near-saturated hydraulic conductivity only. Physically based models that account for the complex interactions between rainfall, infiltration, and the near-surface hydraulic properties are powerful tools for increasing process understanding (Assouline, 2004). Models of surface seal development and water flow through sealed soils have been shown to reproduce measured data on an event basis, but their implementation has been hampered by a lack of data for long-term model evaluations under field conditions (Assouline, 2004).

Figure 8.5-123: Hourly rainfall measured at the field site and average surface runoff during the growing season of 2012. Field operations and dates when bulk samples for

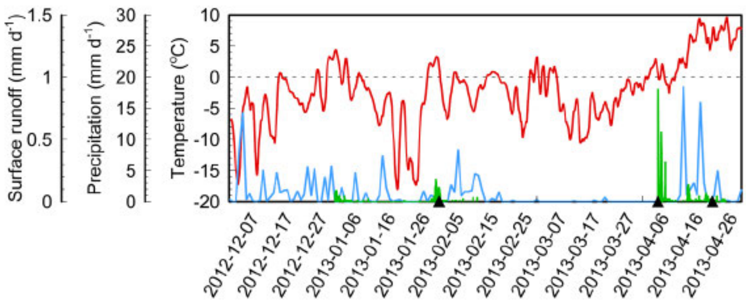
pesticide analysis were taken and tension infiltrometer measurements were performed are indicated



Runoff Events during the Winter Seasons

Surface runoff was generated during three snowmelt periods in 2013, once in January and twice in April. Data on runoff volumes were unfortunately lost for one of these periods. The total runoff volumes for the remaining two periods were between 130 and 2100 L (0.38-6.0 mm). The runoff coefficient for the period December 2012 to March 2013 was 2.6%. Daily air temperatures and precipitation during the periods December 2012 to March 2013 and December 2013 to March 2014 are presented in Figure 8.5-124. The total precipitation in these two periods was 124 and 185 mm, respectively. Corresponding average temperatures were -3.9 and 1.4°C. The long periods with temperatures below 0°C during the winter of 2012-2013 resulted in snow accumulation on the field and soil freezing. These conditions produced surface runoff during three snowmelt periods. This indicates that the soil remained frozen, which reduced the infiltration capacity. In contrast, the limited amount of precipitation during cold periods in the winter of 2013-2014 did not result in significant snow accumulation on the field. It also seems likely that the infiltration capacity was less affected by freezing due to the higher temperatures during the winter of 2013-2014. There were no significant effects of buffer zone treatment or block on runoff volumes.

Figure 8.5-124: **Daily precipitation (blue line) and air temperature (red line) data from Ultuna climate station and average surface runoff (green line) measured at the field site during winter 2012-2013. Surface runoff sampling times are indicated by triangles.**



Pesticide Concentrations

Spring-Applied Pesticides

All applied compounds were detected in all samples. Average concentrations were higher (0.83-7.3 µg/L) during the first runoff event compared with the second event (0.55-4.1 µg/L) for all compounds, although differences were significant only for MCPA. Riise *et al*. (2004) and Siimes *et al*. (2006) also reported the highest concentrations in surface runoff in the first events after pesticide application. Swedish water quality standards below which no effects on surface water ecosystems are assumed have been estimated by the Swedish Chemicals Agency for about 100 pesticides and degradation products (Swedish Chemicals Agency, 2016). Concentrations in surface runoff exceeded water quality standards in all samples during the growing season for diflufenican and pirimicarb. Concentrations of MCPA exceeded water quality standards in all samples taken on 26 June. However, these are in-field concentrations, and whether pesticides in runoff reach surface waters depends on the connectivity to the stream. In addition, dilution would significantly reduce concentrations in receiving surface waters, considering the small surface runoff volumes. All of the applied pesticides were also found in surface runoff collected during snowmelt in the winter of 2012-2013. There were no significant effects of buffer zone treatment or block on pesticide concentrations. Concentrations were about two orders of magnitude lower than in the preceding summer. During the intervening period, residues of the spring-applied pesticides were incorporated by autumn plowing and also degraded and leached into the soil profile. All these processes acted to reduce concentrations in surface runoff. Average concentrations of diflufenican exceeded Swedish water quality standards values for all three sampling occasions during snowmelt.

The fungicide carbendazim, which was not applied to the field, was detected in all samples at concentrations in the same range as some of the recently applied pesticides. Carbendazim has not been included in any products approved for use in Sweden since 1999. This result suggests that degradation of carbendazim is either much slower under Nordic conditions than would be indicated or that there was another source of this compound. Carbendazim is a metabolite of the fungicide thiophanate-methyl, which has been registered for use in Sweden since the mid-1970s, with one product currently approved. However, the degradation in soil of thiophanate-methyl to carbendazim is very fast (PPDB, 2016), and we have no record of any recent use of thiophanate-methyl at the site.

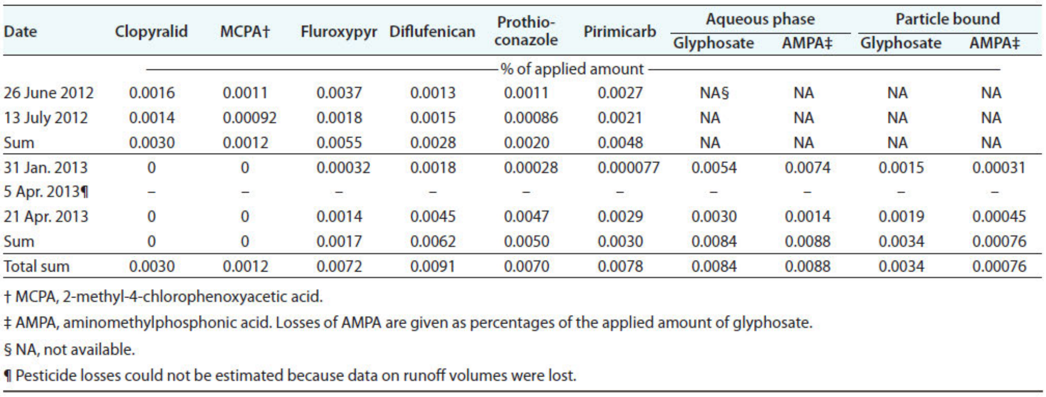
Glyphosate and Aminomethylphosphonic Acid

Concentrations of glyphosate in aqueous phase and bound to particles ranged from 0.12 to 7.4 µg/L and from 0.12 to 2.7 µg/L, respectively; the corresponding AMPA concentrations ranged from 0 to 2.7 µg/L and from 0 to 0.85 µg/L. It is possible that some of the glyphosate and AMPA found in surface runoff originated from the glyphosate application in 2010. There were no significant effects of buffer zone treatment or block on glyphosate or AMPA concentrations. Average concentrations of both substances in the aqueous phase decreased (although not significantly) from the first sampling occasion to the last. Concentrations of glyphosate and AMPA in the aqueous phase were on average 2.2- and 5.1-fold higher, respectively, than in the particle-bound fraction. However, the only statistically significant differences were found between concentrations of AMPA in solution and bound to particles for the sampling on 4 and 21 April. There were no significant correlations between runoff volumes and concentrations for glyphosate and AMPA. The only comparable study that we are aware of (Siimes *et al.*, 2006) reported glyphosate concentrations in the aqueous phase in runoff during snowmelt of between 0.08 and 0.94 µg/L. However, in their study glyphosate was sprayed on bare soil (silt loam) in July at half the dose used in our study.

Pesticide Losses

It was not possible to calculate pesticide losses from the samples taken on 5 Apr. 2013 because data on runoff volumes were not available. The number of plots that generated surface runoff was 10 (31 January), 7 (5 April), and 4 (21 April) for the three events during snowmelt in 2013. This suggests that the losses on 5 April were of the same order of magnitude as the losses during the other two runoff events. Tile drainage has been shown to reduce pesticide losses through surface runoff (Burgoa and Wauchope, 1995; Kladivko *et al*., 2001). It is therefore likely that pesticide losses during snowmelt would have been larger if the buffer zones had not been drained. Quantification of the effects of the tile drainage on the losses through surface runoff was beyond the scope of this study. The total relative losses of the spring-applied pesticides varied between 0.0012% for MCPA and 0.0091% for diflufenican (Table 8.5-160). These losses in surface runoff were small compared with those reported by Riise *et al.* (2004) and Siimes *et a*l. (2006) because the fraction of rainfall routed to surface runoff was smaller. Although runoff concentrations were much higher during the growing season than in snowmelt, winter losses of the spring-applied pesticides were of the same order of magnitude due to the much larger runoff volumes. The coefficients of variation in total losses for the spring-applied pesticides were between 70 and 100% and between 220 and 350% for the growing season and snowmelt periods, respectively. One of the plots dominated (66-100 %) the losses of most of the spring-applied compounds during snowmelt. There were no significant effects of buffer zone treatment or block on pesticide losses. The total losses of glyphosate and AMPA in both phases were 0.021% of the applied amount of glyphosate. Due to the small runoff volumes, losses were small compared with the 0.13% losses reported by Siimes *et al*. (2006). We did not find any clear relationships between compound properties and the relative losses in surface runoff (Table 8.5-160), but the timing of runoff losses was significantly affected.

Table 8.5-160: Losses of pesticides in surface runoff



Date	Clopyralid	MCPA†	Fluroxypyr	Diflufenican	Prothio-conazole	Pirimicarb	Aqueous phase		Particle bound	
							Glyphosate	AMPA‡	Glyphosate	AMPA‡
	% of applied amount									
26 June 2012	0.0016	0.0011	0.0037	0.0013	0.0011	0.0027	NA§	NA	NA	NA
13 July 2012	0.0014	0.00092	0.0018	0.0015	0.00086	0.0021	NA	NA	NA	NA
Sum	0.0030	0.0012	0.0055	0.0028	0.0020	0.0048	NA	NA	NA	NA
31 Jan. 2013	0	0	0.00032	0.0018	0.00028	0.000077	0.0054	0.0074	0.0015	0.00031
5 Apr. 2013¶	–	–	–	–	–	–	–	–	–	–
21 Apr. 2013	0	0	0.0014	0.0045	0.0047	0.0029	0.0030	0.0014	0.0019	0.00045
Sum	0	0	0.0017	0.0062	0.0050	0.0030	0.0084	0.0088	0.0034	0.00076
Total sum	0.0030	0.0012	0.0072	0.0091	0.0070	0.0078	0.0084	0.0088	0.0034	0.00076

† MCPA, 2-methyl-4-chlorophenoxyacetic acid.

‡ AMPA, aminomethylphosphonic acid. Losses of AMPA are given as percentages of the applied amount of glyphosate.

§ NA, not available.

¶ Pesticide losses could not be estimated because data on runoff volumes were lost.

Conclusions

Our results show that the temporal variation in near-saturated hydraulic conductivity during the growing season may be large and that this variation influences the potential risk for pesticide losses in surface runoff. This study also shows that the weather conditions during winter that determine snow accumulation and soil freezing affect pesticide losses in runoff during snowmelt periods. Both spring-applied pesticides and glyphosate, which was applied in the autumn, were found in snowmelt surface runoff samples when runoff occurred. Modeling approaches for pesticide losses through surface runoff should account for the temporal variability in soil hydraulic properties due to seedbed consolidation and surface sealing and, for cold climate, should include the effects of freezing and thawing on the infiltration capacity of the soil. The modeling approaches currently used in risk assessment for pesticides in the European Union do not explicitly account for these processes (FOCUS, 2001, 2014).

<u>Assessment and conclusion by applicant</u>:

The article describes a runoff experiment on a field site in Sweden with realistic cultivation conditions.
The runoff of glyphosate and AMPA was measured over a period of 3 years.
The article is considered reliable

Assessment and conclusion by RMS:

The article is considered reliable but the results are linked with particular snowmelt surface runoff conditions.
Also it provides information on the concentrations of glyphosate and AMPA in surface runoff samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

Glyphosate was applied at 1440 g/ha in autumn (October) of 2012 and 2013 during experiment.

Article reports concentrations of glyphosate in aqueous phase and bound to particles ranging from 0.12 to 7.4 µg L^{-1} and from 0.12 to 2.7 µg L^{-1}, respectively; AMPA concentrations ranging from 0 to 2.7 µg L^{-1} and from 0 to 0.85 µg L^{-1}

Data point:	CA 7.5/005
Report author	Napoli, M. *et al*.
Report year	2016
Report title	Transport of Glyphosate and Aminomethylphosphonic Acid under Two Soil Management Practices in an Italian Vineyard
Document No	Journal of Environmental Quality 45:1713-1721 (2016)
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable (but concentration in surface runoff from field, and not surface water)

The article was found relevant for multiple subchapters. The summary is provided in the soil monitoring subchapter of this document.

Assessment and conclusion by RMS:
This study is considered reliable
It reports a runoff experiment in a vineyard in Italy. The runoff was measured for glyphosate and AMPA residues. This is however in the context of the vineyard with great slope (16%), indicating important losses through run-off, while the results also indicate that transport of glyphosate and AMPA on a hillslope varies over time and according to the soil management practices (harrowed plot *vs* grass covered plot).

The following glyphosate uses on the plots are reported: Application of glyphosate every year in March. Equivalent dose of 34.8 g per plot of 283 m^2 (equivalent to 1225 g/ha)

It provides information on the concentrations of glyphosate and AMPA in surface runoff samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

Concentration in runoff water were monitored for 4 years from March 2007 to February 2011. Runoff and associated sediment from each plot were intercepted by a Gerlach trough placed along the lower side of the plot. A downstream automated runoff gauge was used for measuring the runoff volume (RV) for separate rainfall events. The runoff gauges collected runoff aliquots of about 0.2 L every 300 L of RV.

Maximum concentrations of glyphosate and AMPA dissolved in runoff were respectively 128.9 µg/L and 151.9 µg/L for harrowed plots while the maximum concentration glyphosate and AMPA were 78.4 µg/L and 144.8 µg/L for grass covered plot.

Data point:	CA 7.5/046
Report author	Schreiner, V. *et al.*
Report year	2016
Report title	Pesticide mixtures in streams of several European countries and the USA
Document No	Science of the Total Environment 573 (2016) 680-689
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Given the multitude of pesticides used in agriculture, adjacent streams are typically exposed to pesticide mixtures. Previous studies analysed the ecological risks of a few pesticide mixtures or were limited to an individual region or crop, whereas a large scale analysis of pesticide mixtures is missing. Routine monitoring data from Germany, France, the Netherlands and the USA comprising a total of 4532 sites and 56,084 sampling occasions was analysed with the aim of identify the most frequently detected pesticides, their metabolites and mixtures. The most frequently detected compounds were dominated by herbicides and their metabolites. Mixtures mostly comprised of two up to five compounds, whereas mixtures in the USA and France had clearly less compounds than those of Germany and the Netherlands. The number of detected pesticides and thereby the size of mixtures is positively correlated to the number of measured pesticides (r = 0.57). In contrast, a low relationship was found to the ratio of agricultural areas within the catchment (r = 0.17), and no relationship was found to the size of the catchment (r = 0.06). Overall, our study provides priority mixtures for different countries that may be used for future ecotoxicological studies to improve risk assessment for stream ecosystems.

Materials and Methods

We compiled pesticide monitoring data of lotic surface waters from databases from Germany, France, the Netherlands, and the USA (Table 8.5-161). We retrieved the data from France from EIONET (Reporting Obligations Database (ROD); River quality (EWN-1) - Eionet, 2014), the data from the Netherlands from www.bestrijdingsmiddelenatlas.nl and the data from Germany were provided by the regional water quality authorities. The US dataset was generated by harmonizing and combining datasets from the National Water-Quality Assessment Program (NAWQA Data Export, 2014) and the Water Quality Data Portal (WQP, 2014). Sites within a 10 m distance from both datasets were considered as identical and entries from them were merged. The data from France, the Netherlands and the USA covered the country-level, whereas the German data were restricted to four German states (Rhineland-Palatinate, North Rhine-Westphalia, Saxony and Baden-Württemberg). Nevertheless, we refer to this data as Germany to enhance readability. The used chemical concentrations originated exclusively from grab water samples. Data pre-processing consisted of the following steps: (I) To obtain a spatially-balanced monitoring data set for each region and country, and thus to enhance comparability, we used the Generalized Random Tessellation Stratified method (GRTS; R package: spsurvey) and randomly sampled subsets with maximised spatial balance. The subset size was chosen as the maximum number of sites that showed no spatial clustering (as measured by the $\chi 2$ statistic). This method reduced the used number of sites per country (Table 8.5-161). (II) Non-detects and duplicate entries were removed after assigning a Chemical Abstract Service (CAS) registry number to each chemical. (III) We limited the data to the years of 2008-2012 (only for the German states of Baden-Württemberg and Rhineland-Palatinate the years of 2006-2010 and for North Rhine-Westphalia the years of 2005-2009 were used), because these data had an increased number of sampling occasions compared to preceding years.

These steps resulted in a total of 4532 sites with 56,084 sampling occasions. On average, 12 sampling occasions were performed per site, ranging from 6 in the USA to 27 in France. Up to 779 different pesticides and their metabolites were included in the analysis, with the data set from Netherlands contributing most with 637 different pesticides and their metabolites (Table 8.5-161; Figure 8.5-125). Differences in the analysed pesticides and their metabolites between the different countries were illustrated using multidimensional scaling based on the binary Jaccard distance.

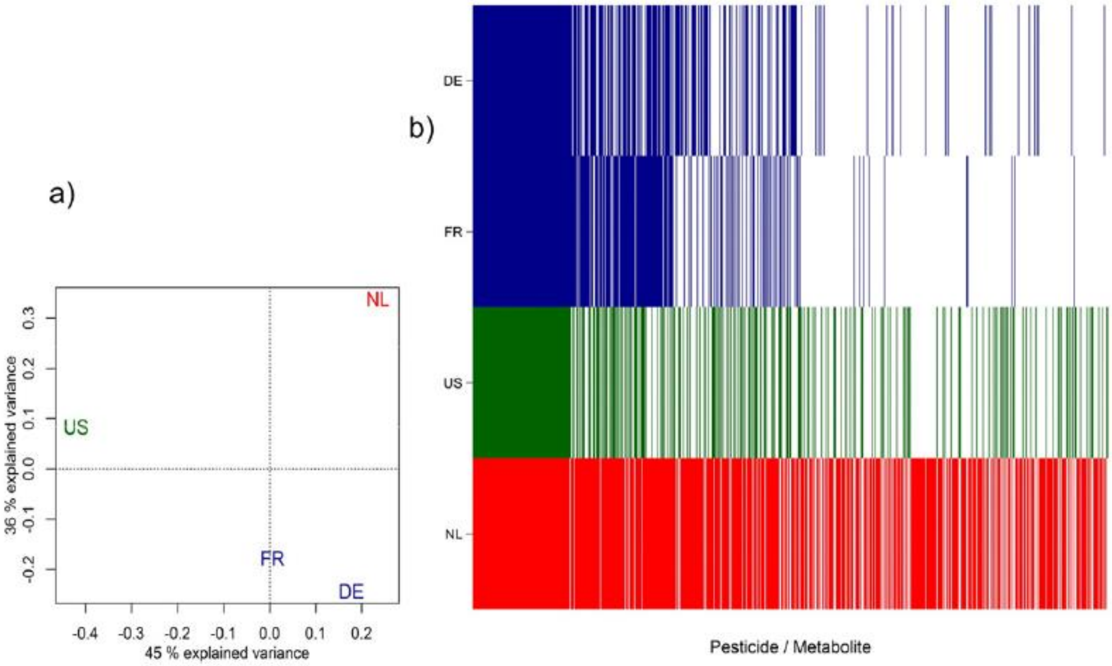
Table 8.5-161: **Overview of data sets analysed with information of detection rates and numbers of compounds and mixtures within the different countries**

	DE	FR	NL	US
Sites remaining after GRTS [%]	72	63	70	62
Sites after GRTS	1037	950	320	2225
Sampling occasions after GRTS	12,177	25,586	5112	13,209
Median sampling occasions per site	8	26	8.5	3
Analysed compounds	297	292	637	324
Mean No. compounds analysed per sampling occasion	85.1	27.6	83.4	36.2
Detected compounds	205	115	267	127
No. most frequent compounds	132	25	69	14
Mean size mixtures all compounds, ±SD	7.0 ± 4.8	3.0 ± 1.6	4.8 ± 3.0	3.2 ± 1.2
Sites with compounds, all compounds [%]	85.1	78.1	90.3	23.5
Sites with mixtures, all compounds [%]	49.4	12.7	65.3	16.2
Sampling occasion with pesticide exposure, all compounds [%]	69.3	32.7	82.1	26.1
Detected core compounds	40	40	38	29
No. most frequent core compounds	33	14	19	9
Mean size mixtures core compounds, ±SD	4.7 ± 2.5	2.5 ± 1.0	3.6 ± 1.8	2.5 ± 0 7
Max size mixture, core compounds	20	9	14	6
Sites with compounds, core compounds [%]	80.3	73.1	85.3	21.4
Sites with mixtures, core compounds [%]	36.2	7.6	36.1	15.0
Sampling occasion with pesticide exposure, core compounds [%]	59.9	24.8	60.2	24.6

DE: Germany; FR: France, NL: Netherlands, US: United States of America. "No. most frequent (core) compounds": number of compounds after establishing level of most frequent compounds (c.f. Fig. S2). Compounds = pesticides + metabolites, GRTS = Generalized Random Tessellation Stratified, SD = standard deviation. For the same table with differentiation between the German states see Table S2.

Figure 8.5-125: a) Multidimensional scaling of the analysed pesticides and their metabolites in the different countries. b) Comparison of the analysed pesticides and metabolites from the different countries.

Each line represents one compound. France and Germany were coded with the same colours in both graphs to highlight concordance of the analysed compounds (see a). For number of analysed pesticides andmetabolites in each country, see Table 8.5-161. DE: Germany; FR: France, NL: Netherlands, US: United States of America.



Identifying most frequently detected pesticides and mixtures

We calculated the relative occurrence (p) of each pesticide and metabolite (compound) (i) for sampling occasions as well as at sites as: $pi = \Sigma y_i/n$ where n is the number of sampling occasions or sites and y is 1 if compound was found in a site or on a sampling occasion, otherwise 0. Additionally, we calculated the percentage of sites and sampling occasions were at least one compound was detected (percentage of sites and sampling occasions where $\Sigma pi > 0$). We identified most frequent mixtures composed of different types of pesticides (herbicides, insecticides and fungicides). Compounds that occurred at <5% of sites were omitted from further analysis as they lead to an inflation of the number and occurrence frequency of mixtures. For example, consider the case of two compounds A and B occurring on 100 sampling occasions and the compounds X, Y, and Z each occurring on 4 sampling occasions. This could result in multiple ternary (ABX, ABY, ABZ) or quaternary (ABXY, ABXZ, ABYZ) mixtures with low relative occurrence frequency. Subsequently, for each mixture the absolute number of compounds (size), the number of the different pesticide types and the occurrence frequency at sites as well as sampling occasions was calculated. For the German data set, the analysis was firstly conducted separately for the four German states and subsequently the results were aggregated weighted by the number of analysed sites or sampling occasions.

Calculation of size and relative land cover of catchment areas in Germany

For each site analysed in Germany, we quantified land cover types in its catchment by following a four step procedure: (i) Extraction of the stream network from a digital elevation model that shows the highest concordance with a mapped stream network of the German state, using the open-source software algorithm ATRIC, (ii) snapping the sites to the nearest segment of the extracted stream network, (iii) automatically delineating the upstream catchment polygon for each fitted site from the DEM using ATRIC and (iv) overlaying the catchment polygons with the CORINE land cover datasets and subsequently calculating the percentage of six land cover types (arable land, permanent crop, forest, meadows, water bodies and other). The analysis was limited to Germany because only for Germany mapped stream networks were readily available. Besides, in the case of the Netherlands, geomorphology does not allow for derivation of stream networks from a DEM.

Associations with monitoring characteristics

We scrutinised whether characteristics of the monitoring programs influence the detection of pesticides and its mixtures using the following response variables: size of mixtures and number of detected compounds. We correlated (Pearson's correlation) these response variables with the number of analysed pesticides and metabolites per sampling occasion and the size of catchment areas of sampling sites. For Germany, we also correlated the response variables with the areal proportion of agriculture, of arable land and of permanent crop land within the upstream catchment. This was done using a cubic regression spline with a Poisson distribution.

Direct comparison of mixtures from different countries - core compounds

Given that the compound spectrum varied between countries (Figure 8.5-125), we analysed the data for 44 core compounds that were measured in all countries and German states. Most of these (29) were herbicides and metabolites with a herbicide as parent compound. Additionally eleven insecticides and four fungicides were part of the core compounds. These core compounds enabled a direct comparison of mixtures from different countries. We tested for differences in the size of mixtures between the countries as well as for differences in mixtures composition using analysis of variance (ANOVA) followed by a Tukey-HSD (Honestly Significant Difference) test for pairwise comparison. Pre-processing of data, statistical analysis and visualisations were performed using R, version 3.1.1.

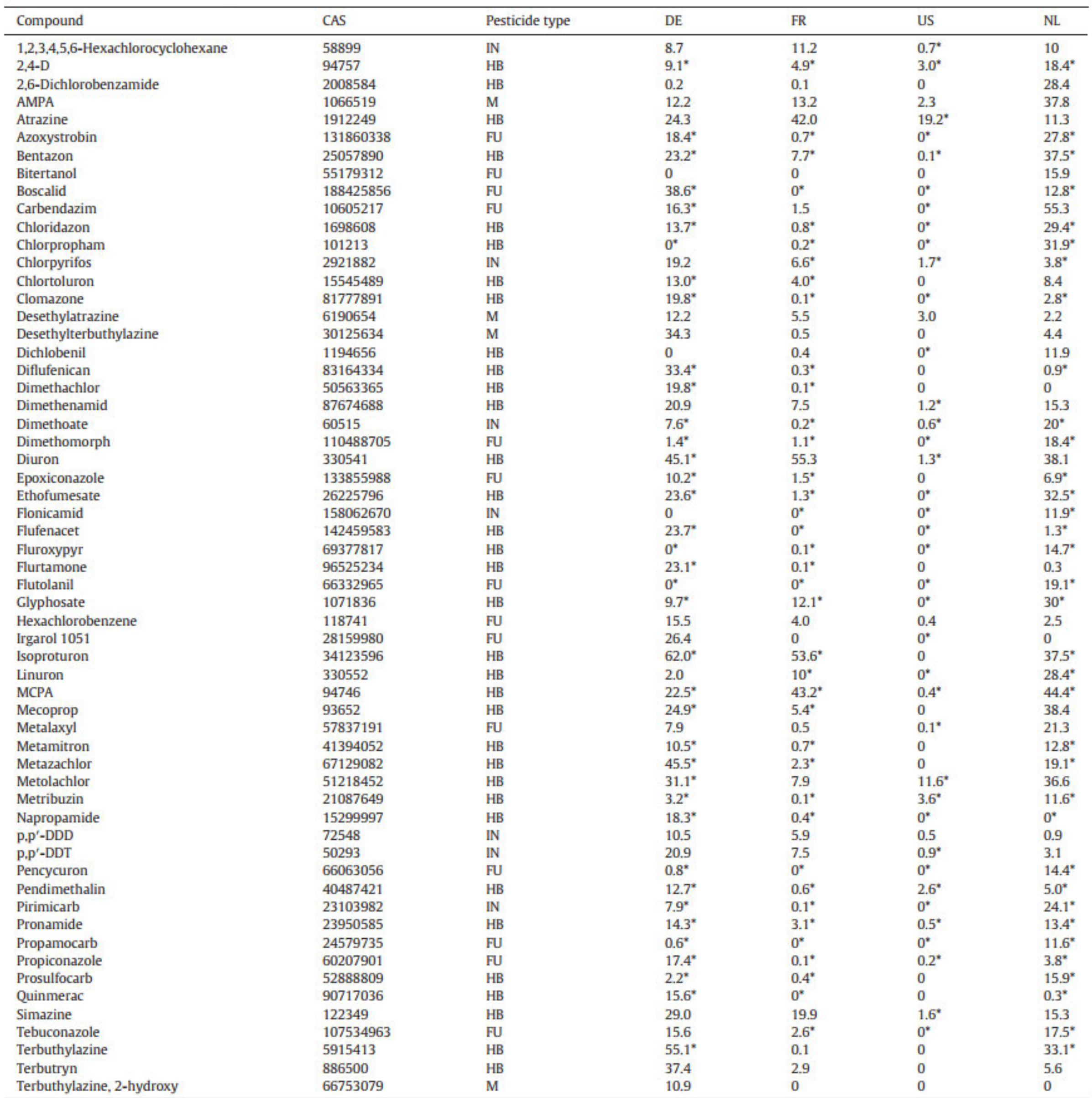
Results

Most frequently detected pesticides and metabolites

The spectrum of analysed pesticides and metabolites varied strongly between countries (Figure 8.5-125a and b). The monitoring data of France and Germany showed a high concordance in the total number of analysed compounds (Germany: 297, France: 292, Table 8.5-161) and identity of analysed compounds in comparison to the Netherlands and the USA (shown with different colours in Figure 8.5-125). The different spectrum of analysed pesticides and metabolites resulted, in several compounds among the most frequent pesticides and metabolites that were country-specific, particularly for the Netherlands, such as Bitertanol, Flonicamid and Flutolanil (Table 8.5-162).

Table 8.5-162: List of the most frequently detected pesticides and metabolites with their relative occurrence at sites of the different countries

The compounds are ordered alphabetically. Each listed compound occurred in at least one country at a minimum of 10 % of the sites

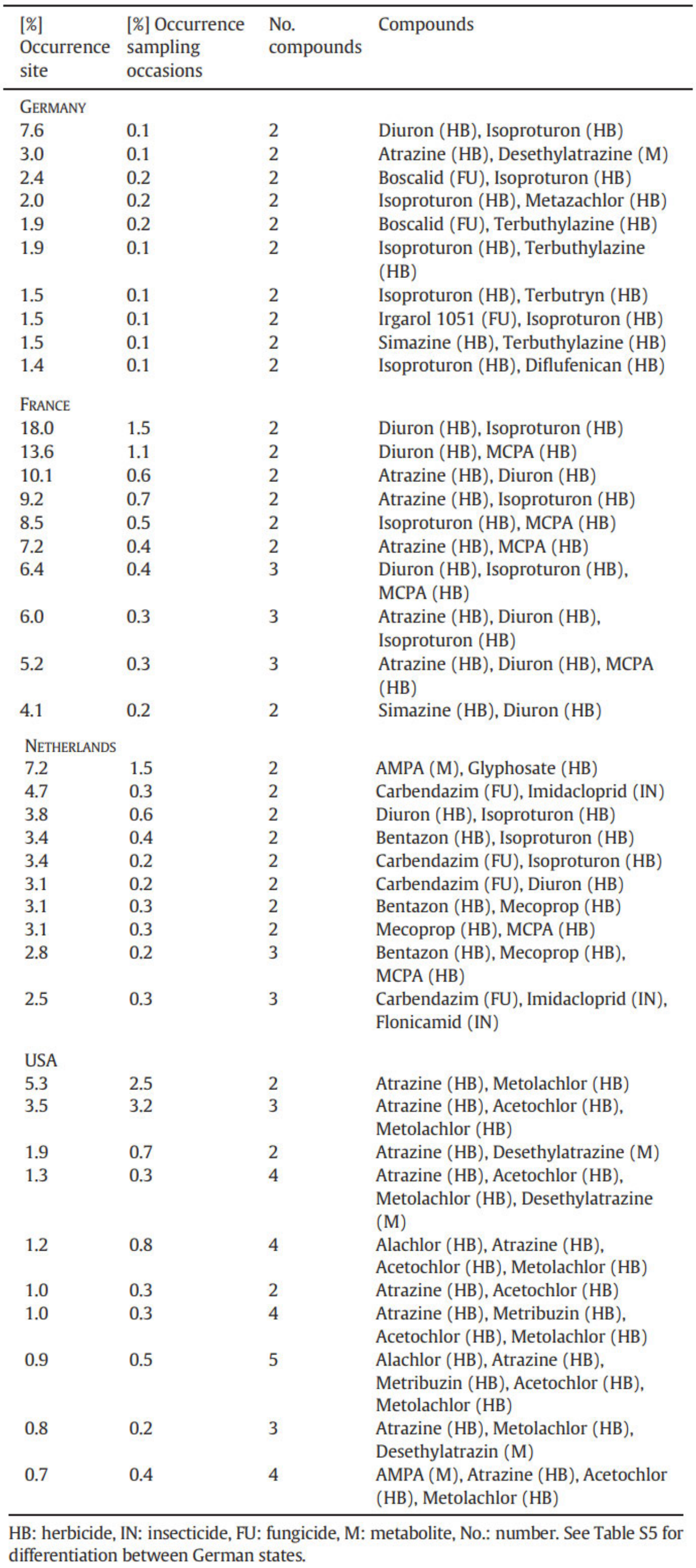


Compound	CAS	Pesticide type	DE	FR	US	NL
1,2,3,4,5,6-Hexachlorocyclohexane	58899	IN	8.7	11.2	0.7*	10
2,4-D	94757	HB	9.1*	4.9*	3.0*	18.4*
2,6-Dichlorobenzamide	2008584	HB	0.2	0.1	0	28.4
AMPA	1066519	M	12.2	13.2	2.3	37.8
Atrazine	1912249	HB	24.3	42.0	19.2*	11.3
Azoxystrobin	131860338	FU	18.4*	0.7*	0*	27.8*
Bentazon	25057890	HB	23.2*	7.7*	0.1*	37.5*
Bitertanol	55179312	FU	0	0	0	15.9
Boscalid	188425856	FU	38.6*	0*	0*	12.8*
Carbendazim	10605217	FU	16.3*	1.5	0*	55.3
Chloridazon	1698608	HB	13.7*	0.8*	0*	29.4*
Chlorpropham	101213	HB	0*	0.2*	0*	31.9*
Chlorpyrifos	2921882	IN	19.2	6.6*	1.7*	3.8*
Chlortoluron	15545489	HB	13.0*	4.0*	0	8.4
Clomazone	81777891	HB	19.8*	0.1*	0*	2.8*
Desethylatrazine	6190654	M	12.2	5.5	3.0	2.2
Desethylterbuthylazine	30125634	M	34.3	0.5	0	4.4
Dichlobenil	1194656	HB	0	0.4	0*	11.9
Diflufenican	83164334	HB	33.4*	0.3*	0	0.9*
Dimethachlor	50563365	HB	19.8*	0.1*	0	0
Dimethenamid	87674688	HB	20.9	7.5	1.2*	15.3
Dimethoate	60515	IN	7.6*	0.2*	0.6*	20*
Dimethomorph	110488705	FU	1.4*	1.1*	0*	18.4*
Diuron	330541	HB	45.1*	55.3	1.3*	38.1
Epoxiconazole	133855988	FU	10.2*	1.5*	0	6.9*
Ethofumesate	26225796	HB	23.6*	1.3*	0*	32.5*
Flonicamid	158062670	IN	0	0*	0*	11.9*
Flufenacet	142459583	HB	23.7*	0*	0*	1.3*
Fluroxypyr	69377817	HB	0*	0.1*	0*	14.7*
Flurtamone	96525234	HB	23.1*	0.1*	0	0.3
Flutolanil	66332965	FU	0*	0*	0*	19.1*
Glyphosate	1071836	HB	9.7*	12.1*	0*	30*
Hexachlorobenzene	118741	FU	15.5	4.0	0.4	2.5
Irgarol 1051	28159980	FU	26.4	0	0*	0
Isoproturon	34123596	HB	62.0*	53.6*	0	37.5*
Linuron	330552	HB	2.0	10*	0*	28.4*
MCPA	94746	HB	22.5*	43.2*	0.4*	44.4*
Mecoprop	93652	HB	24.9*	5.4*	0	38.4
Metalaxyl	57837191	FU	7.9	0.5	0.1*	21.3
Metamitron	41394052	HB	10.5*	0.7*	0	12.8*
Metazachlor	67129082	HB	45.5*	2.3*	0	19.1*
Metolachlor	51218452	HB	31.1*	7.9	11.6*	36.6
Metribuzin	21087649	HB	3.2*	0.1*	3.6*	11.6*
Napropamide	15299997	HB	18.3*	0.4*	0*	0*
p,p′-DDD	72548	IN	10.5	5.9	0.5	0.9
p,p′-DDT	50293	IN	20.9	7.5	0.9*	3.1
Pencycuron	66063056	FU	0.8*	0*	0*	14.4*
Pendimethalin	40487421	HB	12.7*	0.6*	2.6*	5.0*
Pirimicarb	23103982	IN	7.9*	0.1*	0*	24.1*
Pronamide	23950585	HB	14.3*	3.1*	0.5*	13.4*
Propamocarb	24579735	FU	0.6*	0*	0*	11.6*
Propiconazole	60207901	FU	17.4*	0.1*	0.2*	3.8*
Prosulfocarb	52888809	HB	2.2*	0.4*	0	15.9*
Quinmerac	90717036	HB	15.6*	0*	0	0.3*
Simazine	122349	HB	29.0	19.9	1.6*	15.3
Tebuconazole	107534963	FU	15.6	2.6*	0*	17.5*
Terbuthylazine	5915413	HB	55.1*	0.1	0	33.1*
Terbutryn	886500	HB	37.4	2.9	0	5.6
Terbuthylazine, 2-hydroxy	66753079	M	10.9	0	0	0

DE: Germany; FR: France, NL: Netherlands, US: United States of America. IN: insecticide, HB: herbicide, FU: fungicide, M: metabolite. * indicates that the respective pesticide was approved during the time frame of the data used for this study (EC, 2015; EPA, 2016 personal communication). See Table S4 for differentiation between German states.

In addition, pesticide detections varied strongly between the countries across sampling occasions (26% for USA to 82% Netherlands) and sites (24% for USA to 90% for the Netherlands (Table 8.5-161). The most frequently detected compounds, occurring at least at 10% of sites, were mainly herbicides and their metabolites belonging to the chemical classes of phenylurea (Diuron (DCMU), Isoproturon), chlorotriazine (Terbuthylazine, Atrazine) and organophosphorus herbicides (Glyphosate) (Table 8.5-162). In some countries, fungicides (Propiconazole, Germany; Boscalid, Germany; Carbendazim, the Netherlands) and insecticides (Lindane (γ-HCH), France; Fipronil, USA; Imidacloprid, the Netherlands) were among the most frequently detected pesticides. Although 34% and 19% of the analysed compounds were insecticides and fungicides, both pesticide types were less frequently detected in comparison to herbicides.

Table 8.5-163: List of the most frequent mixtures from the different countries with the ratio of occurrence at sites and sampling occasions as well as the number of compounds (size). Order of compounds based on CAS numbers.



[%] Occurrence site	[%] Occurrence sampling occasions	No. compounds	Compounds
GERMANY			
7.6	0.1	2	Diuron (HB), Isoproturon (HB)
3.0	0.1	2	Atrazine (HB), Desethylatrazine (M)
2.4	0.2	2	Boscalid (FU), Isoproturon (HB)
2.0	0.2	2	Isoproturon (HB), Metazachlor (HB)
1.9	0.2	2	Boscalid (FU), Terbuthylazine (HB)
1.9	0.1	2	Isoproturon (HB), Terbuthylazine (HB)
1.5	0.1	2	Isoproturon (HB), Terbutryn (HB)
1.5	0.1	2	Irgarol 1051 (FU), Isoproturon (HB)
1.5	0.1	2	Simazine (HB), Terbuthylazine (HB)
1.4	0.1	2	Isoproturon (HB), Diflufenican (HB)
FRANCE			
18.0	1.5	2	Diuron (HB), Isoproturon (HB)
13.6	1.1	2	Diuron (HB), MCPA (HB)
10.1	0.6	2	Atrazine (HB), Diuron (HB)
9.2	0.7	2	Atrazine (HB), Isoproturon (HB)
8.5	0.5	2	Isoproturon (HB), MCPA (HB)
7.2	0.4	2	Atrazine (HB), MCPA (HB)
6.4	0.4	3	Diuron (HB), Isoproturon (HB), MCPA (HB)
6.0	0.3	3	Atrazine (HB), Diuron (HB), Isoproturon (HB)
5.2	0.3	3	Atrazine (HB), Diuron (HB), MCPA (HB)
4.1	0.2	2	Simazine (HB), Diuron (HB)
NETHERLANDS			
7.2	1.5	2	AMPA (M), Glyphosate (HB)
4.7	0.3	2	Carbendazim (FU), Imidacloprid (IN)
3.8	0.6	2	Diuron (HB), Isoproturon (HB)
3.4	0.4	2	Bentazon (HB), Isoproturon (HB)
3.4	0.2	2	Carbendazim (FU), Isoproturon (HB)
3.1	0.2	2	Carbendazim (FU), Diuron (HB)
3.1	0.3	2	Bentazon (HB), Mecoprop (HB)
3.1	0.3	2	Mecoprop (HB), MCPA (HB)
2.8	0.2	3	Bentazon (HB), Mecoprop (HB), MCPA (HB)
2.5	0.3	3	Carbendazim (FU), Imidacloprid (IN), Flonicamid (IN)
USA			
5.3	2.5	2	Atrazine (HB), Metolachlor (HB)
3.5	3.2	3	Atrazine (HB), Acetochlor (HB), Metolachlor (HB)
1.9	0.7	2	Atrazine (HB), Desethylatrazine (M)
1.3	0.3	4	Atrazine (HB), Acetochlor (HB), Metolachlor (HB), Desethylatrazine (M)
1.2	0.8	4	Alachlor (HB), Atrazine (HB), Acetochlor (HB), Metolachlor (HB)
1.0	0.3	2	Atrazine (HB), Acetochlor (HB)
1.0	0.3	4	Atrazine (HB), Metribuzin (HB), Acetochlor (HB), Metolachlor (HB)
0.9	0.5	5	Alachlor (HB), Atrazine (HB), Metribuzin (HB), Acetochlor (HB), Metolachlor (HB)
0.8	0.2	3	Atrazine (HB), Metolachlor (HB), Desethylatrazin (M)
0.7	0.4	4	AMPA (M), Atrazine (HB), Acetochlor (HB), Metolachlor (HB)

HB: herbicide, IN: insecticide, FU: fungicide, M: metabolite, No.: number. See Table S5 for differentiation between German states.

Most frequently detected mixtures

The 10 most frequently detected mixtures were mostly binary or ternary and composed of herbicides and consisted of compounds that represented the most frequent individual compounds in the countries.

The number of compounds constituting the 10 most frequent mixtures ranged from 5 in France to 12 in Germany (Table 8.5-163).

Associations with monitoring characteristics

The number of detected compounds as well as mixture size (Table 8.5-161) correlated moderately positive with the total number of analysed compounds per sampling occasion (Figure 8.5-126). Both correlated negligibly with catchment size for all countries, and only weakly with the fraction of arable land or of total agricultural area within the catchment areas of Germany (Table 8.5-164). However, the mean number of detected pesticides increased from 3 to 7 compounds when the fraction of total agricultural area within the catchment area increased from 20% to 40%.

Figure 8.5-126: Relationship between number of detected and of analysed compounds (on a logscale)

Solid line indicates a 1:1 ratio of detected: analysed compounds, dashed lines indicate 1:5, 1:10, 1:20 and 1:50 ratios. Colours indicate the number of individual sampling occasions with this respective relationship.

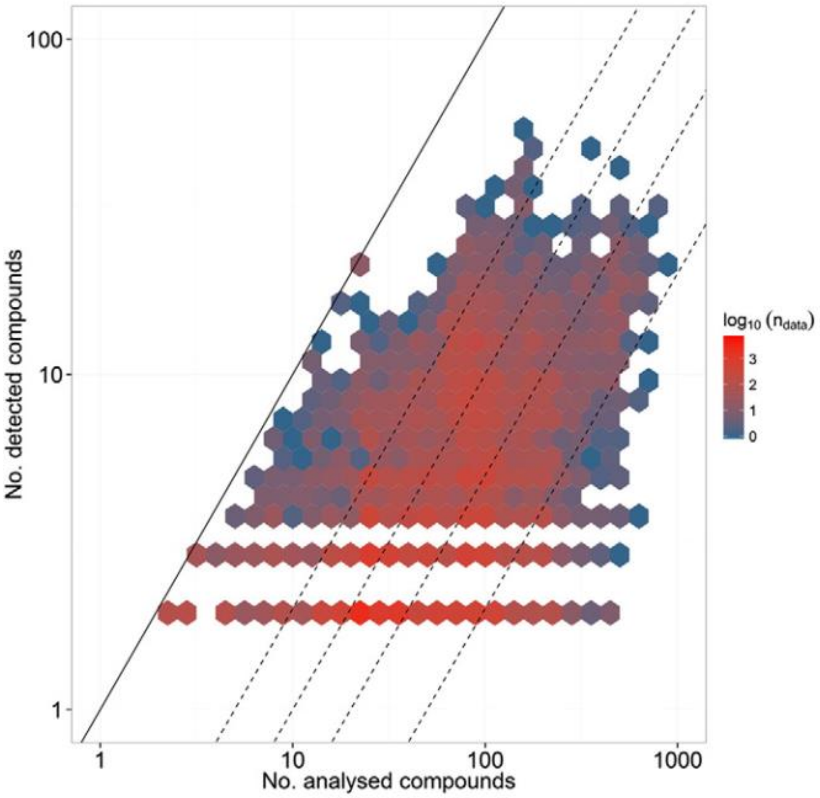
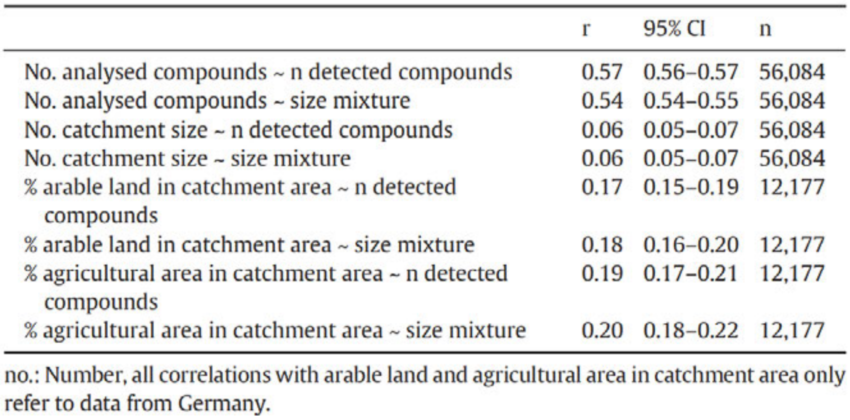


Table 8.5-164: **Correlation coefficients and corresponding confidence intervals (CI) concerning associations with monitoring characteristics**



	r	95% CI	n
No. analysed compounds ~ n detected compounds	0.57	0.56–0.57	56,084
No. analysed compounds ~ size mixture	0.54	0.54–0.55	56,084
No. catchment size ~ n detected compounds	0.06	0.05–0.07	56,084
No. catchment size ~ size mixture	0.06	0.05–0.07	56,084
% arable land in catchment area ~ n detected compounds	0.17	0.15–0.19	12,177
% arable land in catchment area ~ size mixture	0.18	0.16–0.20	12,177
% agricultural area in catchment area ~ n detected compounds	0.19	0.17–0.21	12,177
% agricultural area in catchment area ~ size mixture	0.20	0.18–0.22	12,177

no.: Number, all correlations with arable land and agricultural area in catchment area only refer to data from Germany.

Core compounds - composition and size of detected mixtures

The pesticide mixtures for the core compounds that were analysed in all countries consisted mainly of herbicides (Figure 8.5-127), where Atrazine, Simazine and the metabolites AMPA with a herbicide as parent compound were dominating. For France, herbicide mixtures accounted for 94% of mixtures, whereas for Germany, only 48% of mixtures were solely comprised of herbicides, due to frequent mixtures with fungicides (e.g. Metalaxyl, Propiconazole) and insecticides (Chlorpyrifos). For all countries, insecticides contributed negligibly to mixtures, although one quarter of the analysed core compounds were insecticides. Considering that only four of the 44 analysed core compounds were fungicides, they were comparatively overrepresented in the mixtures of Germany and Netherlands with 41 % and 18 % of all mixtures containing fungicides (Figure 8.5-127). Generally, the relative occurrence of mixtures decreased with an increase of mixture size (Figure 8.5-128). Binary and tertiary mixtures dominated in surface waters as detected in all countries. Only for the German data, larger mixtures occurred also frequently, which was mainly based on mixtures from the German state Baden-Württemberg. Baden-Württemberg also had significantly larger mixture sizes compared to the other countries and German states (all p <0.001, all 95% confidence intervals exclude 0).

Figure 8.5-127: **Relative amount of mixtures from core compounds for the main pesticide types.**

DE: Germany; FR: France, NL: Netherlands, US: Unites States of America. Dark green: mixtures of only herbicides, light green: herbicides in mixture, blue: fungicide in mixtures, red: insecticides in the mixtures. Metabolites were assigned the pesticide type of their parent compound.

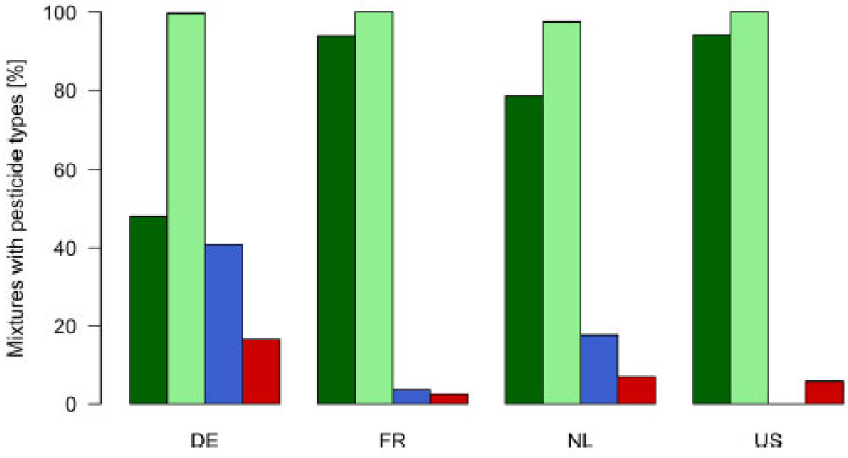
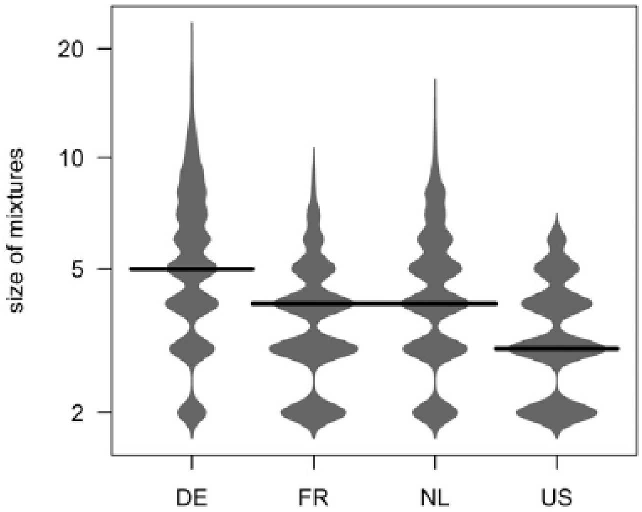


Figure 8.5-128: **Distribution of mixture size for the different countries for the core compounds**
The black solid line gives the median. Y-axis on logarithmic scale. DE: Germany, FR: France, NL: Netherlands, US: United States of America.



Discussion

Most frequently detected pesticides and mixtures
Herbicides and metabolites with herbicides as parent compounds were the most frequently detected pesticide group in our study, of which Isoproturon, MCPA and Atrazine were the most frequent herbicides. This result is in accordance with several other studies that identified herbicides as the most frequently detected compound group. With approximately 83,000 t, the combined herbicide use in France, Germany and the Netherlands was a factor of 12 higher than insecticide and 50 % higher than fungicide use. Based on these application quantities, herbicides enter streams usually in relatively high concentrations, which together with their typical high water solubility and persistence simplifies detection in chemical analysis, especially in comparison to insecticides. Despite herbicides in the USA being applied 2.5 times more frequently than insecticides, presumably due to different climate conditions than in Europe, the ratio of herbicide to insecticide detections was similarly low as for the European countries. In our study, Glyphosate was not considered in the analysis for the USA, although it is frequently applied, due to a lack of data from the regular monitoring. Other monitoring programs included Glyphosate and detected it frequently. The exclusion of the Glyphosate and its metabolites in the regular monitoring can be attributed to its difficult analysis, where the high polarity complicates detection using liquid chromatography, and high costs using alternative methods. Fungicides were in our study detected in all countries except for the USA, in contrast to other studies which detected fungicides in the USA. This lack of detection in the USA may be explained by the fact that fungicides were rarely part of large scale monitoring programs used in our analysis. Additionally, the usual application pattern of fungicides leads to relatively low but continuous concentrations of these compounds in streams.

The limits of quantification (LOQ) for the USA for fungicides in our study were in average 12-fold higher as those of other countries, which might contribute to the low detection frequency. The streams in the German state Baden-Württemberg showed a high percentage of mixtures with fungicides (93%) in comparison to other countries and German regions (0-24%). This is mainly due to the most frequently detected fungicides Metalaxyl and Propiconazole, which occurred at 58% and 90% of the sites respectively. In Baden-Württemberg, the compounds were analysed in almost all sites (98% for both) and all sampling occasions (94% and 92% for Metalaxyl and Propiconazole). In the other regions and countries, except for the German state Saxony where the monitoring was similar to that of Baden-Württemberg, they were analysed in <66% and 36% of sites and sampling occasions. In the other countries the rather high detection rate of Metalaxyl and Propiconazole can also be attributed to the comparatively low LOQ of 1 ng/L for both compounds that was only reached for Baden-Württemberg and was for example 15-fold higher in Saxony.

The LOQ from these compounds in the other German states and countries ranges from 5-fold higher in Rhineland-Palatinate up to 80-folds higher in France. Finally, differences in agricultural land use and consequently in pesticide use may partially explain differences in detection patterns. A study in Switzerland showed that by decreasing the LOQ in pesticide analysis, the number of detected compounds could be increased up to 67% corresponding to 30 to 50 individual compounds in this study. This decrease of LOQs can be necessary to appropriately evaluate potential ecological risks from pesticides. For our dataset, the ratio of LOQ and LC_{50} of the most sensitive taxa differed strongly from 0.0003 (10th percentile) to 4.1 (90th percentile). Decreasing the LOQs is still required for many compounds for a comprehensive ecological assessment. Insecticides were the least frequently detected compound group. The most frequently detected insecticides were DDT, Pirimicarb and Chlorpyrifos. The most frequently detected mixtures from the different countries consisted of two or three compounds with mainly herbicides and metabolites with a herbicide as parent compound. This small size of frequently detected mixtures is partly also due to the limitation to compounds detected at >5% of sites. Without this limitation the average size of the mixtures would be higher. The single compounds of the most frequent mixtures reflect the most frequent single compounds from all analysed surface waters. Frequently detected mixtures in corn and soybean growing areas showed comparable number of compounds to our study (two to four compounds and were exclusively composed of herbicides (Belden *et al*., 2007). Mixtures with Acetochlor, Metolachlor and Atrazine dominated the most frequently detected mixtures in this study from the USA as well as in our results from the US monitoring data. Mixtures with these compounds were absent in other countries, which can be explained by to the fact that the herbicide Acetochlor is not authorized in the EU. Compounds such as Diuron, Atrazine, Simazine and Isoproturon that were often contained in frequently detected mixtures were also detected in a different climate zone.

Associations of detected compounds and mixtures with monitoring characteristics

Our results show that the number of detected pesticides and size of mixtures were correlated to the number of analysed compounds. On average, to detect one pesticide, between 5 and 20 pesticides had to be analysed (Figure 8.5-126). Due to analysis of a high number of randomly detected compounds might not be feasible during routine monitoring, a selection of compounds motivated by current use of pesticides, sales or crop-related use recommendations should be included to analysis.

The number of detected compounds and size of mixtures were not associated with the size of the upstream catchment (r = 0.06). We expected that a larger catchment size would result in a higher number of detected pesticides due to (i) higher amount of pesticide use in a larger catchment, and (ii) a typically larger variety of crops in larger catchments, associated with a higher diversity of applied pesticides. The lack of such a relationship with catchment size may be a result of dilution, i.e. that water body size also increases with catchment size and dilutes pesticide concentrations. Increasing catchment size is related to longer stream distances and consequently transport times of compounds, and increasing transport time may lead to different degradation and transformation processes, as well as partitioning into the sediment phase, which in turn decreases concentrations, and consequently detection frequency. Flow velocity (not considered in analysis due to lack of data) might be a factor in determining, in addition to the duration a compound occurs in a stream and the related dilution factor and degradation, the amount and grain size of sediments, which might influence adsorption from compounds and subsequently the detection rate of pesticides in grab samples.

In contrast to the size of the catchment upstream of the sampling site, the fraction of agricultural area was weakly correlated with the number of detected pesticides and size of mixtures in Germany (r = 0.17). Nevertheless, the number of detected pesticides increased from 3 to 7 when the agricultural area in the catchment area exceeded 20% based on the larger area with pesticide use. Other studies in different countries found a clear footprint of agriculture in terms of effects in stream ecosystems for a higher ratio of agriculture within the catchment of 40% in Germany and France and the USA.

Differences in pesticide detections between countries

The size of mixtures in countries differed between Germany and the Netherlands on the one hand (mean size of mixtures of 7.0 and 4.8, respectively) and USA and France on the other hand (mean mixture size of 3.2 and 3.0, respectively). These groups also differed in the number of analysed compounds per sampling occasion. Whereas in Germany and the Netherlands over 80 compounds were analysed, in the USA and France only 30 compounds were analysed (Table 8.5-161). This stresses again, as already shown above and other studies, that a high number of analysed compounds is crucial for a representative picture of the pesticide load of streams. Even when restricting the analysis to the core group of pesticides measured in all countries, these differences prevailed, though to a lower degree. France and the USA had a mean size of mixtures of 2.5 core compounds, whereas average mixtures in Germany and the Netherlands contained 4.7 and 3.6 compounds. These differences in the size of mixtures of core compounds may be caused by differences in the LOQ between the different countries. For 52% of all compounds, the LOQs were lowest in Germany, potentially increasing the detection frequency. The USA had the lowest LOQ for only 5% of compounds and, presumably partly related to this, the lowest detection frequencies. The low number of core compounds detected in the USA and France compared to Germany and the Netherlands could be caused by: (i) soil properties, (ii) the slope and (iii) the distance of agricultural areas, but also by (iv) crop type.

For instance, in the USA and France legumes are grown on relatively large area (36% and 12%) in comparison to Germany and the Netherlands (0.5% and 6%) and legumes were shown to reduce runoff during rainfall events and the related pesticide input in streams by up to 95% for full gown plants. Finally, agricultural areas in the USA are often dominated by large fields and crop monocultures (average farms of 95 ha) and compared to the other countries (average farms: France 54 ha, Germany 56 ha, the Netherlands 26 ha) a lower farm density. Based on the assumption of a lower farm density and of a homogeneous selection of pesticides within a farm, the number of different pesticides in streams could be lower due to the lower number of pesticides applied. This study provides priority pesticides and pesticide mixtures from streams of Germany, France, the Netherlands and the USA. Using these priority mixtures in ecotoxicological risk assessment could help to improve the estimation of mixture effects in aquatic ecosystems. Additionally, this study suggests that through improved routine pesticide monitoring, by increasing the number of analysed pesticides, improving analytical performance in terms of lowering LOQs and the use of alternative sampling methods to grab sampling, monitoring would provide a more realistic picture of the exposure situation and the number of detected pesticides would likely increase.

Conclusions

Pesticides in streams typically occur in mixtures of two to five compounds, in which herbicides are clearly dominating. The size of detected mixtures is influenced by the number of analysed compounds, the LOQs, but also the proportion of agriculture in the upstream catchment and the sampling method. We identify frequently detected pesticides which may inform the ecological risk assessment for stream ecosystems. Nevertheless, a comprehensive assessment of exposure to pesticide mixtures, would require a decrease of the LOQ for many compounds and widening the spectrum of compounds considered in monitoring programs.

Assessment and conclusion by applicant:

The article summarizes monitoring results of pesticides in some EU Member States and the USA. Glyphosate measurements were derived from databases of national or regional government agencies in Germany, France, the Netherlands and the USA and were reported and evaluated.
The article is considered reliable.

Assessment and conclusion by RMS:

This article deals with analysis of monitoring results from Germany, France, the Netherlands and the USA to identify the most frequently detected metabolites and mixtures. Also this article tested the correlation between the number of detected compounds with other parameters such as the size of the catchment area, the fraction of the agricultural area within the catchment or the total number of analysed compounds per sampling occasion.

However, the study is considered reliable with restrictions since does not give concentration measurement results from the monitoring programs.

Data point:	CA 7.5/047
Report author	Stenrød, M.
Report year	2015
Report title	Long-term trends of pesticides in Norwegian agricultural streams and potential future challenges in northern climate
Document No	Acta Agriculturae Scandinavica, Section B - Soil & Plant Science, 2015 Vol. 65, No. Supplement 2, 199–216
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted under GLP/Officially recognised testing facilities (Bioforsk)
Acceptability/Reliability:	Reliable with restrictions

The objective of the present study was to identify environmental challenges of pesticide use in the northern climate by evaluating long-term pesticide monitoring data compiled by the Norwegian Agricultural Environmental Monitoring Programme. Pesticide use data and pesticide concentrations measured in stream water from six small agricultural catchments in Norway were analysed. Observed trends in pesticide detection frequencies, measured concentrations and cumulative risk from the six monitoring sites were compared. The results demonstrated the need for continued focus on the herbicides metribuzin and aclonifen, and potential concerns regarding use of the fungicide prothioconazole and the insecticide imidacloprid. The six monitoring sites represented the diversity of intensively cropped areas in Norway and differed with respect to estimated cumulative risk. Vegetable and potato cropping areas showed not only the highest level of total environmental risk, but also a statistically significant decreasing trend over the monitoring period. Cereal cropping areas exhibited no statistically significant time-dependent trends in the studied parameters but did show an increase in fungicide use that requires continued attention. The need for risk assessment of mixture toxicity effects and improved monitoring strategy is also discussed. In conclusion, the present results imply that the current global focus on multiple stressors and mixture toxicity of pesticides in stream water is equally relevant in cold climatic conditions.

Materials and Methods

Monitoring sites

Monitoring data representative of pesticide use in Norwegian agriculture are obtained through annual farmer surveys of pesticide applications in the Skuterud, Mørdre, Heia, Vasshaglona and time catchments, which cover areas dominated by production of cereals, potatoes and vegetables, as well as meadows and pastureland. Here, pesticide application data are given as total area (ha) sprayed with herbicides, fungicides and/or insecticides (not reflecting the number of applications per season) and total amount (kg) of the different groups of pesticides applied.

Water sampling and pesticide analyses

The water sampling is mainly by flow proportional composite sampling on average over a period of 14 days. A small water samples is taken each time a predetermined volume of water passes the monitoring station and all sub-samples are collected and stored in a glass container kept in a refrigerator. During the growing season (April–October), the water samples are analysed for pesticides.

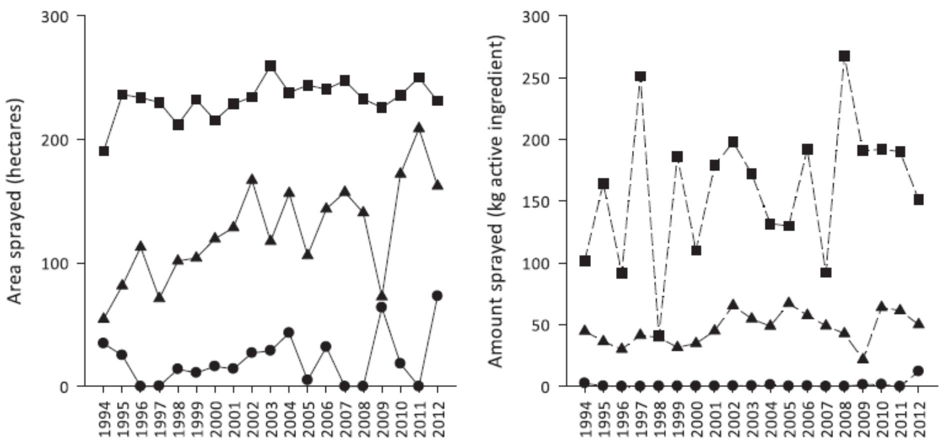
Results

Pesticide use

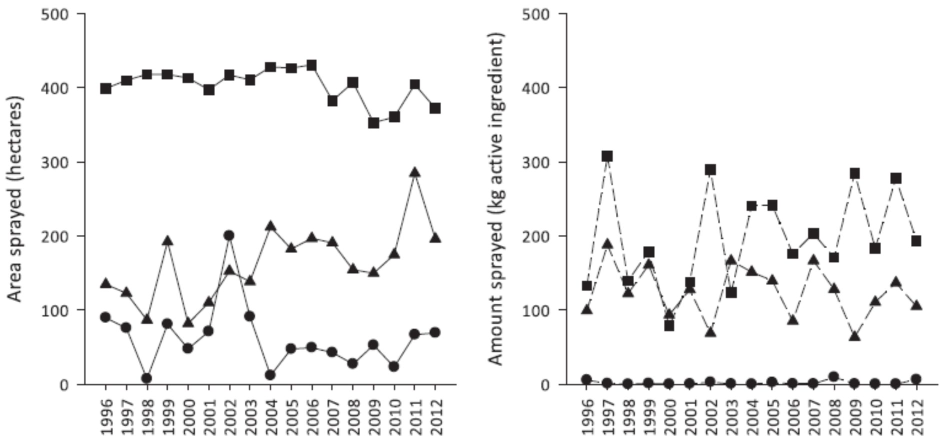
The data collected in the JOVA catchments indicate considerable variation in the use of different pesticides over time (Figures 7.5-123 to 7.5-125). Herbicides have dominated in cereal production (Figure 8.5-129), but the changes in use over the monitoring period differed between the catchments. Considering the area sprayed with herbicides, there has been an increasing trend for Skuterud (r = 0.5, p = 0.035) but a decreasing trend in Mørdre (r = -0.5, p = 0.037). Also, the area sprayed with fungicides increased markedly in both Skuterud (r = 0.7, p = 0.001) and Mørdre (r = 0.6, p = 0.005). The amounts applied varied substantially between years, but no significant trend over time was detected. No statistically significant trends in insecticide use were found for the monitoring period, and application of such chemicals was generally low, although larger areas were sprayed in some years. For the catchments with agricultural production dominated by a combination of potatoes and cereals (Heia) or vegetables and potatoes (Vasshaglona; Figure 8.5-130) the area sprayed with pesticides was quite stable throughout the monitoring period, and no statistically significant time-dependent trends could be discerned.

Figure 8.5-129: **Area (left panel) and amounts (right panel) of herbicides (■), fungicides (▲) and insecticides (●) applied in the JOVA catchments Skuterud (a) and Mørdre (b) throughout the monitoring period 1995–2012**

a) Skuterud



b) Mørdre

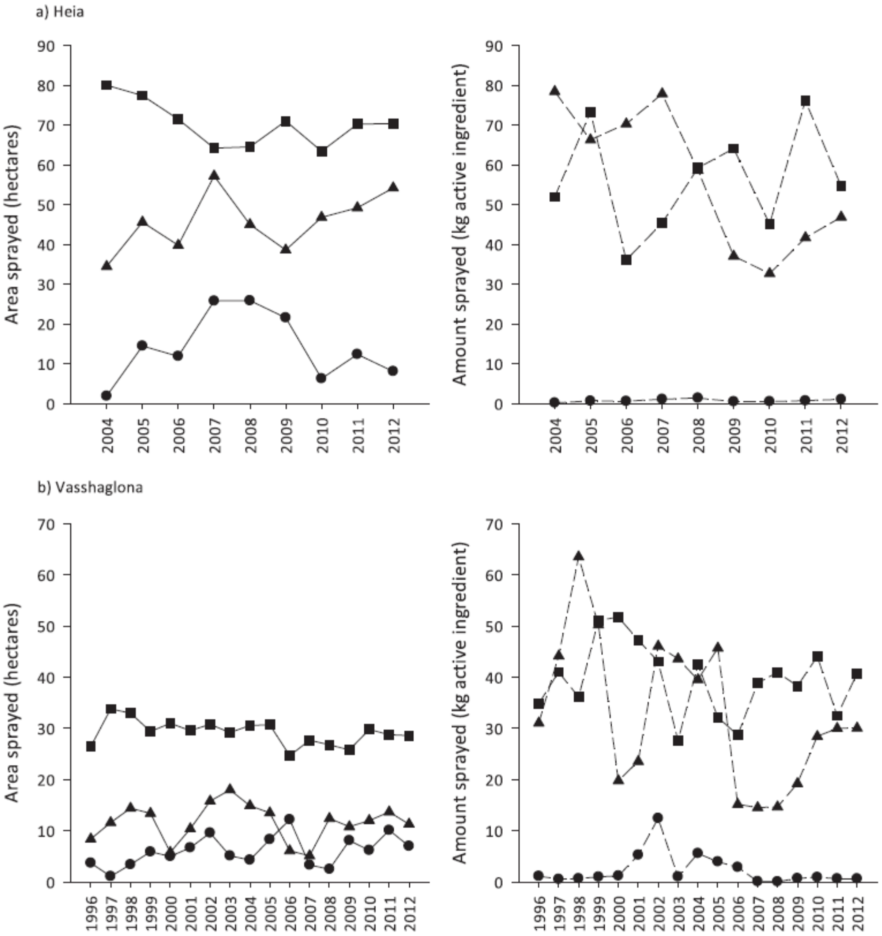


However, a statistically significant decreasing trend in amount of fungicide applied was noted for both the Heia (r = -0.8, p = 0.007) and the Vasshaglona (r = -0.5, p = 0.042) catchment. Analysis of data from the Time catchment, an area dominated by meadows and pasture, showed less use of pesticides (Figure 8.5-131) and no statistically significant time-dependent trends.

Pesticide detections

The JOVA programme has detected 61 different pesticides (including both active ingredients and metabolites) in stream water in the monitored catchments; 24 herbicides (Table 8.5-165), 25 fungicides (Table 8.5-166) and 12 insecticides (Table 8.5-167). The results indicated that although herbicides constituted 77% of all pesticide detections, only about 9% were at concentrations exceeding the corresponding MF values. Fungicides represented 20% of all detections, and 6% of those were at levels above the MF value. Relatively few insecticides were detected (only 3% of the detections), but up to 50% of these exceeded the MF value. In all over the 18-year monitoring period, pesticides were detected at concentrations exceeding the MF value on 408 occasions (excluding double sampling in 2004 and 2007 in the Heia catchment; Table 8.5-168). These detections gave a MEC/MF ratio ≥ 1 and are here assumed to indicate risk to aquatic organisms. Throughout the entire monitoring period and for all six catchments, a mean of two pesticides were detected in each sample analysed, and the corresponding figure for 2011 and 2012 was three pesticides per sample (data not shown). Calculation of the cumulative risk, that is, the measured concentrations of all pesticides in a sample in relation to the respective MF value, resulted in 367 samples with $\Sigma(MEC/MF) \geq 1$ (Table 8.5-168). In these 367 samples, 57 different pesticides were detected, which included those with MEC higher than the MF values (Tables 7.5-149 to 7.5-151); two exceptions to this were DDT and terbuthylazine, which were at levels higher than the MF values in samples not reaching a cumulative risk score of >1.

Figure 8.5-130: Area (left panel) and amount (right panel) of herbicides (■), fungicides (▲) and insecticides (●) applied in the JOVA catchments Heia (a) and Vasshaglona (b) throughout the monitoring period 1995–2012. The boundaries for the Heia catchment were altered in 2004, and hence, only data for the years 2004–2012 are shown



Trends in pesticide detections

Statistically significant differences ($p < 0.001$) between the monitoring sites were found for the median cumulative risk values (Table 8.5-169, Figure 8.5-132). The results indicated statistically significant differences between the Heia catchment dominated by potatoes/vegetables/cereals and those with mainly grain/fodder crops. Furthermore, there was a tendency (i.e. $p \leq 0.1$) towards differences between Heia (after 2004) and Vasshaglona catchments ($p = 0.091$) and Vasshaglona and Time catchments ($p = 0.066$; Table 8.5-169). However, no such statistically significant differences could be found for the 75th percentile values. The multiple comparisons method used assures low risk of false rejection of a H_0 hypothesis assuming equality between groups but also makes it difficult to assert statistically significant differences in the data due to the large variability and large proportion of zero values within each group.

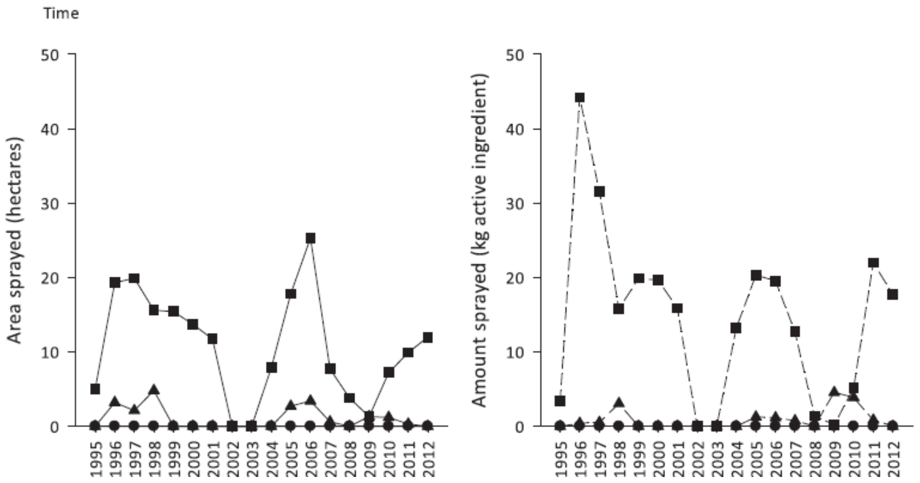
Trend analysis on the individual monitoring sites, showed statistically significant time-dependent trends towards reduction in the Heia, Vasshaglona and Time catchments during the period 1996–2012 (Table 8.5-170). The sampling site and area monitored in the Heia catchment were changed in 2004, but the positive development seen as reduced detection frequency, measured concentrations and cumulative risk could be shown for the sampling points and areas used during both of the monitoring periods in this catchment (i.e. 1996–2004 and 2004–2012). No statistically significant time-dependent trends were evident for the Skuterud, Mørdre and Hotran catchments.

Discussion

Pesticide use

The large year-to-year variation in pesticide use observed in the JOVA catchments (Figures 7.5-123 to 7.5-125) indicates the need for long-term time series as a reference for evaluating single-year results. The trend in herbicide use increased in one of the grain crop catchments (Skuterud) but decreased in the other catchment with such crops (Mørdre), which might be explained by differences in tillage practices (ploughless tillage vs spring ploughing).

Figure 8.5-131: Area (left panel) and amount (right panel) of herbicides (■), fungicides (▲) and insecticides (●) applied in the JOVA catchment time throughout the monitoring period 1995–2012

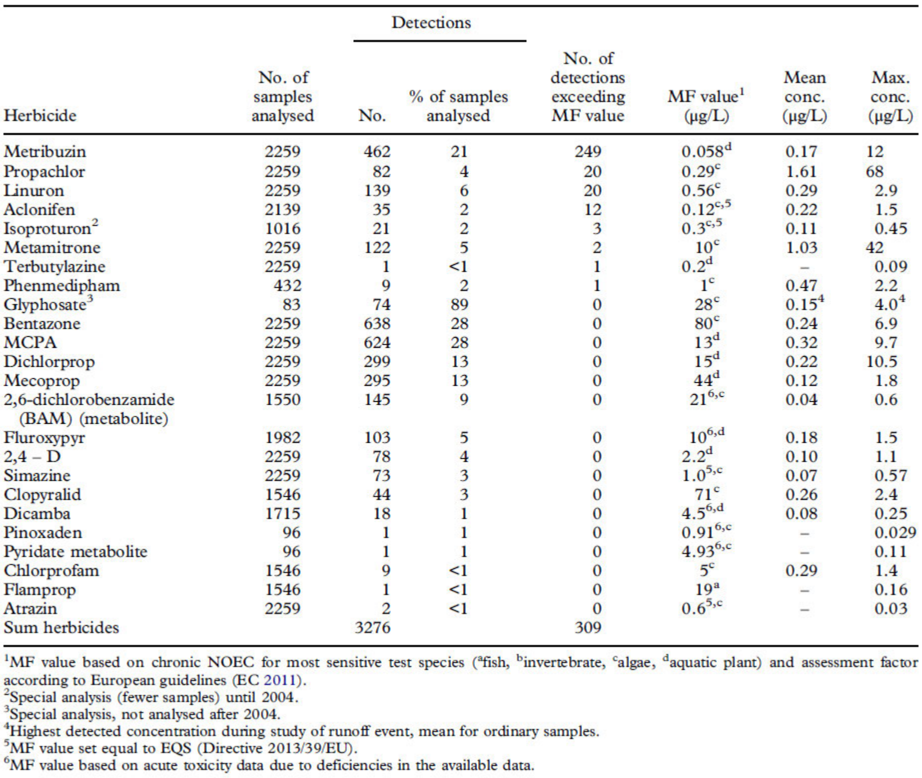


The illustrated data clearly demonstrate the substantial variability caused by management practices and weather conditions, which in turn affects the necessity and possibility of plant protection, and the changes in use caused by approval conditions (e.g. bans, reduced recommended doses and new approvals), and pricing and taxation of plant protection products. However, the influence of these factors is not given further consideration here.

Detected pesticides and potential concerns

The substantial number and levels of pesticide detections shown by the JOVA monitoring data for the period 1995–2012 document the potential environmental concerns connected with the present practices in pesticide use in Norway. Furthermore, climate change projections indicate a forthcoming increase in use of these chemicals in the northern countries. Metribuzin, propachlor, linuron and aclonifen are systemic herbicides, which affect the photosynthesis in selected weeds in potato and vegetable production, and were among the pesticides most frequently found to exceed the MF value over the monitoring period (Table 8.5-166). Two of these compounds, metribuzin and aclonifen, are still in use.

Table 8.5-165: Detections of herbicides in rivers and streams of the JOVA catchments during the monitoring period 1995–2012, categorised according to frequency of detections exceeding the MF level (MF values for 31 December 2013)



Herbicide	No. of samples analysed	Detections		No. of detections exceeding MF value	MF value[1] (µg/L)	Mean conc. (µg/L)	Max. conc. (µg/L)
		No.	% of samples analysed				
Metribuzin	2259	462	21	249	0.058^{d}	0.17	12
Propachlor	2259	82	4	20	0.29^{c}	1.61	68
Linuron	2259	139	6	20	0.56^{c}	0.29	2.9
Aclonifen	2139	35	2	12	$0.12^{c,5}$	0.22	1.5
Isoproturon[2]	1016	21	2	3	$0.3^{c,5}$	0.11	0.45
Metamitrone	2259	122	5	2	10^{c}	1.03	42
Terbutylazine	2259	1	<1	1	0.2^{d}	–	0.09
Phenmedipham	432	9	2	1	1^{c}	0.47	2.2
Glyphosate[3]	83	74	89	0	28^{c}	0.15^{4}	4.0^{4}
Bentazone	2259	638	28	0	80^{c}	0.24	6.9
MCPA	2259	624	28	0	13^{d}	0.32	9.7
Dichlorprop	2259	299	13	0	15^{d}	0.22	10.5
Mecoprop	2259	295	13	0	44^{d}	0.12	1.8
2,6-dichlorobenzamide (BAM) (metabolite)	1550	145	9	0	$21^{6,c}$	0.04	0.6
Fluroxypyr	1982	103	5	0	$10^{6,d}$	0.18	1.5
2,4 – D	2259	78	4	0	2.2^{d}	0.10	1.1
Simazine	2259	73	3	0	$1.0^{5,c}$	0.07	0.57
Clopyralid	1546	44	3	0	71^{c}	0.26	2.4
Dicamba	1715	18	1	0	$4.5^{6,d}$	0.08	0.25
Pinoxaden	96	1	1	0	$0.91^{6,c}$	–	0.029
Pyridate metabolite	96	1	1	0	$4.93^{6,c}$	–	0.11
Chlorprofam	1546	9	<1	0	5^{c}	0.29	1.4
Flamprop	1546	1	<1	0	19^{a}	–	0.16
Atrazin	2259	2	<1	0	$0.6^{5,c}$	–	0.03
Sum herbicides		3276		309			

[1] MF value based on chronic NOEC for most sensitive test species (^{a}fish, ^{b}invertebrate, ^{c}algae, ^{d}aquatic plant) and assessment factor according to European guidelines (EC 2011).
[2] Special analysis (fewer samples) until 2004.
[3] Special analysis, not analysed after 2004.
[4] Highest detected concentration during study of runoff event, mean for ordinary samples.
[5] MF value set equal to EQS (Directive 2013/39/EU).
[6] MF value based on acute toxicity data due to deficiencies in the available data.

These compounds currently represent the herbicides most often detected above MF levels and hence, they require continued attention. Swedish national pesticide monitoring has provided comparable results regarding these substances with concentrations measured in stream water higher than MF values in 49% and 22% of the detections, respectively. An environmental quality standard for aclonifen was included in the list of priority substances of the WFD in 2013 (Directive 2013/39/EU), confirming the broader relevance of apprehension regarding this herbicide. Fenpropimorph, propiconazol, prochloraz and the metabolite prothioconazole-desthio were the top four fungicides in the JOVA data with respect to detections exceeding the MF value (Table 8.5-167), and all of these compounds are currently in use. Prothioconazole-desthio is the major metabolite of a fungicide that was recently (in 2008) approved in Norway for control of Fusarium spp. in grain crops. Due to rapid degradation of the parent compound prothioconazole in the environment this metabolite which is moderately persistent in field soil, is most often encountered in stream water samples. Prothioconazole-desthio is also more toxic to aquatic organisms (especially fish) than the parent compound, which implies potential future concern in Norway.

The insecticides found at concentrations exceeding the MF value (Table 8.5-168) have mainly been used in production of vegetables, potatoes and berries. In general, insecticides are highly toxic to aquatic organisms (mainly invertebrates (Daphnia spp.) and fish) and, consequently, have very low MF values. The present results call for increased attention on measuring environmental concentrations of the fungicide metabolite prothioconazole-desthio and the insecticide imidacloprid (included in the analysis since 2011), which were detected in a large proportion of the analysed samples and frequently at concentrations above MF (in 64% and 44% of the detections, respectively). By comparison, the national pesticide monitoring in Sweden detected quantifiable amounts of prothioconazole-desthio and imidacloprid in nearly 20% of the samples that were assessed and the measured concentrations were above MF in 27% and 8% of the samples, respectively. These results regarding detections as percentage of samples analysed are comparable to the JOVA data, whereas the percentage above MF is considerably lower. Mesocosm studies with the invertebrate test species Chironimus riparius (EFSA 2008b) have demonstrated the potential toxicity of imidacloprid (a neonicotinoid) in the aquatic environment.

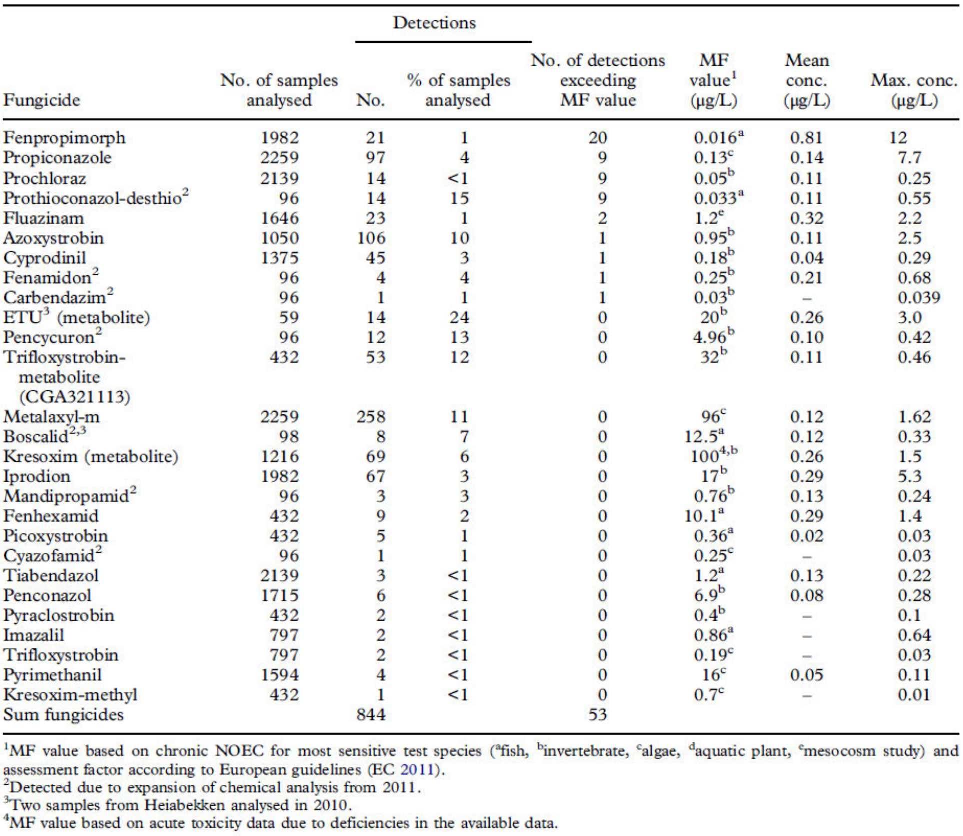
Trends in pesticide detections

Taking into account the high input of pesticides (due to production of potatoes and vegetables, which require frequent use of pesticides) Heia and Vasshaglona had the highest cumulative risk compared to the other JOVA catchments. The Time catchment, which has very little use of pesticides and a low cumulative risk, also showed a reduction in environmental load over the period, possibly chiefly due to some high concentrations of insecticides measured early in the monitoring. Notwithstanding, considering the large increase in the number of substances analysed during the monitoring period as well as a substantial lowering of the quantification limits in the analyses, an increase in environmental load could have been expected instead, especially in the catchments dominated by grain crops with increased use of pesticides. The reduction in load that was noted might have been partly due to the coverage of the analyses still being incomplete in comparison with the vast variety of plant protection products used in the JOVA catchments. It has been reported that the more comprehensive a pesticide screening is, the more reliable are the results of water quality assessments. The herbicide diquat dibromide, which is a desiccant that has been used in potatoes and other crops for several decades, is not assessed in the JOVA catchments. The environmental load caused by this long-term use should be studied to ensure that leaching and negative effects in soil are low, despite the strong sorption of diquat dibromide to soil that can lead to increased persistence and potential accumulation. The catchments dominated by grain crops (Skuterud, Mørdre and Hotran) showed no statistically significant time-dependent trends. However, this might not provide the complete picture, because several currently used fungicides were only recently (2011) included in the analyses, and the widely used glyphosate and sulfonylurea herbicides were not assessed at all.

Need for risk assessment of mixture toxicity effects

The present results on pesticide concentrations and potential cumulative risk in agricultural streams imply that although pesticide use is lower in northern European countries compared to the EU countries with more intensive agricultural practices and pesticide-demanding crops (e.g. France, Spain, Italy), there are concerns regarding residues in stream water and potential negative effects on aquatic organisms. Such effects assumedly include impacts of herbicides on growth of aquatic plants and algae, of fungicides on invertebrates (i.e. Daphnia spp.), fish and algae, and of insecticides on invertebrates (water dwelling growth stages for insects) and fish, with reference to the most sensitive test species indicated above (Tables 7.5-149 to 7.5-151). Furthermore, considering that samples from the main spraying season often contain more than 10 different pesticides, it seems that mixture toxicity should be included in the interpretation and follow-up of monitoring results.

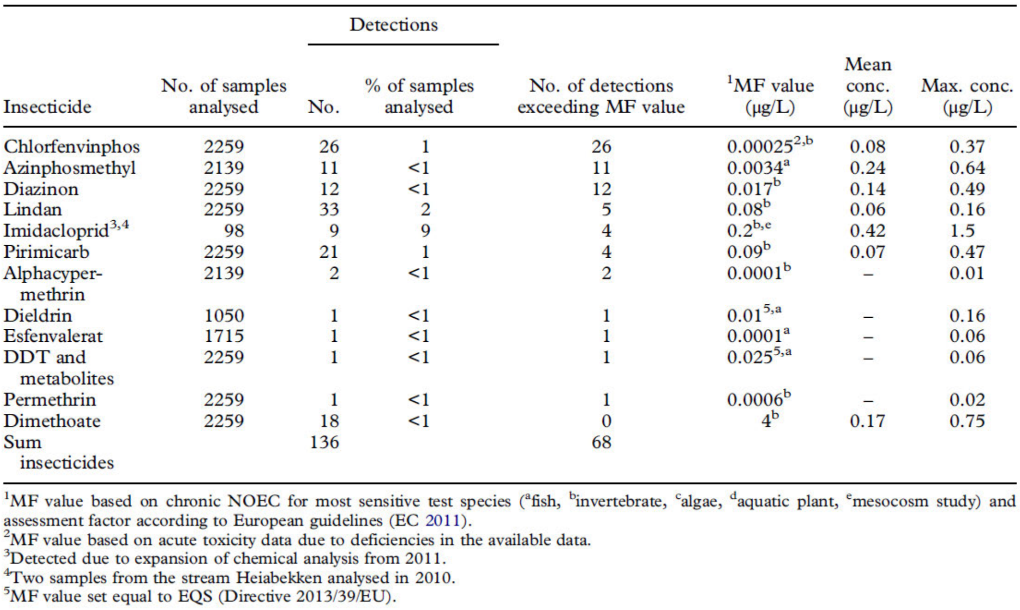
Table 8.5-166: Detections of fungicides in rivers and streams of the JOVA catchments during the monitoring period 1995–2012, categorised according to frequency of detections exceeding the MF level (MF values for 31 December 2013)



		Detections					
Fungicide	No. of samples analysed	No.	% of samples analysed	No. of detections exceeding MF value	MF value[1] (µg/L)	Mean conc. (µg/L)	Max. conc. (µg/L)
Fenpropimorph	1982	21	1	20	0.016[a]	0.81	12
Propiconazole	2259	97	4	9	0.13[c]	0.14	7.7
Prochloraz	2139	14	<1	9	0.05[b]	0.11	0.25
Prothioconazol-desthio[2]	96	14	15	9	0.033[a]	0.11	0.55
Fluazinam	1646	23	1	2	1.2[e]	0.32	2.2
Azoxystrobin	1050	106	10	1	0.95[b]	0.11	2.5
Cyprodinil	1375	45	3	1	0.18[b]	0.04	0.29
Fenamidon[2]	96	4	4	1	0.25[b]	0.21	0.68
Carbendazim[2]	96	1	1	1	0.03[b]	–	0.039
ETU[3] (metabolite)	59	14	24	0	20[b]	0.26	3.0
Pencycuron[2]	96	12	13	0	4.96[b]	0.10	0.42
Trifloxystrobin-metabolite (CGA321113)	432	53	12	0	32[b]	0.11	0.46
Metalaxyl-m	2259	258	11	0	96[c]	0.12	1.62
Boscalid[2,3]	98	8	7	0	12.5[a]	0.12	0.33
Kresoxim (metabolite)	1216	69	6	0	100[4,b]	0.26	1.5
Iprodion	1982	67	3	0	17[b]	0.29	5.3
Mandipropamid[2]	96	3	3	0	0.76[b]	0.13	0.24
Fenhexamid	432	9	2	0	10.1[a]	0.29	1.4
Picoxystrobin	432	5	1	0	0.36[a]	0.02	0.03
Cyazofamid[2]	96	1	1	0	0.25[c]	–	0.03
Tiabendazol	2139	3	<1	0	1.2[a]	0.13	0.22
Penconazol	1715	6	<1	0	6.9[b]	0.08	0.28
Pyraclostrobin	432	2	<1	0	0.4[b]	–	0.1
Imazalil	797	2	<1	0	0.86[a]	–	0.64
Trifloxystrobin	797	2	<1	0	0.19[c]	–	0.03
Pyrimethanil	1594	4	<1	0	16[c]	0.05	0.11
Kresoxim-methyl	432	1	<1	0	0.7[c]	–	0.01
Sum fungicides		844		53			

[1] MF value based on chronic NOEC for most sensitive test species ([a]fish, [b]invertebrate, [c]algae, [d]aquatic plant, [e]mesocosm study) and assessment factor according to European guidelines (EC 2011).
[2] Detected due to expansion of chemical analysis from 2011.
[3] Two samples from Heiabekken analysed in 2010.
[4] MF value based on acute toxicity data due to deficiencies in the available data.

Table 8.5-167: Detections of insecticides in rivers and streams of the JOVA catchments during the monitoring period 1995–2012, categorised according to frequency of detections exceeding the MF level (MF values for 31 December 2013)

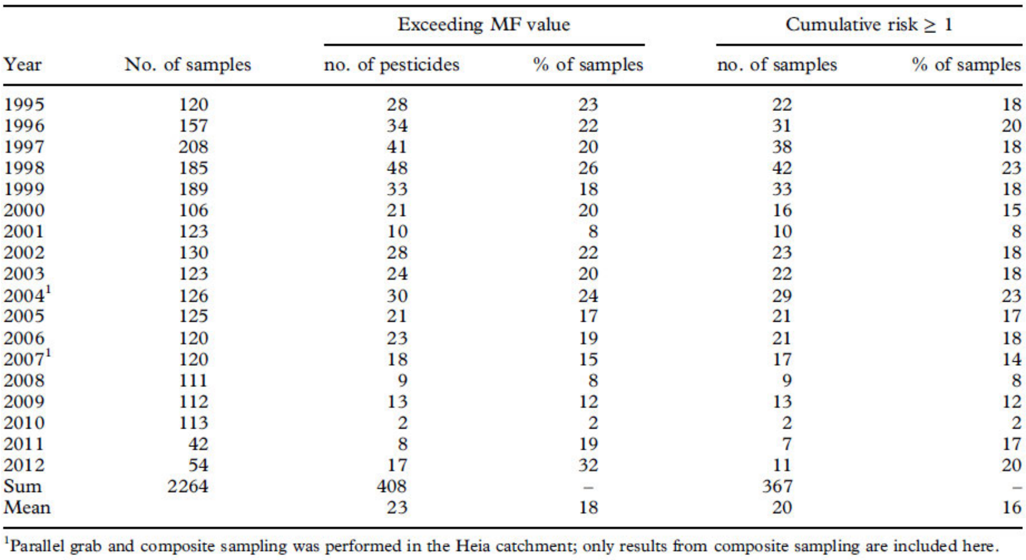


		Detections					
Insecticide	No. of samples analysed	No.	% of samples analysed	No. of detections exceeding MF value	[1]MF value (µg/L)	Mean conc. (µg/L)	Max. conc. (µg/L)
Chlorfenvinphos	2259	26	1	26	0.00025[2,b]	0.08	0.37
Azinphosmethyl	2139	11	<1	11	0.0034[a]	0.24	0.64
Diazinon	2259	12	<1	12	0.017[b]	0.14	0.49
Lindan	2259	33	2	5	0.08[b]	0.06	0.16
Imidacloprid[3,4]	98	9	9	4	0.2[b,e]	0.42	1.5
Pirimicarb	2259	21	1	4	0.09[b]	0.07	0.47
Alphacypermethrin	2139	2	<1	2	0.0001[b]	–	0.01
Dieldrin	1050	1	<1	1	0.01[5,a]	–	0.16
Esfenvalerat	1715	1	<1	1	0.0001[a]	–	0.06
DDT and metabolites	2259	1	<1	1	0.025[5,a]	–	0.06
Permethrin	2259	1	<1	1	0.0006[b]	–	0.02
Dimethoate	2259	18	<1	0	4[b]	0.17	0.75
Sum insecticides		136		68			

[1] MF value based on chronic NOEC for most sensitive test species ([a]fish, [b]invertebrate, [c]algae, [d]aquatic plant, [e]mesocosm study) and assessment factor according to European guidelines (EC 2011).
[2] MF value based on acute toxicity data due to deficiencies in the available data.
[3] Detected due to expansion of chemical analysis from 2011.
[4] Two samples from the stream Heiabekken analysed in 2010.
[5] MF value set equal to EQS (Directive 2013/39/EU).

A mixture toxicity risk evaluation of the JOVA pesticide monitoring data from 2012 suggested that single substances or simple mixtures tend to predominate in the calculated cumulative risk quotients based on the sum of MEC/PNEC ratios and the sum of toxic units for each standard test species group.

Table 8.5-168: Detections of pesticides exceeding the MF value (values for 31 December 2013) and number of stream water samples with cumulative risk ≥ 1 in Norwegian agricultural catchments monitored in the JOVA programme during the period 1995–2012



		Exceeding MF value		Cumulative risk ≥ 1	
Year	No. of samples	no. of pesticides	% of samples	no. of samples	% of samples
1995	120	28	23	22	18
1996	157	34	22	31	20
1997	208	41	20	38	18
1998	185	48	26	42	23
1999	189	33	18	33	18
2000	106	21	20	16	15
2001	123	10	8	10	8
2002	130	28	22	23	18
2003	123	24	20	22	18
2004[1]	126	30	24	29	23
2005	125	21	17	21	17
2006	120	23	19	21	18
2007[1]	120	18	15	17	14
2008	111	9	8	9	8
2009	112	13	12	13	12
2010	113	2	2	2	2
2011	42	8	19	7	17
2012	54	17	32	11	20
Sum	2264	408	–	367	–
Mean		23	18	20	16

[1] Parallel grab and composite sampling was performed in the Heia catchment; only results from composite sampling are included here.

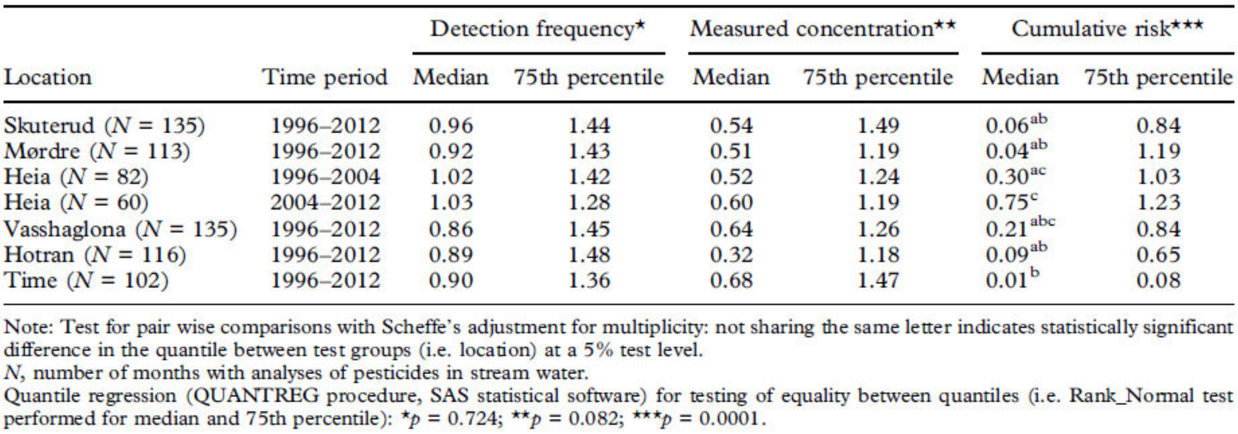
Need for improved monitoring approaches

A continuous challenge is to ensure that the analytical methods employed are updated in relation to the plant protection products that are in use, while at the same time keeping the costs of monitoring at a minimum. Several of the most widely used pesticides are not included in the evaluations performed within the JOVA programme due to analytical and economic limitations, and this incomplete coverage affects the risk assessments based on the monitoring results. The most evident deficiencies in the JOVA analyses concerns the sulfonylurea herbicides and herbicides with glyphosate as the active ingredient. Another important challenge in monitoring of pesticide residues in surface water is being able to measure the (peak) pesticide concentrations that actually occur. The main sampling method in the JOVA catchments (i.e. flow-proportional composite sampling) involves a period of storage before analysis, and other technical aspects connected with sample pre-processing and analysis might lead to an underestimation of the pesticides present in a water sample from a given time period. For some pesticides the quantification limits of the analyses are too high to allow determination at environmentally relevant concentrations, and thus, these substances might occur at potentially harmful levels even though they are not detected through the monitoring. However, lower concentrations can be detected by using passive sampling devices rather than composite water sampling. Also, the sampling of stream water in the JOVA catchments is restricted to the spraying season (May–September), which might yield insufficient monitoring results under such cold climatic conditions. There are indications that degradation of pesticides is delayed in cold climates, which entails an elevated risk of transport during autumn, winter and spring flow events. Furthermore, research has suggested that the mobility of pesticides is increased by soil freezing and by large losses during snowmelt.

Conclusion

The main objective of the present study was to identify environmental challenges associated with use of pesticides in the northern climate by examining trends in detection frequencies, measured concentrations and cumulative risk observed in the long-term pesticide monitoring data collected in the JOVA programme. These data indicate that the environmental load of pesticides used in Norwegian agriculture has decreased in the JOVA catchments from 1995 to 2012. During this monitoring period both the frequency of detections and pesticide concentrations in streams were reduced in areas predominantly growing heavily sprayed potato and vegetable crops, and possibly also in areas dominated by meadows and pasture and thus with lower levels of pesticide use.

Table 8.5-169: Median and 75th percentiles for the summed monthly relative detection frequency, measured concentration, and cumulative risk, for Norwegian agricultural catchments monitored in the JOVA programme



		Detection frequency*		Measured concentration**		Cumulative risk***	
Location	Time period	Median	75th percentile	Median	75th percentile	Median	75th percentile
Skuterud (*N* = 135)	1996–2012	0.96	1.44	0.54	1.49	0.06^{ab}	0.84
Mørdre (*N* = 113)	1996–2012	0.92	1.43	0.51	1.19	0.04^{ab}	1.19
Heia (*N* = 82)	1996–2004	1.02	1.42	0.52	1.24	0.30^{ac}	1.03
Heia (*N* = 60)	2004–2012	1.03	1.28	0.60	1.19	0.75^{c}	1.23
Vasshaglona (*N* = 135)	1996–2012	0.86	1.45	0.64	1.26	0.21^{abc}	0.84
Hotran (*N* = 116)	1996–2012	0.89	1.48	0.32	1.18	0.09^{ab}	0.65
Time (*N* = 102)	1996–2012	0.90	1.36	0.68	1.47	0.01^{b}	0.08

Note: Test for pair wise comparisons with Scheffe's adjustment for multiplicity: not sharing the same letter indicates statistically significant difference in the quantile between test groups (i.e. location) at a 5% test level.
N, number of months with analyses of pesticides in stream water.
Quantile regression (QUANTREG procedure, SAS statistical software) for testing of equality between quantiles (i.e. Rank_Normal test performed for median and 75th percentile): *p = 0.724; **p = 0.082; ***p = 0.0001.

The JOVA catchments chiefly characterised by cereal production plausibly face future challenges related to increased use of fungicides, and they showed no significant reduction in the environmental load of pesticides over the monitoring period. In general, the presence of pesticides in stream water can be explained mainly by the use of pesticides on nearby land areas and the prevailing weather conditions. Most of the pesticides detected in stream water in the JOVA catchments are currently used in Norwegian agriculture. The present results indicate that continued attention should be focused on the herbicides metribuzin and aclonifen, which were monitored throughout the period 1995–2012. Concerns are also emerging with regard to the fungicide prothioconazole (i.e. the metabolite prothioconazole-desthio) and the insecticide imidacloprid, which was more recently included in the JOVA programme, and thus these substances should be scrutinised in the coming years. In many cases, detection frequencies and concentrations of the mentioned pesticides are comparable to those noted in areas with more intensive agriculture than that performed in Norway and the Nordic countries. Pesticide use is probably lower in colder climates compared to more temperate zones, but the current results do not indicate that the environmental challenges of pesticides are at a lower level in the colder areas. It is not possible to draw broader conclusions from this study due to the following limitations: incomplete coverage of pesticides and metabolites, insufficient sampling techniques that did not consider short-term peak concentrations, and inadequate data on yearly variations in pesticide occurrence. The detection frequencies, measured concentrations and estimates of cumulative risk observed in this study imply that the current global focus on multiple stressors and mixture toxicity of pesticides in stream water is equally relevant in cold climatic conditions. This suggests that risk assessment of monitoring results and MEC should be based on a more holistic approach that includes pesticide monitoring, ecotoxicity studies of pesticide mixtures occurring in the field, and modelling strategies.

Figure 8.5-132: **Summed monthly relative cumulative risk over the monitoring period shown for the six JOVA catchments**

x denotes grab samples from the first sampling site [1996–2003]; + indicates samples from the 2nd [current] sampling site [2004–2012]). Month number refers to January 1994 as month number 1.

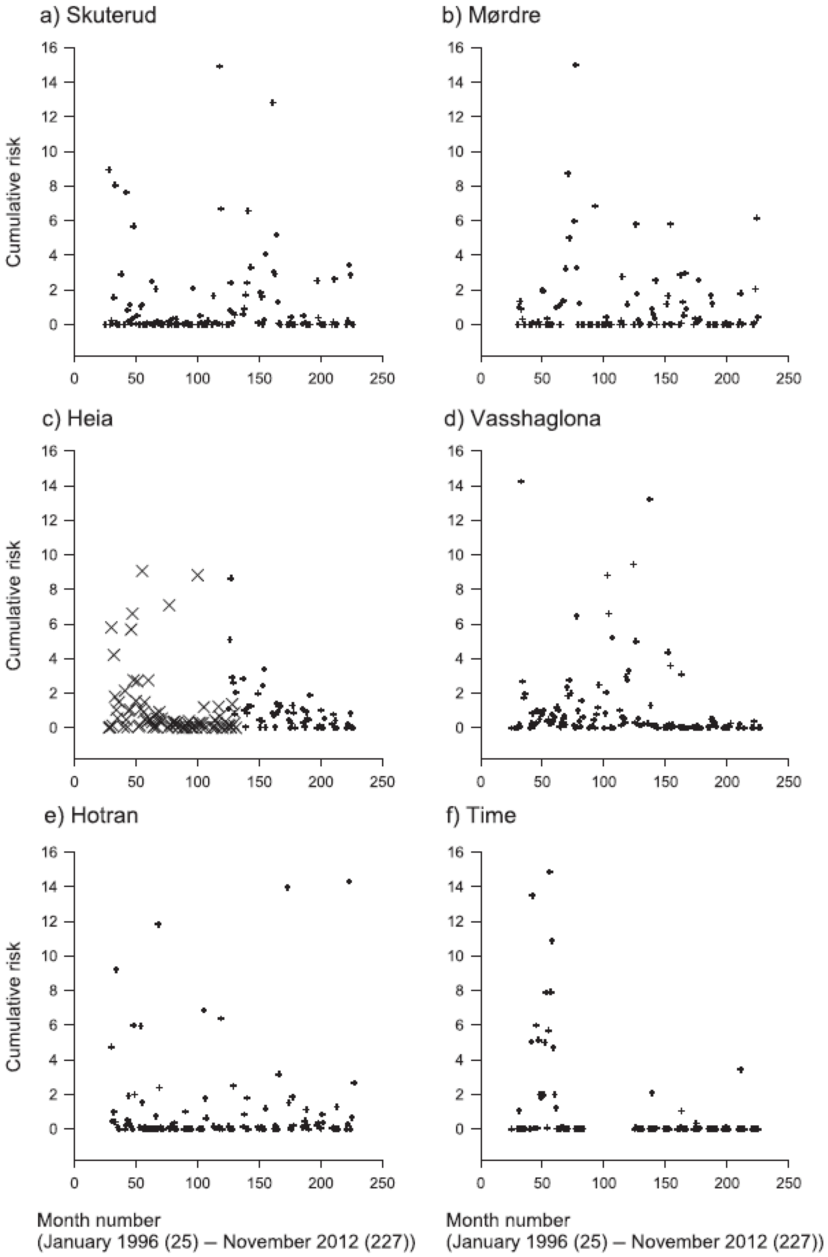
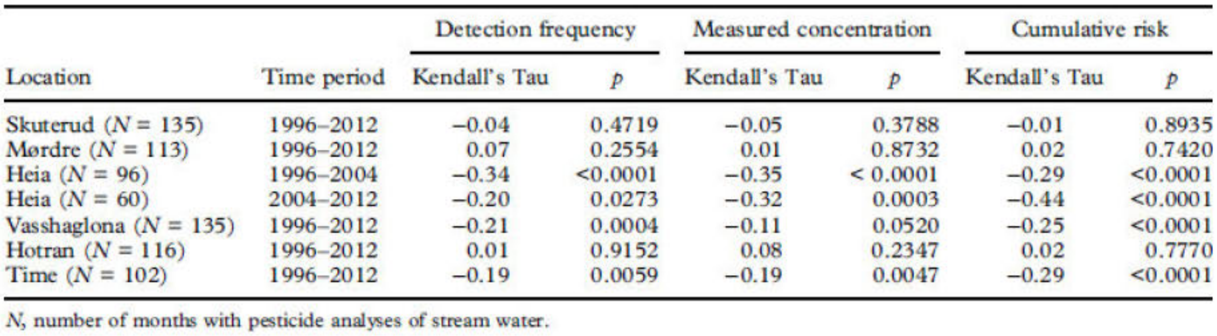


Table 8.5-170: Summary of the results of non-parametric trend analysis (Kendall's Tau) for the summed monthly relative detection frequency, concentration, and cumulative risk, for Norwegian agricultural catchments monitored in the JOVA programme



		Detection frequency		Measured concentration		Cumulative risk	
Location	Time period	Kendall's Tau	*p*	Kendall's Tau	*p*	Kendall's Tau	*p*
Skuterud (*N* = 135)	1996–2012	−0.04	0.4719	−0.05	0.3788	−0.01	0.8935
Mørdre (*N* = 113)	1996–2012	0.07	0.2554	0.01	0.8732	0.02	0.7420
Heia (*N* = 96)	1996–2004	−0.34	<0.0001	−0.35	< 0.0001	−0.29	<0.0001
Heia (*N* = 60)	2004–2012	−0.20	0.0273	−0.32	0.0003	−0.44	<0.0001
Vasshaglona (*N* = 135)	1996–2012	−0.21	0.0004	−0.11	0.0520	−0.25	<0.0001
Hotran (*N* = 116)	1996–2012	0.01	0.9152	0.08	0.2347	0.02	0.7770
Time (*N* = 102)	1996–2012	−0.19	0.0059	−0.19	0.0047	−0.29	<0.0001

N, number of months with pesticide analyses of stream water.

Assessment and conclusion by applicant:

The article evaluates data from Norwegian monitoring programs for pesticides to identify trends and future challenges for the Norwegian agriculture. For glyphosate, deficiencies in the monitoring methods were reported and only few information on the active ingredient is reported. Maximum glyphosate concentration of 4 µg/L.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions.

However, the defficiencies in monitoring methods and analyses for glyphosate are not perfectly clear. The article says "The most evident deficiencies in the JOVA analyses concerns the sulfonylurea herbicides and herbicides with glyphosate as the active ingredient."

It is understood that glyphosate and AMPA were therefore only occasionnaly assessed within the monitoring program, and not after 2004 (only 83 samples analysed for glyphosate).

The maximum reported glyphosate concentration is 4 µg/L.

The article is considered reliable with restrictions.

Data point:	CA 7.5/048
Report author	Székács, A., *et al.*
Report year	2015
Report title	Monitoring Pesticide Residues in Surface and Ground Water in Hungary: Surveys in 1990–2015
Document No	Journal of Chemistry, Vol. 2015, 717948, 01.01.2015
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted under GLP/Officially recognised testing facilities (Agro-Environmental Research Institute, National Agricultural Research and Innovation Centre)

Acceptability/Reliability:	Reliable with restrictions

Over 2000 surface, ground and raw drinking water samples have been analyzed in the frame of different monitoring projects in Hungary and watercourses in neighboring countries between 1990 and 2015. Effects of pesticide contamination on ecological farming and drinking water supply have been assessed. Main water pollutant ingredients of agricultural origin in Hungary are herbicides related to maize production. After EU pesticide re-registration, diazinon, atrazine, and trifluralin gradually disappeared as contaminants. High levels of water soluble pollutants (e.g., acetochlor) in surface water result in temporarily enhanced levels in raw drinking water as well. Extreme levels observed for herbicide residues were of agrochemical industrial origin.

Materials & Methods

In this work, a total of 49 pesticide residues and degradation products, belonging to different chemical classes, were monitored in Hungary. Water samples have been collected in the frame of seven monitoring projects in over twenty sampling campaigns between 1990 and 2015. Each sampling campaign had defined objectives and corresponding sampling regimes. In certain sampling campaigns, soils on cultivation fields were also sampled. Selection of target pesticides was done on the basis of their use and persistency. Determination of the selected analytes was performed using solid phase extraction (SPE) of water samples (1000x concentration factor) followed by GC-MS with or without derivatization, while determination of neonicotinoid insecticides was carried out by HPLC and glyphosate was measured by ELISA.

GC Analysis. Analytical sample preparation and GC/MS procedure was a multiresidue pesticide analysis method applied by survey authorities in Hungary and modified and validated in our laboratory. Acidic ingredients, for example, chlorophenoxy acid type herbicides, were eluted from graphitized carbon black SPE cartridges in a second fraction and were then subjected to derivatization to silyl esters using t-butyldimethylsilyl N, N-dimethylcarbamate as silylating agent and trifluoroacetic acid catalyst. GC-MS analysis was performed on a Varian Saturn 2000 workstation equipped with a Varian CP 8200 autosampler (Varian Inc., Walnut Creek, CA, USA). Quantification of the selected pesticides was performed using matrix-matched calibration. The estimated values of the limits of detection (LODs) were in the range 0.4–5.5 ng/L.

HPLC Analysis. Determinations of neonicotinoid type pesticide active ingredients were performed on Younglin YL9100 HPLC system equipped with YL9150 autosampler (Younglin Co., Anyang Korea). Compounds were separated on a C18 column (Agilent Extend-C18, 150 mm × 4.6 mm i.d., 5 μm) equipped with an Agilent Guard column (12.5 mm × 4.6 mm i.d., 5 μm) at 40 degrees. UV detector signals were recorded at λ = 252 nm and λ = 269 nm. Eluent flow rate was 1.0 mL/min during the isocratic elution until 8 minutes (70 : 30 = A : B eluents, A = 90% water: 10% MeOH, B = MeOH). External calibrations based on the results for standard solutions (Pestanal) were used for quantification. If low concentration ranges required, HPLC-MS/MS measurements were carried out on a Bruker AmaZon SL ion trap instrument (Bruker AXS GmbH, Karlsruhe, Germany) operated in the positive electrospray ionization mode, upon SPE preparation of samples. Retention times were 2.42 min for thiamethoxam and 3.38 min for its decomposition product, clothianidin. LOD determined with standard solutions and with UV detector lied at 10 μg/L. External calibration based on the results obtained for 12 standard solutions in the range of concentrations between 10 μg/L and 150 mg/L. Determinations obtained upon SPE (Sep-Pak C18) with standard solutions and with MS/MS detector allowed LODs of 4 ng/L for thiamethoxam and 17 ng/L for clothianidin. Calibration solutions were prepared from a stock solution by dilution with water.

ELISA. As desirable low LODs for glyphosate and AMPA were not achieved even after their labor-intensive extraction followed by derivatization prior to GC-MS analysis, for determination of glyphosate in ground and surface water, an immunoanalytical method, the commercially available ELISA method (PN 500086) by Abraxis LLC (Warminster, PA, USA), was applied. Measurements were carried out in 96-well microtiter plates according to manufacturer instructions. Comparative results with LC-MS or LC-MS/MS demonstrated the reliability of this competitive ELISA method; therefore, we have used it in our monitoring studies. The main drawback of the method is that it does not detect AMPA; therefore, due to the fast decomposition of glyphosate its environmental occurrence can be underestimated. On the other hand a comparative study has established that immunoassay overestimated glyphosate and detected a trace level in a sample deemed uncontaminated by LC-MS/MS.

Results

Nationwide Survey of Pesticide Residues in Surface Water in Hungary. A national survey (Project OMFB 02193/1999; Monitoring of pesticide residues in surface and ground water, 1999–2002) was launched together with the National Service for Plant and Soil Protection (NSPSP) to assess chemical contamination levels in water bases in Hungary, to explore the points of vulnerability, and to identify pesticide residues in surface and ground water throughout the country. An additional aim was to inspect whether chemical loads on the environment decreased due to the introduction and implementation of integrated pest management (IPM) practices and the spread of ecological (organic) agriculture and to indicate whether pesticide contamination occur as point source or diffuse contaminants. Thus, 332 surface and raw drinking water samples were collected at 90 sites in Hungary. The overall numbers of water samples collected and analyzed were 118, 119, and 95 in 2000, 2001, and 2002, respectively. Among these samples 24, 16, and 11 were tap-water samples provided by Wedeco Waterworks Hungary or collected in the region of Vác in 2000–2002, respectively. In the first year of the survey (2000) 32% of water samples were found to be contaminated mainly by acetochlor and atrazine up to the level of 10000 ng/L and prometryn have also been found at lower concentrations (1–10 ng/L). Two point contamination sources of industrial origin were identified in the region of Balatonfüzfö and the Northern Hungarian Chemical Works (Sajoécseg). In 2001, 58% of samples contained pesticide residues above the LODs. Earlier mentioned ingredients showed similar pattern; 36% of samples were polluted by atrazine and among them 3% are at concentrations above 1000 ng/L, whereas the same ratios for acetochlor were 16% and 6%. Thus, acetochlor occurred less frequently, but higher concentrations have been determined. Prometryn was found in 7% of the samples at levels of 100–10000 ng/L. Among other pollutants trifluralin (10–10000 ng/L), metribuzin (100– 1000 ng/L), and terbutryn (10–1000 ng/L) were detected in 1– 3% of samples. Although diazinon was often (36%) found, its levels were usually low (10–100 ng/L). Regarding seasonal variation of residues it is worthy of note that one-third of samples polluted by atrazine and/or diazinon were collected prior to pesticide application, indicating persistency of these active ingredients under appropriate circumstances. The last year of the project (2002) focused on contaminated areas; therefore, 91% of collected samples contained one or more pesticide active compound. Maximum levels for atrazine and acetochlor remained high (over 15000 ng/L and 46000 ng/L) and contamination rates for these ingredients were 44% and 31%, respectively. Prometryn was detected in 18% of samples up to 1270 ng/L. Frequently found diazinon (65%) at levels 10–100 ng/L and in 3% of samples terbutryn (467–1671 ng/L) were determined. Regarding raw drinking water samples there was only a single case when acetochlor has been detected during the first two years. However, in the autumn of 2002, acetochlor contamination in raw drinking water was observed in the region of Vác near river Danube. Its concentration in raw drinking water occurred to be near 100 ng/L, sometimes exceeding the MRL for drinking water in the EU. To our surprise simultaneously collected surface water samples from river Danube contained similar concentration of this ingredient (80 ng/L). Acetochlor contamination of raw drinking water was also detected in Veröce (34–64 ng/L), but here the levels remained under MRL. As the contamination levels in the river were not extremely high, results indicated the pesticide content passed through bank filtration and water treatment (e.g., chlorination) and occurred at unmodified levels in tap water.

Assessment of Point Source Pesticide Contamination in Hungary.
On the basis of results obtained in the nationwide survey, regions of identified point source contamination sites were monitored (Project KvVM-KAC; Revision of pesticide active ingredients regarding environmental assessment and monitoring results, 2003). Sampling was carried out mainly near Lake Velence and in two regions of Lake Balaton (Balatonfüzfö and Tihany). This project, supported by the Hungarian Ministry of Environment and Water, was also connected to the revision of pesticides considering environmental aspects and pesticide residue monitoring data. In the region of Balatonfüzfö extensive sampling was performed (62 samples) in order to assess the extent and severity of earlier detected point source contamination of industrial origin. Additional 21 sites at Lake Balaton, 14 sites at Lake Velence, and 11 sites in Budapest and other regions were sampled. Surface and raw drinking water samples were collected at 80 sites in May and at 28 additional sites in June and August, 2003. Sampling was repeated at

polluted sites in June and/or August. Thus, overall 135 surface and raw drinking water samples were analyzed during the project.

The contamination rate was found to be as high as 61%, and in accordance with earlier results, surface water samples collected in the region of Balatonfüzfö contained high or extremely high levels of atrazine and acetochlor. Maximum concentration of atrazine was 8240 ng/L and 7540 ng/L in surface water and ground water, respectively. The corresponding values for acetochlor were found to be 13950 ng/L and 10070 ng/L, respectively. In addition, acetochlor could be measured in 56% of the tap water samples reaching the level 1075 ng/L. Lower levels of prometryn (up to 1025 ng/L) and terbutryn (up to 605 ng/L) have also been found. The quality of effluent waters originated from the industrial site of Nitrokémia Chemicals Works was of high concern, as contaminated water bodies flow through basins and ponds into stream Séd and then reach Lake Balaton. Concentrations of atrazine and/or acetochlor in these water courses were in the range of 2000–6000 ng/L, and sometimes exceeded the level of 10000 ng/L. Additional 18 sites in the neighborhood showed higher levels for acetochlor probably due to its leaching from contaminated soil around the area of Nitrokémia Works.

Atrazine was not detected and diazinon occurred in a single case at a level of 538 ng/L. In the region of Tihany, the highest concentration was found to be 424 ng/L in surface water, 359 ng/L in Lake Balaton, and unfortunately appeared in a drinking water sample at a level of 249 ng/L (Csopak). South from the point contamination source half of samples from Lake Balaton were contaminated by acetochlor reaching the maximum concentration of 1547 ng/L, whereas 332 ng/L was measured in Channel Sió. A similar pattern was observed at Lake Velence: 316 ng/L was determined in a surface water sample, whereas high contamination rates (88%) were observed in the lake itself with levels up to 702 ng/L and 2970 ng/L as a peak concentration. Comparing the concentrations determined in water samples collected at a certain polluted site in May, July, and September, the levels of acetochlor, terbutryn, and prometryn ingredients decreased and similar tendency have been usually observed for levels of atrazine. High levels for atrazine and acetochlor have been detected due to improper technology applied for washing pesticide containers (Papkeszi). More than half (56%) of the raw drinking water samples collected in this polluted region near to Nitrokémia Works or above LOD. Contamination levels were in the range of 116 to 1075 ng/L.

Transnational Survey of Seasonal Pesticide Contamination in Rivers in the Carpathian Basin.
To assess the extent of pesticide contamination carried by rivers, in given cases through national frontiers (Project HUSK/0901/2.1.2/0076; Agrowater, 2011–2013), samples collected from Danube, Tisza and Vág rivers, streams, Lake Balaton, and other surface waters and some of drinking water samples were analyzed. Samples were collected in February 2011 before pesticide application along the Danube River, and the same sites from Hainburg (Austria) through Bratislava-Komarno (Slovakia) to numerous sampling points in Hungary, Mohács being the most Southern point, were revisited for repeated sampling after pesticide application during a one-month period after the middle of May. Other sites in the catchment area (Tisza, Balaton, and Vág) and tap water have also been sampled. Monitoring was conducted at eleven sampling sites along the river in the winter and at 31 sampling sites in the summer. Monitoring continued in 2012 and 2013, but sampling has been restricted to Danube River (Budapest). Sixteen surface water samples from Danube and 12 tap water samples were taken twice a week in May and June and four additional samples from Lake Velence in the middle of June in 2012. Similar sample collection from Danube has been performed in 2013, but sometimes it had to be cancelled due to flood in the middle of June. Therefore only twelve samples were analyzed in that year. All surface water samples contained traces of some pesticide residues (trifluralin, alachlor, and chlorophenoxy acids) in February indicating their slow degradation and dissipation rate. Withdrawn ingredient, alachlor, could be detected only in the winter sampling regime at low levels (0.7–10.3 ng/L). In the summer sampling regime (May-June) the ratio of surface water samples that exceeded the maximum concentration of 100 ng/L for individual pesticides was 41%, and 18% of samples contained total pesticide residue above 500 ng/L. Regarding the ingredients and the typical levels results were in accordance with those obtained for samples in Békés county earlier. Acetochlor was the most frequently found pollutant. It was present in all but one surface water samples collected in May and June and typically higher concentrations (75–711 ng/L) have been observed in May than in June (23– 162 ng/L). Metolachlor the second most frequently detected ingredient polluted 65% of samples collected and levels in Danube were 31–241 ng/L. No special pattern for pollutants’ concentrations could be observed along the river. Earlier often detected and banned persistent water pollutants also appeared in samples

collected in May and June. Similarly to results found in 2011–2013, atrazine was detected in 13% of samples at levels 17–40 ng/L, in addition trifluralin (25%, 4–31 ng/L) and ethofumesate (19%, 12–27 ng/L) also often occurred. Less frequently diazinon (16%, 6–10 ng/L) and prometryn (10% 7–40 ng/L) were observed.

Results in 2014 and 2015 (Project AD006; Assessment of (bio)chemical, biological main and side-effects of organic microcontaminants of agricultural origin, monitoring, and determination in environmental and biological samples, 2014–2016) showed a similar pattern seen in 2011, but acetochlor the earlier most frequently found pollutant has not been observed, in contrast to metolachlor that was present in 75% surface water samples collected in May and June (45–365 ng/L). No special temporal variation in time for metolachlor concentrations could be observed. Atrazine could be detected in 13% of samples at levels 17–40 ng/L, often occurred trifluralin (25%, 4–31 ng/L) and ethofumesate (19%, 12–27 ng/L). Less frequently were observed diazinon (13%, 6– 10 ng/L) and prometryn (6% 7–40 ng/L). The vast majority of surface water samples (92%) contained neonicotinoids below LOD, while the highest concentrations (10–41 μg/L) were measured from temporary shallow water bodies after rain events in early summer. Only thiamethoxam and its decomposition product clothianidin were detected among neonicotinoids. These levels are in agreement with recent findings reported for neonicotinoids as surface water polluting contaminants.

Ecotoxicological Analysis.
Given surface water contaminants were subjected to targeted ecotoxicological analysis. Thus, special emphasis was given the combined toxicity and ecotoxicity of glyphosate and its formulating adjuvants, as well as to distribution and ecotoxic effects of neonicotinoid active ingredients. Although glyphosate presents lower acute toxicity than other herbicides, its widespread use and difficulties in detection prompts cautious assessment for combination effects as well. It has been evidenced to cause toxicity and genotoxicity in aquatic organisms and amphibians and teratogenicity in amphibians and birds and has been shown to induce endocrine disrupting effects as well, the latter effect being highly synergized by polyethoxylated tallowamine (POEA) and other commonly used formulating agents in glyphosate-based herbicide preparations. As an immediate consequence of the above toxicological and ecotoxicological concerns and as these substances have proven to be persistent under typical application conditions, glyphosate and its metabolite AMPA are required to be regularly monitored in surface and ground waters. Combinational ecotoxicological effects were proven in our hands as well, on various aquatic organisms. Moreover, adjuvant enhanced cytotoxicity has been evidenced on cell lines of animal and human origin. Our preliminary results indicate that a newly emerging pesticide class of neonicotinoids can be found in environmental water samples as well. Sporadically clothianidin was found in ponds near to maize and sunflower crops emerged from treated seeds. These compounds are used mainly as seed dressings, and the portions not uptaken by target crops contaminate the environment. They accumulate in soil and due to their good water solubility they appear in water resources. As neonicotinoids exert systemic action, the active compounds are translocated and distributed throughout the entire plant; therefore, consumption of different parts of plants (pollen, nectar) could be harmful to insects. Novel ways of intoxication for bees have also been explored, that is, water collection from guttation liquid. They appeared in potatoes and high contamination rates were reported for fruits and vegetables, as well as honey samples. Serious bee poisoning events and risk assessment of EFSA in January 2013 led the European Commission to the conclusion that a high risk for bees cannot be excluded except by imposing further restrictions for two years involving withdrawal of authorization of neonicotinoids and ban of treated seeds for different crops. The restriction applies to the use of 3 neonicotinoid active ingredients (clothianidin, imidacloprid, and thiamethoxam) for seed treatment, soil application (granules), and foliar treatment on crops attractive to bees, including certain cereals. Our findings prompted us to expand our investigations to these target compounds as well as to other polar pollutants amendable only by LC-MS analysis.

Discussion
Pesticides residues in surface waters have routinely been detected in nationwide studies. The rate of contaminated (detectable) samples ranged between 2 and 51%. In the period of 1994–2000, the most common contaminants were atrazine (6%), acetochlor (4%), propisochlor (1.5%), metolachlor (1.5%), diazinon (1%), and 2,4-D (1%). Key contaminants were atrazine and to some extent isoproturon, being found in several cases at above 100000 ng/L. Results of the national survey between 1999 and 2002 and other studies on problem areas also indicated diffuse contamination of surface and ground water in

Hungary. Surprisingly high contamination rate, 32–61%, was found in monitoring projects. Two point contamination sources of industrial origin were identified in the region of Balatonfüzfö (Nitrokkfonf Chemicals Works) and Sajóecseg (Northern Hungarian Chemical Works) connected to former pesticide producers. Atrazine and acetochlor were found in soils in Balatonfüzfö (Nitrokémia Ipartelepek) at alarmingly high concentrations reaching 10–400 ng/g; therefore, the levels of these ingredients in surface waters in surroundings, for example, in the Séd stream, exceeded the level of 10000 ng/mL. Extremely high levels were measured around Sajóecseg not only for acetochlor, but occasionally concentrations for atrazine, prometryn, and terbutryn were above 1000 ng/L in the same sample. Sometimes concentrations in soil were as high as ingredient content in formulated pesticides. At these sites due to exceedingly high residue levels phytoremediation is impossible. Point contamination source due to illegal pesticide deposit has also been explored in Gyomaendröd. Apart from these extremities typically more than half of surface and ground water samples contained one or more pesticide active ingredient. Temporal alterations of residue concentrations have been characterized by bimodal pattern. Whereas pesticide contamination in soil samples appeared to be more uniform in time, contamination rates and levels in water are time dependent. As amounts of precipitation strongly influence leaching of pesticides, levels determined depend not only on pesticide application, but also on meteorological conditions. As expected, the highest levels of pesticide pollution appeared in water samples collected in late spring and autumn campaigns but rarely occurred in waters sampled in August. Although high contamination rates have been found, but due to the improvements of analytical methods, low LODs can be achieved for most target compounds and trace levels of contaminants are detected. One of the minimum performance criteria for analytical methods applied for monitoring chemical pollutants corresponds to the limit of quantification (LOQ). According to the WFD, LOQs should be equal or less than 30% of the relevant Environmental Quality Standards (EQSs). Legally only concentrations measured above the MRL are significant and samples containing pollution below the MRL are regarded as pesticide-free by authorities. Independently from toxicological considerations for individual ingredients, MRLs for pesticide residues in drinking water and ground water in the EU have been set to a common standard value (100 ng/L). Directive 2013/39/EU proposed maximum allowable concentrations (MAC) and annual average (AA) for levels of priority compound sand certain other pollutants in inland surface and other surface waters as EQSs. Values were set for a number of pesticides including alachlor, atrazine, simazine, diuron, isoproturon, chlorfenvinphos, chlorpyrifos, endosulfan, trifluralin, hex-achlorocyclohexanes (HCHs), DDT, aldrin, dieldrin, endrin, and isodrin. MAC values for some of detected water pollutants in Hungary are 700 ng/L and 2000 ng/L for alachlor and atrazine, respectively, but for trifluralin no MAC value is applicable. In our surveys, these levels have rarely been exceeded, only in the cases of point contaminations, where higher concentrations were determined for atrazine. In contrast to the above mentioned limits, pesticide-free means zero level of residues for the public, and it is often a source of confusion or contradiction between the authorities and civil society.

The results confirmed that ecological fields could be contaminated *via* irrigation water; therefore, it should also be monitored especially in corn cultivation regions. Although withdrawal of some water pollutants (atrazine in 2007, diazinon in 2008 and trifluralin in 2009) probably improved water quality, the use of certain water resources as irrigation water in ecological farming should/has to be restricted. As it was observed later in project MONTABIO, withdrawal of the above mentioned ingredients resulted in their gradual disappearance. Atrazine could be detected only in samples collected at Gyomaendröd in 2010, while earlier it had been detected in samples from Békéscsaba and Orosháza. Trifluralin often detected as a soil pollutant has, due to its limited water solubility, quite long dissipation time. Therefore, it could be detected in water samples in all years between 2008 and 2010. Diazinon was often found in water samples collected in 2008, not detected in 2009, but in 2010 eight ground water samples contained this insecticide. They appeared even in 2011; thus their dissipation is slow. Frequent occurrence and temporarily high levels of acetochlor, as well as metolachlor, might be related to their use instead of atrazine in Hungary. Detections of acetochlor in surface water probably contributed to its withdrawal in EU in 2012. The temporal pollution "plaques" of herbicide residues in rivers upon broad field application of herbicides pollute potential irrigation water sources and pose risk to the drinking water supply. Concentrations of acetochlor and metolachlor reported in this study are comparable to those found in the Danube River basin in Serbia (80 and 150 ng/L). In contrast to this Serbian study terbuthylazine was not detected in the surveys.

Atrazine was used predominantly as herbicide in maize monocultures in Hungary. In contrast to DDT, which was banned first in the world in Hungary in 1968, atrazine was being used up to the last date possible by derogation measures upon its ban in EU in 2007. It was often detected in the US, for example, in ground water together with other pesticide active ingredients (simazine, metolachlor, etc.). Diazinon insecticide was also banned in 2007. Trifluralin active ingredient is banned in Hungary since 2009; acetochlor used mainly as a herbicide in maize crops was banned in 2012. Some of these compounds are on the list of the 45 priority substances. Atrazine was present at higher levels only in samples belonging to extreme point source contamination. Concentrations at these sites sometimes exceeded the values of 2000 ng/L established by the legislation as the MAC for atrazine in inland surface waters. Its levels in other water samples were far below the MRL, and upon withdrawal, its levels and occurrence frequency seem to decrease. Trifluralin, which is often detected as a water pollutant in our studies at low concentrations due to its poor water solubility, is also listed as priority substance, although with no applicable MAC value. Compared to our findings (19–70 ng/L) lower levels were reported for atrazine (<5 ng/L) from all parts of Danube in August, 2011, but its metabolite desethylatrazine could be detected at levels 5–20 ng/L with maximum levels around Budapest. Regarding chlorophenoxy acid type herbicides 2,4-D is one of the most widely used herbicides in the world and mixtures of mecoprop, dichlorprop, and MCPA are often applied. As our results indicate these compounds often occur in surface water and amounts of 2,4-D can be usually quantified (56–186 ng/L in 2011). Similar results have been reported in a study conducted in August and September, 2011, with limited number of target compounds belonging to pesticides. The highest concentrations for 2,4-D were found in the area around Budapest (∼50 ng/L), whereas in the Austrian-Slovakian part of the Danube and in the downstream part lower concentrations (∼20 ng/L, ∼10 ng/L) were measured. Despite of the fact that glyphosate is the most frequently used herbicide in Hungary, as well as worldwide, there is little known information about its levels in the environment. Due to its fast decomposition and low detectability it is rarely measured. Regarding contamination rates and levels of glyphosate, the great contrast between sampling regimes is explained by differing agricultural locations, and, to a greater extent, catchment area characteristics, resulting in varying leaching or runoff of glyphosate to surface water. Contamination rates and levels found are strongly influenced by amounts of natural precipitation. Glyphosate contamination reported in large scale environmental water contamination studies was similar to our results. Byer *et al*. analyzed over 700 samples in Canada using an ELISA method. Concentrations were above LOD (100 ng/L) in 33% of the samples collected in 2007, with peak values (up to 12000 ng/L) in late spring/early summer and fall. A monitoring study in Norway found frequent occurrence of glyphosate and AMPA in surface water (54% of 540 surface water samples in 1995–1999). Monitoring in Catalonia, Spain, between 2007 and 2010, reported a 41% contamination rate in the ground water samples analyzed. Similar findings were reported in the United States, as well as in Canada in 2004-2005 (21% of 502 samples contained glyphosate or AMPA at very high maximum concentrations of 41 and 30 ng/mL, respectively).

Conclusion

During this period detectable pesticide residues at low concentrations occurred in alarming proportions of the surface water samples analyzed over decades. Hardly were found samples with pesticide residues below the analytical LOD, even in natural protection or recreational areas. Among monitored pesticides, the most frequently found ingredients are mainly used in maize production. High and periodic herbicide residue levels mostly reflect current herbicide usage, while low to moderate levels of certain pesticides (e.g., trifluralin) indicate a general diffuse contamination countrywide. However, high concentrations observed at point sources were not due to agricultural pesticide application but were related to the pesticide production industry. Contamination levels in ecological fields were substantially lower than that of intensively cultivated fields. However, residues are present in organic cultivation and cause exposure due to persistent organic pollutants (POPs) in soil and due to contamination of irrigation water. Occurrence of banned ingredients may indicate illegal pesticide use or slow decomposition in the given environmental matrix. Among often detected water pollutants some ingredients (atrazine, diazinon, and trifluralin) have been withdrawn in the meantime that can improve water quality. However, as the obtained results show, these compounds and their residues can still be detected in environmental matrices due to their slow degradation rate. Observed pesticide residue levels in surface waters correlate with current pesticide applications and rates. The ongoing process of pesticide reevaluation in the EU resulted in reregistration of only 27% of the authorized pesticide active ingredients between 1995 and 2009. In turn, the range of available pesticides registered for crop and horticultural plant protection has substantially changed in Hungary after 2004 as the country became a full member of the EU. Among insecticides and acaricides, as well as fungicides and antimicrobials, numerous active ingredients have been withdrawn and replaced by new types (novel pyrethroid, neonicotinoid insecticides, triazole, and strobilurin fungicides). The most radical changes occurred among herbicides that represent over half of the pesticide market. In addition to several thiocarbamates (EPTC, butylate), major triazines (atrazine, cyanazine, terbutryn, and prometryn) and chloroacetamides (propachlor, alachlor, propisochlor, and acetochlor) have been gradually banned. Moreover, the shrinkage in herbicide active ingredients led to the predominance of glyphosate on the herbicide market with over 30 various currently registered glyphosate-based formulations. However, on the basis of the resulting increase in environmental occurrence and exposure routes of glyphosate, as well as its recent classification in Group 2A (probably carcinogenic to humans) by the International Agency for Research on Cancer glyphosate is likely to face restrictions on its use in the near future, which will, in turn, affect its levels in environmental matrices. Certain replacement (and only later banned) compounds (e.g., acetochlor) occurred as surface water contaminants. Thus, main surface water contaminants were triazines (atrazine, propisochlor), chloroacetamides (acetochlor, metolachlor), and phenoxycarboxylic acids (2,4-D, MCPA) during the late nineties, followed by triazines (atrazine, prometryn, and diazinon) and chloroacetamides (acetochlor) after the turn of the millennium, while glyphosate and neonicotinoids are more frequently detected advancement of analytical techniques.

Assessment and conclusion by applicant:
The article reports monitoring results for pesticide residues in surface and groundwater in Hungary. For Glyphosate a specific analytical method was used as with the methods used for other substances, no reliable LOD’s were achieved. Only limited information on the results for glyphosate were reported. A maximum glyphosate concentration of 1 µg/L was reported.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant’s conclusions. The article is considered reliable with restrictions.

Only limited information on the results for glyphosate were reported. In the full text article, range of concentration for glyphosate were reported as 0.5 to 1 µg/L in surface water samples.

The main information available in the paper are the following:
“The concentration of glyphosate was [..] determined by ELISA method in 42 surface and ground water samples collected from B´ek´es county in Hungary. Half of the 42 surface and ground water samples collected in September 2010 were contaminated by glyphosate at concentrations of 540–980 ng/L. Exceedingly high glyphosate levels (nearly 1000 ng/L) were measured in five ground water samples and significant concentrations (540–760 ng/L) were determined in 16 cases (3 surface and 13 ground water samples).”

Data point:	CA 7.5/049
Report author	Tang, T. *et al.*
Report year	2015
Report title	Quantification and characterization of glyphosate use and loss in a residential area
Document No	Science of the Total Environment 517 (2015) 207–214
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No

Acceptability/Reliability:	Reliable (but concentration in urban runoff and not surface water)

Urban runoff can be a significant source of pesticides in urban streams. However, quantification of this source has been difficult because pesticide use by urban residents (e.g., on pavements or in gardens) is often unknown, particularly at the scale of a residential catchment. Proper quantification and characterization of pesticide loss via urban runoff requires sound information on the use and occurrence of pesticides at hydrologically-relevant spatial scales, involving various hydrological conditions. A monitoring study in a residential area (9.5 ha, Flanders, Belgium) was conducted to investigate the use and loss of a widely-used herbicide (glyphosate) and its major degradation product (aminomethylphosphonic acid, AMPA). The study covered 13 rainfall events over 67 days. Overall, less than 0.5% of glyphosate applied was recovered from the storm drain outflow in the catchment. Maximum detected concentrations were 6.1 µg/L and 5.8 µg/L for glyphosate and AMPA, respectively, both of which were below the predicted no-effect concentration for surface water proposed by the Flemish environmental agency (10 µg/L), but were above the EU drinking water standard (0.1 µg/L). The measured concentrations and percentage loss rates could be attributed partially to the strong sorption capacity of glyphosate and low runoff potential in the study area. However, glyphosate loss varied considerably among rainfall events and event load of glyphosate mass was mainly controlled by rainfall amount, according to further statistical analyses. To obtain urban pesticide management insights, robust tools are required to investigate the loss and occurrence of pesticides influenced by various factors, particularly the hydrological and spatial factors.

Materials and Methods

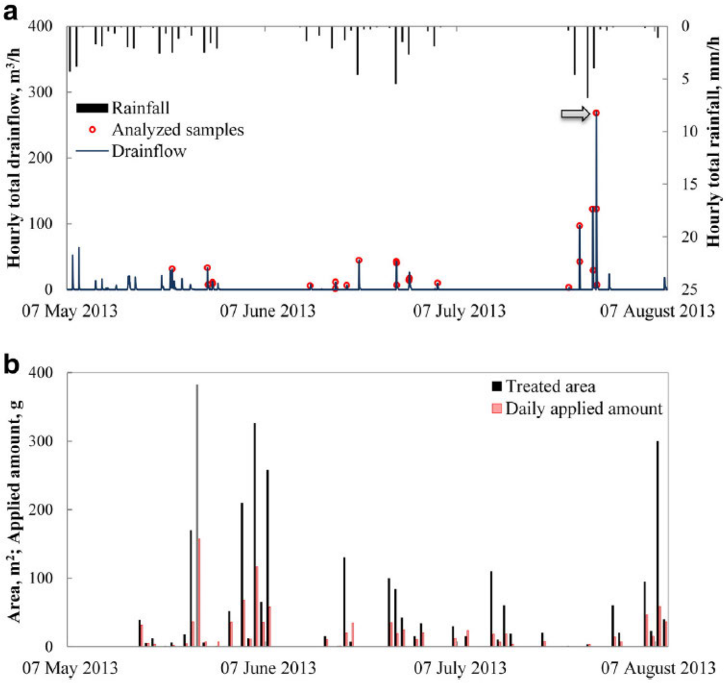
Site description

The residential area was situated in the municipality of Meerhout, northern Belgium (Flemish region). The area was deliberately selected such that it had a separate storm drain system, had no glyphosate inputs from agriculture, industry or government authorities, and represented a typical Belgian residential coverage by non-hard and hard surfaces. Government authorities confirmed that herbicides were not applied by the municipality before and during the study period in the area.

Survey on glyphosate use

The survey was conducted by visits to all the households and questionnaires, between mid-May and early August. 100 households (89%) were interviewed about their general pesticide usage behaviors and asked to participate in the study on 15–18 May 2013. Households, who agreed to participate, were given a questionnaire to record their glyphosate use. The recorded information included date and hour of application; type of surface, surface material and weed level; treated area and treatment methods (spot or areal treatment). Meanwhile, upon their requests, participants were supplied with commercial glyphosate products of either 1 L (Roundup Spray, 8069G/B) or 5 L (Roundup Spray Pump'N Go, 10100G/B). Bottles of the products were weighed before being supplied to and after collection from the participants to determine the total amount used by each household during the study.

Figure 8.5-133: **(a) Rainfall, drainflow and analyzed samples during the study, with indication of the peak discharge (grey arrow, hourly total: 286 m^3/h; minute measurement: 9.1 m^3/min) of the period, and (b) daily treated area (m^2) and daily applied amount (g) of glyphosate, indicating maximum daily treated area and maximum applied amount (gray bar, 382.5 m^2 with 157.4 g)**



Water sampling and chemical analysis

Rainfall was recorded by an ISCO 674 rain gauge that was installed near the outlet of the storm drain. Discharge was measured by an ISCO 750 area velocity module at the outlet. Both rainfall and discharge were recorded at 1-minute intervals, between 7 May and 7 August 2013. Samples were analyzed using liquid chromatography and tandem mass spectrometry (LC–MS/MS), after the standard pretreatment procedure, which include filtration, derivatization and extraction. The limits of quantification (LOQ) were 0.1 µg/L for both glyphosate and AMPA. Stability tests were carried out by spiking water samples from the drain outflow with two glyphosate additions (1 µg/L and 36 µg/L). For feasibility reasons, a selected number of samples were analyzed (Figure 8.5-133a), including 23 event samples from13 rainfall events, 1 background sample and 1 dry-weather sample.

Table 8.5-171: Influencing factors that were statistically analyzed against the concentration and load of glyphosate

Type of factors	Factors	Definition/method of calculation
Factors related to application	Antecedent applied amount	The total amount applied by all residents before a given rainfall event and after the previous event
	Cumulative applied amount	The total applied amount since the start of load calculation at a given time
	Weighted residence time	Average duration between the start of rainfall and the time of all applications before a given rainfall event, weighted by the amount of each application
	Application rate	Antecedent applied amount divided by the total treated area before a given rainfall event
Hydrological factors	Rainfall amount	Depth of rainfall in a given rainfall event
	Antecedent dry period	The duration between the given and its previous rainfall event
	Rainfall intensity	Rainfall amount divided by the rainfall duration in a given event

Data analysis

The mass of glyphosate recovered from the outflow during a given event, referred as event load, was calculated from the measured discharge and concentrations in a time-weighted manner. The event loss rate of glyphosate was subsequently calculated as event load divided by the applied amount of glyphosate between the given and its antecedent rainfall event. For the whole period, the overall loss rate was calculated as total load divided by the total applied amount. The load calculations were done for a period of 67 days between the first (23 May) and last (28 July) event with sample analysis. Glyphosate concentration and event load were analyzed statistically to identify their relationships with a set of predefined controlling factors. The predefined factors mainly included hydrological factors and the pattern of glyphosate use (Table 8.5-171). The dependent variables included glyphosate event load, concentrations of glyphosate and AMPA for the first two analyzed samples from the 13 rainfall events, and the event mean concentration (EMC, event load/event discharge). Via Microsoft Excel 2010, two statistical approaches were applied, bivariate analysis and multivariate analysis, using the correlation analysis and regression analysis, respectively. Linear relationships were assumed during initial bivariate analyses.

Table 8.5-172: Treated area by surface material, as defined in the questionnaire

Type of surface materials	Applied amount		Treated area	
	g	%	m^2	%
Asphalt or tile with cemented jointing	60	5.8%	112	4.0%
Concrete (or clay) slab with sand jointing	654	63.1%	1892	67.6%
Cobblestone with sand jointing	96	9.3%	241	8.6%
Gravel, stone	173	16.7%	425	15.2%
Path on bare soil	9	0.8%	13	0.5%
Vegetated soil	34	3.3%	75	2.7%
Not classified	11	1.0%	40	1.4%
Total	1036	100%	2798	100%

Results and discussion

Hydrology

Field evidence shows no direct runoff flowed to the receiving stream, other than discharge from the storm drain system. The 3-month total discharge corresponds to 12.7% of the total rainfall volume from the study area, with event transfer rates (= event discharge/event rainfall volume) of 6.7%–23.6%. According to the bivariate analyses, the event transfer rate was most significantly affected by rainfall amount, followed by rainfall intensity (Table 8.5-173).

Glyphosate use, detection and loss

Glyphosate use

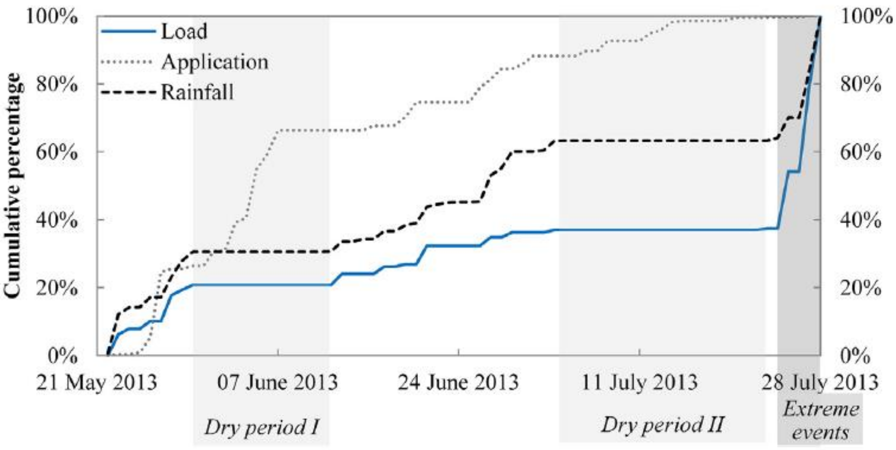
The use by local residents was likely the only source of glyphosate in the study area during the study, based on our surveys. 57 households (51%) participated and 50 households (45%) used the products during the study, though interviews during the first survey showed that only 36 households (32%) used herbicides and 21 households (19%) used glyphosate-containing herbicides on an annual basis. It was therefore assumed that the remaining 49% of households did not use glyphosate during the study. The 45% of households who applied the products was somewhat high, compared with typical residential outdoor use of weed killers. The high percentage in the study was ascribed to the participation of some residents (22 households, 20%) who do not commonly use weed killers due to the provision of free products, and the high number of retired residents (53%) in the study area, which was not the case in generic surveys cited above. Consequently, the 45% herein represents a worst-case scenario for Belgian residential use, though no national data is available for further comparison. As expected, glyphosate was mainly applied on hard surfaces, such as driveways and paths in gardens, and two-thirds of the treated surfaces were concrete slabs (67.6%, Table 8.5-172). During the study, total treated area amounted to approximately 2798 m^2 (Figure 8.5-133b), with a total amount of 1.04 kg. The maximum daily amount (157.4 g, Figure 8.5-133b) was contributed by 8 households on 27 May. 74% of this amount was applied by 3 households, two of which were located close to the drain outlet. Application on this day resulted in the highest glyphosate concentration during the study on the next day (28 May).

Detection of glyphosate and AMPA

The background sample had concentrations of 0.3 μg/L for both glyphosate and AMPA, indicating that glyphosate had likely been applied in 2013 before the study started. However, the glyphosate residues, due to applications before the study started, had limited influence on the detection of glyphosate and AMPA, and the estimation of load and loss rate. According to previous studies, the majority of glyphosate loss takes place within the first 5 mm of rainfall after application and repeated rainfall events further reduce the available residues. While within the 10 days before the survey started, the study area had 4 rainfall events with rainfall amount > 5 mm and another 4 events with rainfall amount between 1 mm and 5 mm (Figure 8.5-133a). These rainfall events can wash off most of the available residues either on landscapes or in the storm drain system. Both glyphosate and AMPA were detected in all analyzed samples, with maximum concentrations of 6.1 μg/L and 5.8 μg/L, respectively. The maximum glyphosate concentration resulted from the large quantity applied (157.4 g) on the previous day and the short distance of the major application sites to the drain outlet, as mentioned above.

The concentrations described here agree with those found in more urbanized catchments, though glyphosate concentration varies by orders of magnitude among different catchments. All measured concentrations in this study were below the predicted no-effect concentration (PNEC, 10 μg/L) for surface water proposed by the Flemish environmental agency, but higher than the EU drinking water standard for individual pesticides (0.1 μg/L). Glyphosate from this residential area is hence likely to have low ecotoxicological significance. An additional sample was automatically taken at the end of the first dry period (Figure 8.5-134), probably related to runoff from irrigation in gardens or from car wash. The sample had glyphosate and AMPA concentration of 3 μg/L and 16 μg/L, respectively. The high concentration of AMPA can be ascribed to the long residence time (19 days), compared with event samples. Because AMPA degrades reportedly slower than glyphosate, it accumulated on hard surfaces or in drainage standing water and resulted in high AMPA levels. Meanwhile, AMPA may have originated from other sources, such as car wash detergents. Car wash detergents may contain phosphonate-containing compounds as chelating agents and AMPA is a key metabolite of such compounds.

Figure 8.5-134: **The evolution of cumulative load primarily follows that of the cumulative rainfall, and extreme events after dry period II (dark gray) significantly contributes to the total load of glyphosate**



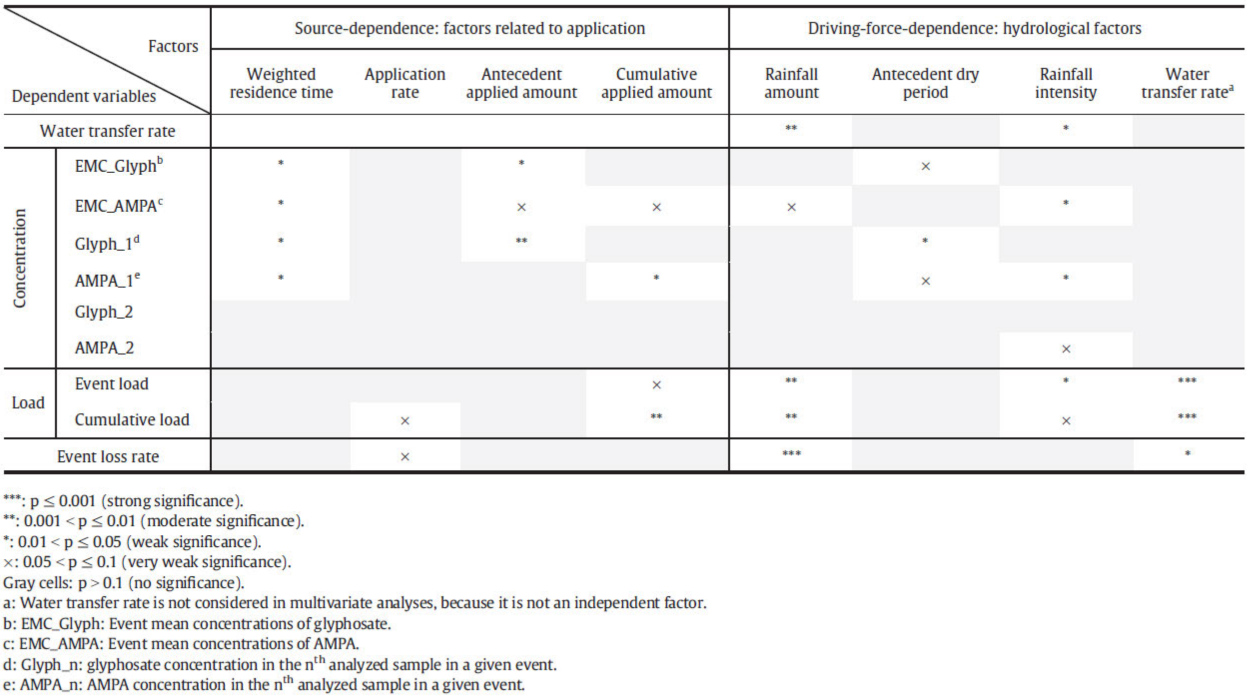
Loads and loss rates

The total glyphosate load from the 14 events (including load from dry-weather discharge) amounted to approximately 3.7 g, 0.45% of the applied amount of glyphosate during the 67 days. Nevertheless, the 3 unanalyzed events also carried glyphosate load and should be considered. Assuming glyphosate concentration therein equaled to the mean measured concentration of all samples (2.32 µg/L), total glyphosate load was 3.9 g, 0.48% of the applied amount. Furthermore, accounting for the loads of both glyphosate and AMPA, loss rates were 0.79% and 0.84%, without and with the inclusion of the unanalyzed events, respectively. Therefore, the overall loss of glyphosate alone is expected to be lower than 0.5%, while including loads from both compounds resulted in a loss rate of less than 1%. Nevertheless, including both compounds can overestimate the total loss, due to other sources of AMPA.

Glyphosate loads and temporal dynamics.

As shown in Figure 8.5-134, the evolution pattern of the cumulative load (as fractions, including load from unanalyzed events) resembled that of cumulative rainfall, but was disproportionate to that of cumulative applied amount, reflecting the dominant influence of rainfall on glyphosate fluxes. Moreover, the cumulative percentage of load was constantly lower than that of rainfall and applied amount, resulting from the substantial contribution of loads by relatively heavy rainfall events after dry period II (dark grey, Figure 8.5-134). The 4 days had one-third of the total rainfall of the 67 days, including the two heaviest rainfall events. This rainfall resulted in two-thirds of the glyphosate load of the period, despite that the antecedent applied amount was very limited. The result implies that a high proportion of retained glyphosate can be washed off from the applied sites during heavy rainfall events. Considering that more than 90% of the treated areas were hard surfaces (Table 8.5-172), this highlights the importance of heavy rainfall events in glyphosate loss from hard surfaces.

Table 8.5-173: Levels of significance by bivariate correlation analysis of the factors influencing the concentration, event load and loss rate of glyphosate



Dependent variables	Factors	Source-dependence: factors related to application				Driving-force-dependence: hydrological factors			
		Weighted residence time	Application rate	Antecedent applied amount	Cumulative applied amount	Rainfall amount	Antecedent dry period	Rainfall intensity	Water transfer rate[a]
Water transfer rate						**		*	
Concentration	EMC_Glyph[b]	*		*			×		
	EMC_AMPA[c]	*		×	×	×		*	
	Glyph_1[d]	*		**			*		
	AMPA_1[e]	*			*		×	*	
	Glyph_2								
	AMPA_2							×	
Load	Event load				×	**		*	***
	Cumulative load		×		**	**		×	***
Event loss rate			×			***			*

***: $p \leq 0.001$ (strong significance).
**: $0.001 < p \leq 0.01$ (moderate significance).
*: $0.01 < p \leq 0.05$ (weak significance).
×: $0.05 < p \leq 0.1$ (very weak significance).
Gray cells: $p > 0.1$ (no significance).
a: Water transfer rate is not considered in multivariate analyses, because it is not an independent factor.
b: EMC_Glyph: Event mean concentrations of glyphosate.
c: EMC_AMPA: Event mean concentrations of AMPA.
d: Glyph_n: glyphosate concentration in the nth analyzed sample in a given event.
e: AMPA_n: AMPA concentration in the nth analyzed sample in a given event.

Loss rates

Since we did not consider the glyphosate residues before the antecedent rainfall event, the event loss rates calculated in our study are expectedly higher than the actual rates and considered worst-case scenarios. Event loss rates ranged from 0.04% to 23.36%, though the overall loss rate was below 0.5%. The widely-varying rates confirm the need to cover a wide range of rainfall events to better estimate and characterize glyphosate loss. Notably, the percentage loss referred herein resulted from glyphosate attenuation and retention not only on land surfaces, but also in the storm drain system. The overall loss rate (<0.5%) agrees with previous glyphosate studies in urban catchments, but is considerably lower than direct loss from hard surfaces or roadsides. Many reasons can explain the low loss rate in this study and other field studies. In this study, major reasons included the relatively high percentage of permeable surfaces, high fraction of concrete blocks as application sites, and strong adsorption of glyphosate onto concrete and deposits. In this study, more than 90% of treated areas were hard surfaces, such as sidewalks and driveways (Table 8.5-172). First, some hard surfaces are connected to permeable surfaces, such as front gardens. Glyphosate runoff can be routed to permeable surfaces, retained and infiltrated thereon, as confirmed by the low water transfer rate. Second, the majority of treated surfaces (63%) are made of small concrete slabs with sand jointing.

Concentration of glyphosate and AMPA

Based on the bivariate analyses, glyphosate concentrations, particularly those of the 1st analyzed samples and EMCs, were mainly influenced by antecedent applied amount, weighted residence time and antecedent dry period (with decreasing level of significance), while AMPA concentrations were mainly influenced by rainfall intensity, weighted residence time and cumulative applied amount. The discrepancy reflects the wash-off behavior of glyphosate is probably different from that of AMPA. The former depends mainly on the glyphosate availability, determined by the applied amount and site dissipation as a function of residence time and field conditions. Whereas for AMPA, the strong influence of rainfall intensity implies that AMPA wash-off is associated with wash-off of particulates. Overall, significance levels of the correlations range from weak to moderate. Multivariate analyses of the factors gave unsatisfactory results with model significance $p > 0.01$ and variable significance $p > 0.1$ in all tests ($N = 10$, 7 tests in total, details not shown). Therefore, no dominating factors can be attributed to the concentration variation of glyphosate and AMPA from our dataset. The unsatisfactory predictions indicate that these factors cannot sufficiently explain the concentration dynamics. One important unaccounted factor is the spatial properties of the catchment and application sites, which influenced the hydrological behaviors and the complex interactions among glyphosate, surface runoff and treated surfaces. Therefore, more spatially-explicit considerations are needed for the catchment properties, particularly materials of the treated surfaces and their connectivity to the storm drain inlets or streams.

Event load and loss rate

According to the bivariate analyses, event glyphosate load is mainly influenced by the rainfall amount, intensity and is weakly influenced by cumulative applied amount (Table 8.5-173). The three factors can explain 70% of the variations in the event load ($p = 0.003$, N=13), according to the multivariate analyses. The resulting regression model confirms the significant influence of rainfall amount ($p = 0.002$), but rejects that of rainfall intensity ($p = 0.11$) and cumulative applied amount ($p = 0.42$). There have been no reported studies in which factors contributing to herbicide loss were directly investigated under field conditions. Notably, the regression model is site-specific and the statistical significance should be carefully considered due to the uncertainties originated from load estimation, quantification of the factors and the limited number of events in the statistical analysis. Additionally, a strong correlation ($p < 0.005$) between loss rate and rainfall amount was observed, underlining again the hydrological dominance on glyphosate loss.

Conclusions

This study investigated the use and loss of glyphosate from a typical Belgian residential area, aiming to realistically quantify glyphosate loss via surface runoff related to use by local residents and to investigate the controlling factors. The study covered 13 rainfall events of various amounts and intensities, and provided a representative quantification of glyphosate loss. It is among the few studies that have quantified pesticide loss from residential catchments over a relatively long period (67 days) and addressed the influencing factors under field conditions. Despite that a high number of households used glyphosate during the study, glyphosate was found at concentrations below the surface water PNEC proposed by VMM. The overall loss rate of glyphosate (<0.5%) was substantially lower than loss from hard surfaces at laboratory and plot scales. However, glyphosate load and loss rate varied considerably among rainfall events. The overall low loss is related partially to the high fraction of permeable surfaces and concrete slabs being the main treated surfaces in the study area, whereas variations in event load and loss rate are predominantly determined by rainfall (amount and intensity). Additionally, multivariate analyses suggested that rainfall and application cannot adequately explain the concentration variations. This promotes the need to account for other important factors, such as the surface material and connectivity to the drain inlets of the application sites. For robust analyses of different factors or to obtain management insights, a spatially-distributed hydrological model is beneficial to account for the spatial properties and urban hydrology. To develop such tools, in-depth understanding of pesticide behaviors in urban environments is needed, including how pesticides interact with different surface materials (e.g., asphalt and concrete), and to what extent adsorption and desorption take place and allows for residue wash-off.

Assessment and conclusion by applicant:

The article describes a modelling exercise to quantify and characterize the loss of glyphosate in a residential area to surface waters in Belgium. Overall, less than 0.5% of applied glyphosate was recovered from the storm drain outflow. Maximum detected concentrations were 6.1 µg/L and 5.8 µg/L for glyphosate and AMPA, respectively. The authors concluded that measured concentrations and percentage loss rates could be attributed partially to the strong sorption capacity of glyphosate and low runoff potential in the study area.

The article is considered reliable.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions, the article is considered reliable. It however provides information on the concentrations of glyphosate and AMPA in urban surface runoff samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

The following information from the article can be retained:

This monitoring study was conducted in a residential area (9.5 ha, Flanders, Belgium) to investigate the use and loss of glyphosate and its metabolite AMPA. The study covered 13 rainfall events over 67 days. 23 event samples from13 rainfall events were analysed for glyphosate and AMPA, plus 1 background sample and 1 dry-weather sample.

The article reports the following use of glyphosate: "glyphosate was mainly applied on hard surfaces, such as driveways and paths in gardens, and two-thirds of the treated surfaces were concrete slabs (67.6%). During the study, total treated area amounted to approximately 2798 $m^{2,}$ with a total amount of 1.04 kg".

Field evidence shows no direct runoff flowed to the receiving stream, other than discharge from the storm drain system.

Overall, less than 0.5% of glyphosate applied was recovered from the storm drain outflow in the catchment. Both glyphosate and AMPA were detected in all analyzed samples, with maximum concentrations of 6.1 µg/L and 5.8 µg/L, respectively. The maximum glyphosate concentration resulted from the large quantity applied (157.4 g) on the previous day and the short distance of the major application sites to the drain outlet.

It is also worth noting that "An additional sample was automatically taken at the end of the first dry period, probably related to runoff from irrigation in gardens or from car wash. The sample had glyphosate and AMPA concentration of 3 µg/L and 16 µg/L, respectively. The high concentration of AMPA can be ascribed to the long residence time (19 days), compared with event samples."

Data point:	CA 7.5/050
Report author	Gasperi, J. *et al.*
Report year	2014
Report title	Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric contributions for a wide range of contaminants in three French sites
Document No	Environmental Science and Pollution Research (2014) 21:5267-5281
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

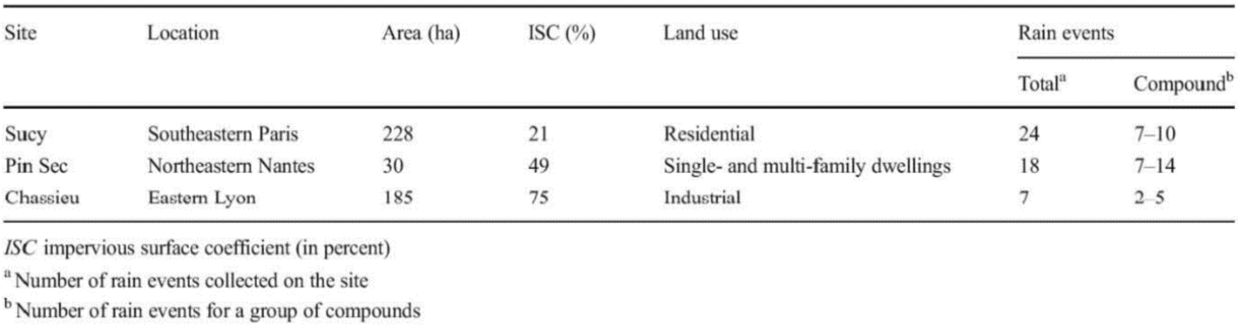
This study is aimed at: (a) providing information on the occurrence and concentration ranges in urban stormwater for a wide array of pollutants ($n = 77$); (b) assessing whether despite the differences between various catchment areas (land use, climatic conditions, etc.), the trends in terms of contamination level are similar; and (e) analyzing the contribution of total atmospheric fallout (TAF) with respect to sources endogenous to this contamination. The studied contaminants include conventional stormwater contaminants (polycyclic aromatic hydrocarbons (PAHs), Zn, Cu, Pb, etc.), in addition to poorly or undocumented pollutants such as nonylphenol and oetylphenol ethoxylates (NPnEO and OPnEO), bisphenol A (BPA), polybrominated diphenyl ethers (PBDEs), a wide variety of pesticides, and various metals of relevance (As, Ti, Sr, V). Sampling and analysis were performed using homogeneous methods on three urban sites with different land use patterns located in three distinct French towns. For many of these pollutants, the results do not allow highlighting a significant difference in stornmwater quality at the scale of the three urban sites considered. Significant differences were, however observed for several metals (As, Cr, Cu, Ni, Sr and Zn), PAHs, and PBDEs, though this assessment would need to be confirmed by further experiments. The pollutant distributions between dissolved and particulate phases were found to be similar across the three experimental sites, thus suggesting no site dependence. Lastly, the contributions of TAF to stormwater contamination for micropollutants were quite low. This finding held true not only for PAHs, as previously demonstrated in the literature, but also for a broader range of molecules such as BPA, NPnEO, OPnEO and PBDEs, whose high local production is correlated with the leaching of urban surfaces, buildings, and vehicles.

Materials and Methods

Site description and sampling procedure

Three urban catchment areas, one on each observatory, were considered in this study, i.e., Sucy in Paris, Pin See in Nantes, and Chassieu near Lyon. These areas are all drained by conventional separate storm sewers (Table 8.5-174). They range from 30 to 228 ha, and their impervious surface coefficients vary between 27% (Sucy) and 75% (Chassieu). Heavy traffic loads are reported in Sucy. On each site, total atmospheric fallout (TAF) and stormwater at the catchment outlet were simultaneously collected. Depending on the site, between seven and 24 events were sampled (Table 8.5-175).

Table 8.5-174: Urban catchment characteristics and description



Site	Location	Area (ha)	ISC (%)	Land use	Rain events	
					Total[a]	Compound[b]
Sucy	Southeastern Paris	228	21	Residential	24	7–10
Pin Sec	Northeastern Nantes	30	49	Single- and multi-family dwellings	18	7–14
Chassieu	Eastern Lyon	185	75	Industrial	7	2–5

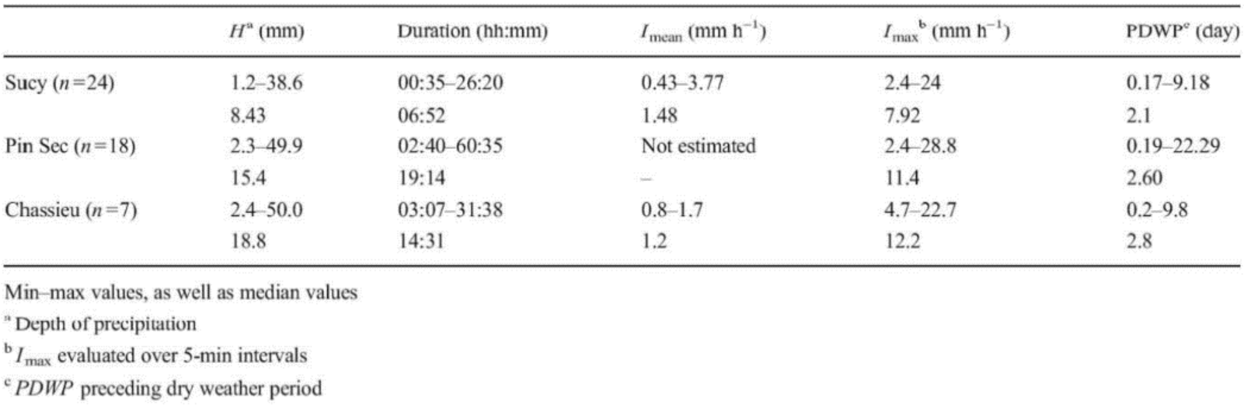
ISC impervious surface coefficient (in percent)

[a] Number of rain events collected on the site

[b] Number of rain events for a group of compounds

Sampling was conducted over a 23- month period (from July 2011 to May 2013). Due to the large volumes required for these analyses (more than 20 1 for all pollutants in order to obtain suitable TSS masses for the particulate phase), it was not possible to analyze all contaminants during each single rain event. Two sampling configurations were thus deployed on each site: one for APnEO, polybrominated diphenyl ether (PBDE), and pesticide monitoring and another configuration for PAH, glyphosate, AMPA, and metal monitoring. Hence, between two and 14 events were sampled for a given family of compounds on a given catchment (Table 8.5-174). The number of rain events considered for each family and each catchment is listed in the individual result tables. The main characteristics of these events, including precipitation depth (*H*, in millimeters), mean intensity over the rain event and maximum 5-min intensity (I_{mean} and I_{max}, in millimeters per hour), and preceding dry weather period (PDWP; in days), are shown in Table 8.5-175. These rain events feature relatively low rainfall intensities, with no extreme rainfall amounts collected. Precipitation depth (from 1.2 to 50 mm) and duration (00:35 to 60:35) both cover wide ranges. To avoid contamination or sorption, TAF was collected in a l-m^2 stainless steel collector for organic pollutants and two 0.5-m^2 plastic collectors for metals and glyphosate. TAF values were measured for the period spanning the studied rain event and the preceding dry weather period. Atmospheric collectors were set up on rooftops at two sites and/or away from potential local sources, such as heavy road traffic, on all three sites. At the catchment outlet, stormwater was sampled using automatic samplers equipped with Teflon® pipes and plastic or glass bottles; samples were then controlled through a flowmeter in order to derive flow proportional EMC.

Table 8.5-175: Rain event characteristics on the three study sites (min-max and median values)



	H^{a} (mm)	Duration (hh:mm)	I_{mean} (mm h^{-1})	$I_{\mathrm{max}}{}^{b}$ (mm h^{-1})	PDWP^{c} (day)
Sucy (n=24)	1.2–38.6	00:35–26:20	0.43–3.77	2.4–24	0.17–9.18
	8.43	06:52	1.48	7.92	2.1
Pin Sec (n=18)	2.3–49.9	02:40–60:35	Not estimated	2.4–28.8	0.19–22.29
	15.4	19:14	–	11.4	2.60
Chassieu (n=7)	2.4–50.0	03:07–31:38	0.8–1.7	4.7–22.7	0.2–9.8
	18.8	14:31	1.2	12.2	2.8

Min–max values, as well as median values

[a] Depth of precipitation

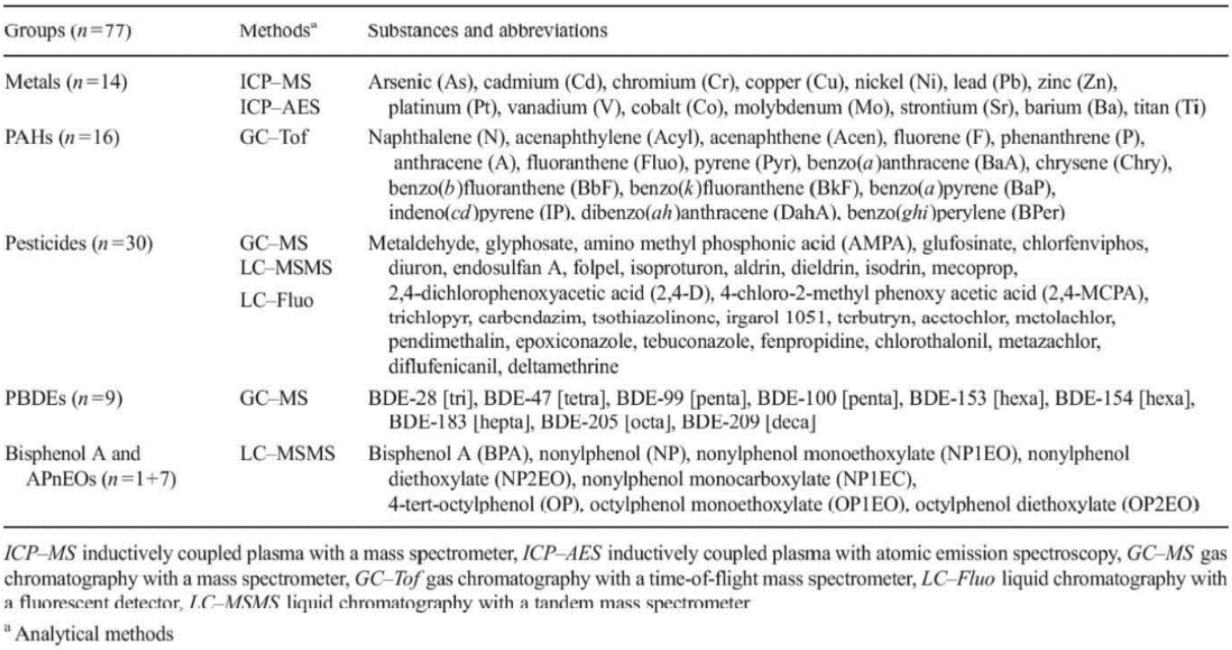
[b] I_{max} evaluated over 5-min intervals

[c] *PDWP* preceding dry weather period

Conventional water quality parameters and pollutants analyzed

Conventional water quality parameters, such as total suspended solids (TSS) and total dissolved and particulate organic carbon (TOC, DOC, and POC), were analyzed for each rain event collected in terms ofTAF and stormwater. A total of 77 pollutants were monitored, including 14 metals, 30 pesticides, 16 PARs, nine PBDEs, bisphenol A (BPA), and seven alkylphenols (APnEO, including nonylphenol (NP) and nonylphenol mono- (NP1EO) and diethoxylates (NP2EO), octylphenol (OP) and octylphenol mono- (OP1EO) and diethoxylates (OP2EO), and nonylphenol acetic acid (NP1EC)). Table 8.5-176 provides the full list of targeted molecules, the analytical methods employed, and the usual abbreviations. All compounds were analyzed over both the dissolved and particulate phases in order to evaluate their potential for transfer and further treatment processes. For all organic compounds, the dissolved and particulate phases were analyzed separately and not deduced from the total and dissolved phases because separate extraction of the two phases was found to be essential for an accurate quantification of contaminant levels.

Table 8.5-176: Pollutants analyzed and analytical methods



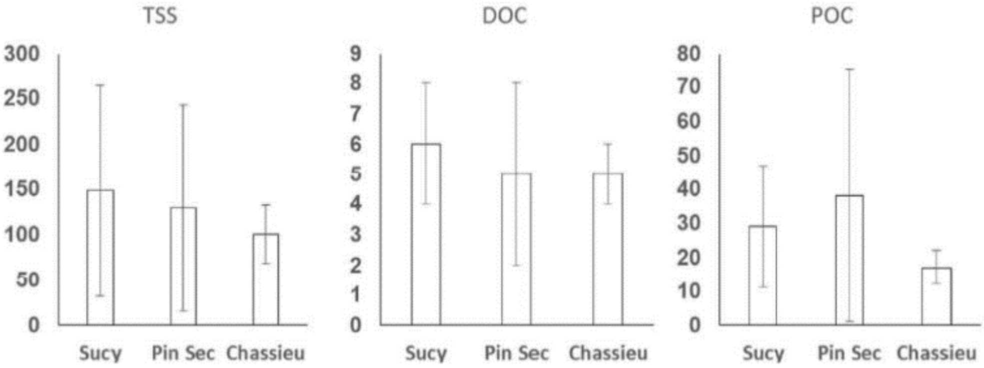
Groups (n=77)	Methods^{a}	Substances and abbreviations
Metals (n=14)	ICP–MS ICP–AES	Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), platinum (Pt), vanadium (V), cobalt (Co), molybdenum (Mo), strontium (Sr), barium (Ba), titan (Ti)
PAHs (n=16)	GC–Tof	Naphthalene (N), acenaphthylene (Acyl), acenaphthene (Acen), fluorene (F), phenanthrene (P), anthracene (A), fluoranthene (Fluo), pyrene (Pyr), benzo(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*a*)pyrene (BaP), indeno(*cd*)pyrene (IP), dibenzo(*ah*)anthracene (DahA), benzo(*ghi*)perylene (BPer)
Pesticides (n=30)	GC–MS LC–MSMS LC–Fluo	Metaldehyde, glyphosate, amino methyl phosphonic acid (AMPA), glufosinate, chlorfenviphos, diuron, endosulfan A, folpel, isoproturon, aldrin, dieldrin, isodrin, mecoprop, 2,4-dichlorophenoxyacetic acid (2,4-D), 4-chloro-2-methyl phenoxy acetic acid (2,4-MCPA), trichlopyr, carbendazim, tsothiazolinone, irgarol 1051, terbutryn, acetochlor, metolachlor, pendimethalin, epoxiconazole, tebuconazole, fenpropidine, chlorothalonil, metazachlor, diflufenicanil, deltamethrine
PBDEs (n=9)	GC–MS	BDE-28 [tri], BDE-47 [tetra], BDE-99 [penta], BDE-100 [penta], BDE-153 [hexa], BDE-154 [hexa], BDE-183 [hepta], BDE-205 [octa], BDE-209 [deca]
Bisphenol A and APnEOs (n=1+7)	LC–MSMS	Bisphenol A (BPA), nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenol monocarboxylate (NP1EC), 4-tert-octylphenol (OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO)

ICP–MS inductively coupled plasma with a mass spectrometer, *ICP–AES* inductively coupled plasma with atomic emission spectroscopy, *GC–MS* gas chromatography with a mass spectrometer, *GC–Tof* gas chromatography with a time-of-flight mass spectrometer, *LC–Fluo* liquid chromatography with a fluorescent detector, *LC–MSMS* liquid chromatography with a tandem mass spectrometer

[a] Analytical methods

As regards the analytical methods employed, metals were analyzed by inductively coupled plasma (ICP)-mass spectrometry for the most part or by inductively coupled plasma with atomic emission spectroscopy for Zn. All organic pollutants were analyzed by either gas or liquid chromatography with a fluorescence detector or with a simple, tandem, or time-of-flight mass spectrometer for both the dissolved and particulate tractions. All pollutants were quantified using internal standards. To avoid analytical bias, all analyses for a given class of contaminant were conducted by the same reference laboratory. Field blank results indicate no particular contamination from sampling devices and/or sample pre-treatment procedure for most pollutants monitored (*n* = 77). A low contamination by nonylphenol could, however, be observed (<5 ng/L), but this value was far less than levels found in TAF or stormwater.

Figure 8.5-135: Concentrations (mean ± SD, in milligrams per liter) of conventional water quality parameters for stormwater on the Suey (*n* =24), Pin Sec *(n* = 18), and Chassieu *n* = 7) catchments



Result interpretation methodology

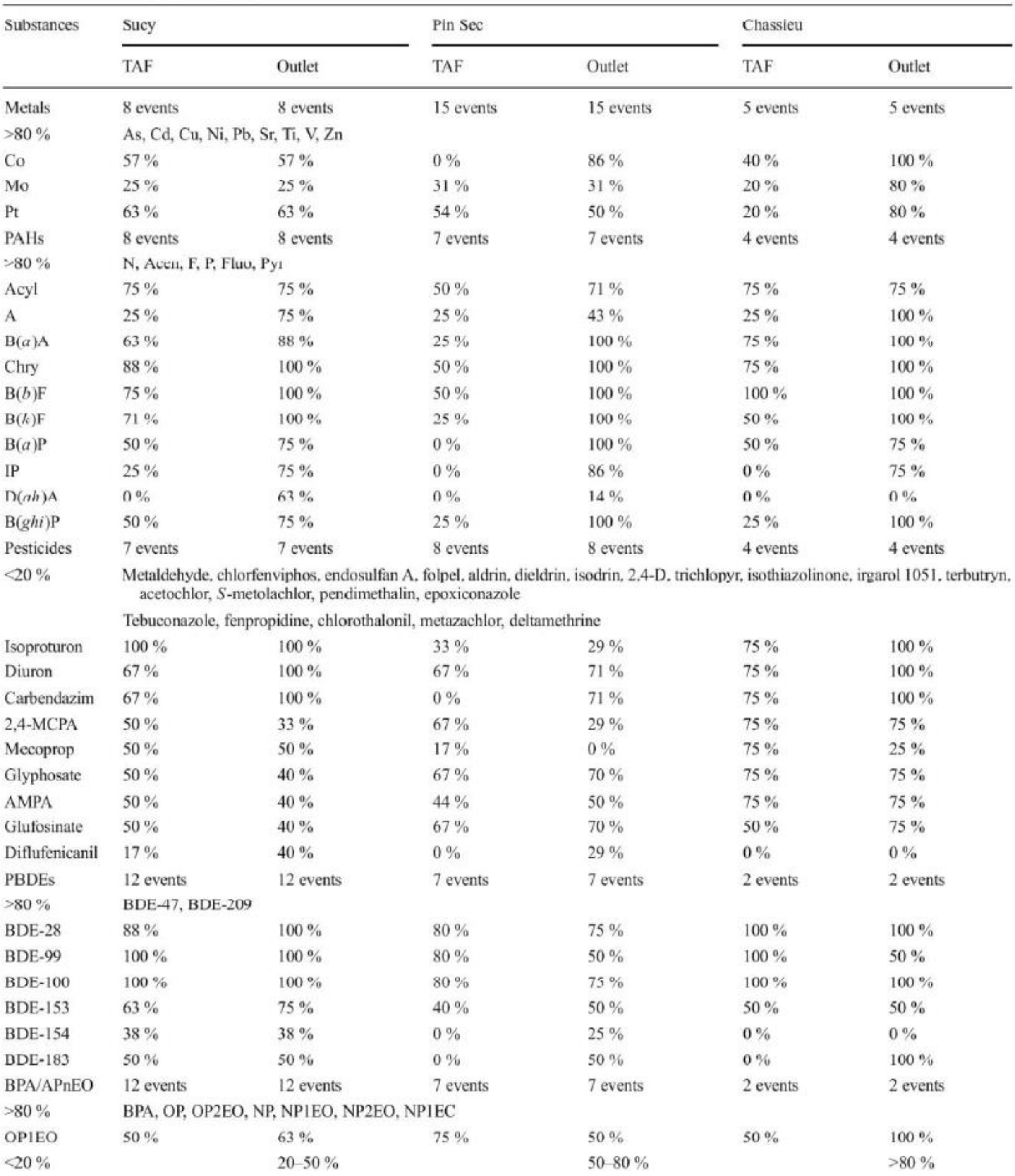
Concentrations will be compared first across study sites and then to data from the literature, i.e., NURP database for the USA and QASTOR database in France. To compare sites, the statistical distribution of stormwater EMC data for each site will be assessed. In this study, log-normal distributions have been tested at 5% significance levels hence both the mean and standard deviation (SD) of EMCs (estimated distribution) have therefore been calculated first in log space and then transformed into arithmetic space. Based on similar methodology, the statistical distributions of each pollutant EMC will be evaluated and the differences in pollutant EMCs across sites assessed using the Kruskal-Wallis test at 5%. For pollutants showing site-to-site differences, individual site concentrations will be presented. When no difference has been identified, data from all three sites will be pooled and global statistical parameters provided. The last parts will present the distribution of pollutants between the dissolved and particulate phases, as well as the contributions of total atmospheric fallout to stormwater contamination.

Results and discussion

Conventional water quality parameters

Conventional water quality parameters (TSS in milligrams per liter, DOC and POC in milligrams of C per liter) are provided in Figure 8.5-135. On each site, EMCs for TSS, DOC, and POC are log-normally distributed (Shapiro-Wilk test, α = 0.05, *W*=0.93 for Sucy and Pin Sec, *W*=0.79 for Chassieu), and no significant differences appear across the three sites (Kruskal-Wallis test, α =0.05, *p* value=0.478, 0.167, and 0.102 for TSS, DOC, and POC, respectively).

Table 8.5-177: Occurrence (in percent) of pollutants in TAF and stormwater



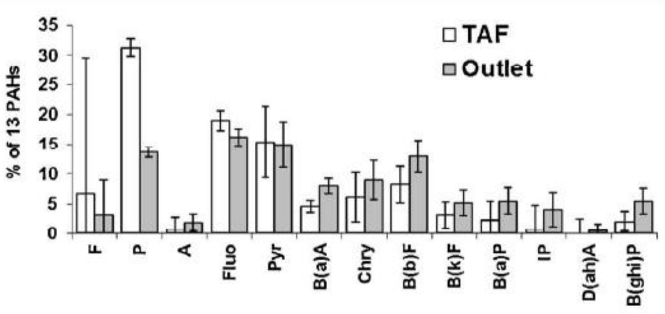
Substances	Sucy		Pin Sec		Chassieu	
	TAF	Outlet	TAF	Outlet	TAF	Outlet
Metals	8 events	8 events	15 events	15 events	5 events	5 events
>80 %	As, Cd, Cu, Ni, Pb, Sr, Ti, V, Zn					
Co	57 %	57 %	0 %	86 %	40 %	100 %
Mo	25 %	25 %	31 %	31 %	20 %	80 %
Pt	63 %	63 %	54 %	50 %	20 %	80 %
PAHs	8 events	8 events	7 events	7 events	4 events	4 events
>80 %	N, Acen, F, P, Fluo, Pyr					
Acyl	75 %	75 %	50 %	71 %	75 %	75 %
A	25 %	75 %	25 %	43 %	25 %	100 %
B(*a*)A	63 %	88 %	25 %	100 %	75 %	100 %
Chry	88 %	100 %	50 %	100 %	75 %	100 %
B(*b*)F	75 %	100 %	50 %	100 %	100 %	100 %
B(*k*)F	71 %	100 %	25 %	100 %	50 %	100 %
B(*a*)P	50 %	75 %	0 %	100 %	50 %	75 %
IP	25 %	75 %	0 %	86 %	0 %	75 %
D(*ah*)A	0 %	63 %	0 %	14 %	0 %	0 %
B(*ghi*)P	50 %	75 %	25 %	100 %	25 %	100 %
Pesticides	7 events	7 events	8 events	8 events	4 events	4 events
<20 %	Metaldehyde, chlorfenviphos, endosulfan A, folpel, aldrin, dieldrin, isodrin, 2,4-D, trichlopyr, isothiazolinone, irgarol 1051, terbutryn, acetochlor, *S*-metolachlor, pendimethalin, epoxiconazole					
	Tebuconazole, fenpropidine, chlorothalonil, metazachlor, deltamethrine					
Isoproturon	100 %	100 %	33 %	29 %	75 %	100 %
Diuron	67 %	100 %	67 %	71 %	75 %	100 %
Carbendazim	67 %	100 %	0 %	71 %	75 %	100 %
2,4-MCPA	50 %	33 %	67 %	29 %	75 %	75 %
Mecoprop	50 %	50 %	17 %	0 %	75 %	25 %
Glyphosate	50 %	40 %	67 %	70 %	75 %	75 %
AMPA	50 %	40 %	44 %	50 %	75 %	75 %
Glufosinate	50 %	40 %	67 %	70 %	50 %	75 %
Diflufenicanil	17 %	40 %	0 %	29 %	0 %	0 %
PBDEs	12 events	12 events	7 events	7 events	2 events	2 events
>80 %	BDE-47, BDE-209					
BDE-28	88 %	100 %	80 %	75 %	100 %	100 %
BDE-99	100 %	100 %	80 %	50 %	100 %	50 %
BDE-100	100 %	100 %	80 %	75 %	100 %	100 %
BDE-153	63 %	75 %	40 %	50 %	50 %	50 %
BDE-154	38 %	38 %	0 %	25 %	0 %	0 %
BDE-183	50 %	50 %	0 %	50 %	0 %	100 %
BPA/APnEO	12 events	12 events	7 events	7 events	2 events	2 events
>80 %	BPA, OP, OP2EO, NP, NP1EO, NP2EO, NP1EC					
OP1EO	50 %	63 %	75 %	50 %	50 %	100 %
<20 %		20–50 %		50–80 %		>80 %

The measured TSS concentrations are in good agreement with those reported on the same sites in previous studies. On the Chassieu catchment, based on on-line turbidity measurements from 2004 to 2011, the average TSS concentration during storm events was estimated at around 75 mg/L. The concentrations found on these sites (mean values of 148, 129, and 100 mg/L) are much lower, however, than those previously reported in France by Saget (1994): a TSS of between 170 and 550 mg/L (with a median of roughly 420 mg/L) on Paris sites (QASTOR database). High concentrations of TSS found by Saget (1994) might reflect poor quality local sewer connections leading to the discharge of wastewater into the separate sewer. Since 1994, considerable EMCs display similar statistical parameters to those reported in the NURP database, i.e., a mean and median TSS concentration of approximately 174 and 113 mg/L, respectively.

Micropollutants

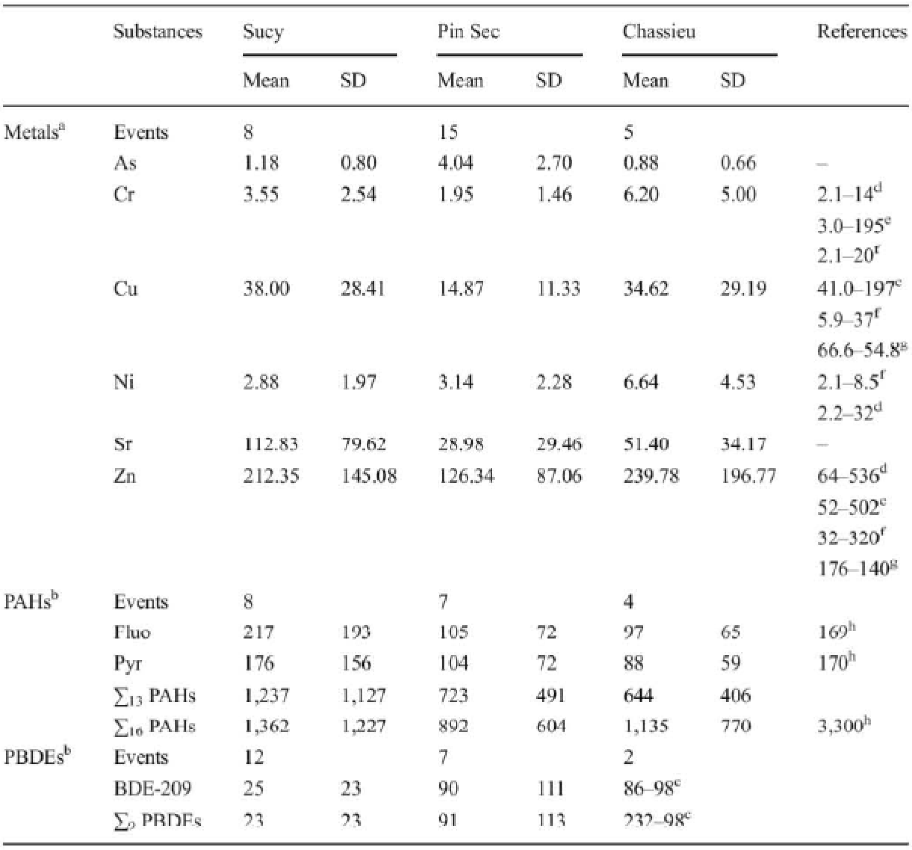
Occurrence of micropollutants on each catchment
The occurrences (in percent) for each pollutant monitored, as well as the number of rain events considered, are reported in Table 8.5-177 for TAF and stormwater. Out of 77 pollutants monitored, between 42 and 48 substances (including metals, PAHs, PBDEs, APnEOs, and BPA) were systematically detected, while 20 to 25 substances exhibited occurrence rates of less than 25%.

Figure 8.5-136: PAH fingerprints (in percent, mean ± SD) in TAF and stormwater at the catchment outlet



Overall, the occurrence profiles were quite homogenous across the three sites, except for some pesticides or low-level compounds. Out of 14 metals monitored, almost all were systematically detected in TAF and stormwater at each catchment outlet, except for Co, Mo. and Pt. As regards their occurrence rates, no clear difference appeared from atmosphere to catchment outlet. It would therefore appear that the 14 trace metals analyzed within the scope of this survey were ubiquitous in both atmospheric deposition and stormwater, with no significant differences across the three sites. For Co, Mo, and Pt, the levels in TAF and runoff were below their detection limits. For PAHs, six compounds (N, Acen, F, P, Fluo, and Pyr) were systematically observed in TAF and stormwater regardless of the site considered. Regardless of the site under investigation, the PAH fingerprints were quite homogenous from one rain event to the next and from one site to the next. Yet, as illustrated in Figure 8.5-136, TAF and stormwater present different PAH fingerprints. PAH patterns for TAF: are characterized by the predominance of low molecular weight PAHs (LMW; two to four aromatic rings) compared to heavy molecular weight PAHs (HMW; i.e., five to six aromatic rings) as attested by a mean LMW/HMW ratio of approximately 12. This difference traduces direct deposition on urban surfaces of HMW PAHs emitted by either combustion (vehicle exhaust) or petroleum sources (rubber tires, oil leakage, asphalt materials) whereas the LMW PAHs can be transported over large distance via the atmosphere, as, in urban context, the PAH distributions in stormwater reflect a mixture of pyrolytic and petrogenic contamination.

Table 8.5-178: Pollutant concentrations (mean ± SD) in stormwater Substances Sucy displaying site-to-site differences

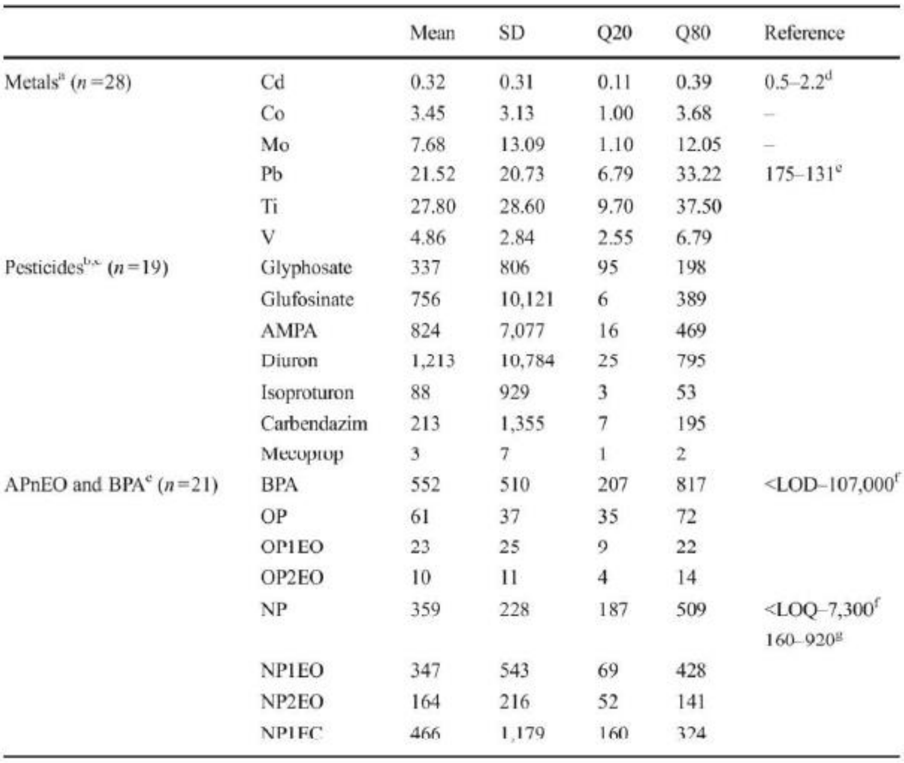


	Substances	Sucy		Pin Sec		Chassieu		References
		Mean	SD	Mean	SD	Mean	SD	
Metals[a]	Events	8		15		5		
	As	1.18	0.80	4.04	2.70	0.88	0.66	–
	Cr	3.55	2.54	1.95	1.46	6.20	5.00	2.1–14[d] 3.0–195[e] 2.1–20[f]
	Cu	38.00	28.41	14.87	11.33	34.62	29.19	41.0–197[e] 5.9–37[f] 66.6–54.8[g]
	Ni	2.88	1.97	3.14	2.28	6.64	4.53	2.1–8.5[f] 2.2–32[d]
	Sr	112.83	79.62	28.98	29.46	51.40	34.17	–
	Zn	212.35	145.08	126.34	87.06	239.78	196.77	64–536[d] 52–502[e] 32–320[f] 176–140[g]
PAHs[b]	Events	8		7		4		
	Fluo	217	193	105	72	97	65	169[h]
	Pyr	176	156	104	72	88	59	170[h]
	$\sum_{13}$ PAHs	1,237	1,127	723	491	644	406	
	$\sum_{16}$ PAHs	1,362	1,227	892	604	1,135	770	3,300[h]
PBDEs[b]	Events	12		7		2		
	BDE-209	25	23	90	111	86–98[c]		
	$\sum_{9}$ PBDEs	23	23	91	113	232–98[c]		

[a] Metal concentrations in micrograms per liter, [b] Concentrations in nanograms per liter for organic pollutants, [C] Only two events collected, [d] Lamprea and Ruban 2011a, [e] Rossi (1998), [f] Sabin *et al.* (2005), [g] NURP database, mean and median values, [f] Zgheib *et al.* (2011a, b), median values

Of the 30 pesticides evaluated, 19 compounds broken down into five herbicides (metazachlor, terbutryn, pendimethalin, trichlopyr, and acetochlor), five fungicides (folpel, epoxiconazole, fenpropidine, chlorothalonil, and tebuconazole), six insecticides (chlortenviphos, endosultan, aldrin, dieldrin, isodrin, and deltamethrine), and three algaecides/imolluscicides (isothiazolinone, irgarol 1051, and metaldehyde)-were never detected in stormwater or with an occurrence rate of below 20%, regardless of the catchment considered. The detection limits of most of these compounds lie in the range of 2 - 7 ng/L. Of these compounds, some (such as aldrin and dieldrin) are now banned: The non-detcction may be explained by having been phased out from use in France. In spite of reports surrounding the leaching of additives from recent construction materials, terbutryn, irgarol 1051, and isothiazolinone were also not detected. As a matter of fact seven herbicides (glyphosate. glufosinate and its degradation product AMPA, diuron, isoproturon, mecoprop, and 2,4-MCPA) and one fungicide (carbendazim) were frequently observed in stormwater, and this finding remained independent of the site tested. In general, these compounds exhibited occurrences varying between 20 and 100% in runoff, e.g., mecoprop 0-50%, isoproturon 29- 100%, and 2,4-MCPA 29- 75%. More details on their occurrence rates are provided in Table 8.5-178. A similar trend was observed in TAF. As regards occurrence, slightly higher rates of these herbicides were noted at the scale of larger basins (i.e., Sucy and Chassieu), compared to Pin Sec. Given that the pesticide presence in stormwater is highly dependent on site and peripheral activities, this could suggest that the pesticide use could tend to be more limited and specific on smaller sites. This finding may also reflect the results of the new policy being implemented in the Nantes Metropolitan Area targeting a drastic reduction in pesticide use on public spaces. The Pin Sec catchment is in fact affected by the same kind of this policy. Chassieu, which has, the less restrictive policy in terms of pesticide reduction, shows the higher level of occurrence in TAF and Stormwater for most of the pesticides analyzed.

Table 8.5-179: Pollutant concentrations (mcan ± SD, Q20 and Q80) in stormwater displaying no site-to-site differences



		Mean	SD	Q20	Q80	Reference
Metals[a] (*n* = 28)	Cd	0.32	0.31	0.11	0.39	0.5–2.2[d]
	Co	3.45	3.13	1.00	3.68	–
	Mo	7.68	13.09	1.10	12.05	–
	Pb	21.52	20.73	6.79	33.22	175–131[e]
	Ti	27.80	28.60	9.70	37.50	
	V	4.86	2.84	2.55	6.79	
Pesticides[b,c] (*n* = 19)	Glyphosate	337	806	95	198	
	Glufosinate	756	10,121	6	389	
	AMPA	824	7,077	16	469	
	Diuron	1,213	10,784	25	795	
	Isoproturon	88	929	3	53	
	Carbendazim	213	1,355	7	195	
	Mecoprop	3	7	1	2	
APnEO and BPA[c] (*n* = 21)	BPA	552	510	207	817	<LOD–107,000[f]
	OP	61	37	35	72	
	OP1EO	23	25	9	22	
	OP2EO	10	11	4	14	
	NP	359	228	187	509	<LOQ–7,300[f] 160–920[g]
	NP1EO	347	543	69	428	
	NP2EO	164	216	52	141	
	NP1EC	466	1,179	160	324	

[a] Metal concentrations in micrograms per liter, [b] For pesticides, the site-to-site differences were not tested, [c]oncentrations in nanograms per liter for organic pollutants, [d] Rossi (1998), [e] NURP database, mean and median values, [f] Kalmykova *et al.* (2013), [g] Bressy *et al.* (2012), d10-d90 values

Diuron and glyphosate are used as total herbicides, and their presence in stormwater may be explained by its application on different types of urban surfaces. At the scale of the Paris conurbation and prior to 2008, diuron accounted for about 31 % of urban pesticide use. At present, in spite of its recent ban in France (December, 2008) from phytophannaceutical products, diuron is being increasingly added to building facade paints and renders in order to provide antialga1 and antifungal protection. Glyphosate is widely used by municipalities and home gardeners; this tendency has been verified in a recent survey conducted at Pin Sec, which showed that in spite of information delivered by local authorities, herbicides (and especially glyphosate) are still being used.

Table 8.5-180: Percentage of metals and organic pollutants in the particulate phase of stormwater (mean ± SD)

	<20 %	<50 %	50–80	>80 %
Metals	Sr (13±10)	As (48±18)	Cd (63±30) Mo (63±40) Ni (54±18) V (62±18) Zn (60±23) Cu (73±13)	Co (80±34) Cr (85±11) Pb (94±4) Ti (94±9)
PAHs		N (44+28)	A (60+44) F (70±31)	Acyl (90+37) Acen (82±28) P (84±12) Fluo (93±5) Pyr (93±5) B(*a*)A (100±22) Chry (97±4) B(*b*)F (99±2) B(*k*)F (99±2) B(*a*)P (100±1) IP, d(*ah*)A (100[a]) B(*ghi*)P (99±1)
Pesticides	Diuron (6±41) Glyphosate (14±43)	Glufosinate (43±46) Isoproturon (42±43)		
PBDEs			BDE-28 (71±33), BDE-100 (55±34)	BDE-47 (95±33) BDE-99 (86±42) BDE-209 (99±7)
APnEO and BPA	BPA (18±11) OP1EO (14±23)	OP (45±22) OP2EO (32±16) NP (40±22) NP1EO (39±20) NP2EO (29±17) NP1EC (38±30)		

[a] Detected only in the particulate phase

Based on experimental batch tests conducted on surfaces of varying imperviousness, Blanchoud *et al.* (2007) estimated the transfer coefficients (i.e., the ratio between quantity of pollutants at the catchment outlet and quantity of pollutants input on this catchment) to equal roughly 60% for diuron and 25% for glyphosate. Carbendazim were also reported to be leached from new antifouling paints and renders. Mecoprop and 2,4-MCPA are mainly applied for yards, parks, and railway maintenance.

Out of the nine PBDEs monitored, high occurrence rates were observed for five compounds (BDE-28, 47, 99, 100, and 209) while other congeners (BDE- 153, 154, 183, and 205) were less frequently detected. Due to growing environmental and human health concerns, penta- and octa-BDE and, more recently, deca-BDE have been banned in Europe though they are still being detected. To date, however, no study has focused on their occurrence in runoff. Their presence in runoff was nevertheless anticipated since PBDEs are found in TAF and have commonly been added to building materials, automotive parts, plastics, and electronic equipment. Lastly, BPA and APnEO (NP, NPIEO, NP2EO, NPIEC, OP, OPI EO, and OP2EO) were systematically observed in runoff and TAF. Nonylphenol ethoxylate (NPnEO; 80%) and octylphenol ethoxylate (OPnEO; 20%) are widely used in industrial and domestic applications, such as lubrication, oil additives, detergents, and antistatic agents.

The presence of NP and OP in stormwater had been expected since both compounds are used in paints, concrete, building materials, asphalt, and certain vehicle parts. Nonylphenol acetic acid (NPI EC), which is a degradation product of NPnEO, is also frequently identified in both matrices. BPA is primarily used as a monomer in the manufacturing of polycarbonate plastics, renowned for its high resistance to shocks and temperature (e.g., plastic windows, car bumpers), as well as in epoxy resins. BPA is also an admixture introduced during the production of PYC, varnishes, and paints and in the formulation of some car products (brake fluid, tires).

Concentration ranges of pollutants in Stormwater
The statistical parameters of EMC distributions are indicated in Table 8.5-178 for pollutants that display site-to-site differences and Table 8.5-179 for the other pollutants.

Metals - From an overall standpoint, metal EMC ranges varied by one or more orders of magnitude from one sample to another. It should be highlighted that the INOGEV project has contributed new information on the elements As, Co, Mo, Pt, Sr, Ti, and V, which had seldom been reported in the literature previously. For Mo (1 - 12 µg/L, Q20 and Q80), CO (1 - 3.5 µg/L), Pb (7- 35 µg/L), V (3- 7 µg/L), Ti (10-37 µg/L), and Cd (0.12- 0.42 µg/L), our results do not indicate any site-to-site differences at the scale of the three urban sites studied. Statistical parameters of the EMC distribution are reported in Table 8.5-179. For As, Cu, Cr, Ni, Zn, and Sr, differences between sites appeared and concentrations on each site are given in Table 8.5-178. Higher Cr and Ni concentrations were found at Chassieu, most likely as a result of local industrial activities. The highest Cu. Zn. Sr. and Ti concentrations were reported at Sucy. Interestingly, these metals are known to originate from vehicle brake linings and tires, thus suggesting that differences could be highly correlated with traffic density. Initial estimations actually revealed significantly different traffic densities on each site. The Zn contamination might also be attributed to leaching from roofs, gutters, street fumiture, etc. The higher Ni and Cr concentrations measured at Chassieu could be explained by the presence of industries on this catchment, but these concentrations did remain low.

PAHs -The PAH results are discussed on the basis of total concentrations, Whereas no significant difference was found for TAF across the three sites, statistical analyses revealed significant site-to-site differences for total PAH concentrations in stormwater. Moreover, Chassieu (644 ng/L for Σ_{13} PAHs, Table 8.5-179) and Pin Sec (723 ng/L) presented lower concentrations than Sucy (1,237 ng/L). Another interesting point is that even though TSS concentrations vary within the same range on all three sites, the differences observed are primarily tied to the PAH contents of the particles collected. The median PAR content found in Sucy (approximately 19,000 ng/g) far surpasses that reported for Chassieu (6,000 ng/g) or Pin Sec (7,000 ng/g). On the whole, the stormwater concentrations are much higher than those observed in TAF, thus indicating a local production source. No correlation was found between PAHs, TSS, and dissolved and particulate organic carbon levels (Speam1an lest, R^2 <0.3). In addition and based on the limited number of rain events, no seasonal correlation was identified. As previously mentioned for vehicle-derived metals, the contamination in stormwater likely reflects a difference in road traffic density and type from one catchment to another. In accordance with the extensive literature, PAHs are indeed emitted by vehicle traffic via gas exhaust, tire wear, and spilled oil. The highest concentrations were consistently found for Sucy, which is subjected to much higher traffic density. The industrial catchment of Chassieu generated the lowest PAH concentrations, except for the extremely high concentrations of naphthalene measured on some samples. These low PAH concentrations were unexpected, due to the numerous industrial and logistics activities in Chassieu as well as the proximity to Lyon's dense highway corridor, yet they remain consistent with the low traffic density inside the catchment.

Pesticides - Among the most widely detected pesticides, glyphosate (95- 198 ng/L, Q20 and Q80), AMPA (16-469 ng/L), diuron (25- 795 ng/L), and glufosinate (6-389 ng/L) are all non-selective herbicides and were predominantly in stormwater. Isoproturon (3- 53 ng/L) and carbendazim (7- 195 ng/L) were detected at lower concentration levels, while the remaining pesticides (mecoprop, 2,4-D, 2,4-MCPA) did not generally exhibit concentrations reaching 5 ng/L. Given the limited number of rain events for these compounds (from four to eight events, depending on the site), the difference in herbicide concentrations between sites was not statistically tested and instead the data were pooled (Table 8.5-179).

High glyphosate concentrations were measured on Pin Sec, where municipal use of this pesticide is limited. At the scale of our three study sites, it can reasonably be assumed that glyphosate is being used by private gardeners. Diuron and carbendazim were reported to be leached at high concentrations from new antifouling paints and renders. This source would be consistent with the much lower concentrations measured on Chassieu (with industrial –type buildings), compared to Sucy and Pin Sec, though it remains limited to relatively new or recently renovated facades. Despite the ban, dated supplies of diuron-based pesticides might still be in use by private gardeners or it has accumulated in the soils. High herbicide concentrations were occasionally observed (1,500-3,000 ng/L) independent of the site or period under consideration. These high concentrations depend on various factors affecting the quantity of pesticides remobilized, such as the time interval between applications and rainfall, the level of imperviousness of the treated surface, or the characteristics of the rain events.

PBDEs - Of the eight PBDEs detected in runoff, deca-BDE (BDE-209) displayed the highest concentration, in ranging from 23 to 251 ng/L (Q20 and Q80 on the full dataset) and with a median relative contribution to Σ_8 PBDEs of around 90%. The other congeners varied overall within the 0.5- 3.0- ng/L range. For tri- to hepta-BDEs, BDE-47 and BDE-99 were the most abundant congeners, with mean relative abundances of 5 and 3%, respectively. While the PBDE contamination of the atmospheric compartment is known, no experimental data on PBDE levels in stormwater were available. Although no geographical difference was noticed for TAF contamination, significant site-to-site differences were observed for stormwater contamination (Σ_9 PBDE, Kruskal-Wallis test, $\alpha = 0.05$, p value=0.017, Table 8.5-178). This finding suggests that land use and/or building materials applicable to these sites might affect runoff differently. Lower PBDE concentrations were actually found in Sucy, as compared to the other sites. To date, any more comprehensive explanation has not been provided. For all sites under consideration, BDE-209 concentrations at the catchment outlet were significantly higher than those either measured in TAF during this study (0.4-8.6 ng/L) or reported for Sweden in urban areas (2.5- 14.4 ng/L for Σ_8, PBDEs).

Bisphenol A and APnEO - For BPA and APnEO, no site differences were observed (Kruskal-Wallis test, $\alpha = 0.05$, p value = 0.035 for BPA and p value = 0.111 for APnEOs). The statistical parameters associated with their distributions are listed in Table 8.5-179. The mean EMCs of BPA and NP were estimated at 552 and 359 ng/L. For both compounds, these concentrations were much higher than those reported for rainwater in Paris and in the same overall range as results for runoff and landfill leachate in Sweden. On the French national scale, NP levels were also comparable to those reported by Bressy *et al.* (2012), NP and nonylphenol ethoxylates (NP1EO and NP2EO) were predominant, in comparison with OP and octylphenol ethoxylates (OP1EO and OP2EO). In our study, NP tends to exhibit higher concentrations than NP1EO and NP2EO; these findings contrast with the Swedish results. Regardless of the site and rain event considered, the alkylphenol distributions remained fairly homogenous, as characterized by the following order: NP (42±25%>NP1EO (25±11%) ~NP1EC (21±9%>NP2EO (12±4%). For the first time, the presence of NP1EC has been reported in runoff, with concentrations significantly greater than those measured in TAF (<3 ng/L).

Table 8.5-181: Contributions (in percent) of TAF to stormwater pollution (mean ± SD)

	$C_{[\mathrm{TAF}]}/C_{[\mathrm{Outlet}]}<10\ \%$	$C_{[\mathrm{TAF}]}/C_{[\mathrm{Outlet}]}<20\ \%$	$C_{[\mathrm{TAF}]}/C_{[\mathrm{Outlet}]}>20\ \%$
Water parameters	TSS (8±11) POC (9±13)		DOC (25±15)
Metals	As (7±4) Sr (9±7)	Ti (13±24) Pb (11±12) Cu (20±17)	Cu (20±17) Cr (32±53) Ni (32±31) Cd (33±29)
	$\mathrm{Sr}_{\mathrm{Sucy}}$ (3±1) $\mathrm{Sr}_{\mathrm{Chassieu}}$ (5±3) $\mathrm{Zn}_{\mathrm{Sucy}}$ (9±5) $\mathrm{Cr}_{\mathrm{Sucy}}$ (10±5) $\mathrm{Cr}_{\mathrm{Chassieu}}$ (8±6)	$\mathrm{Sr}_{\mathrm{Pin\ Sec}}$ (14±6) $\mathrm{Zn}_{\mathrm{Chassieu}}$ (15±9)	$\mathrm{Zn}_{\mathrm{Pin\ Sec}}$ (86±127) $\mathrm{Cr}_{\mathrm{Pin\ Sec}}$ (55±68)
PAHs	B(*a*)P (4±11) I(*cd*)P (1±4), B(*ghi*)P (4±8)	A (13±34) Fluo (17±19) Pyr (14±14) Chry (13±20) B(*b*)F (14±21) B(*k*)F (11±20) B(*a*)A (11±15)	N (68±32) Acyl (24±25) Acen (40±45) F (28±20) P (26±22)
PBDEs	BDE-47 (6±4) BDE-99 (9±15) BDE-154 (5±6)	BDE 28 (18±24) BDE-100 (16±14) BDE-153 (12±16) BDE-209 (11+19)	
APnEO and BPA	BPA (4±3) NP1EC (4±10) OP (8±5) BPA (4±4)	NP (19±16) NP1EO (18±21) OP1EO (16±21) OP2EO (17±13)	NP2EO (32±21)

$C_{[\mathrm{TAF}]}/C_{[\mathrm{outlet}]}$ concentrations found for total atmospheric fallout/concentrations measured in stormwater at the catchment outlet

Distribution of pollutants between dissolved and particulate phases

The distributions of all pollutants between dissolved and particulate phases are shown in Table 8.5-180. For all pollutants examined, no significant differences across the three sites were remarked, thus suggesting that this distribution is not site-dependent but rather correlated with the physical and chemical properties of the compound under consideration. This assessment could prove useful in the choice of stormwater treatment device. Most metals were mainly bound to the particulate phase (>50%), except for Sr. This tendency was more pronounced for Co, Cr, Pb, and Ti and to a lesser extent for Cu. The remaining metals (As, Cd, Ni, Y, Mo, and Zn) yielded an intermediate behavior since the mean particulate phase ranged from 48± 18% (As) to 63±40% (Mo). In accordance with typical stormwater findings, most organic pollutants studied herein are preferentially associated with particles. Despite the fact that log K_{ow} does not accurately describe the behavior of all pesticides, this coefficient can still be used as an indicator to predict the pollutant distribution between dissolved and particulate fractions. Other parameters however, might also affect the partitioning, e.g., molecular structures and charges.

Contribution of atmospheric deposition to storm water pollution

For each pollutant, the contributions of total atmospheric fallout to stormwater pollution have been calculated. At the scale of the rain event, the ratio between TAF and stormwater concentrations was evaluated; the mean +SD values of this ratio are given in Table 8.5-181. Except for several individual substances, the contributions of TAF were on the whole rather weak and median values generally did not exceed 30 %. For metals and as a result of low concentrations found on all three sites for TAF total atmospheric fallout accounted for less than 20 % of the stormwater pollution for six metals (As, Pb, Sr, Ti, V, and Cu) though in some cases (Cd, Cr, Ni) did exceed 30%. For As, Sr, and V, this contribution did not exceed 10%. Overall, the ratios between TAF and stormwater were quite similar at the scale of these three sites, except for Cr, Sr, and Zn. Differences were readily observed for Cr (55% at Pin Sec vs. 8% and 10% at Chassieu and Sucy), Sr (14% at Pin Sec vs. 5% and 3% at Chassieu and Sucy), and Zn (86% at Pin Sec.

vs. 9% and 15% at Chassicu and Suey). A very high atmospheric Zn contribution was observed on Pin Sec (86± 127%), which was mainly due to the first three campaigns (December 2011 through March 20 12), during which unusually high atmospheric concentrations were measured (122- 537 µg/L). These increased concentrations may be attributed to specific works involving zinc sheets in the vicinity of the sampling device; however, this hypothesis could not be verified. Long-range transportation is rejected as an explanation since TSS did not increase during this period.

For PAHs, PBDEs, APnEO, and BPA, atmospheric contributions remained low, thus confirming a strong local production for all compounds. Except for PAHs and NP, this production has not been highlighted in the literature for such a broad panel of substances. For other families, such as APnEOs and PBDEs, local production from road, urban surfaces, and vehicle leaching would be expected since these compounds are used in building materials and automobile parts. As mentioned for PAHs, the sources of these compounds now need to be investigated more thoroughly. Consequently, samples from street runoff will soon be analyzed as a follow-up to this work.

Conclusion

This paper has been developed as part of the INOGEV project being carried out by the three French Observatories in Urban Hydrology (OPUR, OTHU, and ONEVU) focusing on stormwater quality and intended to deliver the initial conclusions drawn from a new more extensive French dataset. This study has provided, for a wide array of pollutants and three distinct sites featuring distinct land use patterns and contexts, a knowledge and comparison of their occurrence rates and concentration ranges in stormwater with the same experimental procedures for each site. Relevant data have been derived for newly targeted metals (As, Ti, Sr and V) and heretofore poorly documented organic pollutants, such as nonylphenol and octylphenol ethoxylates, PBDEs, certain pesticides, and BPA. Such a database could be used to develop a relevant decision-making aid for urban Stormwater practitioners and watershed managers in evaluating the stormwater contribution to the pollution of receiving waters. For many pollutants, the results obtained during this monitoring program do not highlight any significant difference in stormwater quality across the three urban sites studied, with variability from one site to another being of the same order of magnitude or less than variability from one event to another.

This study has not only confirmed the initial conclusions drawn at the scale of three Paris sites (Zgheib *et al*. 2012 a) but has reinforced them since the urban sites considered in the INOGEV project are more highly contrasted than those initially examined. This study, however, also underscores significant site-to-site differences for several metals (As, Cr, Cu, Ni, Sr, and Zn), as well as for PAHs and PBDEs.

Like for stormwater quality, this study reveals no significant differences in the distribution between dissolved and particulate phases across all sites, which suggests that this distribution is not site-dependent but instead correlated with the physical and chemical properties of the compound being examined. In accordance with typical stormwater observations, most metals were primarily bound to the particulate phase: (a) >50% for As, Cd, Mo, Ni, V, Cu, and Zn and (b) >80% for Co, Cr, Pb, and Ti. for organic pollutants, their distributions between dissolved and particulate phases depend heavily on their chemical and physical properties; moreover, it appears that the octanol-water coefficient (log K_{ow}) of these substances may be used to roughly predict their behavior. Log K_{ow} serves as an empirical predictive approach for easily determining the distributions between dissolved and particulate phases of pollutants, yet the relation between K_{ow} (or another coefficient, like K_{oc} or K_d) and substance distribution in stormwater still requires further investigation.

In conclusion, this study has highlighted that the contributions of TAF were either rather low or very low for quality parameters and micropollutants, with median values not exceeding 30% except for certain individual substances. This extremely relevant finding underscores local production not only for PAHs, as previously demonstrated in the literature, but also for a broader range of substances such as BPA, APnEOs, and PBDEs. This local production is correlated with leaching from urban surfaces, buildings, and vehicles, although their actual sources must now be more thoroughly investigated. In pursuing this work and in addition to the initial conclusions delivered, a deeper analysis between groups of pollutants (correlation trends) will be carried out in order to select representative substances to be studied. Atmospheric and stormwater fluxes at various temporal scales will also soon be evaluated and compared in order to assess the relative contribution of atmospheric inputs. Stormwater quality relative to rain event characteristics will also be studied. Subsequent investigations will rely on developing a methodology and tools for estimating annual stormwater pollutant fluxes at the scale of urban sites based on on-line turbidity measurements.

Assessment and conclusion by applicant:

The article reports the results from a monitoring exercise for micropollutants in total atmospheric fallout (TAF) and stormwater of three French urban catchment areas. Occurrence of glyphosate and AMPA (in percent) were reported in TAF and stormwater. Among other pollutants, the concentrations of glyphosate and AMPA, expressed as mean ± SD, Q20 and Q80 were also reported. The results provide a comprehensive overview on the occurrence of glyphosate and AMPA in the stormwater of urban areas. However, the focus is not on agricultural areas.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

This study provides information on the concentrations of glyphosate and AMPA in stormwater samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

RMS notes that between 7 and 24 events were sampled, but the detailed concentrations results for each event are not reported. Concentration in atmospheric fallout and stormwater for glyphosate among other pollutants are reported as mean ± SD, Q20 and Q80 of the pooled concentrations results of the 3 sites, since the study authors indicate that there were no site-to-site differences in the results (using the Kruskal-Wallis test at 5%). RMS however notices that the calculated standard deviation is quite huge compared to the mean concentration.
These results cannot be related to use of glyphosate in the catchment areas. No indication for seasonal variation is either given.

The study is considered reliable with restrictions

Data point:	CA 7.5/051
Report author	Maillard E., Imfeld G.
Report year	2014
Report title	Pesticide Mass Budget in a Stormwater Wetland
Document No	Environmental Science & Technology 2014, 48, 8603−8611
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Wetlands are reactive landscape zones that provide ecosystem services, including the improvement of water quality. Field studies distinguishing pesticide degradation from retention to evaluate the sink and source functions of wetlands are scarce. This study evaluated based on a complete mass budget the partitioning, retention, and degradation of 12 pesticides in water, suspended solids, sediments, and organisms in a wetland receiving contaminated runoff. The mass budget showed the following: (i) dissolved pesticides accounted for 95% of the total load entering the wetland and the pesticide partitioning between the dissolved phase and the suspended solids varied according to the molecules, (ii) pesticides accumulated primarily in the <250 μm bed sediments during spring and late summer, and (iii) the hydrological regime or the incoming pesticide loads did not influence the pesticide dissipation, which varied according to the molecules and the wetland biogeochemical conditions. The vegetation enhanced the pesticide degradation during the vegetative phase and the pesticides were released during plant senescence. The dithiocarbamates were degraded under oxic conditions in spring, whereas glyphosate and aminomethylphosphonic acid (AMPA) degradation occurred under reducing conditions during the summer. The complete pesticide mass budget indicates the versatility of the pesticide sink and source functions of wetland systems.

Materials and Methods

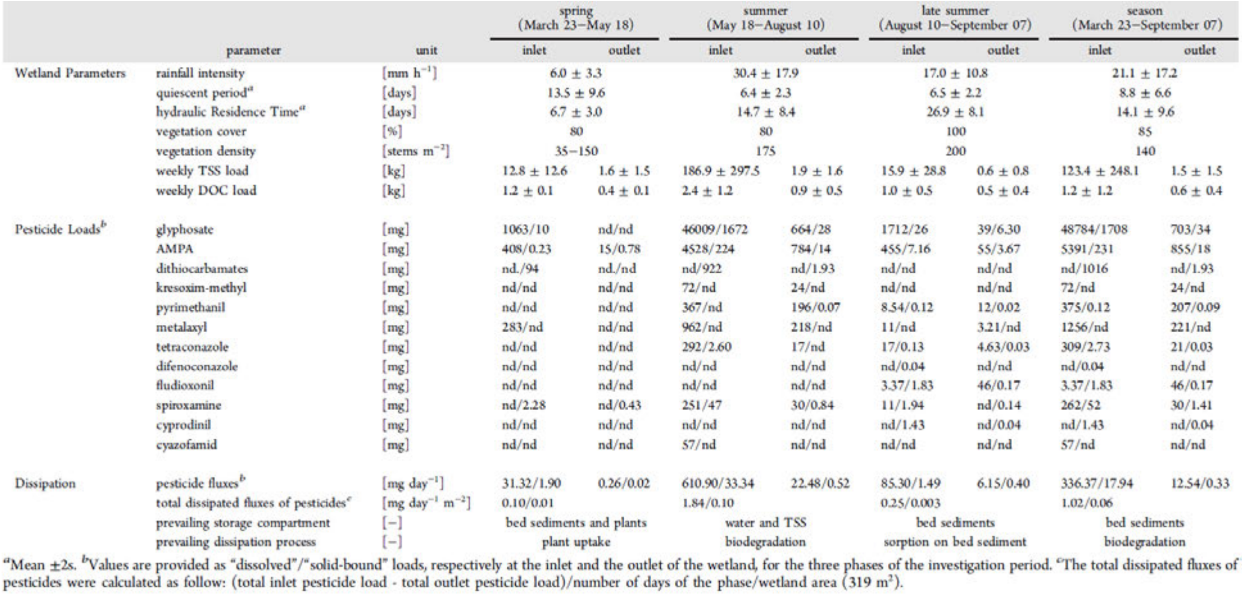
Description of the Stormwater Wetland

The studied stormwater wetland is located at the outlet of a 42.7 ha vineyard catchment in Rouffach (Alsace, France). The daily rainfall and evapotranspiration were measured at a weather station located on the catchment (Meteo France, station no. 68287003).

Sampling of Water, Organisms, and Sediments in the Wetland

The runoff discharges and volumes were continuously monitored from March 23 to September 28, 2011 (i.e.,over 189 days) using bubbler flow modules combined with a Venturi channel at the inlet and a V-notch weir at the outlet of the stormwater wetland. Water samples (300 mL) were collected at the wetland inlet and outlet every 3 m^3 using automatic samplers. Integrative water samples (150 mL) were also collected at the center of the wetland forebay every 2 h to be representative of the forebay water. The detailed hydrological budget is provided in Table 8.5-182. Discrete flow- and time-proportional water samples obtained over a week were combined in single composite samples prior to analysis. Additional sampling campaigns were conducted monthly in the wetland from 23 March (day 0) to 07 September (day 168), 2011 on days 0, 28, 56, 84, 111, 140, and 168 to quantify the pesticides in the wetland compartments, that is, the aqueous phase, TSS, bed sediments, vegetation, algae, and invertebrates. A grid-cell sampling was conducted by dividing the forebay area into four equal rectangular cells (9 × 6 m). The subsamples were collected at the center of each cell, and the four subsamples were pooled to obtain a single composite sample for each wetland compartment. For each sample type and sampling campaign, a portion of the fresh collected composite samples was weighted, dried at 80 °C for 1 week, and weighted again to estimate the (bio) mass of the wetland compartment, and another portion was maintained at -20 °C for chemical analyses.

Table 8.5-182: Hydrological and Pesticide Mass Budget in the Stormwater Wetland (Rouffach, Alsace, France)



			spring (March 23–May 18)		summer (May 18–August 10)		late summer (August 10–September 07)		season (March 23–September 07)	
	parameter	unit	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet
Wetland Parameters	rainfall intensity	[mm h^{-1}]	6.0 ± 3.3		30.4 ± 17.9		17.0 ± 10.8		21.1 ± 17.2	
	quiescent period[a]	[days]	13.5 ± 9.6		6.4 ± 2.3		6.5 ± 2.2		8.8 ± 6.6	
	hydraulic Residence Time[a]	[days]	6.7 ± 3.0		14.7 ± 8.4		26.9 ± 8.1		14.1 ± 9.6	
	vegetation cover	[%]	80		80		100		85	
	vegetation density	[stems m^{-2}]	35–150		175		200		140	
	weekly TSS load	[kg]	12.8 ± 12.6	1.6 ± 1.5	186.9 ± 297.5	1.9 ± 1.6	15.9 ± 28.8	0.6 ± 0.8	123.4 ± 248.1	1.5 ± 1.5
	weekly DOC load	[kg]	1.2 ± 0.1	0.4 ± 0.1	2.4 ± 1.2	0.9 ± 0.5	1.0 ± 0.5	0.5 ± 0.4	1.2 ± 1.2	0.6 ± 0.4
Pesticide Loads[b]	glyphosate	[mg]	1063/10	nd/nd	46009/1672	664/28	1712/26	39/6.30	48784/1708	703/34
	AMPA	[mg]	408/0.23	15/0.78	4528/224	784/14	455/7.16	55/3.67	5391/231	855/18
	dithiocarbamates	[mg]	nd./94	nd./nd	nd/922	nd/1.93	nd/nd	nd/nd	nd/1016	nd/1.93
	kresoxim-methyl	[mg]	nd/nd	nd/nd	72/nd	24/nd	nd/nd	nd/nd	72/nd	24/nd
	pyrimethanil	[mg]	nd/nd	nd/nd	367/nd	196/0.07	8.54/0.12	12/0.02	375/0.12	207/0.09
	metalaxyl	[mg]	283/nd	nd/nd	962/nd	218/nd	11/nd	3.21/nd	1256/nd	221/nd
	tetraconazole	[mg]	nd/nd	nd/nd	292/2.60	17/nd	17/0.13	4.63/0.03	309/2.73	21/0.03
	difenoconazole	[mg]	nd/nd	nd/nd	nd/nd	nd/nd	nd/0.04	nd/nd	nd/0.04	nd/nd
	fludioxonil	[mg]	nd/nd	nd/nd	nd/nd	nd/nd	3.37/1.83	46/0.17	3.37/1.83	46/0.17
	spiroxamine	[mg]	nd/2.28	nd/0.43	251/47	30/0.84	11/1.94	nd/0.14	262/52	30/1.41
	cyprodinil	[mg]	nd/nd	nd/nd	nd/nd	nd/nd	nd/1.43	nd/0.04	nd/1.43	nd/0.04
	cyazofamid	[mg]	nd/nd	nd/nd	57/nd	nd/nd	nd/nd	nd/nd	57/nd	nd/nd
Dissipation	pesticide fluxes[b]	[mg day^{-1}]	31.32/1.90	0.26/0.02	610.90/33.34	22.48/0.52	85.30/1.49	6.15/0.40	336.37/17.94	12.54/0.33
	total dissipated fluxes of pesticides[c]	[mg day^{-1} m^{-2}]	0.10/0.01		1.84/0.10		0.25/0.003		1.02/0.06	
	prevailing storage compartment	[–]	bed sediments and plants		water and TSS		bed sediments		bed sediments	
	prevailing dissipation process	[–]	plant uptake		biodegradation		sorption on bed sediment		biodegradation	

[a] Mean ±2s. [b] Values are provided as "dissolved"/"solid-bound" loads, respectively at the inlet and the outlet of the wetland, for the three phases of the investigation period. [c] The total dissipated fluxes of pesticides were calculated as follow: (total inlet pesticide load - total outlet pesticide load)/number of days of the phase/wetland area (319 m^2).

Chemical Analyses

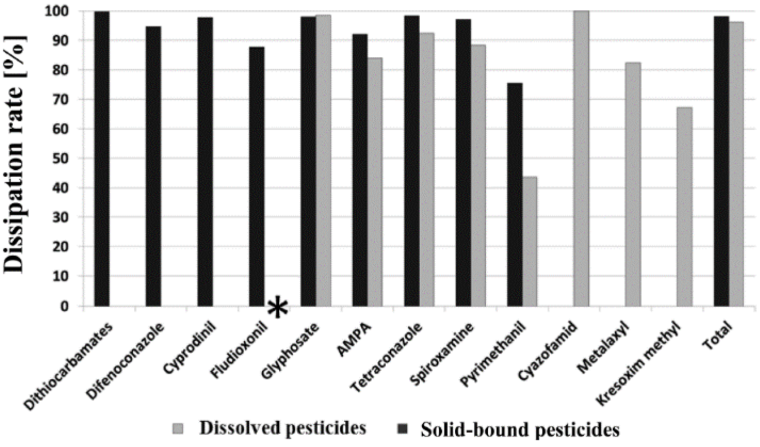
The dissolved oxygen, pH, conductivity, redox potential and temperature were directly measured in the field using WTW multi 350i portable sensors at the center of the four cells of the forebay and in the 6 piezometers of the gravel filter. The hydrochemical characteristics (TIC, DIC, NPOC, DOC, TKN, $PO4^{3-}$, P_{tot}, NO_3^-, NO_2^-, NH_4^+, Mn^{2+}, Fe^{2+}, Fe_{tot}, SO_4^{2-}, Mg^{2+}, Na^+, Cl^-, and K^+) were determined in the water samples using FR EN ISO standards and laboratory procedures. Ten fungicides that is, cyazofamid, cyprodinil, difenoconazole, dithiocarbamates (metiram-zinc and mancozeb), fludioxonil, kresoxim methyl, metalaxyl, pyrimethanil, spiroxamine, tetraconazole, 1 herbicide, glyphosate, and its degradation product AMPA were analyzed because of their widespread use and high frequency of application on the catchment. The fungicides and herbicides were quantified by LC−MS/MS following SPE extraction according to the NF XPT 90-210 standards and procedures. The dithiocarbamates (metiram-Zn + mancozeb) were quantified by GC−MS/MS via the headspace quantification of CS2 following the acid-catalyzed hydrolysis of dithiocarbamate in a $SnCl_2$+HCl solution. Glyphosate and AMPA were quantified following derivatization with fluorenemethoxycarbonyle (FMOC).

Results and Discussion

Pesticide Dissipation by the Wetland

The dissipation rate of the total pesticide loads by the wetland was 96.3%. The total dissolved pesticide load that entered the wetland during the investigation period (23 March to 28 September) was 56.6 ± 13.2 g (<0.7 µm) and 58.9 ± 13.9 g (<0.22 µm) and accounted for 95% of the total inflowing load, whereas the load of solid-bound pesticides was only 3.0 ± 1.0 g. The dissolved pesticides loads in the fractions <0.7 and <0.22 µm did not significantly differ at the inlet and at the outlet of the wetland. This highlights that pesticides were predominantly transported in the dissolved phase, in agreement with previous study. During the investigation period, 2.1 g of dissolved pesticides and 0.06 g of solid-bound pesticides were released by the wetland (the average daily flux of total pesticides was 11.6 mg/day) (Table 8.5-182). The average Kd and Koc values calculated for the pesticide significantly differed between the wetland inlet and outlet, and the forebay. Field Kd and Koc values should be cautiously considered as limits of pesticide quantification in TSS (10 µg/kg) were 2 orders of magnitude higher than limits in water (0.1 µg/L) due to the analytical difficulty to extract solid bound-pesticides.

Figure 8.5-137: Dissipation rates of dissolved (<0.7 µm) and solid-bound pesticides (>0.7 µm) in the stormwater wetland (Rouffach, Alsace, France) from 23 March to 7 September 2011. ∗fludioxonil dissipation in the dissolved phase was negative (−1267%).

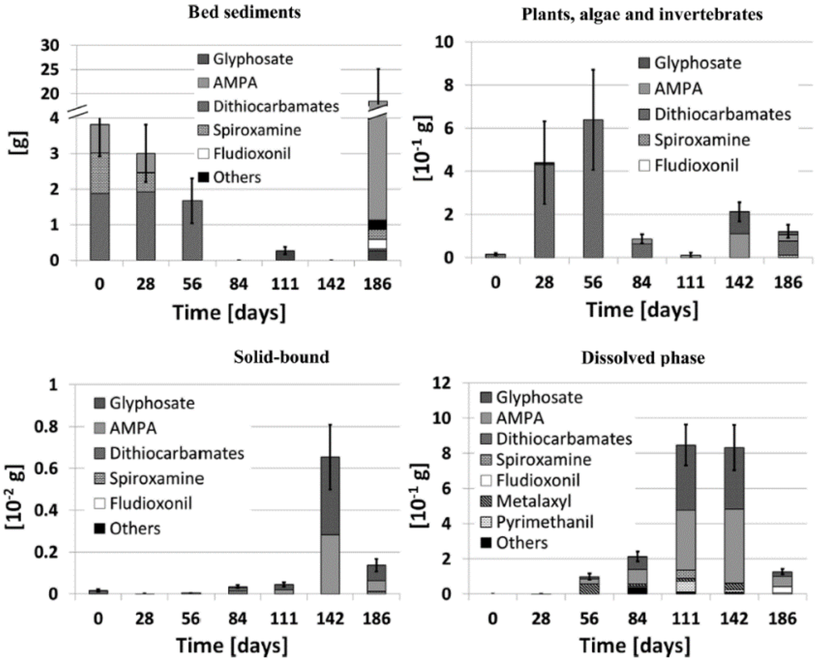


The weekly dissipation rates of the dissolved pesticides averaged 96.2 ± 8.2%, but ranged from negative values forfludioxonil (−1266%) to 100% for cyazofamid (Figure 8.5-137). Fludioxonil entered the wetland during the late summer (after day 147) and larger fludioxonil loads were released by the wetland (59.3 mg) compared with those entering (4.3 mg), which indicates the persistence of fludioxonil since the previous agricultural season. The dissipation rate of the total solid-bound pesticides (>0.7 µm) was 98% and ranged from 75.5% for pyrimethanil to 99.8% for the dithiocarbamates (Figure 8.5-137), underscoring the high capacity of the wetland to trap solidbound pesticides through settling processes. The hydrological conditions did not influence the dissipation of the dissolved and the solid-bound pesticides because no correlation was found on a weekly basis between the dissipation of total pesticide loads and the average quiescent period (the time between two runoff events) or the hydraulic retention time (HRT) in the wetland. Glyphosate (48.8 g; 86.3%), AMPA (5.4 g; 9.5%), metalaxyl (1.3 g; 2.2%), pyrimethanil (0.4 g; 0.7%) and tetraconazole (0.3 g; 0.5%) primarily contributed to the inflowing load of dissolved pesticide (<0.7 µm), whereas glyphosate (1.7 g; 56.7%), the dithiocarbamates (1.0 g; 33.7%), AMPA (0.2 g; 7.7%), spiroxamine (0.05 g; 1.7%) and tetraconazole (0.003 g; 0.1%) contributed to the solid-bound load. The mean AMPA fraction (%AMPA, calculated on a weekly basis as a percentage of the total molar loads of glyphosate and AMPA) was 27.6 ± 20.4% at the wetland inlet and 68.5 ± 33.0% at the outlet, which indicates that glyphosate was degraded into AMPA in the wetland as described previously. The overall dissipation rate of glyphosate was 98.5%, whereas that of AMPA was 84.3%, which highlights that AMPA was more persistent in the wetland compared to glyphosate.

Due to the dense wetland vegetation cover and the relatively high photodegradation half-life times (DT_{50} photolysis > 10 days), significant pesticide photodegradation is not expected for the studied pesticides, with the exception of cyazofamid (DT_{50} photolysis = 0.1 days), which contributed to only 0.1% of the total inflowing pesticide load. Hydrolysis is expected to be negligible in the wetland conditions, except for the dithiocarbamates (with a DT_{50} of 1.3 days, pH 7, and 20 °C). It is noteworthy that the dithiocarbamates were only found in association with the suspended solids, which supports the idea that solid-bound dithiocarbamates were more stable than dissolved dithiocarbamates. Pesticide loss by volatilization can be neglected in the mass budget for pesticides with a lowvapor pressure (<0.18 mPa), and estimates of the total mass loss by volatilization for pyrimethanil, metalaxyl and spiroxamine (vapor pressure <3.5 mPa, nondimensional Henry constant $<10^{-7}$) are in the range of the analytical error (<1% of the total mass budget). Consequently, in our study, a negative pesticide mass budget that cannot be attributed to storage in any of the wetland compartments can be attributed to biodegradation, except in the case of cyazofamid. The pesticide mass budget made it possible to distinguish three seasonal phases during the investigation period with respect to pesticide inputs, distribution, degradation and retention, as follows: spring (23 March (or day 0) to 18 May), summer (19 May to 10 August) and late summer (11 August to 07 September (or day 168)) (Table 8.5-182, Figures 7.5-132 and 7.5-133).

Seasonal Change in the Pesticide Distribution and the Wetland Source/Sink Functions.
On day 0 (March 23), the amount of pesticides stored in the wetland was 3.8 g, 91.6% of which was found in the fine bed sediments (50−250 µm), 8% in the medium bed sediments (250−1000 µm), 0.2% in the vegetation and <0.3% in the other compartments. The dithiocarbamates (1.9 g), spiroxamine (1.1 g) and AMPA (0.8 g) primarily contributed to the total pesticide load. The amount of pesticides stored on day 0 corresponds to the pesticides used in the previous winegrowing period because no pesticides were used in the catchment before day 0.

Figure 8.5-138: **Monthly pesticide mass budget (g) in the bed sediments, plants and invertebrates, suspended solids and dissolved phase of the stormwater wetland (Rouffach, Alsace, France). The error bars correspond to the analytical uncertainty. The errors for the pesticide loads were calculated via error propagation based on the uncertainty of the individual pesticide concentration measurements and the mass estimate for each wetland compartment.**

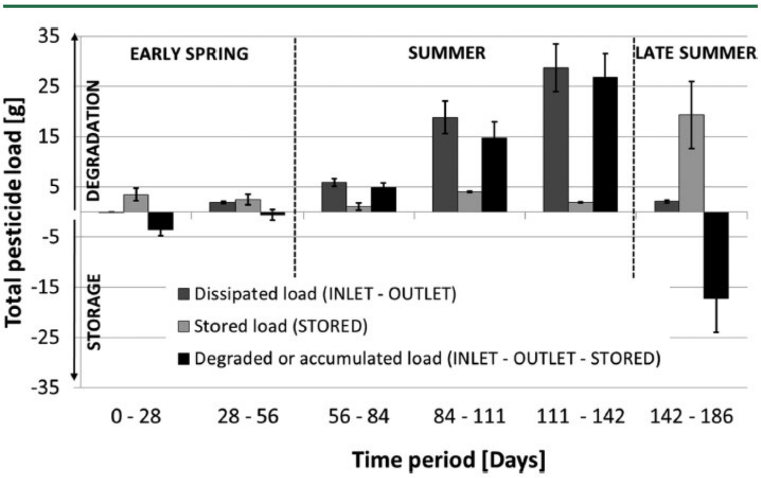


Spring

During the spring (day 0 to day 56), the wetland received 3.1% of the total incoming load during the investigation period and acted as a pesticide sink. The dissolved pesticides accounted for 94.3% of the total incoming load. Metalaxyl and spiroxamine were only found in the dissolved phase, whereas the dithiocarbamates were exclusively associated with the TSS and accounted for 88% of the total solid-bound load. 16.3 mg of pesticides were released by the wetland, corresponding to 0.9% of the inflowing load. The pesticides accumulated in the wetland sediments (1.7 g on day 56; 69.3% of the total load stored) and the vegetation (0.6 g; 26.4%) because the amount of pesticides found in the wetland on day 56 (2.4 g) exceeded that entering the wetland (1.8 g) (Figure 8.5-139, Table 8.5-182). However, the pesticide amount stored in the wetland decreased from 3.8 to 2.4 g. The primary contributors to the total pesticide load in the wetland compartments were as follows: the dithiocarbamates >spiroxamine > AMPA > glyphosate. Biodegradation of spiroxamine, glyphosate and AMPA occurred in the wetland as indicated by (i) decreasing load of spiroxamine and AMPA in the bed sediments (from 1.1 g to 0 for spiroxamine and from 0.8 to 0.03 g for AMPA) without any increase in the other compartments, and (ii) the release of only 15.9 mg of AMPA (the maximum AMPA concentration was 0.2 µg/L), 0.4 mg of spiroxamine and no glyphosate, although 1.1 g of glyphosate and 0.4 g of AMPA entered the wetland during the spring. The degradation of spiroxamine and AMPA occurred under aerobic conditions prevailing in the wetland forebay during the spring, as indicated by the average oxygen concentration (3.9 ± 4.1 mg/L), the redox potential (50 mV ± 160 mV), as well as release of nitrate and sulfate by the wetland. Nitrate release may either occur by nitrification or result from vegetation decay, and the release of sulfate by the wetland supports sulfite and sulfide oxidation. Pesticides were partly translocated from the bed sediments to the vegetation during the spring. The biomass of the aerial plant parts increased from 0.5 to 3.7 kg/m^2 and that of the roots from 1.6 to 8.2 kg/m^2 during the vegetative phase. The dithiocarbamates were taken up by the plants, as indicated by a decrease of the dithiocarbamates load in the fine bed sediments (from 1.6 to 1.3 g between days 0 and 56) and an increase in the vegetation (from 7.1 mg to 508.7 mg in the roots and from 9.1 mg to 128.0 mg in the aerial parts), whereas 2.3 mg of the dithiocarbamates were found in the algae on day 56 (i.e., <0.1% of the total pesticide load stored in the wetland). Dithiocarbamates did not accumulate during the summer in the wetland, although the degradation of dithiocarbamates decreased over time (Figure 8.5-138).

Figure 8.5-139: Pesticide mass budget highlighting the pesticide storage vs degradation in the stormwater wetland (Rouffach, Alsace, France)

The dissipated pesticide load (INLETload − OUTLETload) refer to the load stored (STOREDload) or degraded (INLETload − OUTLETload − STOREDload >0). The accumulated load (INLETload − OUTLETload − STOREDload <0) is the load accumulated in the wetland from one period to another. The errors for the pesticide loads were calculated via error propagation based on the uncertainty of the individual pesticide concentration measurements and the mass estimate for each wetland compartment.



Summer

During the summer (day 56 to day 142), the wetland acted as a pesticide sink and degradation was the primary dissipation process. This resulted in low pesticide accumulation in the wetland despite large pesticide inputs (Figures 7.5-132 and 7.5-133, and Table 8.5-182). During the investigation period, 52.5 g of dissolved and 2.9 g of solid-bound pesticides entered into the wetland, which represented 93% of the total input load. The total pesticide amount released by the wetland during the summer was 1.9 g, corresponding to 3.4% of the total inflowing load. Anoxic conditions prevailed, as indicated by the dissolved oxygen concentrations (0.3 ± 0.3 mg/L) and the redox potential values (−20 to −120 mV), whereas the nitrate and sulfate mass budgets indicate nitrate (−69 ± 42%) and sulfate reduction (−51 ± 25%) in the wetland from the end of June (day 91). Anoxic conditions in the wetland were compatible with pesticide degradation, as shown for glyphosate and AMPA, whereas dithiocarbamates degradation appeared to be less efficient.

The total pesticide amounts stored in the wetland were 0.3, 1.2, and 1.1 g between days 56 and 84, day 84 and 111, and day 111 and 140, respectively, which accounted for less than 6% of the total load entering the wetland. This result indicates that pesticide degradation was the prevailing process during the summer (Figures 7.5-132 and 7.5-133). The stored pesticide loads were 1 order of magnitude lower than that found during the spring, even though the pesticide input in the wetland was larger during the summer (Table 8.5-182). The largest pesticide loads were found in the dissolved phase of the wetland forebay (203.0 mg on day 84 and 765.4 mg on day 142), which indicates limited pesticide storage in the sediments and vegetation due to the regular mixing of the forebay water during runoff events (the average quiescent period was 6.4 ± 2.3 days, indicating more frequent runoff events in the summer than in the spring). Other relevant storage compartments in the wetland were the fine bed sediments (270.7 mg on day 111) and the plant roots (from 55.8 mg on day 84 to 177.5 mg on day 142). The average vegetation density was 175 stems/m^2, that is, 4 times higher than in early spring (Table 8.5-182). The plant roots accumulated glyphosate (101.0 mg or 0.3 mg/m^2 wetland) and AMPA (76.5 mg or 0.2 mg/m^2 wetland) (Figure 8.5-138), indicating sorption onto the roots and/or plant uptake. The pesticide loads in the algae and invertebrates accounted for 10.4% (31.3 mg) and 0.13% (0.4 mg), respectively, of the total stored pesticide load on day 84. Algae were not observed in the wetland after day 84 and during the late summer. It is noteworthy that pesticides taken up by organisms may be quickly and irreversibly conjugated in less-extractable forms, leading to an underestimation of the pesticide amounts stored in plants, algae, and invertebrates.

Late summer

During the late summer, the wetland mostly acted as a pesticide sink with moderate pesticide degradation and primary storage in the fine bed sediments. Pesticides were not used in the vineyard catchment after day 132 (02 August). Anaerobic conditions prevailed, as indicated by the mass depletion of nitrate (37%) and sulfate (28 ± 53%) by the wetland. 2.2 g of dissolved pesticides and 38.8 mg of solid bound pesticides entered wetland, corresponding to only 3.8% of the total inflowing pesticide load (Table 8.5-182). The total pesticide amount released by the wetland during the late summer was 0.2 g, corresponding to 7.3% of the inflowing load. The pesticides were stored as follows: in the fine bed sediments (18.4 g of pesticides) > plant roots (122.6 mg) >dissolved phase (105.4 mg) > coarse bed sediments (46.1 mg) > the TSS of the forebay (12.1 mg). The total pesticide load stored in the wetland consisted of AMPA (17.4 g), glyphosate (321.2 mg), fludioxonil (306.5 mg), and spiroxamine (284.1 mg) and was greater than during the summer, except in the dissolved phase, the TSS and the vegetal biomass, which primarily stored pesticides during the summer (Figure 8.5-138). Although the vegetation cover was denser during the late summer (200 stems/m^2), the plant root biomass was lower than in the summer (−32%) and the evapotranspiration decreased, indicating vegetation senescence during the late summer. Hence, plant decay may also have contributed to the pesticide accumulation in the bed sediments by increasing both the content of organic matter and the diversity of the carbonaceous sorbent materials. The accumulation of AMPA in the fine bed sediments during the late summer can be related to the longer average HRT (26.9 ± 8.1 days) compared with that in summer. The longer HRT enhanced the settling of solid-bound pesticides from the water column, thus increasing the contact time of the dissolved AMPA−sediment interactions (Figures 7.5-132 and 7.5-133). This result is in agreement with previous studies showing that AMPA is more sorptive than glyphosate and primarily sorbs to the metal (hydro)oxides in clay materials and humic substances. AMPA was also found to be more persistent than glyphosate in soils due to the formation of non extractable residues, which stabilizes AMPA and lowers its bioavailability. In addition, the clay fraction of the fine bed sediment increased by 22% from day 0 to day 168, which potentially increased the specific surface area for the AMPA-clay metal (hydr)oxide interactions (Figure 8.5-138), thus lowering AMPA bioavailability and degradation during the late summer. The occurrence of a persistent stock of AMPA in the wetland sediments, which can be released during the winter, must be carefully considered in the management of wetland systems receiving pesticide runoff.

Environmental Implications for Wetlands Receiving Pesticide Fluxes

This study represents a first attempt to establish a complete pesticide mass balance in a wetland system under field conditions for assessing dissipation processes. The seasonal change in the partitioning, degradation, and distribution of the pesticides was quantified in a stormwater wetland to evaluate the dynamics of the pesticide sink and source functions. Although wetland field studies are invariably dependent on the system configuration and the study context, our results provide a rational basis for interpreting pesticides dissipation in planted stormwater wetlands collecting contaminated runoff under temperate climates. Our data highlight that the wetland system could act primarily as pesticide sinks from spring to summer. Stormwater wetlands can efficiently remove dissolved and solid-bound pesticides, even when the pesticides are predominately transported in the dissolved phase. The solid-bound molecules were efficiently retained by the wetland whereas mostly dissolved molecules, such as AMPA or fludioxonil, were moderately transported and less retained during the spring and late summer. Plant roots and fine sediments (50 and 250 μm) were the primary contributors to the retention of glyphosate, AMPA and dithiocarbamates. The pesticides did not accumulate in the vegetation except in the vegetative stage during the spring. The wetland vegetation enhanced pesticide degradation in the rhizosphere, and pesticide degradation corresponded to the development of the vegetation. Pesticide mass degradation was maximal during the summer when the vegetation was mature, under prevailing anoxic conditions, and when large pesticide loads entered the wetland. During the spring and late summer, the wetland mostly accumulated pesticides in the fine wetland bed sediments. AMPA accumulation in the fine sediments in late summer raises the issue of the ecotoxicological risk posed by the accumulation and the release of poorly described degradation products from wetland systems. Wetland systems can act not only as pollutant sinks, but also as pollutant sources, which raises concerns on the degradation, retention, and release of pesticides and degradation products in wetlands intercepting pesticide runoff. This study shows that quantitative understanding of the pesticide sink and source functions can support the evaluation and the management of services provided by wetland ecosystems to improve water quality.

Assessment and conclusion by applicant:
The article reports the pesticide loss and input in a stormwater wetland in an agricultural region in France. Several pesticides were analyzed, among them glyphosate and AMPA. Analytical methods were poorly described in the article but were provided in the supporting information. Mostly dissolved molecules, such as AMPA or fludioxonil, were moderately transported and less retained during the spring and late summer. Plant roots and fine sediments (50 and 250 µm) were the primary contributors to the retention of glyphosate, AMPA. AMPA accumulation in the fine sediments in late summer raises the issue of the ecotoxicological risk posed by the accumulation and the release of poorly described degradation products from wetland systems.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:
Agrees with applicant's conclusions.

RMS highlights that information from laboratory water sediment studies (B.8.2.2) conducted on glyphosate or AMPA also indicate a potential accumulation of AMPA in sediment.
It is worth noting that the results are expressed as loads (mg) in wetland compartments (inlet and outlet) for the three phases of the investigation period, and not in concentration. However the study of Infeld *et al,* 2013 (CA7.5/055) reports glyphosate and AMPA concentrations for the same period on the same vineyard.

The article is considered reliable with restrictions.

Data point:	CA 7.5/021
Report author	Norgaard, T. *et al.*
Report year	2014
Report title	Leaching of Glyphosate and Aminomethylphosphonic Acid from an Agricultural Field over a Twelve-Year Period
Document No	Vadose Zone J. doi:10.2136/vzj2014.05.0054
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The article was found relevant for multiple subchapters. The summary is provided in the groundwater monitoring subchapter of this document.

Assessment and conclusion by RMS:

This study analyzed the results from a unique 12-yr field-scale monitoring program measuring the leaching of glyphosate and AMPA. Measurements were made in a shallow drainage system beneath a 1.26-ha field. Therefore the results can reflect both leaching concentration and drainflow concentration before entry into surface water.

See summary under GW section.
The study is reliable with restrictions. It provides information on the concentrations of glyphosate and AMPA in drainflow samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

Maximum measured concentration for glyphosate of 31 µg/L is dated 2005.

Data point:	CA 7.5/052
Report author	Ramwell, C. *et al*.
Report year	2014
Report title	Contribution of household herbicide usage to glyphosate and its degradate aminomethylphosphonic acid in surface water drains
Document No	Society of Chemical Industry (wileyonlinelibrary.com) DOI 10.1002/ps.3724
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable (but concentration in urban surface runoff, and not surface water)

It is necessary to understand the extent to which different sources of pesticides contribute to surface water contamination in order to focus preventive measures appropriately. The extent to which glyphosate use in the home and garden sector may contribute to surface water contamination has not previously been quantified. The aim of this study was to quantify the widely used herbicide glyphosate and its degradation product aminomethylphosphonic acid (AMPA) in surface water drains (storm drains) that could be attributed to amateur, non-professional usage alone. Maximum glyphosate and AMPA concentrations in surface water drains were 8.99 and 1.15 µg/L, respectively after the first rain event following the main application period, but concentrations rapidly declined to <1.5 and <0.5 µg/L. The AMPA:glyphosate ratio was typically 0.35. Less than 1% of the applied glyphosate was recovered in drain water. Glyphosate and AMPA losses from urban areas that arise solely from amateur usage have been quantified. In spite of overdosing occurring, the authors reported that glyphosate concentrations in drain flow were lower than concentrations reported elsewhere from professional use in urban areas.

Materials and methods

A catchment suitable for the investigation of glyphosate in drain flow from purely domestic usage would ideally have the following attributes: no agricultural inputs of glyphosate, separate foul and surface water drains (the latter being reasonably accessible), a mix of hard/impermeable and permeable surfaces and a low probability of vandalism of the monitoring equipment. A small, residential catchment (5.16 ha) where the houses had separate foul sewers and surface water drains was identified in York, England as study site. Two ISCO 6172 automatic water samplers were installed to sample water (120 mL) from the final drain every 5 min, with the water from three consecutive samples being directed to a single bottle, giving one composite sample (360 mL) every 15 min. One sampler was triggered when rainfall exceeded 0.4 mm within 2 h; the other was triggered when the water level in the drain was >0.01 m. This approach was taken to minimise missing a sampling event because of equipment failure. Rainfall was monitored using a tipping-bucket rain gauge (resolution 0.1 mm) sited on top of one of the boxes used to house the water samplers. Discharge was measured using an ISCO 750 area/velocity flow module.

The study was undertaken in early summer (June–July 2009) when herbicide applications in private gardens are common in response to the favourable weather conditions for weed growth. Samples were taken during the first rain event (15 June 2009) after the equipment was installed (22 May 2009) and prior to the survey of the residents in order to monitor any ‘background’ levels of glyphosate. After that, samples were collected in response to all rain events until the end of July 2009. Samples were collected within 24 h.

Samples were decanted from the glass collection bottles into high-density polyethylene (HDPE) bottles on return to the laboratory and stored in the freezer until dispatched for analysis.

The inputs of glyphosate into the catchment were established by means of a questionnaire. All houses in the catchment were approached by door-to-door visits over a period of 5 days during the day, in the evening and at the weekends. Fast Action Roundup Ready-To-Use (RTU) weedkiller (glyphosate 7.2 g/L MAPP 14481) in either a 1 L trigger sprayer or a 5 L 'pump and spray' container was supplied to those participants who requested it, or participants used products that they already had (*n*=2; Tesco's own-brand glyphosate and Pathclear – containing glyphosate, oxadiazon + diflufenican). The 1 L bottles were weighed before and after use in order to quantify the amount used. This was not possible with the 5 L RTUs as these were too heavy for field-portable scales.

It was necessary to estimate the amounts applied for 39% of the residents. Similarly, only the total quantity of glyphosate used per household was known, so the amount used per application was calculated from knowledge of the weed density and area treated, as indicated on their pro forma, in order to distribute the total amount of glyphosate spray solution used between each application date.

Samples were analysed using an existing validated method. Samples were thawed, homogenised by shaking and then left to settle. Samples were not filtered in order to avoid potential glyphosate losses. Samples were derivatised prior to analysis: an aliquot of sample (50 µL) was transferred by pipette into a 10 mL reactivial, and reagent (2 mL) was slowly added (freshly prepared 2:1 mixture of trifluacetic anhydride and 2,2,3,3,4,4,4-heptafluorbutanol cooled to −20°C). The vial was then sealed and heated to 95°C for 2 h. After cooling, the excess reagents were removed under a stream of nitrogen at 40°C until dry. The sample was then dissolved in ethyl acetate containing 0.2% citral (1 mL) and transferred to a vial ready for analysis. The limits of detection were 0.002 µg/L for glyphosate and 0.003 µg/L for AMPA, and the limits of quantification were 0.007 and 0.01 µg/L, respectively. All calibration graphs were linear over the standard range, with a typical linear correlation coefficient of 0.999. Recoveries at 0.05 µg/L were 108 ± 31% for glyphosate and 121±17% for AMPA.

Measurements of concentration and discharge were used to calculate the total mass of glyphosate leaving the catchment. Discharge measurements were collected every minute, whereas bulk drain water samples were collected every 15 min. It was therefore necessary to extrapolate the chemical data. It was assumed that there was a linear increase or decrease in concentration between successive samples, enabling a concentration per minute to be estimated. In addition, two total masses per rainfall event were calculated. The first was the total load between the first and last measured concentration. However, as this was not always the very first or very last sample generated, because some samples had insufficient volume for analysis, a second calculation was made where a concentration of zero was assumed as soon as the water sampler was triggered, and concentrations up to the first analysed sample were calculated by linear extrapolation as described above. The final total glyphosate loss per event was calculated from the sum of the loads for glyphosate + AMPA, where the final mass of AMPA was calculated from initial mass of AMPA × (molecular weight of glyphosate/molecular weight of AMPA).

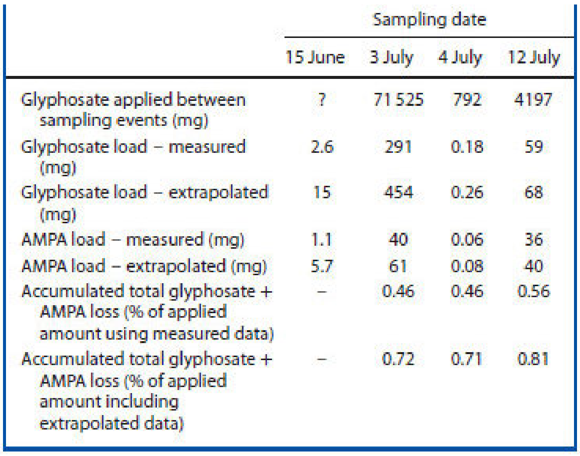
Results

Of the 148 houses in the catchment, 82 separate households were interviewed and, of these, 34 agreed to participate in the study. The majority of applications occurred within the first 2 weeks of the study, with a notable 53 g of glyphosate being applied on a single day. More than half of this application could be attributed to a single person who applied 5 L (and therefore 36 g of Roundup) over a period of 2 days primarily to an area of ∼10 m^2 that had a high weed infestation rate of >50% for weeds that were ∼10 cm high. Maximum concentrations of 1 µg/L of glyphosate and 0.43 µg/L of AMPA were detected in the 'background' drain samples, and the concentrations dipped to 0.33 and 0.37 µg/L, respectively, 5 h after the start of the rainfall event. The presence of glyphosate in the background sample indicated that there was an incomplete dataset for the total amount of glyphosate applied.

The first rain event after the main application period occurred on 3 July 2009 (2 weeks after the first recorded application), and three further events were monitored. The highest concentrations of glyphosate (8.99 µg/L) and AMPA (1.15 µg/L) occurred during this first rain event, although the concentrations rapidly declined within the first hour to <2 µg/L, with the final sample taken containing <1 µg/L. A short rain event on the following day (4 July 2009) generated further samples (after a further 0.79 g of glyphosate had been applied in the catchment), with peak concentrations of 2.08 µg/L of glyphosate and 0.66 µg/L of AMPA. Glyphosate concentrations in the last monitored rain event were <1 µg/L, in spite of more than 4 g of glyphosate being applied in the intervening dry period between sampling events. AMPA concentrations ranged from 0.17 to 0.54 µg/L in this last event. These concentrations are the same order of magnitude as the initial 'background' samples. It should be noted that the glyphosate and AMPA concentrations reported here are those measured in the surface water drains, where there is relatively low discharge and therefore low dilution, and they are not representative of concentrations in surface water, where it would be expected that significant dilution would occur. The load of glyphosate is needed in order to estimate concentrations in surface water.

The total mass of glyphosate and AMPA detected in the drain was calculated for each rain event, and the results are presented in Table 8.5-183. Although over 71 g of glyphosate was applied prior to the first monitored post-application rain event, less than 0.5% of this glyphosate was detected in surface water drain flow, even when accounting for both the glyphosate +AMPA. Samples collected on the next day, the second rain event after application, added very little glyphosate and AMPA to the total loss, such that the accumulated loss as a percentage of amount applied was still <0.5%. Between 0.56 and 0.81% (for the measured and extrapolated data, respectively) of the applied glyphosate had been recovered in drain flow by the end of the sampling period. These findings highlight that only a very small percentage of the applied glyphosate is recovered in surface water drains, and it is assumed that the majority of the applied glyphosate is retained in the catchment and/or degraded.

Table 8.5-183: Mass of glyphosate applied and recovered for individual rain events



	Sampling date			
	15 June	3 July	4 July	12 July
Glyphosate applied between sampling events (mg)	?	71 525	792	4197
Glyphosate load – measured (mg)	2.6	291	0.18	59
Glyphosate load – extrapolated (mg)	15	454	0.26	68
AMPA load – measured (mg)	1.1	40	0.06	36
AMPA load – extrapolated (mg)	5.7	61	0.08	40
Accumulated total glyphosate + AMPA loss (% of applied amount using measured data)	–	0.46	0.46	0.56
Accumulated total glyphosate + AMPA loss (% of applied amount including extrapolated data)	–	0.72	0.71	0.81

Extrapolating the known usage from the households surveyed (76.5 g glyphosate used by 34 out of 82 households) to the total number of households in the catchment (*n*=148) would give a total of 138 g of glyphosate applied. The quantity of glyphosate detected in the drains would then equate to 0.31 or 0.45% of the amount applied using the measured and extrapolated sampling data respectively.

However, using a directly proportional relationship to augment wash-off to account for the lower-than-average rainfall in the study period gives a glyphosate loss of only 0.69% and 1.01% for the measured and extrapolated water sample data, respectively, which, if further extrapolated to account for glyphosate application in the entire catchment, gives glyphosate losses of 0.38 and 0.56% for the measured and extrapolated water sample data, respectively. The data demonstrate that the loss of glyphosate in the present study (0.6%) is low compared with other studies, in spite of one of the residents considerably overdosing. In the present study, an equivalent of 14.8 g/ha was applied, which compares to an estimate of 0.16 g/ha in another study having an emission factor of 2%. It is likely that the lower quantities of glyphosate detected in drain water in the present study reflect the type of 'impermeable' hard surface treated, affecting the pathways of loss/retention mechanisms.

Conclusion

It is acknowledged that several glyphosate sources such as surface drains and wastewater treatment plants may contribute to the concentrations detected in the larger monitoring programmes, but the calculation above using data from the present study indicates that it is unlikely that losses from residential catchments, following proper usage, will contribute significantly to the total glyphosate load in surface waters compared with other urban areas. The findings of this study can therefore assist in ensuring that mitigation against glyphosate inputs to surface waters are targeted at the appropriate source of emission.

Assessment and conclusion by applicant:

The article describes the contribution of the household usage of glyphosate to concentrations of the active and AMPA in surface water drains. The set-up of the experiment excluded agricultural use. The sample site was an urban residential area in the UK. Overall, less than 0.6% of applied glyphosate was recovered from the storm drain outflow. Maximum detected concentrations were 8.99 µg/L and 1.15 µg/L for glyphosate and AMPA, respectively.

Some information missing, e.g. sample storage.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

The aim of this study was to quantify the widely used herbicide glyphosate and its degradation product aminomethylphosphonic acid (AMPA) in surface water drains (storm drains) that could be attributed to amateur, non-professional use alone.

The study is considered reliable, but however provides information on the concentrations of glyphosate and AMPA in surface runoff samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

Maximum glyphosate and AMPA concentrations in surface water drains were 8.99 and 1.15 µg/L respectively after the first rain event following the main application period, but concentrations rapidly declined to < 1.5 and < 0.5 µL^{-1}. The AMPA:glyphosate ratio was typically 0.35. Less than 1% of the applied glyphosate was recovered in drain water.

Data point:	CA 7.5/006
Report author	Székács, A. *et al.*
Report year	2014
Report title	Monitoring and biological evaluation of surface water and soil micropollutants in Hungary
Document No	Carpathian Journal of Earth and Environmental Sciences, August 2014, Vol. 9, No. 3, p. 47 - 60
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The article was found relevant for multiple subchapters. The summary is provided in the soil monitoring subchapter of this document.

Assessment and conclusion by RMS:

This articles reports results from monitoring program in Hungary.

In the scope of a national monitoring program, 423 soil samples and 202 surface and ground water samples were collected between 2008 and 2013, in uneven annual distribution, from agricultural fields and industrial sites.

Contamination in arable lands and industrial areas has been investigated on 13 plots in 5 replicates. Among agricultural areas, three types of land use have been involved: arable lands under intensive cultivation, organic farming and pasture.

The findings are not detailed and the reported glyphosate findings cannot be assigned to any respective sampling site. A maximum concentration of glyphosate at 0.98 µg/L was reported as an unspecified (SW/GW) water contaminant.

The study is considered reliable with restrictions.

Data point:	CA 7.5/007
Report author	Daouk, S. *et al.*
Report year	2013a
Report title	The herbicide glyphosate and its metabolite AMPA in the Lavaux vineyard area, western Switzerland: Proof of widespread export to surface waters. Part I: Method validation in different water matrices
Document No	Journal of Environmental Science and Health, Part B (2013) 48, 717-724
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable for validation of analytical method used in CA7.5/053 Reliable for surface water concentration

An analytical method for the quantification of the widely used herbicide, glyphosate, its main by-product, aminomethylphosphonic acid (AMPA) and the herbicide glufosinate at trace level was developed and tested in different aqueous matrices. Their derivatization with 9-fluorenylmethyl chloroformate (FMOC-Cl) was done prior to their concentration and purification by solid phase extraction. The concentrated derivates were then analyzed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). Spiking tests at three different concentrations were realized in several water matrices: ultrapure water, Evian© mineral water, river water, soil solution and runoff water of a vineyard. Except for AMPA in runoff water, obtained regression curves for all matrices of interest showed no statistical differences of their slopes and intercepts, validating the method for the matrix effect correction in relevant environmental samples. The limits of detection and quantification of the method were as low as 5 and 10 ng/L, respectively, for the three compounds. Spiked Evian© and river water samples at two different concentrations (30 and 130 ng/L) showed mean recoveries between 86 and 109%, and between 90 and 133% respectively. Calibration curves established in spiked Evian© water samples between 10 and 1000 ng/L showed r^2 values above 0.989. Monitoring of a typical vineyard river showed peaks of pollution by glyphosate and AMPA during main rain events, sometimes above the legal threshold of 100 ng/L, suggesting the diffuse export of these compounds by surface runoff. The depth profile sampled in the adjacent lake near a waste water treatment plant outlet showed a concentration peak of AMPA at 25 m depth, indicating its release with treated urban wastewater.

Materials and Methods

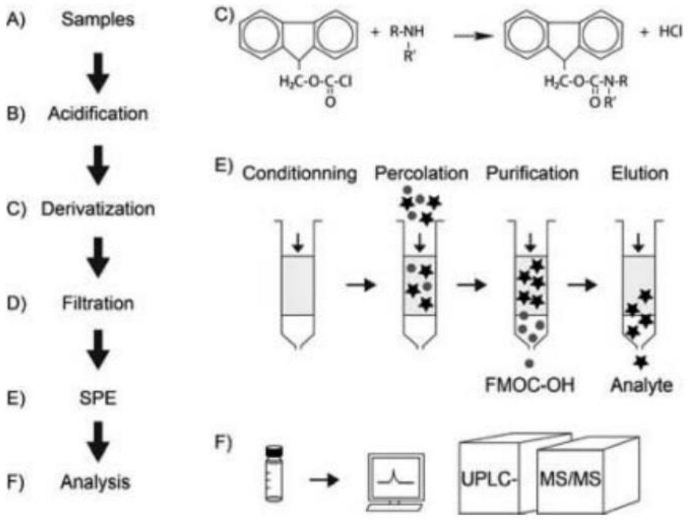
Chemicals

Glyphosate (PESTANAL®, 99.7%), glufosinate-ammonium (PESTANAL®, 99.2%) and AMPA (99%) were obtained from Sigma-Aldrich. Glyphosate-FMOC (98.5%), AMPA-FMOC (97%), glufosinate-FMOC (94%) and the internal standards (IS) labeled with stable isotopes 1,2-;$^{13}C_2$,^{15}N glyphosate (98%) and ^{13}C,^{15}N AMPA (99%) were obtained from Dr. Ehrenstorfer.

Analytical method

The analytical method was adapted from Hanke *et al.* (see Figure 8.5-140).

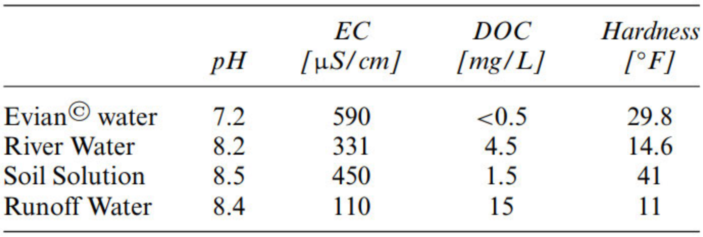
Figure 8.5-140: Main phases of the analytical procedure: a) Samples (80 mL); b) Acidification (1 h); c) Derivatization with FMOC-Cl (2 h); d) Filtration (0.45 µm); e) Solid-phase extraction (SPE); f) Analysis by UPLC-MS/MS



Method validation in different water matrices

Spiking tests were performed in different water matrices in order to validate the method for further monitoring campaigns. The chosen matrices were: ultrapure water, Evian© water, river water, soil solution and runoff water. Natural water samples were collected close to the Lutrive River in a vineyard area located above the village of Lutry, Switzerland. Spiking tests were performed at three different concentrations (40, 80 and 120 ng/L) in all matrices; in natural waters blank subtraction was performed. In each case, samples were spiked and analyzed in triplicate. The main parameters of the different water samples are presented in Table 8.5-184: dissolved organic carbon (DOC) measurements were realized with a Liquitoc (Elementar©, Hanau, Germany), and water hardness was calculated after Ca^{2+} and Mg^{2+} measurements with an ICS-1100 as following: $[CaCO_3] = 2.5[Ca^{2+}] + 4.1[Mg^{2+}]$. Linear curves were obtained by plotting the ratio of the analyte area to the IS area against the ratio of the theoretical concentration of the analyte to the IS one. The corresponding internal standards were used for glyphosate and AMPA, whereas AMPA IS was used for glufosinate as they are both primary amines. The difference of slopes and intercepts for the curves were tested with the Prism® program. The P-values were fixed to 0.05. The accuracy of the method was assessed by calculating mean recoveries between the measured and the spiked concentrations in Evian© and River water, at 30 and 130 ng/L in triplicates. The limits of detection (LOD) and quantification (LOQ) of the method were determined in ultrapure, Evian© and surface water samples as the lowest concentrations with a signal/noise ratio equal or above three and ten respectively.

Table 8.5-184: **Main properties of analyzed water samples: pH, electrical conductivity (EC), dissolved organic carbon (DOC) and hardness, expressed in French degrees [°F]**



	pH	*EC* *[µS/cm]*	*DOC* *[mg/L]*	*Hardness* *[°F]*
Evian© water	7.2	590	<0.5	29.8
River Water	8.2	331	4.5	14.6
Soil Solution	8.5	450	1.5	41
Runoff Water	8.4	110	15	11

Environmental sampling

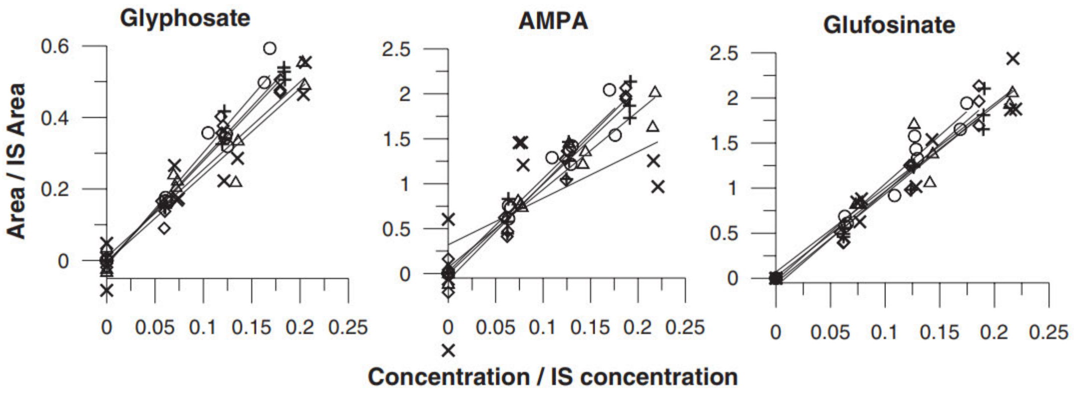
The Lutrive is a local river in the east of the city of Lausanne, at the western limit of the Lavaux vineyard area. Its small watershed (6.4 km^2) is characterized by different land uses: agricultural fields (45%), of which 4.1% are vineyards, urban and impervious surfaces (31%) and forests (24%). Grab samples were collected in the vineyard area during the growing season of 2010 and during both dry- and wet-weather conditions. Daily precipitations data of the meteorological station of Pully, west of the Lutrive River. Lake Geneva was sampled during dry weather on the 1st of July 2010, in the Vidy Bay near the waste water treatment plant (WWTP) outlet at nine different depths: -2, -5, -10, -15, -18.5, -21, -23, -25 and -29 m.

Results and discussion

Linearity and matrix effect

The response factors, i.e. the ratio area/IS area, for the different concentrations, normalized by IS concentration, showed a good linearity for the three compounds (Figure 8.5-141). Coefficients of determination (r^2) were all above 0.916 except for AMPA in runoff water, which was only 0.324. The slopes were varying between 2.4 and 3.1 for glyphosate, 5.1 and 10 .7 for AMPA and between 9.3 and 10.7 for glufosinate; Intercepts varied between -0.072 to 0.069. Both values, slopes and intercepts, were not significantly different between the different matrices samples for glyphosate and glufosinate. For AMPA however, a significant difference with the others was observed for the runoff sample with a slope of 5.1. The same was observable for the intercept that is higher than the others (0.32). These poorer results for AMPA in runoff samples can be explained either by substantial AMPA content in the spiked sample or by the high DOC concentration in this kind of sample (cf. Table 8.5-184). Nevertheless, in general the results confirm the ability of internal standards to compensate signal losses due to the matrix effect, which was stronger for runoff samples and soil solution. Indeed, both showed considerable discrepancies in slopes when compared with ultrapure, Evian© or river water samples before normalization with IS. Thus, with the exception for AMPA in runoff water, the results show the applicability of the method for the monitoring of several types of environmental samples: surface water, soil solution and runoff samples. Moreover, they confirm the suitability of Evian© water as calibration matrix. Indeed and surely due to its mineral content, Evian© water showed more similar slopes to environmental matrices than ultrapure water, making it more suitable for building calibration curves.

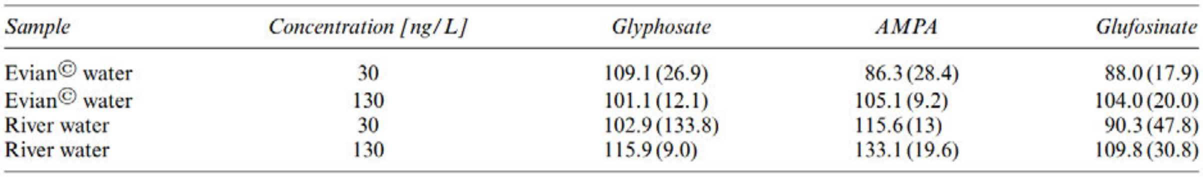
Figure 8.5-141: **Performance of the developed method for the five water types tested: triplicates of spiked water samples of three concentrations (40, 80 and 120 ng/L) normalized by internal standards (IS) labeled with stable isotopes, with the different matrices: Ultrapure water (◦), Evian© water (+), River water (◊), Soil solution (Δ) and Runoff water (×); blank subtraction were performed for soil solution and runoff water samples.**



Precision and accuracy

Calibration curves in spiked Evian© water samples were generated from 10 up to 1000 ng/L. They showed a linear behavior with the following equations and coefficients of determination (r^2): glyphosate=1.222x + 5.204, $r^2 = 0.991$; AMPA = 1.325x + 1.707, $r^2 = 0.989$; glufosinate = 1.249x + 0.372, $r^2 = 0.995$. The inter-day variation of standards responses showed a good reproducibility with relative standard deviations of 9, 17 and 9% for glyphosate, AMPA and glufosinate respectively at 50 ng/L and of 8, 4 and 9% at 1000 ng/L; standard deviations of calibration curve slopes varied with 3, 1.6 and 6.5% respectively. Despite elevated response variations for river water spiked at low concentrations (30 ng/L), the method showed a good accuracy with mean yields of spiked Evian© samples varying from 86 to 109%, whereas for spiked river water samples they varied from 90 to 133% (Table 8.5-185). This variability is substantially reduced at higher concentration (130 ng/L) and can thus be related to blank subtraction.

Table 8.5-185: **Mean recoveries of spiked water samples (n = 3) [%, (SD%)]**



Sample	*Concentration [ng/L]*	*Glyphosate*	*AMPA*	*Glufosinate*
Evian© water	30	109.1 (26.9)	86.3 (28.4)	88.0 (17.9)
Evian© water	130	101.1 (12.1)	105.1 (9.2)	104.0 (20.0)
River water	30	102.9 (133.8)	115.6 (13)	90.3 (47.8)
River water	130	115.9 (9.0)	133.1 (19.6)	109.8 (30.8)

Limits of Detection (LOD) and of Quantification (LOQ)

The limit of quantification (LOQ) in ultrapure and Evian© water samples was 7 ng/L, with a signal/noise ratio (S/N) equal or above 10 for the three compounds, whereas for river water samples S/N was lower. However, at 14 ng/L the S/N ratio was higher than 10. As the concentration of the first standard used to build the calibration curves is 10 ng/L, the LOQ can thus be fixed at this level. Spiked Evian© water at lower concentrations showed S/N ratios above 3 at 5 ng/L. In surface water sample S/N ratios above three were observed at 7 ng/L. Thus, the method LOD and LOQ were fixed at 5 and 10 ng/L respectively.

Environmental samples

Samples taken in the Lutrive River exhibited concentrations between the detection limit and maximum values of 800 ng/L and 300 ng/L for glyphosate and AMPA respectively (Figure 8.5-142). These concentration peaks are well above the legal threshold value defined for pesticides in Switzerland (100 ng/L). This implicates that glyphosate and AMPA may be hazardous for surface waters. These values are in the range of previous results obtained with occasional sampling in different other Swiss rivers. Glyphosate shows a typical pattern for chemicals applied in agriculture, with elevated concentrations during rain events, suggesting the transfer of these compounds from fields to surface water as already shown for other herbicides. The concentration pattern of AMPA also exhibits peaks, suggesting a similar transport pathway than for glyphosate.

Results of the depth profile from the Vidy bay of Lake Geneva in July 2010 (Figure 8.5-143) showed glyphosate concentrations in general below the LOQ. Glufosinate and AMPA were detected in higher concentrations reaching a maximum of 26 and 67 ng/L, respectively, suggesting possible other sources than for glyphosate. For AMPA, the highest concentrations were found at 25 m depth, at which depth dissolved organic carbon (DOC) and major ions measurements show also a concentration peak. In a recent publication, Bonvin *et al*. highlighted the influence of the WWTP outlet and the release of treated wastewater at this specific depth, as confirmed by temperature and conductivity anomalies. This may explain the increase in concentrations of the metabolite AMPA and major ions at this depth as shown for other micropollutants such as pharmaceuticals. It has been suggested that the degradation of phosphonic acids in detergents was also an important source of AMPA in wastewater, especially during dry periods.

Figure 8.5-142: **Results for the Lutrive River from April to September 2010: Concentrations of glyphosate (•), AMPA () and glufosinate (◊); daily precipitations from the Pully meteorological station (Source: MeteoSwiss, histograms); threshold of the federal ordinance on water protection (Oeaux) for pesticides (100 ng/L; -).**

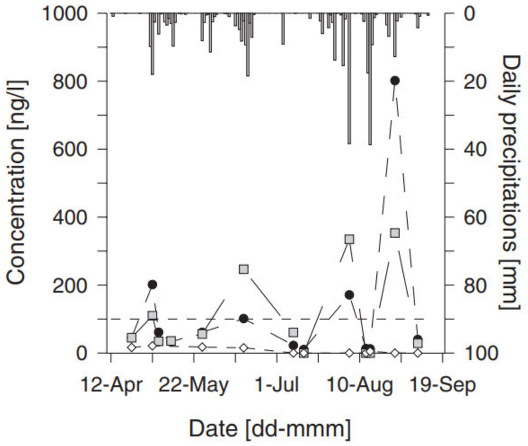
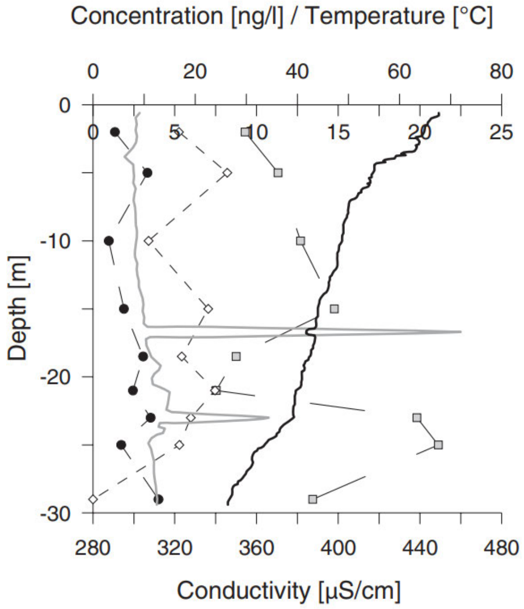


Figure 8.5-143: **Results for the lake depth profile sampled above the WWTP outlet in Vidy Bay, Lake Geneva, the 1st of July 2010; glyphosate (•), AMPA () and glufosinate (◊) concentrations; temperature (black line) and conductivity (grey line) profiles.**



Conclusion

The validation of the method to quantify the herbicide glyphosate, its metabolite AMPA and the herbicide glufosinate at trace level in several types of natural waters was successful and allows following these potential hazardous molecules in the environment. Further investigations to better understand their behavior in soils after their application and their transport to surface water will be possible. Preliminary results of field studies show that river water samples exhibit a frequent pollution by the studied herbicides, which finally end up in Lake Geneva. Several samples showed concentrations above the legal threshold of 100 ng/L. This highlights the importance of monitoring these substances in the aquatic system.

Assessment and conclusion by applicant:

The main focus of the article is the validation of an analytical method in different water matrices. The measured values for glyphosate and AMPA from natural sites can be used for monitoring purposes. They represent a vineyard area in Switzerland.

The article is considered reliable.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions. The article is considered reliable for validation of analytical method in water matrices used in CA7.5/053.

In the frame work of the method validation, surface water samples from the Lutrive River and the lake Geneva were collected and analysed.

The Lutrive is a local river in the east of the city of Lausanne, at the western limit of the Lavaux vineyard area. Its small watershed (6.4 km2) is characterized by different land uses: agricultural fields (45%), of which 4.1% are vineyards, urban and impervious surfaces (31%) and forests (24%).

Grab samples were collected in the vineyard area during the growing season of 2010 and during both dry- and wet-weather conditions

Lake Geneva was sampled during dry weather on the 1st of July 2010, in the Vidy Bay near the waste water treatment plant (WWTP) outlet at nine different depths: -2, -5, -10, -15, -18.5, -21, -23, -25 and -29 m.

Maximum concentrations of 800 ng/L and 300 ng/L for glyphosate and AMPA respectively were measured in the Lutrive river. In the Lake Geneva, glyphosate concentrations were in general below the LOQ. AMPA was detected in higher concentrations reaching a maximum of 67 ng/L The highest AMPA concentrations were found at 25 m depth, at which depth dissolved organic carbon (DOC) and major ions measurements show also a concentration peak

Data point:	CA 7.5/053
Report author	Daouk, S. *et al.*
Report year	2013b
Report title	The herbicide glyphosate and its metabolite AMPA in the Lavaux vineyard area, western Switzerland: Proof of widespread export to surface waters. Part II: The role of infiltration and surface runoff
Document No	Journal of Environmental Science and Health, Part B (2013) 48, 725–736
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable (but concentration in runoff water)

The article was found relevant for multiple subchapters. The summary is provided in the soil monitoring subchapter of this document.

Assessment and conclusion by RMS:

The study is considered reliable but provides measured concentration in runoff water and not in surface water, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

The article reports the mobility of glyphosate and AMPA in soil and runoff to surface water after application of the parent to 2 parcels of a vineyard soil in Switzerland. Slopes are from 13 to 43%. Glyphosate was applied to the two parcels in April of 2010 and 2011, at the application rate of 1080 g/ha.

The following results are reported for concentration of glyphosate and AMPA in the runoff samples:

In 2010, high concentrations of glyphosate and AMPA were found in the two first unfiltered (but decanted) runoff samples after the application: 73 and 110 µg/L, respectively 9 and 14 µg/L. This result is in agreement with the relatively high concentration found (567 ng/L) in the soil solution at 80 cm for the same period (05/05/10). Glyphosate concentrations dropped down to 7 µg/L in May and then to 4 µg/L in early June, before decreasing to 1 µg/L after the succession of rainy days in mid-June.
For AMPA, the decrease in concentrations was less drastic, what can be explained by the fact that it is assumed to be constantly produced by glyphosate degradation. The high concentration (~9 µg/L) observed in early July occurred after only one rainy day after a dry period that probably allowed soil microorganisms to decay glyphosate into AMPA more actively.

In 2011, concentrations were in the same range of values and their decrease was also observed, but to a lower extent. In contrast to 2010, AMPA concentrations were never higher than those of glyphosate. At the end of June, high concentrations were observed again with 95 µg/L of glyphosate and 9 µg/L of AMPA. These values are in same range than right after the application in late April, revealing an application on neighbourhood parcels. Indeed, the important rainfall of more than 40 mm in two days induced certainly a huge runoff, possibly passing across the road situated above the parcel, and penetrating it.

In order to determine whether glyphosate and AMPA were transported in the dissolved state or bound to soil particles, a syringe filtration (Nylon filters) of runoff samples was made: the fraction <0.45 µm still carried between 70 and 90% of the total concentration, with medians of 78% and 73% for glyphosate and AMPA respectively (n = 10, data not shown). Thus, transport of glyphosate and AMPA associated to coarse particle (>0.45 µm) accounted for 20–30%, which is more than in previous studies despite a smaller cut-off (0.24 µm).

Data point:	CA 7.5/054
Report author	Houtman, C. *et al.*
Report year	2013
Report title	A Multicomponent Snapshot of Pharmaceuticals and Pesticides and in the River Meuse Basin
Document No	Environmental Toxicology and Chemistry, Vol. 32, No. 11, pp. 2449-2459
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The river Meuse serves as a drinking-water source for more than 6 million people in France, Belgium, and The Netherlands. Pharmaceuticals and pesticides, both designed to be biologically active, are important classes of contaminants present in this river. The variation in the presence of pharmaceuticals in time and space in the Dutch part of the Meuse was studied using a multicomponent analytical method for pharmaceuticals combined with univariate and multivariate statistical analyses of the results. Trends and variation in time in the presence of pharmaceuticals were investigated in a dead-end side stream of the Meuse that serves as an intake point for the production of drinking water, and 93% of the selected compounds were detected. Highest concentrations were found for the antidiabetic metformin. Furthermore, a spatial snapshot of the presence of pharmaceuticals and pesticides was made along the river Meuse. Principal component analysis was successfully applied to reveal that wastewater-treatment plant effluent and water composition at the Belgian border were the main factors determining which compounds are found at different locations. The Dutch part of the river basin appeared responsible for approximately one-half of the loads of pharmaceuticals and pesticides discharged by the Meuse into the North Sea. The present study showed that multicomponent monitoring in combination with principal component analysis is a powerful tool to provide insight into contamination patterns in surface waters.

Materials and Methods

Chemicals
All chemicals were bought commercially.

Sampling
Grab-water samples were taken in prerinsed bottles of green glass every 4 wk from August 2010 to August 2012 (27 analyses) at the intake site for drinking-water production in the dead-end side stream of the river Meuse.

Analysis of pharmaceuticals with the ultra-HPLC/MS-MS multicomponent method
The analysis method contained 41 pharmaceuticals. In the selection of compounds, specific attention was given to pharmaceuticals with large consumption volumes. Eleven of the 20 most-sold pharmaceuticals were included. Other selection criteria were previous detection, ecotoxicological relevance (e.g., cytostatics, antibiotics, and nonsteroidal anti-inflammatory drugs), and representation of different therapeutic classes. The method was validated by calculating the recovery and standard deviation in surface-water samples from 8 different locations and sampled on different days spiked with pharmaceuticals. The average recovery was 91±14%. Most (n = 32) compounds had a minimum reporting limit of 5 ng/L or lower, of which 18 compounds had a minimum reporting limit between 0.1 ng/L and 1 ng/L. The highest minimum reporting limit was obtained for clofibrate (85 ng/L).

Statistical analyses
Box plot figures representing minimum, first quartile, median, third quartile, and maximum concentrations were made in Excel for pharmaceuticals that were detected in at least 5 samples (20% of the samples). Concentrations less than the minimum reporting limit were artificially set at 25% of the individual minimum reporting limit. The significance of long term time trends and seasonal variation was tested using the statistical software package Trendanalist. For this purpose, the obtained data set was complemented with archived monitoring results for those pharmaceuticals that had also been monitored with enough sensitivity with LC/MS and gas chromatography (GC)/MS methods at the same location from 2005 to 2010 (the test requires results of a period of at least 4.5 yr). Long-term time trends were tested with linear regression (in case of normally distributed data), and the Mann-Kendall test corrected for seasonal effects (if data were not normally distributed). Seasonal variation was tested with Kruskal-Wallis tests.

Spatial snapshot of pharmacuticals along the Meuse

Sampling locations
Water from 16 locations was sampled to generate a snapshot of the chemical water quality of the Dutch part of the rive Meuse. Samples were taken either from the main stream of the river Meuse or from rivers feeding the Meuse (Dommel and As) or from points along the Meuse or Waal nearer the entrance to the North Sea. Sampling points included locations near waste water treatment plants and drinking water abstraction points.

Sampling
Grab samples were collected from the 16 locations in a single sampling campaign between 13 and 16 September 2010. This month had some rain and a low to moderate flow in the river of, on average, 6.8 E6 m^3/d at the Belgian border. From 2 locations (1 and 12) additional samples were taken 1 wk prior (week 1, 9 September) and 1 wk after (week 3, 23 September) the sampling campaign (week 2, 13-16 September) to enable calculation of loads (see section Loads discharged into the North Sea) and to gain an understanding of variation in measured concentrations in the semi-long term. Samples were stored at 4°C and processed within 48 h.

Multicomponent analysis of pharmaceuticals and pesticides

Pharmaceuticals were analyzed on ultra-HPLC/MS-MS as described above. Concentrations of bisoprolol and propranolol were not included in the snapshot study due to uncertainty in the quantification in some samples caused by matrix effects (ion enhancement). The pesticides were analyzed by Aqualab Zuid, according to their own validated protocols. In short, pesticides were analyzed using a multicomponent method for 65 polar pesticides on ultra-HPLC/triple-quadrupole-MSMS. A total number of 140 less polar and more volatile pesticides were analyzed with a multicomponent method by means of GC-mass selective detection. The herbicide glyphosate and its metabolite aminomethylphosphonic acid were derivatized and analyzed by HPLC combined with fluorescence detection.

Statistical analysis
A principal component analysis was performed to cluster activities in the river basin according to contamination patterns using XLStat2008 software. Only compounds detected in at least 20 % of the measurements were included (10 water quality parameters, 19 pesticides, and 29 pharmaceuticals). All concentrations less than the minimum reporting limit were artificially set at 0. First, all concentrations were standardized ([concentration at individual location - average concentration]/standard deviation). A matrix was constituted with the 20 samples (16 locations plus the 2 additional samples at both locations 1 and 12) as loadings and filled with the standardized concentrations of general water-quality parameters, pharmaceuticals, and pesticides as observations. Replicates were included to investigate if these measurements would give factor loadings more similar to each other than measurements at other locations. Principal component analysis was performed to check the cumulative variance explained by the first principle component and then repeated with Varimax rotation to reduce the projection of the variance from projection on 20 components to projection on 3 components.

Loads discharged into the North Sea
Daily loads of pharmaceuticals and pesticides passing through the Meuse were calculated from the measured concentrations using flow data at locations 1, 2, 4, 12, and 16, because flow data for these locations could be provided by the Dutch Ministry of Infrastructure and Environment and the Water Board Aa and Meuse. Single measured concentrations for each individual compound were available for locations 2, 4, and 16. Loads for these locations were calculated using the average flow between 2 and 30 September 2010 as follows

$$\text{Load} = Q_{4\text{ wk average}}\ \text{X}\ c$$

where Q represents the flow and c represents the compound concentration. Three weekly measured concentrations were available for locations 1 and 12. For these locations, average loads were calculated more precisely using the averaging estimators approach with the formula

$$\text{Load} = \left[\sum (c_i \times Q_i) / \sum (Q_i)\right] \times Q_{4\text{ wk average}}$$

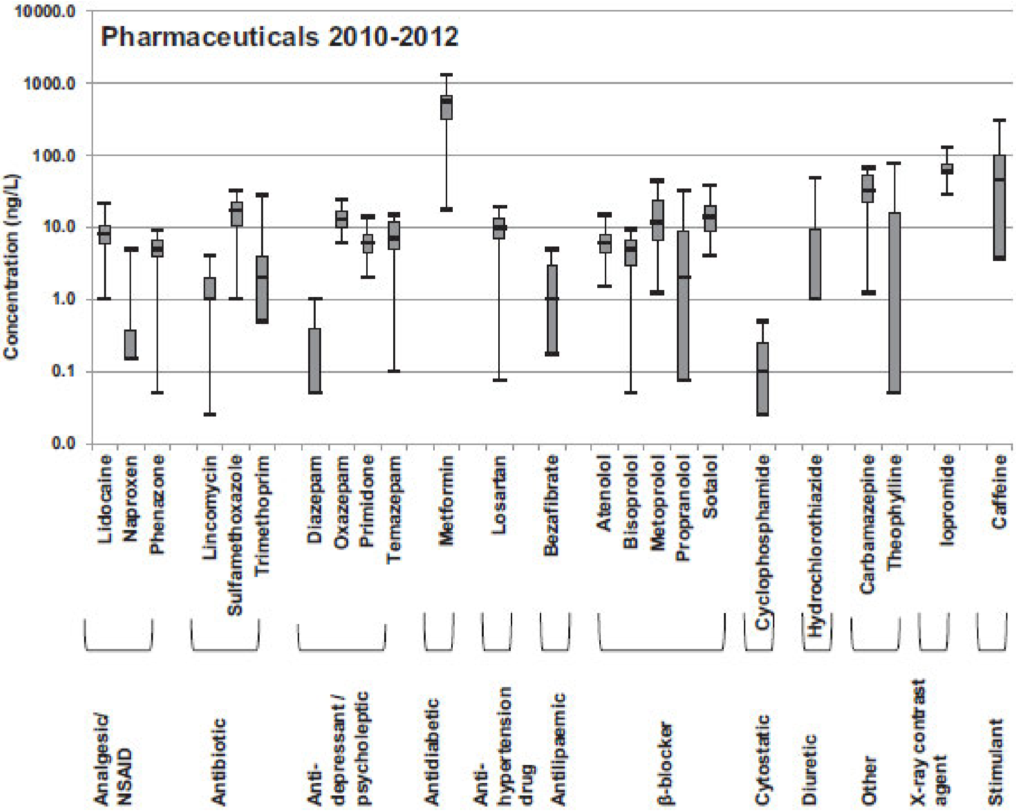
where Qi represents the flow on day i and ci represents the individual compound concentration on day i.

Results and Discussion

Variation and trends of pharmaceuticals in time

Presence of pharmaceuticals
Surface water from the enclosed branch of the Meuse (location 11) was analyzed every 4 wk from August 2010 to August 2012. Thirty-two compounds were detected at least once in the enclosed Meuse, and 20 compounds were detected in >50% of the samples. Most compounds had median concentrations on the order of 10 ng/L, and variations of concentrations in time were seen in orders of magnitude. Figure 8.5-144 provides the concentration characteristics of those pharmaceuticals detected in at least 20 % of the samples, represented as a box plot.

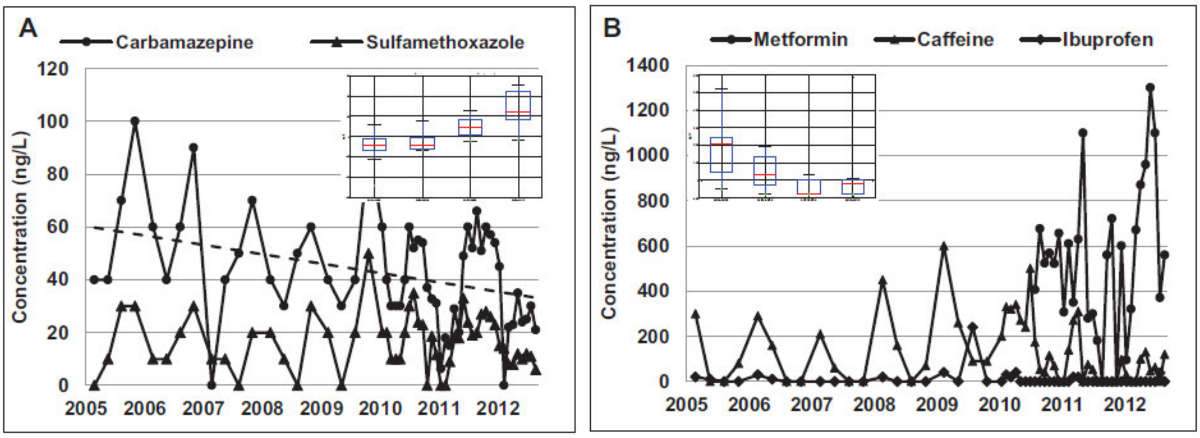
Figure 8.5-144: **Box plot diagram summarizing the median, minimum, maximum, and 25th and 75th percentile concentrations of 4-wk measured concentrations of pharmaceuticals in the enclosed Meuse between August 2010 and August 2012. NSAID: nonsteroidal anti-inflammatory drug.**



Representatives of all investigated therapeutic classes were found during the 2 yr of measurements. Although most individual pharmaceuticals were found in concentrations around 10 ng/L, their combined concentration was between 0.3 µg/L (August 2011) and 1.6 µg/L (May 2012).

By far, the highest concentrations (on average 0.6±0.3 µg/L) were found for the antidiabetic drug metformin (Figure 8.5-145B). Because more than 80% of Dutch diabetes type II patients are treated with this drug with daily doses up to 3 g to lower their serum glucose levels, this drug is number 5 in the top list of most prescribed drugs in The Netherlands (http://www.gipdatabank.nl/); and will probably also be among the top prescribed drugs in Belgium and France.

Figure 8.5-145: Concentration patterns of pharmaceuticals in surface water from the enclosed Meuse between 2005 and 2011. The dotted line represents the measured trend for carbamazepine. Inserted panes show box-whisker plots of seasonal variations in the concentration of carbamazepine (A) and caffeine (B) in the 4 periods of January to March, April to June, July to September, and October to December.



The 2 other compounds that were present in concentrations ≥100 ng/L were the stimulant caffeine and the X-ray contrast agent iopromide. Both compounds were found with median concentrations (46 ng/L and 60 ng/L, respectively) comparable to those previously found for other European rivers (72 ng/L and 100 ng/L, respectively). Six analgesics and nonsteroidal anti-inflammatory drugs were detected. Most prevalent were phenazone and lidocaine present in 96% to 100% of the samples. This is in line with previous findings. Ibuprofen, although belonging to the high-consumption volume compounds, was detected only once (40 ng/L), probably due to its relatively high minimum reporting limit (32 ng/L) and its almost complete removal (99% removed during wastewater treatment.

Of the cholesterol synthesis inhibitors, only atorvastatin was detected once, possibly due to its high removal rate in wastewater treatment (85-90%).

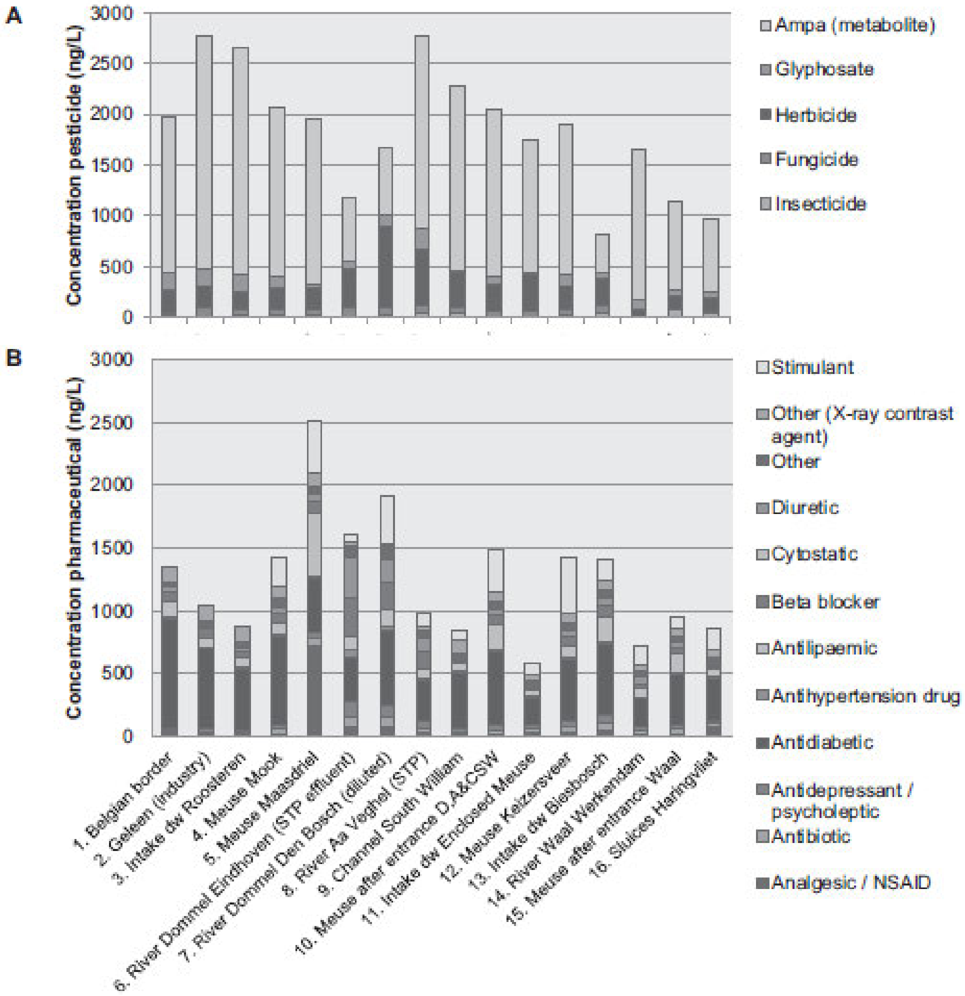
All investigated antidepressants/psycholeptics were detected. The benzodiazepines diazepam, oxazepam, and temazepam (psycholeptics) were included in the method because of their high consumption volumes. The highest concentration was found for oxazepam (24 ng/L). Of the cytostatics, cyclofosfamide was detected more frequently (52%) than ifosfamide (11 %). Both were present at very low concentrations (maximum 1 ng/L) and could be detected only because of a rather low minimum reporting limit in our method for these compounds. The investigated antibiotics clearly divided into 3 (chloramphenicol, oxacillin, sulfaquinoxalin) that were (almost) never found and 3 (lincomycin, sulfamethoxazole, and trimethoprim) that were detected in almost every sample.

Antihypertension drugs, b-blockers and diuretics, the antiepileptic carbamazepine, and theophylline (drug against chronic obstructive pulmonary disease and asthma) were also structurally detected, with frequencies of 89% for losartan and 67% to 100% for all 5 investigated b-blockers.

Carbamazepine was the only compound for which a significant temporal trend was found (Figure 8.5-145A). The concentration decreased by an average of 7.5% (3 ng/L) per year. To investigate if the absolute amount of carbamazepine present in the enclosed Meuse had decreased, calculation of loads is necessary. Unfortunately, suitable flow data were not available for this location.

The concentrations of caffeine ($p < 0.2\%$), carbamazepine ($p < 0.1\%$), ibuprofen ($p < 0.1\%$), and sulfamethoxazole ($p < 1\%$) varied significantly between seasons. Carbamazepine and sulfamethoxazole (Figure 8.5-145A) showed highest concentrations in fall. Caffeine and ibuprofen (Figure 8.5-145B) showed highest concentrations (up to 600 ng/L) in winter and spring. Thirty-five pharmaceuticals were detected during the sampling campaign in the Meuse (Figure 8.5-146B). Remarkably, a high concentration of 442 ng/L of unknown cause of the antilipemic pravastatin was detected in the Meuse at Maasdriel.

Figure 8.5-146: Pesticides (A) and pharmaceuticals (B) in 20 water samples taken in September 2010 in the Dutch part of the Meuse River basin. Combined concentrations of all pharmaceuticals and pesticides are shown according to their class per location. Strictly speaking, glyphosate is a herbicide; however, because its concentration is so high and as such so determinative for the total concentration of herbicides, it is shown separately. NSAID: nonsteroidal anti-inflammatory drug; DW= drinking water.



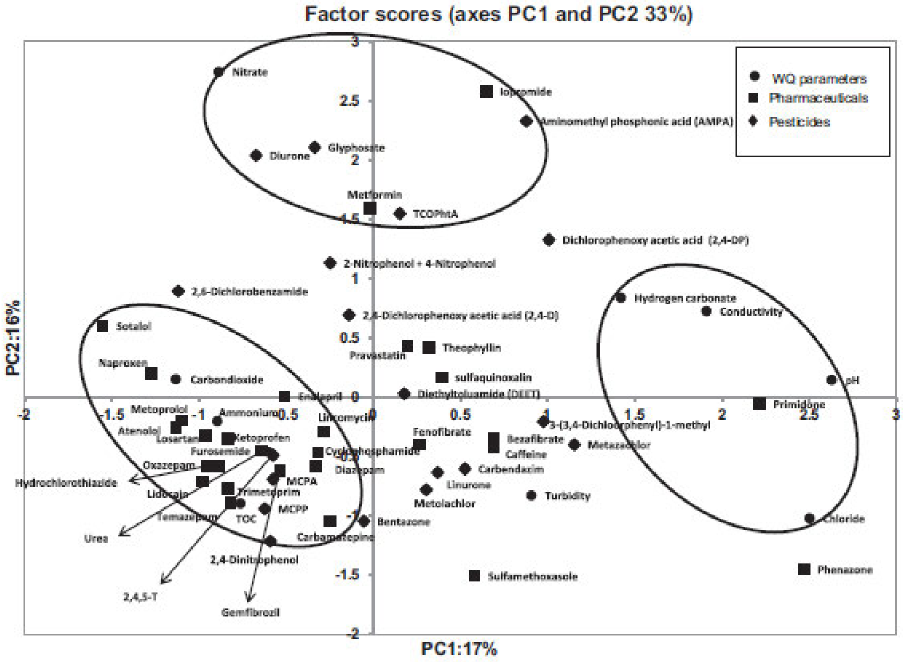
Twenty-eight pesticides were detected. Concentrations varied between less than the minimum reporting limit (10 - 20 ng/L for most pesticides) to 1.3 µg/L for aminomethylphosphonic acid at location 2 (Figure 8.5-146A). Pesticides have long been the most important group of contaminants of concern to drinking-water companies using the Meuse as a water source. In contrast to pharmaceuticals, which are generally of point-source origin to watersheds (e.g. via WWTP outfalls), herbicides are mostly of non-point-source origin because they are applied directly to the land for agricultural purposes. The fact that only 14% of 205 analyzed pesticides were detected might be partly explained by the fact that the multicomponent methods used for pesticides contained many pesticides that are not frequently found in Dutch surface waters anymore but for which monitoring is still obligatory according to European Union or national legislation. Only 4 insecticides were detected: diazinone, bromophos-ethyl, dichlofenthione, and N,N-diethylmeta-toluamide. All were found once, except N,N-diethyl-metatoluamide, which was found in 60% of the samples. The main use of N,N-diethyl-meta-toluamide is not in agriculture but as an insect-repellent by the public. Two fungicides were detected: carbendazim and 2,6-dichlorobenzamide.

Both were present in more than 75% of the samples. Nineteen detected pesticides belong to the class of herbicides. Among them were glyphosate and aminomethylphosphonic acid (its degradation product). They are notorious contaminants in the river Meuse. The main emission pathways to the Dutch part of the Meuse are runoff from pavements. Glyphosate is not well degraded in WWTPs. Degradation to aminomethylphosphonic acid takes place mainly in the environment. Glyphosate and aminomethylphosphonic acid were the only pesticides found in all samples. Relatively high concentrations of pharmaceuticals and pesticides were found in samples from the WWTP effluent receiving rivers feeding the Meuse.

Principal component analysis-factor loadings
Principal component analysis was performed with a data matrix consisting of 20 samples (locations) as variables and 58 parameters as observations (10 water-quality parameters, 29 pharmaceuticals, and 19 pesticides that were detected in at least 20% of the measurements). The analysis showed that of the 20 principle components, the first accounted for 17% of the total variance, the second for 16%, and the third for 14% of the total variance of the data set. Collectively, the first 3 components could thus explain 47% of the total variance. Locations with a positive score on principal component 1 are less influenced by WWTP effluent due to strong dilution (locations 14-16 are situated in the large river Waal and in wide parts of the Meuse) or environmental degradation (e.g., the residence time of water in the enclosed Meuse is about 6 wk). Principal component 2 groups samples mainly according to their geographical location in the river basin. A positive loading is found for locations in the first part of the river basin downstream from the Belgian border. No clear trend was observed in the loadings on principal component 3. This principal component apparently reflects projection of a combination of diffuse factors that could not be straightforwardly interpreted. Therefore, interpretation of scores was done only for principal components 1 and 2.

Principal component analysis-factor scores
Figure 8.5-147 shows the factor score plot for principal component 1 versus principal component 2. It gives an impression of the extent to which types of locations are predictors of the compounds found somewhere. The components belonging to the group of pesticides have factor scores most to the center of the plot and are scattered throughout the plot. This indicates that contamination with pesticides as a group occurs throughout the Meuse River basin and is not very location-specific within or is not projected enough on the first 2 components of the principal component analysis to elucidate a specific clustering of individual pesticides. Water-quality parameters and pharmaceuticals, however, do show distinct clustering and separation. On the left in Figure 8.5-147, the water-quality parameters (circles) CO_2, NH_4^+, TOC, and urea are found. Indeed, NH_4^+ , TOC, and urea are known to be markers for WWTP effluent, especially during rainy periods and sewer overflows. In addition, the majority of pharmaceuticals detected in the present study (18, 62%) are found in this same cluster. This is in agreement with the fact that WWTPs are important sources of pharmaceuticals in surface waters. Besides lack of persistence, for some compounds, such as sulfamethoxazole, sulfaquinoxalin (used in veterinary pharmaceuticals), and iopromide (only used in hospitals), scores outside the cluster can be explained because they have emission routes other than WWTPs. The score of caffeine, also not in the cluster, agrees with its high water solubility and low persistence, which make it a suitable marker for anthropogenic influence but not specific for WWTP effluent. Conductivity, HCO_3^-, pH, and chloride cluster positively on principal component 1.

Figure 8.5-147: Factor score plot of measured parameters of the snapshot study on principal components 1 and 2 (PC1 and PC2, respectively) after Varimax rotation by principal component analysis. The factor scores indicate how the processes projected on the first and second principal components predict the contamination pattern of individual parameters (compounds). WQ = water quality; MCPP = 2-(2-methyl-4-chlorophenoxy) propanoic acid; MCPA = (4-chloro-2-methylphenoxy) acetic acid.



A decrease of HCO_3^- thus leads to higher concentration of CO_2, which was indeed found on the negative part of principal component 1. The highest pH and chloride were measured at locations in the delta area due to influence of intruding seawater and mixing with water from the river Waal.

Principal component 2 was found to represent the water composition of the Meuse at the Belgian border. In the upper part of the score plot, a remarkably high positive score on principal component 2 is found for nitrate and for some pesticides (glyphosate and its metabolite aminomethylphosphonic acid and diurone). This may be explained by leaching of these compounds from the sandy soils in the province of Limburg, which are used for intensive chicken and pig farming and treated with manure.

Calculated loads

The snapshot study was performed in September at low-flow conditions, just before the seasonal rise of flow in the river Meuse occurred. Water flows at the Belgian border were comparable during the first 2 sampling weeks (respectively, 8.2 E6 m^3/d and 8.4 E6 m^3/d) and much lower in the third sampling week (3.4 E6 m^3/d). Therefore, it was important to use all the replicate samples for the calculation of loads. Concentrations did not decrease proportionally (Figure 8.5-146), however, so loads of 18.3 kg/d (6.7 t/yr) of pharmaceuticals and 25.6 kg/d (9.2 t/yr) of pesticides are found at Meuse Keizersveer, indicating an increase in The Netherlands by a factor of 2.0 and 2.6, respectively, between the Belgian border and the Meuse at Keizersveer. In the delta area between Keizersveer and Haringvliet Sluices, a further increase in loads was observed. However, as water in Haringvliet consists of an average 1:4 mixture of water from the rivers Meuse and Waal, concentrations measured here are more representative for the Waal than for the Meuse. The calculated contribution of The Netherlands is higher than expected based on the area of the river basin (23% of the area is situated downstream from the Belgian-Dutch border) and on the population density (40% in The Netherlands). A possible explanation could be a higher consumption of pharmaceuticals and pesticides in The Netherlands in comparison with upstream countries. Another explanation might be that compounds emitted in the French and Belgian parts of the river basin have more time for environmental degradation before they reach the Belgian border and, as such, concentrations in the upper part are less clearly related to emission than those downstream.

Conclusion
Multicomponent methods were successfully applied to investigate the presence of pharmaceuticals in time and space in the river Meuse. Among the detected compounds were those included in the method because of their large consumption volumes and those that were not investigated in the Meuse basin previously, such as metformin and benzodiazepines, confirming the relevance of consumption volume as a selection criterion for analysis of pharmaceuticals in the aquatic environment. It can - ideally, if combined with data on metabolism and degradation - serve to anticipate what can be expected to penetrate into surface waters and thus escape the pattern of focusing environmental monitoring only compounds previously detected (such as carbamazepine). The principal component analysis applied in this snapshot study revealed that emission of WWTP effluent and the composition of Meuse water as it enters The Netherlands at the Belgian border were the most important factors predicting the presence of compounds at locations in the Dutch part of the Meuse River basin. Multicomponent monitoring in combination with principal component analysis thus proved to be a powerful tool to provide insight into the relation between locations (activities in river basin) and compounds. However, pesticides especially occurred throughout the river basin and behaved mutually very differently in the principal component analysis. Therefore, it is not possible without considerable loss of information to select only 1 or a few compounds for monitoring that could represent a large group of environmental contaminants. Monitoring a broad range of compounds thus remains essential to investigate the quality of surface waters, especially if the water functions in the production of drinking water.

Several studies have concluded that measured traces of individual pharmaceuticals in water are too low to give rise to concern. Nevertheless, the structural presence of low concentrations of multiple pharmaceuticals in water abstracted for drinking-water production is an issue requiring further attention. A toxicological risk assessment of the mixture of compounds detected in water sources is the next step of our work. Pharmaceuticals and pesticides were found throughout the Meuse River basin. Because rivers often run through several countries, upstream activities can influence surface-water quality in other countries downstream. A good quantitative view of discharges was lacking for the Meuse. Our study showed that it is not appropriate to speak of the Dutch delta as Europe’s “sewage drain,” because approximately one-half of the discharged pesticides and pharmaceuticals appear to be added in The Netherlands itself. This result stresses the necessity of international collaboration in the protection of water quality in rivers crossing national boundaries.

Glyphosate concentrations in the range of 0.02 to 0.21 µg/L and AMPA concentrations between 0.38 and 2.28 µg/L were reported.

Assessment and conclusion by applicant:
The article describes the results of a monitoring exercise at the river Meuse in the Netherlands, where concentrations of 29 pharmaceuticals and 19 pesticides were reported from a multisite sampling campaign to evaluate the status of the Meuse. Glyphosate concentrations in the range of 0.02 to 0.21 µg/L and AMPA concentrations between 0.38 and 2.28 µg/L were reported.
The article is considered reliable.

Assessment and conclusion by RMS:
The article is considered reliable with restrictions, since describes a one shot sampling campaign.

It aimed at giving an overview of the chemical water quality of the Dutch part of the rive Meuse. Water from 16 locations was sampled once to generate a snapshot of the chemical water quality along the Dutch part of the river Meuse.

The concentrations results of glyphosate and AMPA (among other pharmaceuticals) detected in the snapshot study are reported as raw data in the study. Glyphosate concentrations in the range of 0.02 to 0.21 µg/L and AMPA concentrations between 0.38 and 2.28 µg/L were reported along the river.

Data point:	CA 7.5/055
Report author	Imfeld G. *et al*.
Report year	2013
Report title	Transport and attenuation of dissolved glyphosate and AMPA in a stormwater wetland
Document No	Chemosphere 90 (2013) 1333–1339
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable (but concentration measured in runoff)

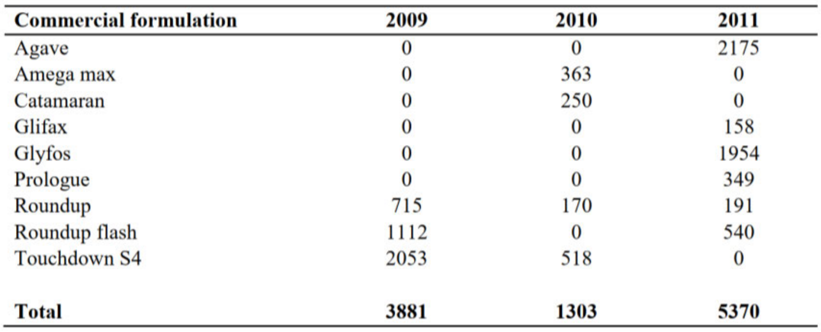
Glyphosate is an herbicide used widely and increasingly since the early 1990s in production of many crops and in urban areas. However, knowledge on the transport of glyphosate and its degradation to aminomethylphosphonic acid (AMPA) in ecosystems receiving urban or agricultural runoff is lacking. Here we show that transport and attenuation of runoff-associated glyphosate and AMPA in a stormwater wetland differ and largely vary over time. Dissolved concentrations and loads of glyphosate and AMPA in a wetland receiving runoff from a vineyard catchment were assessed during three consecutive seasons of glyphosate use (March to June 2009, 2010 and 2011). The load removal of glyphosate and AMPA by the wetland gradually varied yearly from 75% to 99%. However, glyphosate and AMPA were not detected in the wetland sediment, which emphasises that sorption on the wetland vegetation, which increased over time, and biodegradation were prevailing attenuation processes. The relative load of AMPA as a percentage of total glyphosate increased in the wetland and ranged from 0% to 100%, which indicates the variability of glyphosate degradation via the AMPA pathway. Our results demonstrate that transport and degradation of glyphosate in stormwater wetlands can largely change over time, mainly depending on the characteristics of the runoff event and the wetland vegetation. We anticipate our results to be a starting point for considering degradation products of runoff-associated pesticides during their transfer in wetlands, in particular when using stormwater wetlands as a management practice targeting pesticide attenuation.

Materials and Methods

Description of the vineyard catchment
The 42.7 ha vineyard catchment is located in Rouffach, Alsace, France. The study was carried out between 23 March and 30 June 2009, 2010 and 2011 because glyphosate use mainly proceeds in spring, from the end of March (bud-breaking of grapevine) to June (fruit-setting of grapevine). The detailed use of glyphosate in commercial preparations is provided in Table 8.5-186. The use of glyphosate was estimated based on yearly surveys addressed to the vine-growers (surveys covered at least 80% of the vineyard area). The mean precipitation from March 23 to June 30 is 204 ± 70 mm (1998–2011). Rainfall-runoff events do

not generate permanent stream in the catchment and statistically occur every week. During rainfall-runoff events, contaminated runoff converges at the outlet of the catchment where it is collected by the stormwater wetland. Surface runoff constitutes the main route of pesticide entry in the wetland.

Table 8.5-186: Glyphosate commercial preparations and amounts of glyphosate used at the vineyard catchment (Rouffach, Alsace, France) from March 23 to June 30 2009, 2010 and 2011. Values are given in grams of glyphosate.



Commercial formulation	2009	2010	2011
Agave	0	0	2175
Amega max	0	363	0
Catamaran	0	250	0
Glifax	0	0	158
Glyfos	0	0	1954
Prologue	0	0	349
Roundup	715	170	191
Roundup flash	1112	0	540
Touchdown S4	2053	518	0
Total	**3881**	**1303**	**5370**

Description of the stormwater wetland

The wetland was constructed in 2002 to control flooding into the urban area. The stormwater wetland has a surface area of 319 m^2 and a total volume of 1500 m^3. It is composed of a naturally planted forebay (215 m^2). The mean hydraulic retention time was 11.0 ± 8.3 h during the periods of investigation. The water storage capacity of the wetland forebay was 50 m^3. Water depth in the forebay varied from 0.1 to 0.5 m during the investigation periods, depending on the runoff volume entering. A secondary small inflow also contributed to the volume entering the wetland from March to May. The budget of water volumes entering and outflowing the wetland was balanced when direct rainfall and evapotranspiration volumes were included (data not shown). Due to the clayey wetland bed (permeability (k_s) < 10^{-10} m/s) and based on the water balance, water losses by vertical infiltration were negligible.

The chemical composition of wetland sediment was (mean ± SD%; $n = 5$): organic carbon 15.0 ± 0.9, SiO_2 49.6 ± 0.5, Al_2O_3 10.4 ± 1.1, MgO 2.2 ± 0.1, CaO 11.6 ± 1.1, Fe_2O_3 4.5 ± 0.5, MnO 0.1 ± 0.0, Na_2O 0.6 ± 0.1, K_2O 2.4 ± 0.2 and P_2O_5 0.4 ± 0.1. The sediment texture was (%): clay 44, fine silt 33, coarse silt 10, fine sand 5, and coarse sand 8. The pH value was 8.1. Sediments were removed from the wetland forebay on February 2008. Glyphosate and AMPA were analysed in the wetland sediment in 2009 and 2011, as described previously (Maillard *et al*., 2011). In 2009, the vegetation cover (*Phragmites australis, Juncus effusus and Typha latifolia*) in the wetland forebay was <1% of the area in March and April, 10% in May, and 50% in June. In 2010 and 2011, the same plant species were present and the vegetation covered 100% of the forebay area from April to June. *P. australis* (Cav.) represented 90% of the total vegetation cover through the investigation period. No algal growth was observed.

Runoff discharge measurement and sampling procedure

Runoff discharges entering and outflowing the wetland were continuously monitored from 23 March to 30 June 2009, 2010 and 2011. The water depth was measured using bubbler flow modules combined with a Venturi channel at the wetland inlet and a V-notch weir at the outlet. Flow proportional water samples were collected at the inlet using a 4010 Hydrologic automatic sampler and at the outlet using a 6712FR ISCO Teledyne automatic sampler. Water samples (300 mL) were collected in jars, stored in the dark at 4°C after each runoff event, and placed on ice during transportation to the laboratory for chemical analysis. The series of discrete flow proportional water samples taken over a runoff event were combined in a single composite sample prior to analysis.

Chemical analysis

Conductivity, pH, dissolved oxygen and redox potential were directly measured in the field using WTW multi 350i portable sensors. Concentrations of dissolved organic carbon (DOC), total suspended solids, total phosphorus and PO_4^{3-} were determined by FR EN ISO standards and laboratory procedures.

Glyphosate and AMPA were analysed according to the NF XPT 90-210 at the Pasteur Institute of Lille (France), which is accredited by the French National Accreditation Authority, and recognised by the European Cooperation for Accreditation. Water samples were filtered through 1 µm glass fiber filters and solid-phase extracted. Glyphosate and AMPA were extracted from sediment samples by ultrasonic and methanol extraction. Quantification of glyphosate and AMPA was performed after derivatisation with fluorenemethoxycarbonyl. Both compounds had a quantification limit of 0.10 µg/L and 10 µg/kg in water and sediment samples, respectively. Extraction efficiencies of pesticides were obtained for each water sample set by spiking with surrogates. Relative standard deviation was 16% for both compounds. Recovery efficiency was 86% for glyphosate and 81% for AMPA. Further quality control was achieved by using a blank for each set of samples.

Data analysis and calculation

Hydrological and hydrochemical variables were compared using the paired nonparametric Wilcoxon signed rank and the Spearman rank correlation tests. When glyphosate and AMPA concentrations were lower than the quantification limit, the concentrations were set to zero for calculating the occurrence and loading. For quantifying the transport of the total glyphosate loadings in the wetland, AMPA, as a glyphosate-derived compound, was expressed on a glyphosate mass equivalent. The mass equivalent load of glyphosate (MELgly) was calculated according to:

$$MEL_{gly} = Load\ (Glyphosate) + \left\{ Load\ (AMPA)\ \left[\frac{MW_{gly}}{MW_{\mathrm{AMPA}}}\right] \right\}$$

where MW_{gly} = molecular weight of glyphosate (0.16907 kg/mol), and MW_{AMPA} = molecular weight of AMPA (0.11104 kg/mol).

For quantification of the total seasonal glyphosate load as a percentage of the seasonal applied amount of glyphosate on the vineyard catchment, a seasonal export coefficient of glyphosate (SEC_{gly}) was calculated:

$$SEC_{gly} = \frac{MEL_{gly}\ (mass\, season^{-1})}{Glyphosate\ \ application\ \ (mass\, season^{-1})} 100$$

The relationship between AMPA and glyphosate was evaluated by calculating the %AMPA as a percentage of total loads of glyphosate and AMPA:

$$\%\mathrm{AMPA} = \frac{[\mathrm{AMPA}]}{([Glyphosate] + [\mathrm{AMPA}])} 100$$

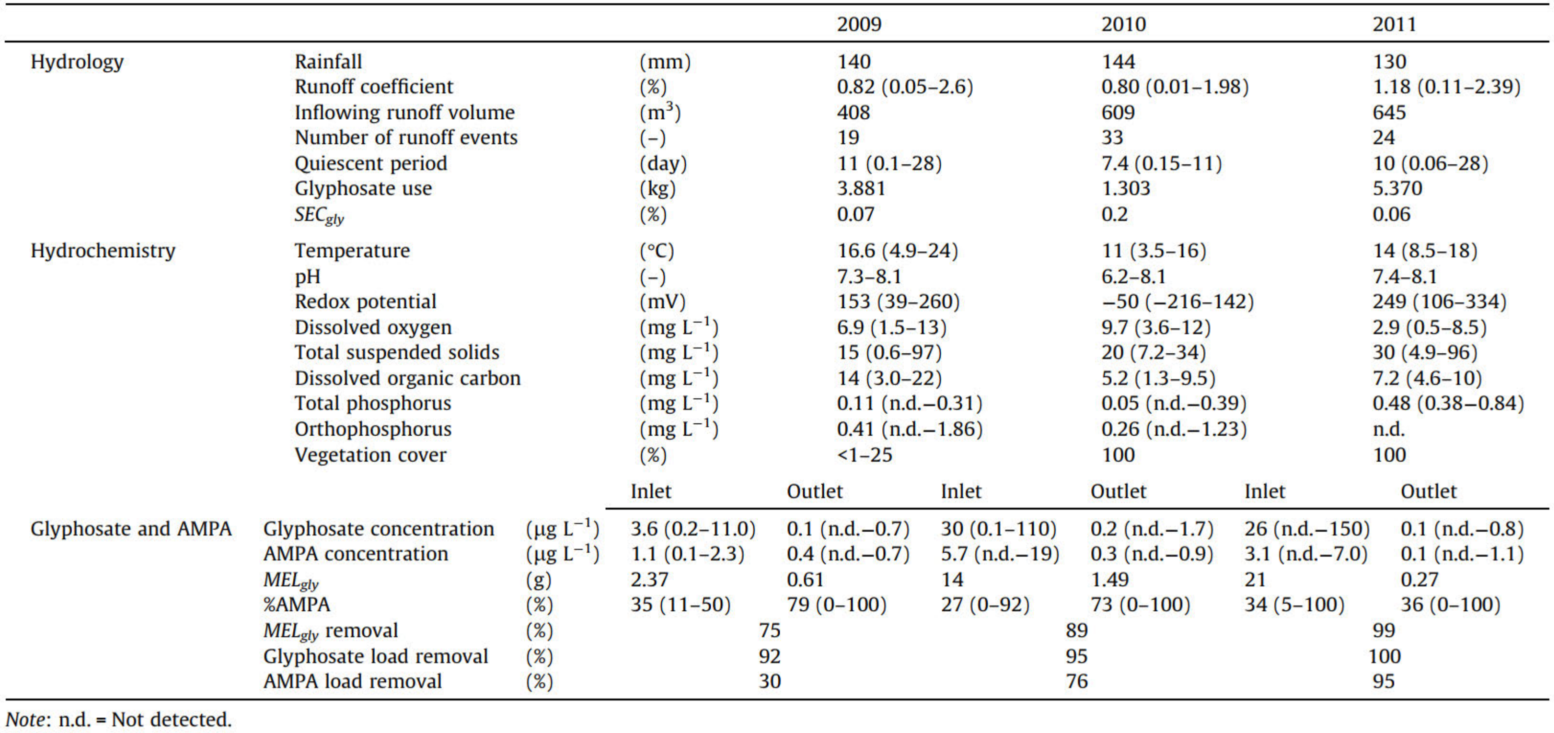
where [AMPA] and [glyphosate] are their respective molar loadings in water. A %AMPA equal to zero indicates either that both AMPA and glyphosate were below the quantification limit or that only AMPA was above it.

Results

Hydrological characteristics and glyphosate export

Climatic and hydrological characteristics from 23 March to 30 June 2009, 2010 and 2011 are summarised in Table 8.5-187 and Figure 8.5-148. Comparison of climatic characteristics revealed that temperature, solar radiation and evapotranspiration values were significantly lower in 2009 compared to those in 2010 and 2011 ($p \leq 0.05$). Runoff events that generated volumes lower than 50 m^3 accounted for more than 80%, indicating that small and moderate runoff events prevailed. The analysis of climatic and hydrological conditions revealed that conditions and rainfall-runoff patterns globally were similar in 2009, 2010 and 2011, although monthly variation occurred.

Table 8.5-187: Hydrology, hydrochemistry and glyphosate at the stormwater wetland (Rouffach, Haut-Rhin, France) from 23 March to June 30, 2009, 2010 and 2011. Values are provided as the mean and ranges.

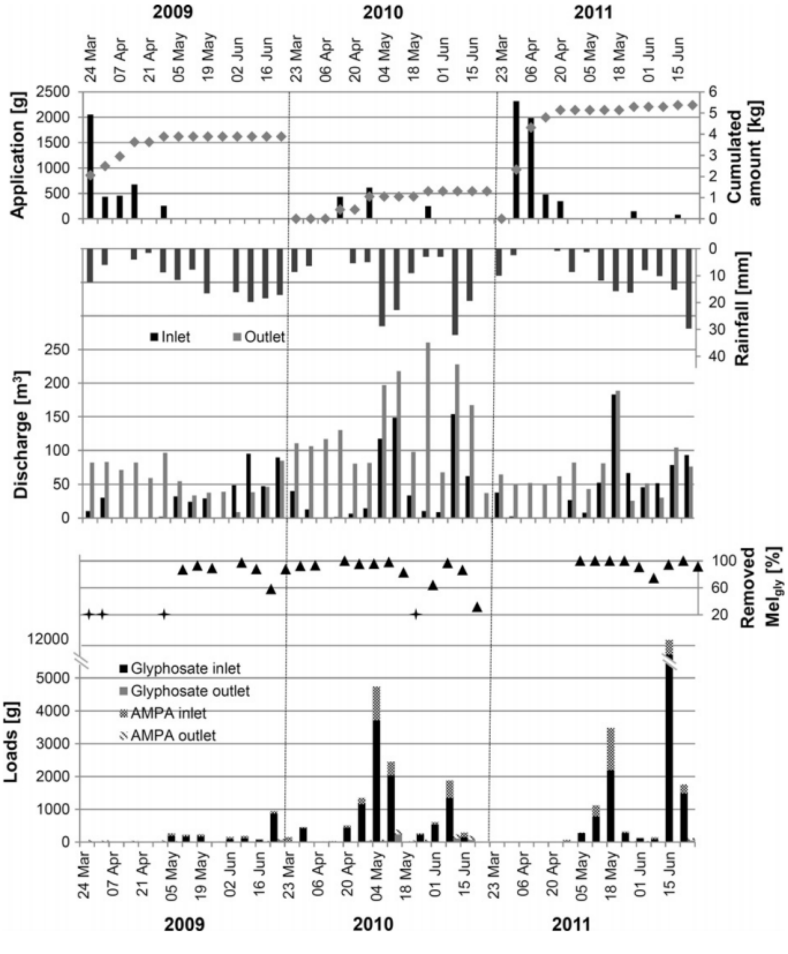


			2009		2010		2011	
Hydrology	Rainfall	(mm)	140		144		130	
	Runoff coefficient	(%)	0.82 (0.05–2.6)		0.80 (0.01–1.98)		1.18 (0.11–2.39)	
	Inflowing runoff volume	(m^3)	408		609		645	
	Number of runoff events	(–)	19		33		24	
	Quiescent period	(day)	11 (0.1–28)		7.4 (0.15–11)		10 (0.06–28)	
	Glyphosate use	(kg)	3.881		1.303		5.370	
	SEC_{gly}	(%)	0.07		0.2		0.06	
Hydrochemistry	Temperature	(°C)	16.6 (4.9–24)		11 (3.5–16)		14 (8.5–18)	
	pH	(–)	7.3–8.1		6.2–8.1		7.4–8.1	
	Redox potential	(mV)	153 (39–260)		−50 (−216–142)		249 (106–334)	
	Dissolved oxygen	(mg L^{-1})	6.9 (1.5–13)		9.7 (3.6–12)		2.9 (0.5–8.5)	
	Total suspended solids	(mg L^{-1})	15 (0.6–97)		20 (7.2–34)		30 (4.9–96)	
	Dissolved organic carbon	(mg L^{-1})	14 (3.0–22)		5.2 (1.3–9.5)		7.2 (4.6–10)	
	Total phosphorus	(mg L^{-1})	0.11 (n.d.–0.31)		0.05 (n.d.–0.39)		0.48 (0.38–0.84)	
	Orthophosphorus	(mg L^{-1})	0.41 (n.d.–1.86)		0.26 (n.d.–1.23)		n.d.	
	Vegetation cover	(%)	<1–25		100		100	
			Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Glyphosate and AMPA	Glyphosate concentration	(μg L^{-1})	3.6 (0.2–11.0)	0.1 (n.d.–0.7)	30 (0.1–110)	0.2 (n.d.–1.7)	26 (n.d.–150)	0.1 (n.d.–0.8)
	AMPA concentration	(μg L^{-1})	1.1 (0.1–2.3)	0.4 (n.d.–0.7)	5.7 (n.d.–19)	0.3 (n.d.–0.9)	3.1 (n.d.–7.0)	0.1 (n.d.–1.1)
	MEL_{gly}	(g)	2.37	0.61	14	1.49	21	0.27
	%AMPA	(%)	35 (11–50)	79 (0–100)	27 (0–92)	73 (0–100)	34 (5–100)	36 (0–100)
	MEL_{gly} removal	(%)	75		89		99	
	Glyphosate load removal	(%)	92		95		100	
	AMPA load removal	(%)	30		76		95	

Note: n.d. = Not detected.

Yearly patterns of glyphosate use are provided in Figure 8.5-148. Most glyphosate is applied in late March and April. There were small applications in May (2010) and two in June (2011). Runoff events generating volume larger than 50 m^3 mainly occurred in May and June and influenced the seasonal pattern of both concentrations and apportionments of both glyphosate and AMPA in runoff entering the wetland. In contrast, MEL_{gly} that entered the wetland in March and April 2009 and 2011 was lower than 70 mg, likely due to the occurrence of less intense rainfall-runoff events. The SEC_{gly} was 0.07 in 2009, 0.2 in 2010 and 0.06% in 2011, which indicates relatively low MEL_{gly} export. Although 3–5 times less glyphosate was used in 2010, MEL_{gly} export was larger compared to 2009 and 2011. This can be explained by more frequent and intense rainfall-runoff events following the applications and lower quiescent period (dry period between two rainfall-runoff events).

Figure 8.5-148: Temporal changes of glyphosate use, hydrological condition in the vineyard catchment (Rouffach, France) and total mass equivalent loads of glyphosate (*MEL_{gly}*) at the stormwater wetland from March to June 2009, 2010 and 2011. Stars represent negative removed *MEL_{gly}*.



Occurrence and concentration of glyphosate and AMPA in the wetland

Concentrations and loadings of glyphosate and AMPA in the wetland are summarized in Table 8.5-187 and in Figure 8.5-148. 98% of water samples ($n = 46$) collected at the inlet of the wetland through the three investigation periods had glyphosate and AMPA concentrations above the quantification limits. In contrast, only 52% and 83% of water samples ($n = 64$) collected at the outlet of the wetland had quantifiable concentrations of glyphosate and AMPA, respectively, which indicates that transport through the wetland reduced the occurrence of glyphosate and AMPA.

Glyphosate concentrations entering the wetland ranged from 0.1 to 150 µg/L. Mean inlet concentration (mean ± SD µg/L) was 3.6 ± 3.6 in 2009, 30 ± 30 in 2010 and 26 ± 48 in 2011, whereas that of AMPA was

1.1 ± 0.7 in 2009, 5.7 ± 4.9 in 2010 and 3.1 ± 2.6 in 2011. The mean concentration of glyphosate in 2009, 2010 and 2011 decreased by 36, 150 and 263 times from the inlet to the outlet of the wetland, respectively, whereas that of AMPA only decreased by 3, 19, 31 times, respectively. This indicates that concentration reduction by the wetland increased over year, although attenuation of glyphosate always was larger than that of AMPA on the seasonal time scale (Table 8.5-187). Concentrations of glyphosate and AMPA in the wetland sediments were below the detection limits in 2009 and 2011, which indicate no significant transfer of dissolved pesticides from the water column to the bed sediments or degradation of glyphosate and AMPA bond to sediment during the study period.

Transport and attenuation of MEL_{gly} in the wetland
In order to quantify the transfer and attenuation of glyphosate and AMPA in the wetland, the MEL_{gly} was evaluated at the wetland inlet and outlet (Figure 8.5-148). The total MEL_{gly} entering the wetland in 2009, 2010 and 2011 was 37.26 g, and that outflowing was 2.29 g, which corresponds to an overall MEL_{gly} removal efficiency of 94%. The seasonal MEL_{gly} removal efficiency increased over time (75% in 2009, 90% in 2010, and 99% in 2011). Interestingly, the MEL_{gly} entering the wetland also increased over time (2.38 g in 2009, 14.10 g in 2010 and 20.79 g in 2011), proportionally to the MEL_{gly} removed by the wetland (1.78 in 2009, 12.61 in 2010 and 20.52 g in 2011). This underscores the absence of threshold at which MEL_{gly} removal by the wetland would decrease at larger loading, which is further supported by a positive correlation between the inlet discharge, runoff-associated MEL_{gly} and MEL_{gly} removal by the wetland on the seasonal time scale ($p < 0.001$). Hence, the stormwater wetland very likely was not saturated by large input of glyphosate and AMPA during the study period, which may be due to the relatively low runoff coefficient at the study site. On a weekly basis, the MEL_{gly} removal efficiencies generally ranged between 80% and 100%, indicating that the wetland maintained its capacity to attenuate varying runoff-associated MEL_{gly} through the investigation period. When no storm event occurred and the wetland still was releasing water from previous storms, the weekly MEL_{gly} exported by the wetland ranged ranged from 18 to 60 mg. In these cases, the outflowing MEL_{gly} was larger than that at the inlet, thus yielding negative MEL_{gly} removal by the wetland.

Transport and attenuation of AMPA in the wetland
From 23 March to 30 June 2009, 2010 and 2011, the total load of AMPA entering and outflowing the wetland was 5.558 and 1.047 g, respectively. This corresponds to a total removal efficiency of 81%, and underscores that possible degradation of glyphosate to AMPA did not result in larger amount of AMPA at the outlet compared to the inlet during the study period. The seasonal AMPA removal efficiency (28% in 2009, 76% in 2010, and 95% in 2011) and the amount of AMPA removed by the wetland (0.188 g in 2009, 2.007 g in 2010 and 2.386 g in 2011) both increased over time. Globally, AMPA removal was lower than that of MEL_{gly} and glyphosate. The accumulation of AMPA following glyphosate degradation in the wetland was evaluated based on the relative proportion of AMPA as a percentage of total glyphosate and AMPA loadings (%AMPA). The %AMPA generally exceeded 60% at the outlet, whereas AMPA rarely prevailed at the inlet. The mean %AMPA through the investigation periods was 32 ± 23% at the inlet and 63 ± 40% at the outlet, which clearly emphasises that the AMPA fraction increased during transport through the wetland. However, %AMPA ranged from 0% to 100% both at the inlet and the outlet of the wetland, which underlines the temporal variability of the AMPA portion in the MEL_{gly}.

Discussion

Several attenuation processes may simultaneously and synergistically control the transfer of dissolved glyphosate and AMPA in wetlands. The transfer and attenuation of glyphosate and AMPA in the wetland is expected to mostly vary according to their partitioning between the aqueous and solid phases, and the biodegradation activity. The partitioning and biodegradation of glyphosate and AMPA are themselves controlled by the runoff characteristics, the apportionment of runoff-related glyphosate, the extent of sediment sorption, as well as climatic and hydrochemical variables. In particular, the gradual increase of MEL_{gly} removal over time and the increase of %AMPA in the wetland suggest an initial fast attenuation of glyphosate entering the wetland driven by sorption to the wetland sediment and the temporal development of the vegetation, followed by a slower attenuation phase controlled by biodegradation.

The gradual increase of MEL_{gly} removal correlated with the larger cover of wetland vegetation (from <1% in March 2009 to 100% in June 2011), which suggests that vegetation also contributed to glyphosate and AMPA attenuation. Owing to large spatial and temporal variations in the vegetal biomass and species in the studied wetland, the contribution of vegetation in glyphosate and AMPA attenuation could not be quantified.

A gradual adaptation of wetland microorganisms for the use of various phosphorus sources, including glyphosate and AMPA may explain the gradual increase of seasonal MEL_{gly} removal. Since the quiescent period (i.e. time between two runoff events) apparently increased when the MEL_{gly} removal decreased, regular and transient runoff passing through the wetland did not seem to result in lower MEL_{gly} removal.

Biodegradation of AMPA generally is slower than that of glyphosate. The %AMPA reflects temporal changes in the glyphosate degradation efficiencies in the wetland. As glyphosate degradation occurred, the amount of dissolved glyphosate available for transport through the wetland decreases, whereas the amount of AMPA relatively increases. Consequently, AMPA may accumulate in the wetland when its degradation efficiency is significantly lower than that of glyphosate.

Conclusion

This quantitatively evaluates the transport and attenuation of dissolved glyphosate and AMPA in a stormwater wetland receiving runoff from a vineyard catchment with respect to the hydrological and hydrochemical conditions. The results indicate that the transport of dissolved glyphosate and AMPA through the wetland differed and largely varied both on seasonal and yearly time scales. Attenuation of glyphosate and AMPA loadings by the wetland generally was larger than 80% and gradually increased over time, which correlated with larger vegetation cover, and possibly with gradual adaptation of glyphosate-degrading microorganisms. However, the fraction of AMPA generally was larger at the wetland outlet, which emphasises the persistence of AMPA and varying efficiencies of glyphosate degradation. Therefore, the transfer of degradation products of runoff-associated pesticides through wetland systems, and in particular those used as a management practice targeting pesticide attenuation, should be carefully considered.

Assessment and conclusion by applicant:

The article reports concentration measurements for glyphosate and AMPA residues in an artificial stormwater wetland in France receiving runoff from a vineyard catchment with respect to the hydrological and hydrochemical conditions. Specific analytical methods were used and the limits of quantification were stated. The maximum glyphosate concentration entering the wetland was 150 µg/L. However, the maximum AMPA concentration was 19 µg/L.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

This article provides a detailed study on glyphosate and AMPA concentration measurements in an artificial wetland in a vineyard. It is considered reliable. It however provides measured concentration in runoff water and not in surface water, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

RMS notes that it is the same vineyard as studied in several other studies at different times (CA 7.5/051, CA 7.5/055, CA 7.5/064, and CA7.5/068).

The following information from the study can be retained:

- The 42.7 ha vineyard catchment is located in Rouffach, Alsace, France.
- The wetland was constructed in 2002 to control flooding into the urban area. The stormwater wetland has a surface area of 319 m^2 and a total volume of 1500 m^3. It is composed of a naturally planted forebay (215 m^2). The mean hydraulic retention time was 11.0 ± 8.3 h during the periods of investigation. The water storage capacity of the wetland forebay was 50 m^3.
- The use of glyphosate was estimated based on yearly surveys addressed to the vine-growers (surveys covered at least 80% of the vineyard area). Cumulated amount of used glyphosate reaches 3.8 kg, 1.3 kg and 5.37 kg respectively in 2009, 2010 and 2011 in the catchment.
- Rainfall-runoff events do not generate permanent stream in the catchment and statistically occur every week. During rainfall-runoff events, contaminated runoff converges at the outlet of the catchment where it is collected by the stormwater wetland. Surface runoff constitutes the main route of pesticide entry in the wetland.
- Runoff discharges entering and outflowing the wetland were continuously monitored from 23 March to 30 June 2009, 2010 and 2011. The water depth was measured using bubbler flow modules combined with a Venturi channel at the wetland inlet and a V-notch weir at the outlet. Flow proportional water samples were

Glyphosate concentrations entering the wetland ranged from 0.1 to 150 µg/L. AMPA concentration ranged from 0.1 to 19 µg/L.

It is indicated that the mean concentration of glyphosate in 2009, 2010 and 2011 decreased by 36, 150 and 263 times from the inlet to the outlet of the wetland, respectively, whereas that of AMPA only decreased by 3, 19, 31 times, respectively. This may not be in accordance with the authors conclusions that “Attenuation of glyphosate and AMPA loadings by the wetland generally was larger than 80%”.

Data point:	CA 7.5/022 CA 7.5/023 (Translation)
Report author	Martin, J. *et al*.
Report year	2013
Report title	Sugar Cane, Herbicides And water Pollution in Reunion Island: Achievements and Perspectives at the End of the First Decade of monitoring
Document No	Conference paper: 22nd Conference of COLUMA. International Days on Weed Control, Dijon, France, December 10-12, 2013 pp.641-651 ref.13
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities
Acceptability/Reliability:	Reliable with restrictions

The article was found relevant for multiple subchapters. The summary is provided in the groundwater monitoring subchapter of this document.

Assessment and conclusion by RMS:
No measured concentration are available from this study. Moreover, it should be noted the results are given for both groundwater and surface and cannot be separated. Overall one third of the 247 water points and analyses concern surface water.
Glyphosate is reported to be the third more frequently detected pesticide above >0.1 µg/L in groundwater/surface water, although representing no more than 7 % of the total pesticide dectection above the trigger.
The article is considered reliable with restrictions.

Data point:	CA 7.5/024
Report author	Mörtl, M. *et al*.
Report year	2013
Report title	Determination of glyphosate residues in Hungarian water samples by immunoassay
Document No	Microchemical Journal 107 (2013) 143–151
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities (Central Food Research Institute, Hungary)
Acceptability/Reliability:	Reliable with restrictions

The article was found relevant for multiple subchapters. The summary is provided in the groundwater monitoring subchapter of this document.

Assessment and conclusion by RMS:

The article describes a monitoring study where immunoassay analytical method was used. In the scope of a national environmental survey, 42 water samples (6 surface water and 36 ground water samples) were obtained on September 7-8, 2010, from 14 sampling sites in Békés county, Hungary. And further 18 surface water samples collected from the Danube River and Lake Velencei in Hungary at 12 sampling sites in 2011

Methods and analysis (ELISA) are well described. The study authors concluded there was no matrix effects on the results of surface water. However, it should be noted that the recovery of the method (tested on spiked samples) in surface water was 127.7% (see Table 8.5-79).

For samples from the Békés county, study authors indicate that both intensive and organic parcels were chosen in all four settlements (4 organic and 4 intensive), so as industrial site. However results are hard to relate to the different sites and cannot be related to any pressure of use of glyphosate.

Detected glyphosate concentrations in the 6 surface water samples in 2010 were 0.422 ± 0.271 ng/mL (with average concentrations in individual samples ranging between 0.12 and 0.68 ng/mL).

From the 2011 samples, results from the Danube river remained, in the vast majority, below the LOD of the assay (0.05 ppb). Only the sample from Lake Velencei showed a concentration higher than the LOD (0.064 ng/ml), while two other samples from the Danube River (Dömös, Kopaszi gát) were near the LOD (0.043 and 0.035 ng/mL, respectively).

The article is considered reliable with restrictions.

Data point:	CA 7.5/056
Report author	Vialle, C. *et al*.
Report year	2013
Report title	Pesticides in roof runoff: Study of a rural site and a suburban site
Document No	Journal of Environmental Management 120 (2013) 48 - 54
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

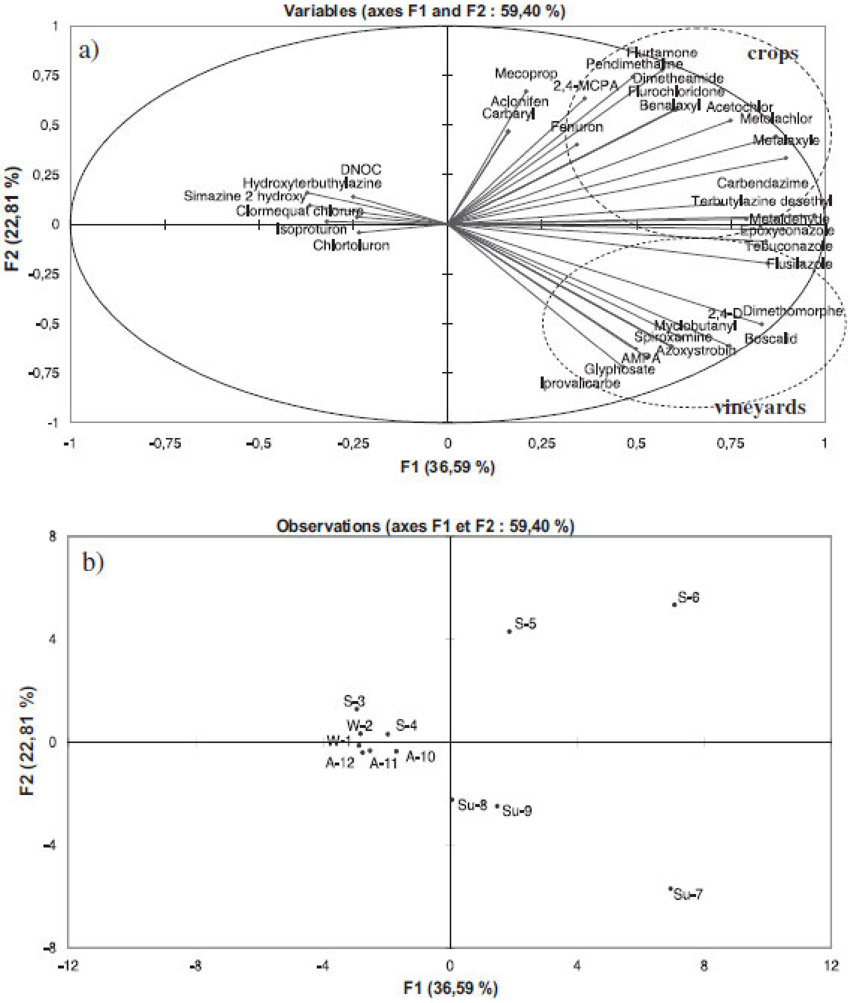
The quality of stored roof runoff in terms of pesticide pollution was assessed over a one-year period. Two tanks, located at a rural and suburban site, respectively, were sampled monthly. The two studied collection surface were respectively a tile slope roof and a bituminous flat roof. Four hundred and five compounds and metabolites were screened using liquid and gas chromatography coupled with various detection systems. Principal Component Analysis was applied to the data sets to elucidate patterns. At the rural site, two groups of compounds associated with two different types of agriculture, vineyard and crops, were distinguished. The most frequently detected compound was glyphosate (83%) which is the most commonly used herbicide in French vineyards. At the suburban site, quantified compounds were linked to agriculture rather than urban practices. In addition, all samples were contaminated with mecoprop which is a roof-protecting agent. Its presence was attributed to the nature of roofing material used for rainwater collection. For both sites, the highest number and concentrations of compounds and metabolites were recorded at the end of spring and through summer. These results are consistent with treatment periods and higher temperatures.

Materials and Methods

Sampling site
Two sites in south-western France were selected to install commercially available domestic rainwater collection systems. Rainwater is first collected from the roof area and then channeled via gutters through pipes to an underground PEHD storage tank in order to be reused later. The first site was a private house surrounded by cultivated fields. The annual average rainfall in this region is 760 mm, and the average temperatures range from 7.9 to 18.3 ^{0}C. Agriculture in this area is characterised by the vineyards of Gaillac and crops such as wheat, maize and colza. The second site was the research building of an engineering school located in the suburban area of Toulouse, which has an urban population of around 860 000 inhabitants. This site is 12 km from the city centre. The annual average rainfall is 668 mm, with average temperature ranging from 8.6°C to 18.1°C. The area is near a well-travelled road and 70 ha of experimental cultivation fields

Sample collection
Stored roof runoff sampling was carried out monthly from January 2009 to December 2009 for site 1 and between November 2009 and October 2010 for site 2. Grab samples of stored roof runoff were taken around 10 cm under the surface water in the tank.

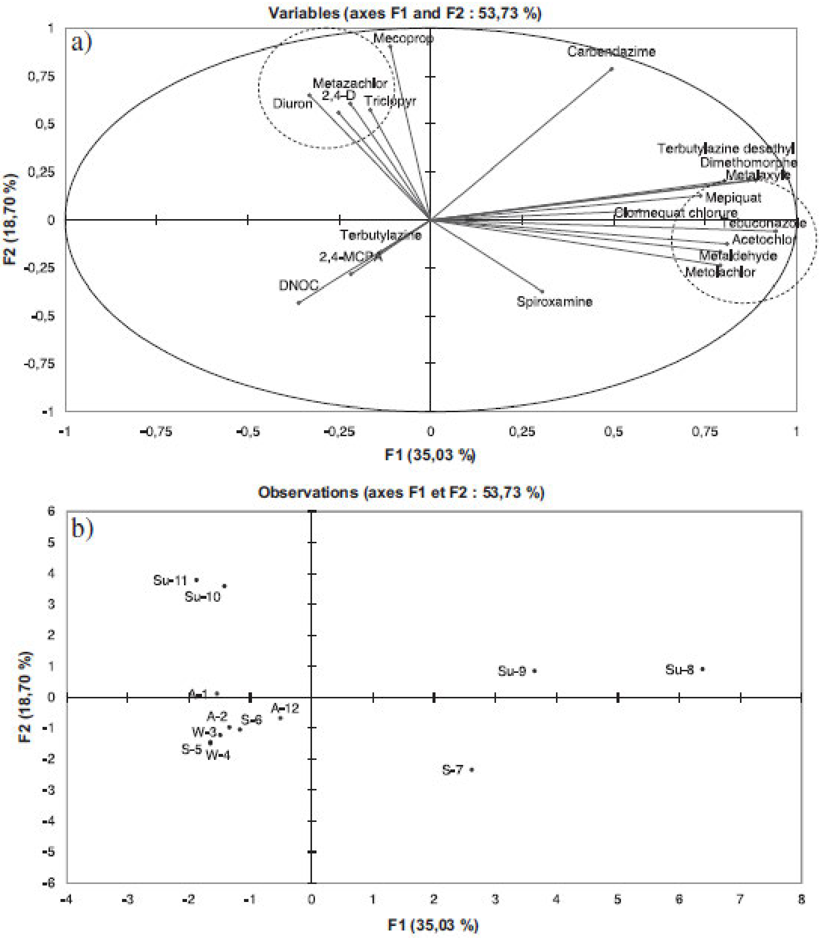
Figure 8.5-149: **a) The square cosines for all detected pesticides at site 1 (rural) in components F1 and F2 account for approximately 59% of the total variance. b) A two-dimensional plot of the 12 observations at site 1 (rural) in F1 and F2. The letters indicate the sampling season and the number precises the sampling month (Su = Summer; A = Autumn, W = Winter, S = Spring; 1 = November; 2 = December; 3 = January; 12 = October).**



Pesticide analysis

Water samples were screened for 405 compounds. Extracts were simultaneously analysed by liquid chromatography (HPLC) and gas chromatography (GC) with systematic multidetection: with diode array detector (HPLC-DAD), coupled with tandem mass spectrometry (HPLC-MS-MS), with an electron capture detector and a nitrogen phosphorus detector (GC-ECD-NPD), or coupled with mass spectrometry (GC-MS). Other sample aliquots were analysed by HPLC after a derivation, or by headspace with GC-MS. Some compounds were quantified by direct injection and analysis by HPLC-MS-MS.

Figure 8.5-150: **a) The square cosines for all detected pesticides at site 2 (suburban) in components F1 and F2 account for approximately 55% of the total variance. b) A two-dimensional plot of the 12 observations at the suburban site in F1 and F2. The letters indicate the sampling season and the number precises the sampling month (Su = Summer; A = Autumn, W = Winter, S = Spring; 1 = January; 2 = February; 11 = November; 12 = December).**



Results and discussion

Loadings for the two first components and square cosines are presented in a circle (Figure 8.5-149 and Figure 8.5-150a). A variable is increasingly well represented by a component as the corresponding square cosine nears unity. Graphically, this is represented as the variable nearing the edge of the circle. To elucidate the seasonal influence on concentrations of compounds, different observations were also represented in planes F1 versus F2 (Figure 8.5-149 and Figure 8.5-150b).

Rural site

At the rural site, the most frequently detected compounds were glyphosate (83%), DNOC (75%), AMPA (58%), metolachlor (R + S) (58%), carbendazim (50%), and 2,4-MCPA (50%). Analysis revealed that the highest concentrations measured were for glyphosate (6 µg/L). In addition, concentrations of several hundreds of ng/L were measured for AMPA, metolachlor, DNOC and metaldehyde in order of decreasing concentrations. Types of compounds detected are consistent with the agricultural practices in the region. In rural zones, herbicides are predominantly used, with fungicides being the next most common. Insecticides are used only to a minor extent. The presence of compounds at the end of spring and in the summer is illustrated in Figure 8.5-149b. Some summer samples are well represented in the first group, corresponding to vineyard pesticides, and the spring sampling is well represented in the second group, corresponding to crop pesticides. As a result, the distinction of samples of the same season is obviously due to agricultural uses. The ambient temperature may also have an influenced.

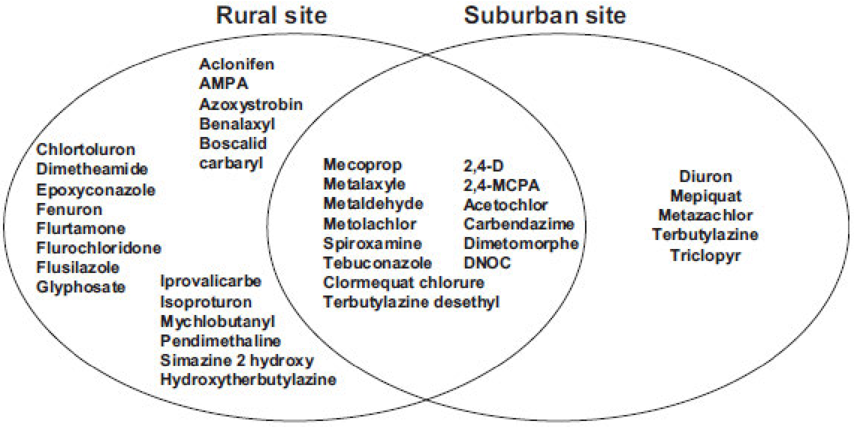
Suburban site

At the suburban site, the most often detected compounds, which appeared in at least 50% of the suburban samples, were mecoprop (100%) and DNOC (75%). The compound with the highest measured concentrations was mecoprop (4.8 µg/L). Up to hundreds of ng/L were quantified for DNOC, metaldehyde, 2,4-MCPA, and metolachlor. The percentage of occurrence of mecoprop in roof runoff at the suburban site was 100%. Mecoprop is a roof-protecting agent. Thus, in this study, this compound comes from the roofing material itself. The release appeared predominantly when the ambient temperature was high. Thus, the maximum concentration was observed in the summer. The suburban site studied seems to be influenced by nearby agriculture pesticide use rather than urban pesticide practices.

Comparison of the two sites

Of the 405 pesticides and metabolites analysed, 34 were detected more than once in the roof runoff samples collected at the rural site, of which 26 were above the limit of quantification at least once. At the suburban site, 15 pesticides were quantified, and only 4 were detected more than once over the twelve samples. The majority of compounds found were herbicides; the next most common compounds found were fungicides. Metabolites were the third most common class of compounds found. Concerning the spatial variation, compounds detected in the tanks are different for the two sites. There were 14 compounds detected at least once at both of the two sites; 20 compounds were found only in the rural zone, and 5 were detected exclusively in the suburban area (Figure 8.5-151). Considering only the number of compounds detected, a greater diversity of compounds was observed in the rural zone. Concerning the seasonal variation of the number of compounds detected, conclusions are identical for the two study sites. The most complex mixtures of compounds were sampled at the end of spring through summer at both sites (Figure 8.5-152).

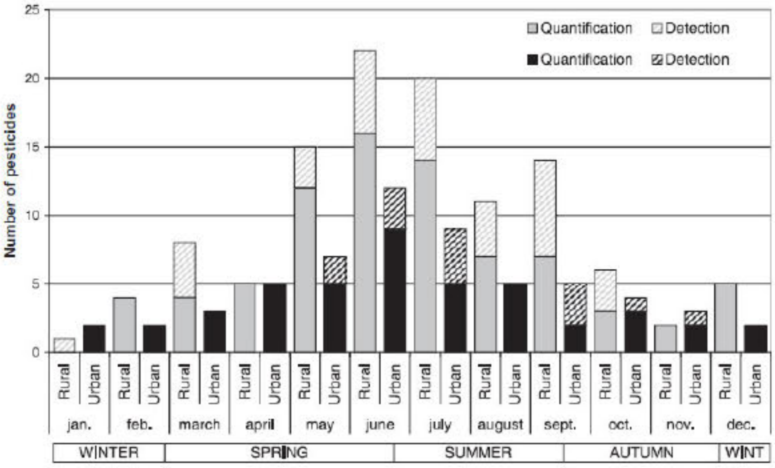
Figure 8.5-151: Pesticides detected according to sampling site



Conclusions

This study presents results concerning the quality of stored roof runoff in terms of pesticide contamination. No less than 405 compounds or metabolites were screened over a year for both a rural and a suburban site in south-west France. Even if this study is based on a limited data set, an effort was made to extract more information from the data set through the use of multivariate analysis techniques. At the rural site, PCA permits distinguishing compounds according to the type of surrounding agriculture, i.e., vineyard and crops. At the suburban site, the presence of compounds seems to be influenced more by local agriculture than by urban practices. Both sites at the end of spring through the summer were identified as particularly sensible seasons for compounds concentration and diversity. High concentrations of a roof-protecting agent were quantified in roof runoff from a bituminous flat roof. In the context of rainwater harvesting, which is becoming a common practice, this study reveals the importance of collected roof runoff pollution in terms of pesticides concentrations. Not only seasonal but also spatial variability of this contamination over the year was monitored.

Figure 8.5-152: Number of pesticides detected or quantified over the year at the two sites



Assessment and conclusion by applicant:

The article reports the concentrations of glyphosate and AMPA among some other hundreds of substances in the roof runoff from two experimental sites in France, one in a rural area, the other one in a suburban area. At the rural site, two groups of compounds associated with two different types of agriculture, vineyard and crops, were distinguished. The most frequently detected compound was glyphosate (83%) which is the most commonly used herbicide in French vineyards. At the suburban site, quantified compounds were linked to agriculture rather than urban practices. The measured maximum concentrations of glyphosate and AMPA were 6 µg/L and 0.9 µg/L, respectively.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions. The article is considered reliable with restrictions.

It reports measured concentrations in roof runoff water and not in water bodies.

The analytical method is only briefly described in the full text study. The accuracy is not given. The LOQ is indicated to be 0.1 µg/L.

Details of monthly measured concentration are reported in the full text study.

From the rural site,

- Glyphosate is detected 83% of the samples, with maximum concentration of 6 µg/L in July 2009 (range 0.2 -6 µg/L)
- AMPA is detected in 58% of samples, maximum concentration 0.9 µg/L in august 2009 (range 0.1-0.9 µg/L)

At the suburban site, neither glyphosate nor AMPA was detected.

Data point:	CA 7.5/057
Report author	Botta F. *et al.*
Report year	2012
Report title	Phyt'Eaux Cités: Application and validation of a programme to reduce surface water contamination with urban pesticides
Document No	Chemosphere 86 (2012) 166–176
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes
Acceptability/Reliability:	Reliable with restrictions

This paper presents first results of Phyt'Eaux Cités, a program put in place by the local water supply agency, the SEDIF (Syndicat des Eaux d'Ile-de-France), in collaboration with 73 local authorities, private societies and institutional offices (365 km^2). The challenges included: measurement of the previous surface water contamination, control of urban pesticide applications, prevention of pesticide hazard on users and finally an overall reduction of surface water contamination. An inquiry on urban total pesticide amount was coupled with a surface water bi-weekly monitoring to establish the impact of more than 200 molecules upon the Orge River. For 2007, at least 4400 kg and 92 types of pesticides (essentially herbicides) were quantified for all urban users in the Phyt'Eaux Cités perimeter. At the outlet of the Orge River (bi-weekly sampling in 2007), 11 molecules were always detected above 0.1 µg L^{-1}. They displayed the mainly urban origin of pesticide surface water contamination. Amitrole, AMPA (Aminomethyl Phosphonic Acid), demethyldiuron, diuron, glyphosate and atrazine were quantified with a 100% of frequency in 2007 and 2008 at the Orge River outlet. During the year, peaks of contamination were also registered for MCCP, 2,4 MCPA, 2,4 D, triclopyr, dichlorprop, diflufènican, active substances used in large amount in the urban area. However, some other urban molecules, such as isoxaben or flazasulfuron, were detected with low frequency. During late spring and summer, contamination patterns and load were dominated by glyphosate, amitrole and diuron, essentially applied by cities and urban users. Both isoproturon and chlortoluron were quantified during autumn and winter months according to upstream agricultural practices. In conclusion, 3 years after the beginning of this programme, the cities reduced the use of 68% of the total pesticide amount. An improvement on surface water quality was found from 2008 and during 2009 for all pesticides. In particular, glyphosate showed a decrease of the load above 60% in 2008, partly related to the Phyt'Eaux Cités action.

Materials and methods

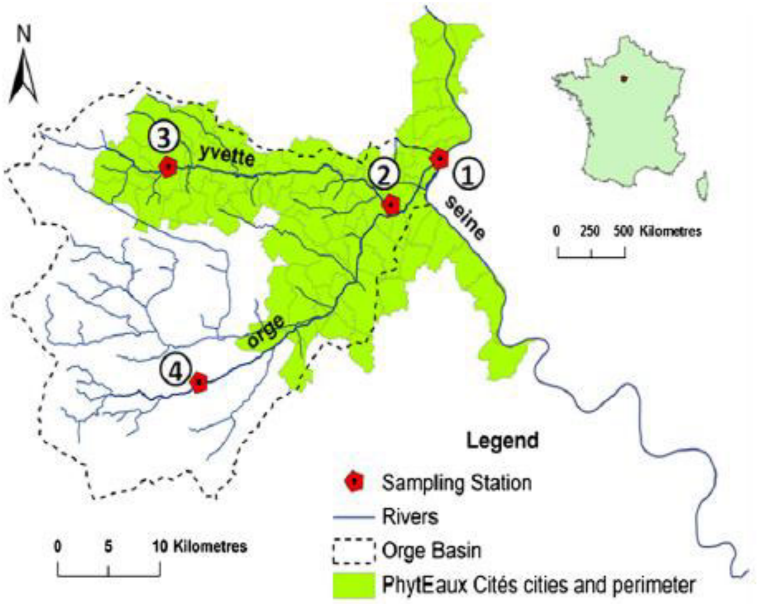
Samplings were conducted by Aspect Environmental Consulting (Ennery, France) and Veolia Water (Paris, France). Manual sampling of surface waters were carried out from bridges in the middle of the water bed with glass grab bottles and samples were stored in 1 L glass bottles. Water samples were transported at 4°C and analyzed within a period of no longer than 1 week.

One hundred eighty nine molecules (active substances and metabolites) in 2007 and 212 in 2008–2009 (implementation after inquiry), were analyzed by the Chemisches Untersuchungslabor (Offenburg, Germany), a laboratory accredited by the German Accreditation Council (DAR). The substances investigated were chosen in accordance with three parameters: molecules with non-agricultural or double uses (from data collected by SIVOA and Phyt'Eaux Cités), molecules detected in urban rivers and molecules followed in other regional pesticide monitoring. Analytical methods were summarized according to extraction method, chromatographic equipment and LQ (limit of quantification). Except for amitrole, all the analytical methods are certified (ISO, DIN or EPA).

To estimate the annual load, discharge data were exported from the database HYDROBANQUE (http://www.hydro.eaufrance.fr/). For the point ''Orge upstream'', (basin area of 112 km^2) concentrations were quantified at Sermaise (no. 4 in Figure 8.5-153) near the associated discharge point (basin of 114 km^2). For the downstream point of the Orge (basin of 936 km^2), Athis-Mons sampling point (no. 1 in Figure 8.5-153) was coupled with Morsang-sur-Orge discharge data (922 km^2). For the Yvette River, pesticide concentrations were registered at Epinay-sur-Yvette (no. 2 in Figure 8.5-153, 279 km^2) and discharge values at Villebon-sur-Yvette (224 km^2). At discharge stations that are not far from sampling stations, it was considered that discharge at the sampling sites can be correlated to the basin size changes. Over the January–December period, daily pesticide fluxes were calculated by multiplying the pesticide concentration of the collected samples from the continuous (bi-weekly) samples by the mean daily flow during that day. The sum of the 24 d load was compared to the average annual stream flow to obtain an annual load according to the equation below (Eq. (1)). Concentrations below the LQ were set to half of the LQ for these statistical calculations.

$$\text{Annual load} = \frac{\sum_{j-2}^{365}([C]j.cont. \times Qjsample.cont.)}{\sum_{j-1}^{365} Qjsample.cont.} \times Qtot \qquad (1)$$

Figure 8.5-153: Phyt'Eaux Cités area and monitoring stations in the Orge basin: no.1 Athis-Mons, no.2 Epinay-sur-Orge, no.3 Chevreuse and no.4 Sermaise



Results

Inquiries about public users were performed in the first semester of 2007. Fifty-seven of the above mentioned 73 local authorities answered to this investigation. The investigated cities declared having used in 2007 at least 167 commercial products with a total of 92 molecules. Totally active ingredient used by cities was 2053 kg year^{-1} in 2007 for the 57 inquired cities (mean of 36 kg year^{-1} for each city) A molecule was chosen as a tracer of this group and used in the following data analysis. First group included molecules essentially used by cities, where glyphosate was chosen as the main applied compound in urban areas. Agricultural applications of glyphosate on this basin were limited. The second group included molecules used by other users (national and regional railways, airport or golfs) in very large amount, most of the time largely applied as compared to city applications. Amitrole was chosen as tracer for group B. Main other users of pesticides were the national and the regional railways companies (846 kg year^{-1} of applied pesticides). Railway spraying is carried out on a surface of 4.93 km^2. Only herbicides were applied (glyphosate essentially, followed by 2,4 D and amitrole). The third group included molecules essentially used by agricultural weed control. No data on agricultural amount were available on agricultural applied amount. The choice of molecules for this group was based on three levels: results of an inquiry on an upstream sub-basin called Remarde (Botta, 2009), water analyzes of Sermaise (agricultural sampling station) samples and on databases on pesticide national homologation by uses. Isoproturon was chosen as tracer for this group. The fourth group included molecules that display mixed sources, such as diuron and mecoprop, homologated as pesticide but also used as biocides. Diuron was chosen as tracer for group D. Herbicides were in all cases the most used family of pesticides. Total urban uses were estimated at 4400 kg for 2007, 1575 kg of which is glyphosate.

In this study, 49 of the 212 active substances and metabolites analyzed during 2007, 2008 and 2009 were detected at the four sampling stations. The sampling campaign for the year 2007 was focused on 189 substances (171 active substances and 18 metabolites). At the outlet of the Orge Basin, 33 substances (29 active substances and 4 metabolites) were quantified and 6 displayed 100% frequencies (glyphosate and its metabolite, diuron and its metabolite, amitrole and atrazine).

Urban substances mainly used by cities

Glyphosate and its degradation product, AMPA, were by far the most detected molecules in the Orge River basin. Very high concentration peaks were registered at Epinay-sur-Orge (no. 2 in Figure 8.5-153) and at Athis-Mons (no. 1 in Figure 8.5-153) during summer periods. In the upstream stations was detected from March to December but an increase in concentrations was found during the summer. Positive outliers and extreme values were mainly detected for glyphosate during its application period for urban weed management. The result was in accordance with the pesticide inquiries. The inquiry documented that 52 local authorities used this herbicides and also 6 of the other public users settled in the Phyt'Eaux Cités area. The maximal recorded concentration of AMPA was 5.1 µg L^{-1} in 2007.

Urban substances mainly from other users

Amitrole was by far the most applied one by the National Railways Society (in 2004 more or less a rate of 2700 g ha^{-1}) and in particular during the spring months. The origin of amitrole in the Phyt'Eaux Cités perimeter can be also related to cities application (19 quotations) and to the other public users, especially by the national railways, where amitrole represents 10% of herbicides amount. Herbicides 2,4 D and 2,4 DP were detected during the first semester of 2007 at very low concentrations in all the monitoring stations.

Substances mainly used by agriculture and analyzes of upstream sampling point

Isoproturon and chlortoluron, are used essentially in wintercrops. They were detected during winter months at the Orge upstream point (concentration level of 1 µg L^{-1}). The highest isoproturon concentration was registered in Sermaise (no. 4 in Figure 8.5-153) during the campaign of December 17, 2007 (1.2 µg L^{-1}). Highest chlorotoluron concentrations were observed in December 2007 at the upstream stations (Sermaise and Chevreuse) (1.5 µg L^{-1}). During the rest of the year, concentrations were between 0.5 and 0.8 µg L^{-1}. At the downstream sampling stations they were detected at low concentrations until June.

Substances with different uses (urban application, biocides and agricultural uses)

Diuron showed 100% of detection frequency in 2007 and 2008. The diuron degradation product, the demethyldiuron was often measured at the Orge stations and in the downstream point of the Yvette River (Epinay-sur-Orge, no. 2 in Figure 8.5-153). Diuron concentrations were fluctuating between 0.5 µg L^{-1} and 1 µg L^{-1} during May, June, July and August. This herbicide was widely used by municipalities inside the Phyt'Eaux Cités action area (quoted 24 times) and by other users (quoted three times).

Change in pesticide occurrence following implementation of the Phyt'Eaux Cités program

A comparison between concentrations median, quantification frequency and loads between the years 2007, 2008 and 2009 is discussed in this section. The objective was to establish if a real decrease of pesticides concentration was registered in surface water during these 3 years.

Glyphosate (agricultural and urban applications) was always detected in the Orge and Yvette downstream stations. One hundred percent of detection frequency in 2007 and of 87.5% in 2008 was noted for glyphosate at the outlet of the Orge River (Athis- Mons). In 2009 a decrease was noted and detection frequency was 66.6%.

The median concentrations decreased between 2007 and 2008, from 0.61 to 0.43 µg L^{-1}. In 2009, glyphosate was still detected in all the four sampling stations. Glyphosate and AMPA still represented the two major contaminants at the end of the third year of the action. The highest load was measured for glyphosate that increased significantly between the upstream point and the downstream point. It was followed by its degradation product AMPA, diuron and amitrole. For glyphosate the estimated annual load was 1.7 kg $year^{-1}$ at the upstream point. The same compounds displayed a 179 kg $year^{-1}$ load at the outlet of Orge catchment. AMPA had an annual load of 156.8 kg $year^{-1}$ at the Orge outlet and 1.7 kg $year^{-1}$ in the upstream point. For the Yvette River annual loads were estimated to be 92.3 kg $year^{-1}$ for glyphosate and 52.8 kg $year^{-1}$ for the AMPA. Yvette loads represented 50% of glyphosate, 30% of AMPA and 70% of chlortoluron of total loads of the Orge River.

Finally the annual load of the group A (Urban application) was compared for 2007, 2008 and 2009. Loads at the outlet of Orge River were considered. Glyphosate load decreased in both streams, Yvette and Orge. At the Orge outlet, the load decreased from 126.6 kg $year^{-1}$ in 2007 to 50.5 kg $year^{-1}$ in 2008, with a diminution of 62%. In the Yvette, a higher decrease is registered (-85%) in 2008 as compared to 2007. A reduction of loads (30%) is also registered for its degradate AMPA. The load decreased more in the Yvette River as compared to the Orge River, probably due to a difference of water discharge volume between 2007 and 2008, higher on the Yvette River.

The Yvette impact on the Orge contamination was mainly due to agricultural pesticides, such as chlortoluron and isoproturon. A particular characteristic of the Orge River catchment is that at least 80% of the urban area is located between the upstream and the downstream point. For chlortoluron and isoproturon, a load increase was observed for 2008, with higher value at the Orge downstream site. For diuron the annual load downstream was 30 times larger than the Orge upstream flow. In the downstream point of the Orge River (Athis-Mons), annual concentration trend was similar to the one in the upstream point (Sermaise, no. 4 in Figure 8.5-153) but concentrations were 10 times lower.

MCPP (mecoprop) was the only molecule that displays a constant detection frequency during the three year and not a significant decrease. Median values were quite similar in 2007, 2008 and 2009. It was difficult to verify an effect of Phyt'Eaux Cités program because MCPP has different sources (agricultural uses, urban uses or biocides). Release of mecoprop will be primarily from its application as a herbicide, but also potentially from its manufacture, transport and storage.

Compared to 2007 data, this load variation might have different interpretations. Hydrological conditions were partly different and rainfall events were less frequent in 2008. To determine the reason for decrease, the glyphosate and diuron loads were divided into dry weather load and wet weather loads based upon the day of sampling. During both years, 13 samples among 24 were collected during a rainy day. The mean discharge for all the rainy days in 2008 (4.37 m3 s^{-1}) was similar to the one measured in 2007 (4.12 m^3 s^{-1}) and the total amount of rainfall during the sampling days was similar for both years as compared to total annual amounts (5.81% in 2007 and 5.71% in 2008). The only load during dry weather days was 4.3 kg $year^{-1}$, lower in 2007 than in 2008, whereas the average concentrations were 0.47 µg L^{-1} in 2007 and 0.57 µg L^{-1} in 2008. If the rainfall load was separated from the dry weather one, the difference between the two loads was sensible. In this case the rainfall load is three times higher in 2007 as compared to 2008. This tendency was not related to a difference of hydrological conditions but rather to highest average concentrations in 2007 (1.7 µg L^{-1}) compared to 0.65 µg L^{-1} in 2008. Consequently, Phyt'Eaux Cités appears likely to play a part in surface water quality improvement during 2008. However, data on pesticide loads were only collected for 2 years and data are scarce to certify that this load decrease was only related to the program impact.

Conclusion

Use of pesticides by municipalities generally decreased from 2007 to the end of 2009. In some cities, chemical treatments were also replaced by other type of weed-control (thermal, mechanical, etc.). The impact of pesticides used in urban settlements on surface water quality was confirmed during campaigns of 2007 and 2008. The urban uses impact on surface water quality was confirmed by coupling the results of investigation and the surface water campaigns. Eighteen of the applied pesticides in urban areas were frequently detected in the four sampling stations and in particular high concentrations were registered for glyphosate, amitrole, diuron, MCPP and 2,4-MCPA. Considering the period between May and July (maximum of application), the pesticide sum frequently exceeded the limit of 5 µg L^{-1} at Athis-Mons (no. 1 in Figure 8.5-153).

The elevated urban pesticide concentrations observed during 2007–2008 justify the Phyt'Eaux Cités action and also the intervention area chosen by the SEDIF. Multivariate analysis using PCA was applied to explain and confirm the main pattern of pesticide distribution. In the Orge River, detected pesticides that were applied in agricultural and urban areas display essentially urban origins. The inquiries displayed a decrease in pesticide use during the program from 2007 (95 kg city $year^{-1}$) until 2009 (35 kg city $year^{-1}$), also in term of kg ha^{-1} (from 2.5 to 0.8 kg ha^{-1}). The sustainable planning was carried out by 28 cities, while four reached at least 75% of the planned BMP by the Phyt'Eaux Cités action and two decided to stop all type of pesticide applications. With those results a decrease of transfer through urban surface water was expected to occur.

The improvement of the program was related with decrease of pesticide detection in surface water. Some substances were not quantified in 2009, whereas they were in 2007–2008. This pattern was observed for molecules frequently used by cities (dicamba and propiconazole) or by other urban applicators, like bromacil. A more important decrease was observed for molecules applied essentially by cities, such as glyphosate. The total load at the outlet of the Orge Basin displayed a spectacular decrease (more than 50%). Phyt'Eaux Cités was a new approach to reduce the contamination of surface water by pesticides. The more knowledge and mobilization of the local authorities could improve the reduction of pesticides use. The programme suggested to city staff specific pest management strategies and general alternative controls. The objective was to reduce overall pesticide use by the end of 2010.

Assessment and conclusion by applicant:

The article describes monitoring data (surface water) for glyphosate among other pesticides for an urban area in France. No agricultural area is considered. Glyphosate and AMPA concentrations are presented as Figures. The maximum recorded concentration of AMPA was 5.1 µg/L.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions. The article is considered reliable with restrictions.

The article describes surface water monitoring data for glyphosate and AMPA among other pesticides for an urban area in France.

Detailed tabulated results are not presented. The maximum recorded concentration of AMPA was 5.1 µg/L (reported in the text). Maximum recorded concentration for glyphosate was 6.6 µg/L in Athis-Mons in 2007 (from supplementary data 4).

The following information from the study can also be retained:

Glyphosate and its degradation product, AMPA, were by far the most detected molecules in the Orge River basin. Very high concentration peaks were registered at Epinay-sur-Orge and at Athis-Mons during summer periods. In the upstream stations was detected from March to December but an increase in concentrations was found during the summer. Positive outliers and extreme values were mainly detected for glyphosate during its application period for urban weed management.

The following figure from the full text study is also reported for additional information on results for the glyhopsate concentration (green triangle on the plots) at the station of Athis-Mons in 2007, 2008 and 2009.

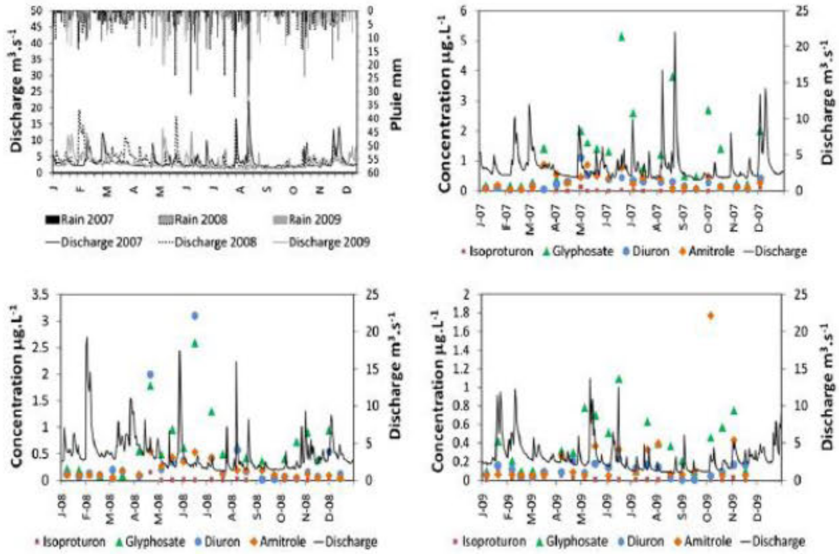


Fig. 4. Example of pesticides concentration trends for each group at the Athis-Mons sampling station (outlet of the Orge River) during 2007, 2008 and 2009.

Data point:	CA 7.5/058
Report author	Coupe, R. *et al.*
Report year	2012
Report title	Fate and transport of glyphosate and aminomethylphosphonic acid in surface waters of agricultural basins
Document No	Society of Chemical Industry (wileyonlinelibrary.com) DOI 10.1002/ps.2212
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Glyphosate [*N*-(phosphonomethyl)glycine] is a herbicide used widely throughout the world in the production of many crops and is heavily used on soybeans, corn and cotton. Glyphosate is used in almost all agricultural areas of the United States, and the agricultural use of glyphosate has increased from less than 10 000 Mg in 1992 to more than 80 000 Mg in 2007. The greatest intensity of glyphosate use is in the midwestern United States, where applications are predominantly to genetically modified corn and soybeans. In spite of the increase in usage across the United States, the characterization of the transport of glyphosate and its degradate aminomethylphosphonic acid (AMPA) on a watershed scale is lacking. This publication included results from an investigation carried out in a catchment in Rouffach, France, and this summary will focus on this investigation.

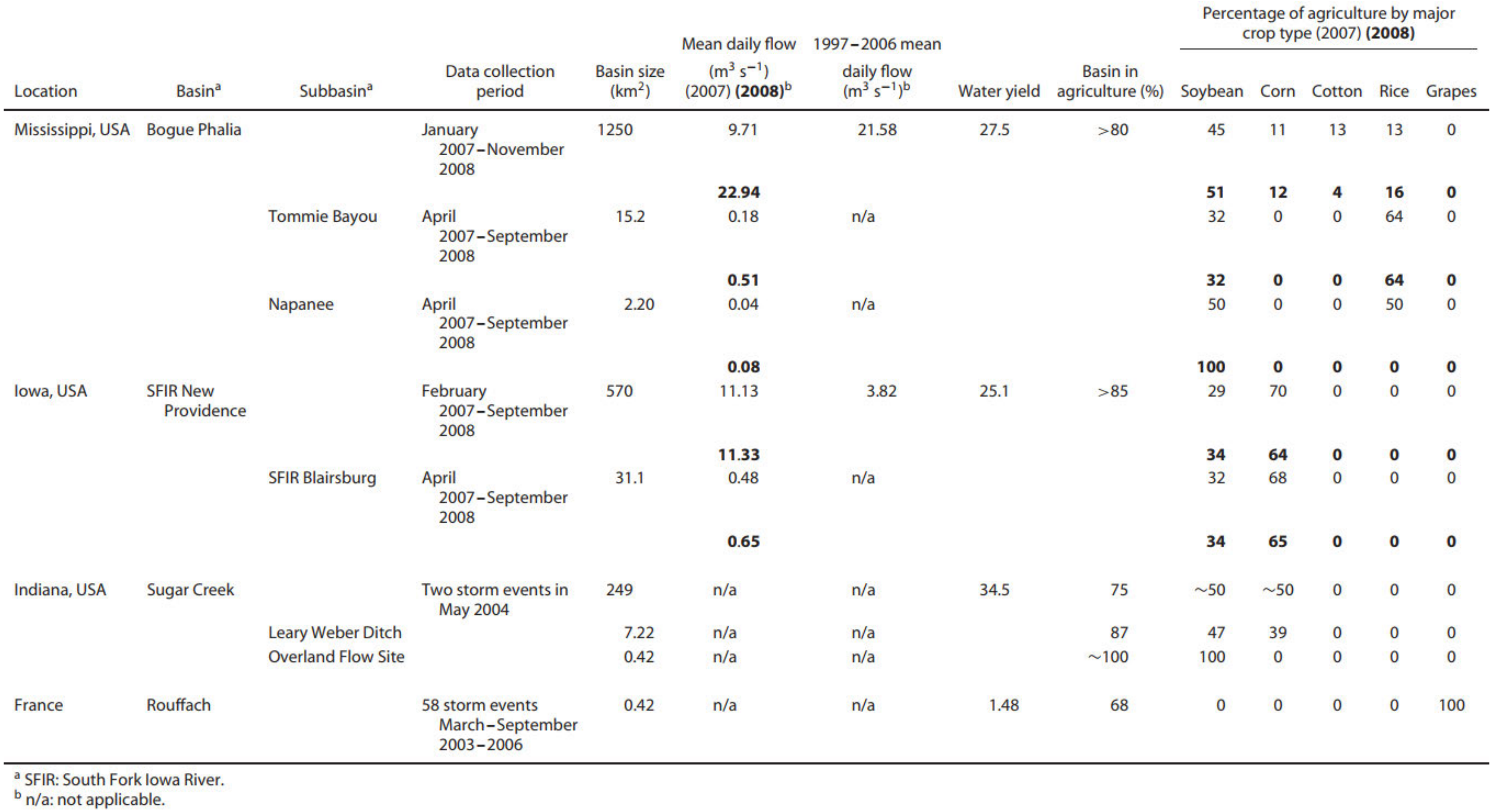
In the French catchment, glyphosate and AMPA were detected in almost every sample: the maximum glyphosate concentration was 86 µg/L, minimum was <0.1 µg/L, and the median was 4.7 µg/L. For AMPA, the maximum concentration was 44 µg/L, the minimum was 0.2 µg/L, and the median was 1.9 µg/L. This catchment could be considered as a worst case, in that glyphosate was used in the catchment almost continuously, and the area, climate and agricultural practice were favourable for runoff.

Glyphosate use in a watershed results in some occurrence in surface water; however, the watersheds most at risk for the offsite transport of glyphosate are those with high application rates, rainfall that results in overland runoff and a flow route that does not include transport through the soil.

Materials and methods

This paper explores the transport of glyphosate and AMPA in seven streams in agricultural basins located in four different environmental settings (Table 8.5-188). Water samples were collected over a 2-year period from two sets of nested basins (Mississippi and Iowa). Water samples were also collected during storm events in Indiana (1 year) and near Rouffach, France (4 years), and the latter investigation will be the focus of this summary.

Table 8.5-188: **Study basins and subbasins with basic hydrological and agricultural characteristics, data collection period, basin size, mean daily stream flow for 2007 and 2008 and 1997 – 2006 mean daily streamflow**



									Percentage of agriculture by major crop type (2007) **(2008)**				
Location	Basin[a]	Subbasin[a]	Data collection period	Basin size (km^2)	Mean daily flow (m^3 s^{-1}) (2007) **(2008)**[b]	1997–2006 mean daily flow (m^3 s^{-1})[b]	Water yield	Basin in agriculture (%)	Soybean	Corn	Cotton	Rice	Grapes
Mississippi, USA	Bogue Phalia		January 2007–November 2008	1250	9.71	21.58	27.5	>80	45	11	13	13	0
					22.94				**51**	**12**	**4**	**16**	**0**
		Tommie Bayou	April 2007–September 2008	15.2	0.18	n/a			32	0	0	64	0
					0.51				**32**	**0**	**0**	**64**	**0**
		Napanee	April 2007–September 2008	2.20	0.04	n/a			50	0	0	50	0
					0.08				**100**	**0**	**0**	**0**	**0**
Iowa, USA	SFIR New Providence		February 2007–September 2008	570	11.13	3.82	25.1	>85	29	70	0	0	0
					11.33				**34**	**64**	**0**	**0**	**0**
		SFIR Blairsburg	April 2007–September 2008	31.1	0.48	n/a			32	68	0	0	0
					0.65				**34**	**65**	**0**	**0**	**0**
Indiana, USA	Sugar Creek		Two storm events in May 2004	249	n/a	n/a	34.5	75	~50	~50	0	0	0
		Leary Weber Ditch		7.22	n/a	n/a		87	47	39	0	0	0
		Overland Flow Site		0.42	n/a	n/a		~100	100	0	0	0	0
France	Rouffach		58 storm events March–September 2003–2006	0.42	n/a	n/a	1.48	68	0	0	0	0	100

[a] SFIR: South Fork Iowa River.
[b] n/a: not applicable.

Study site

Rouffach, France
The Rouffach basin is located in eastern France in the Alsace region south of Strasbourg on the slopes overlooking the Rhine River Valley. The Rouffach basin is small in size, about 0.42 km^2, with an average slope of about 150 m/km. Streamflow is ephemeral, occurring only during rainfall events. Only rainfall events that generated a runoff volume greater than 8 m^3 were monitored. Land use for about 68% of the contributing basin is vineyard.

Data collection, analysis and quality assurance
Water samples from the Rouffach basin were collected using an automatic sampler from March to October.

Water sample collection and processing in the United States followed USGS protocols. Water samples were filtered and analyzed for glyphosate and AMPA using online solid-phase extraction and analysis by HPLC/MS. Water samples collected from the Rouffach basin in France were filtered and analyzed using similar methods, with a reporting level of 0.1 µg/L. The results presented here will only represent the portion of glyphosate and AMPA that is dissolved in water, and not the portion attached to sediment.

Glyphosate application and loads
For the Rouffach basin, annual surveys were sent to the 28 farmers in the basin, asking for information on pesticide application methods, timing and amounts.

When glyphosate or AMPA concentrations were reported as less than the reporting limit, the concentrations were set to zero for percentage detection values and load calculations.

To gain a better understanding of the fate and transport of pesticides, it is often insightful to examine the relation between pesticide degradates and the parent compound. Here, the %AMPA as a percentage of total glyphosate (glyphosate + AMPA) was calculated:

$$\%\ \text{AMPA} = \frac{[\text{AMPA}]}{[\text{Glyphosate}] + [\text{AMPA}] \times 100}$$

For the site in France, a load was calculated for each event by multiplying the concentration (using linear interpolation between measured concentrations) by the instantaneous flow for each minute and then summing over the entire event. The annual load was calculated by summing the individual event loads for each year.

The annual load as a percentage of use (LAPU) was calculated to compare the behavior of glyphosate across scales and between study areas. It was calculated thus:

$$\text{LAPU} = \frac{\substack{\text{annual stream load of glyphosate} \\ \text{from that basin (kg year}^{-1}\text{)}}}{\substack{\text{annual glyphosate use} \\ \text{in that basin (kg year}^{-1}\text{)}}} \times 100 \qquad (2)$$

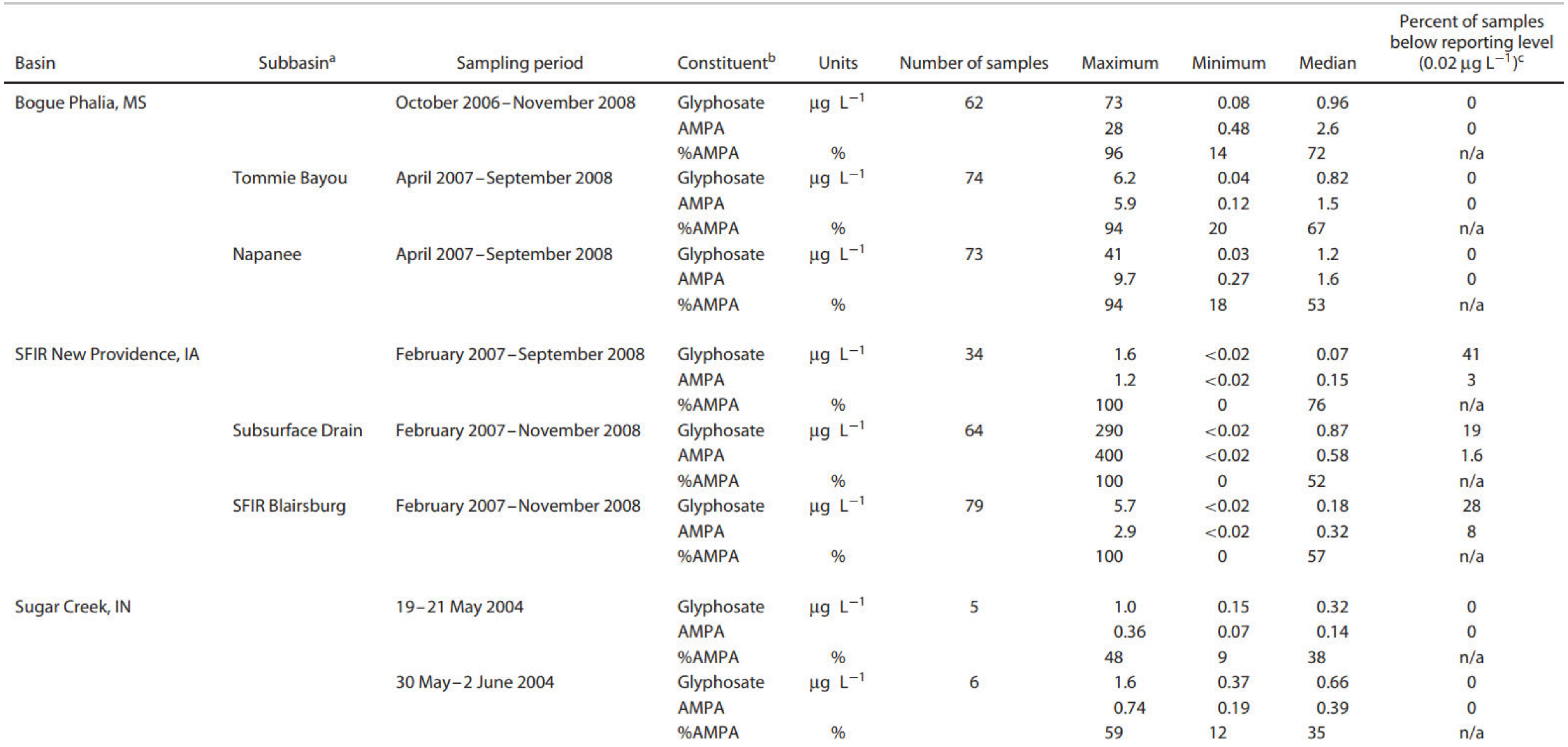
Additionally, for proper quantification of the total glyphosate load as a percentage of use (TGLAPU), the load of AMPA must be expressed on a glyphosate mass equivalent basis and added to the load of glyphosate.

Results

France

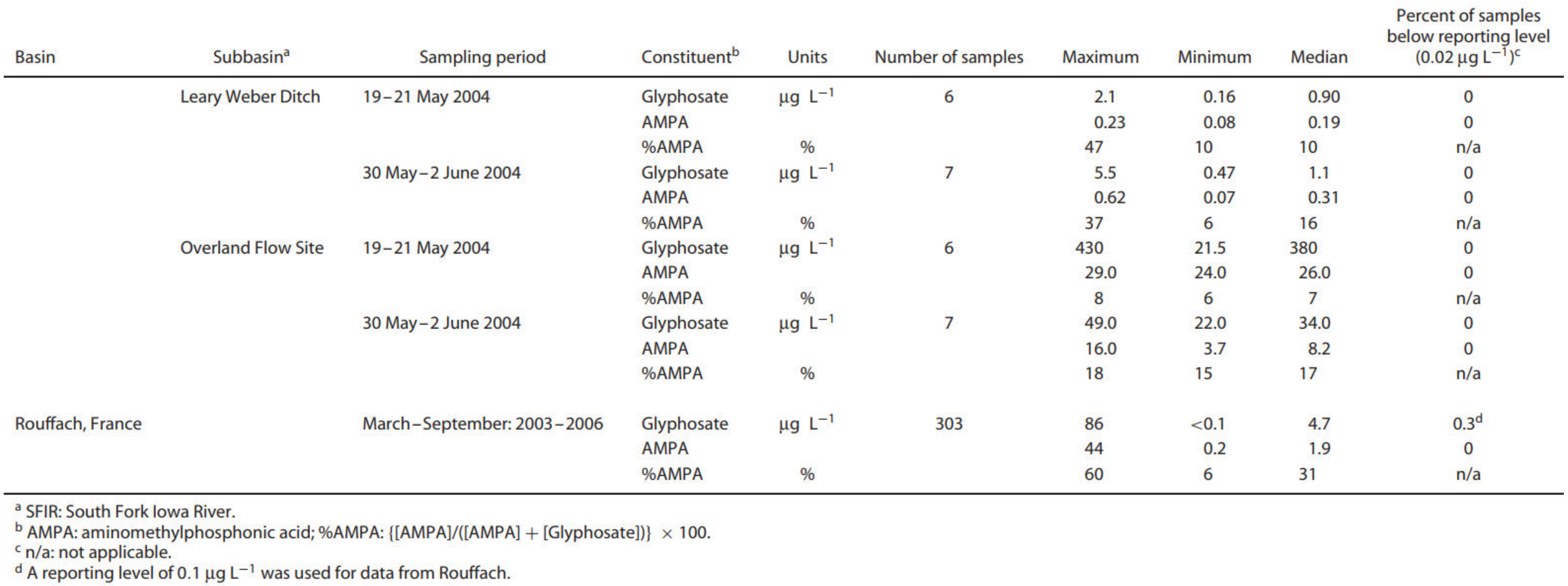
Fifty-eight runoff events from March to September 2003–2006 were sampled, and 303 samples were collected from the Rouffach basin. All but one sample had concentrations of glyphosate above the reporting level of 0.1 µg/L (Table 8.5-189). Every sample had detectable levels of AMPA with maximum concentrations of glyphosate and AMPA of 86 and 44 µg/L (median concentrations: 4.7 and 1.9 µg/L). Generally, the LAPU values for glyphosate (0.009–0.029%) for the Rouffach basin were an order of magnitude less than at the other sites (Table 8.5-190).

Table 8.5-189: **The sampling period, number of samples collected, maximum, minimum and median concentrations of glyphosate, AMPA and %AMPA at each sampling site and the percentage of samples below the reporting limit**



Basin	Subbasin[a]	Sampling period	Constituent[b]	Units	Number of samples	Maximum	Minimum	Median	Percent of samples below reporting level (0.02 $\mu g\ L^{-1}$)[c]
Bogue Phalia, MS		October 2006 – November 2008	Glyphosate	$\mu g\ L^{-1}$	62	73	0.08	0.96	0
			AMPA			28	0.48	2.6	0
			%AMPA	%		96	14	72	n/a
	Tommie Bayou	April 2007 – September 2008	Glyphosate	$\mu g\ L^{-1}$	74	6.2	0.04	0.82	0
			AMPA			5.9	0.12	1.5	0
			%AMPA	%		94	20	67	n/a
	Napanee	April 2007 – September 2008	Glyphosate	$\mu g\ L^{-1}$	73	41	0.03	1.2	0
			AMPA			9.7	0.27	1.6	0
			%AMPA	%		94	18	53	n/a
SFIR New Providence, IA		February 2007 – September 2008	Glyphosate	$\mu g\ L^{-1}$	34	1.6	<0.02	0.07	41
			AMPA			1.2	<0.02	0.15	3
			%AMPA	%		100	0	76	n/a
	Subsurface Drain	February 2007 – November 2008	Glyphosate	$\mu g\ L^{-1}$	64	290	<0.02	0.87	19
			AMPA			400	<0.02	0.58	1.6
			%AMPA	%		100	0	52	n/a
	SFIR Blairsburg	February 2007 – November 2008	Glyphosate	$\mu g\ L^{-1}$	79	5.7	<0.02	0.18	28
			AMPA			2.9	<0.02	0.32	8
			%AMPA	%		100	0	57	n/a
Sugar Creek, IN		19 – 21 May 2004	Glyphosate	$\mu g\ L^{-1}$	5	1.0	0.15	0.32	0
			AMPA			0.36	0.07	0.14	0
			%AMPA	%		48	9	38	n/a
		30 May – 2 June 2004	Glyphosate	$\mu g\ L^{-1}$	6	1.6	0.37	0.66	0
			AMPA			0.74	0.19	0.39	0
			%AMPA	%		59	12	35	n/a

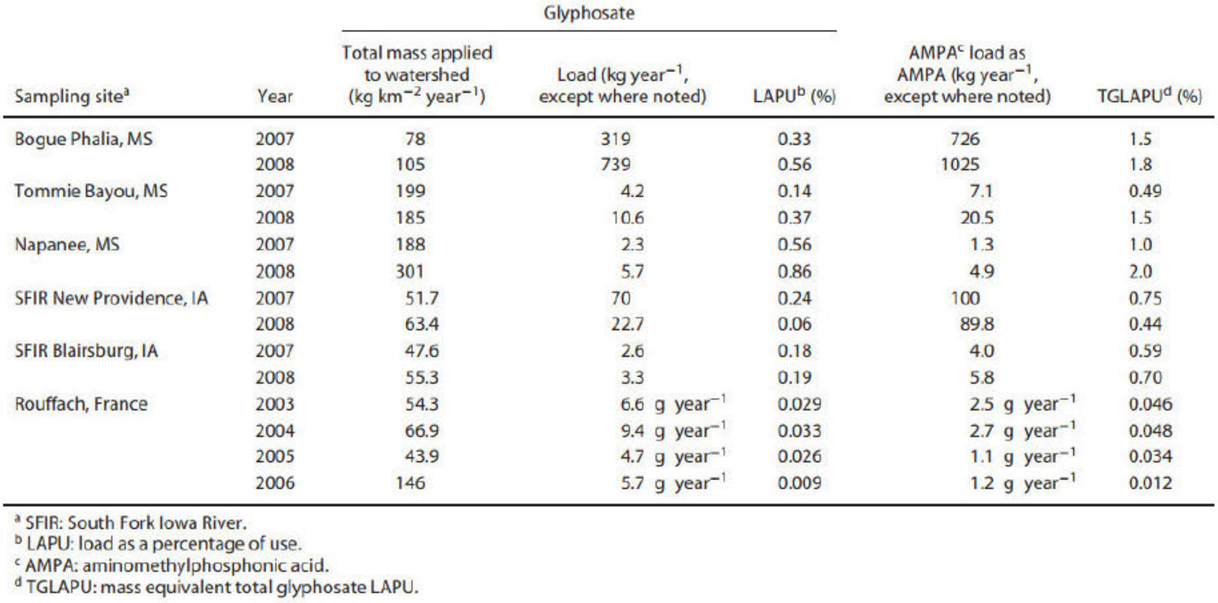
Table 8.5-189 – continued



Basin	Subbasin[a]	Sampling period	Constituent[b]	Units	Number of samples	Maximum	Minimum	Median	Percent of samples below reporting level (0.02 µg L^{-1})[c]
	Leary Weber Ditch	19–21 May 2004	Glyphosate	µg L^{-1}	6	2.1	0.16	0.90	0
			AMPA			0.23	0.08	0.19	0
			%AMPA	%		47	10	10	n/a
		30 May–2 June 2004	Glyphosate	µg L^{-1}	7	5.5	0.47	1.1	0
			AMPA			0.62	0.07	0.31	0
			%AMPA	%		37	6	16	n/a
	Overland Flow Site	19–21 May 2004	Glyphosate	µg L^{-1}	6	430	21.5	380	0
			AMPA			29.0	24.0	26.0	0
			%AMPA	%		8	6	7	n/a
		30 May–2 June 2004	Glyphosate	µg L^{-1}	7	49.0	22.0	34.0	0
			AMPA			16.0	3.7	8.2	0
			%AMPA	%		18	15	17	n/a
Rouffach, France		March–September: 2003–2006	Glyphosate	µg L^{-1}	303	86	<0.1	4.7	0.3[d]
			AMPA			44	0.2	1.9	0
			%AMPA	%		60	6	31	n/a

[a] SFIR: South Fork Iowa River.
[b] AMPA: aminomethylphosphonic acid; %AMPA: {[AMPA]/([AMPA] + [Glyphosate])} × 100.
[c] n/a: not applicable.
[d] A reporting level of 0.1 µg L^{-1} was used for data from Rouffach.

Table 8.5-190: Comparison of glyphosate application and glyphosate and AMPA loads, glyphosate LAPU values and the mass equivalent total glyphosate LAPU between the basins studied



		Glyphosate				
Sampling site[a]	Year	Total mass applied to watershed (kg km^{-2} year^{-1})	Load (kg year^{-1}, except where noted)	LAPU[b] (%)	AMPA[c] load as AMPA (kg year^{-1}, except where noted)	TGLAPU[d] (%)
Bogue Phalia, MS	2007	78	319	0.33	726	1.5
	2008	105	739	0.56	1025	1.8
Tommie Bayou, MS	2007	199	4.2	0.14	7.1	0.49
	2008	185	10.6	0.37	20.5	1.5
Napanee, MS	2007	188	2.3	0.56	1.3	1.0
	2008	301	5.7	0.86	4.9	2.0
SFIR New Providence, IA	2007	51.7	70	0.24	100	0.75
	2008	63.4	22.7	0.06	89.8	0.44
SFIR Blairsburg, IA	2007	47.6	2.6	0.18	4.0	0.59
	2008	55.3	3.3	0.19	5.8	0.70
Rouffach, France	2003	54.3	6.6 g year^{-1}	0.029	2.5 g year^{-1}	0.046
	2004	66.9	9.4 g year^{-1}	0.033	2.7 g year^{-1}	0.048
	2005	43.9	4.7 g year^{-1}	0.026	1.1 g year^{-1}	0.034
	2006	146	5.7 g year^{-1}	0.009	1.2 g year^{-1}	0.012

[a] SFIR: South Fork Iowa River.
[b] LAPU: load as a percentage of use.
[c] AMPA: aminomethylphosphonic acid.
[d] TGLAPU: mass equivalent total glyphosate LAPU.

Conclusion

In the French catchment, where the use is almost continuous, glyphosate and AMPA were detected in almost every sample. The annual stream load of glyphosate as a percentage of annual use was much less in the French catchment, even though the French site had detections in almost every sample at relatively high concentrations, because the amount of water that leaves this basin is small compared with the others.

Glyphosate use in a watershed results in some occurrence in surface water; however, the watersheds most at risk for the offsite transport of glyphosate are those with high application rates, rainfall that results in overland runoff and a flow route that does not include transport through the soil.

Assessment and conclusion by applicant:

The article reports concentration measurements for glyphosate and AMPA residues in stream waters in USA and France. Specific analytical method were used and the limits of reporting were stated. The watersheds most at risk for the offsite transport of glyphosate are those with high application rates, rainfall that results in overland runoff and a flow route that does not include transport through soil. For the French catchment, only runoff events with volumes greater than 8 m^3 were monitored between March and October.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant’s conclusions. The article is considered reliable with restrictions.

Only the results from the French site are considered, since it is unknown whether the US sites could be considered representative of any EU conditions.

The results from the French basin are from the study of Gregoire et al. (2010) reviewed under CA7.5/068. Please refer to this study.

Data point:	CA 7.5/059
Report author	Petersen, J. *et al*.
Report year	2012
Report title	Sampling of herbicides in streams during flood events
Document No	J. Environ. Monit., 2012, 14, 3284
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (Eurofins Denmark A/S)
Acceptability/Reliability:	Reliable

In stream water xenobiotics usually occur as pulses in connection with floods caused by surface run-off and tile drainage following precipitation events. In streams located in small agricultural catchments we monitored herbicide concentrations during flood events by applying an intensive sampling programme of ½ h intervals for 7 h. In contrast to grab sampling under non-flood conditions, clearly elevated concentrations were recorded during the floods, and pulses varying in occurrence, duration and concentration were recorded. Pulses of recently applied herbicides were the most prominent, but also agricultural herbicides used in previous seasons caused pulses in the streams. Asynchronism of chemographs may be related to the characteristics of the compounds as well as their transport pathways and transformation in compartments between the source and the point of sampling in the stream. Thus, the occurrence of chemographs is difficult to predict, which ought to be taken into account when designing a sampling strategy. Even though the chemographs of herbicides and their transformation products (glyphosate and aminomethylphosphonic acid (AMPA) as well as terbuthylazine and desethylterbuthylazine) seem to be synchronous, their occurrence may still be difficult to predict. It is evident that grab sampling under non-flood conditions yields insufficient information on the dynamics of occurrence of herbicides in stream water, both with respect to environmental effects and the calculation of the load to a recipient. In conclusion, the design of a sampling strategy regarding herbicides in stream waters should adequately consider the aim of the investigation.

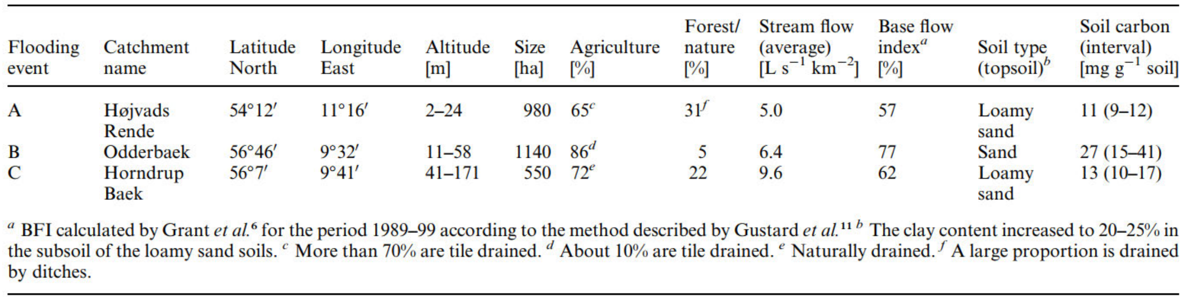
Materials and methods

Intensive sampling of herbicide pulses (chemographs) in streams was planned for surface run-off events in the 2004 spring spraying season in Denmark (April–June). Precipitation events of 10 mm within 1–2 days would expectedly occur on average 4–5 times during the spring spraying season. Precipitation of this order was converted to an expected rise in the water level of the catchment stream depending on stream characteristics, typically 5–10 cm. A floating contact was adjusted to start an automatic sampler at the estimated rise in the stream water level (flood) to catch the chemographs.

The stream water sampling was carried out in three catchments (A, B and C; Table 8.5-191) at a precipitation driven flood event as indicated in Figure 8.5-154. The sampling device was a stainless steel pipe (10 mm i.d.) with a 90° bend 10 cm from the end installed vertically in the middle of the stream. The horizontal tube-end was placed at a height above the bottom corresponding to about 40% of the water level with the opening pointing downstream, and the tube being emptied (blown-out by air pressure) before each sampling. During the flood events sampling was carried out using two ISCO-samplers (no. 3700 with 12 glass bottles of 900 mL annealed at 550 °C). The samplers were programmed to take samples every 15 minutes, and they were combined two by two to represent 30 minute intervals for 5 h, except samples no. 23 and 24 which were taken 6 and 7 h after the start of the sampling, respectively. The 15 minute interval was applied to catch chemograph peak concentrations, and the combination of the samples ensured sufficient material for analysis. In addition, two grab samples (2 L each) were taken on days without preceding precipitation to record concentrations under non-flood conditions in each stream.

The day after receipt at the commercial laboratory (Eurofins Denmark A/S, DK-8464 Galten, DANAK accreditation no. 168), the samples were homogenised, and an internal standard was added. The 1.8 L combined samples and the 2 L grab samples were divided into three subsamples of 500 mL each, and the compounds were extracted and analysed by three methods according to their chemical properties. Owing to the smaller sample volume of sample no. 23 and 24, these were analysed by method 1 only.

Table 8.5-191: Flood event – catchment key and catchment characteristics

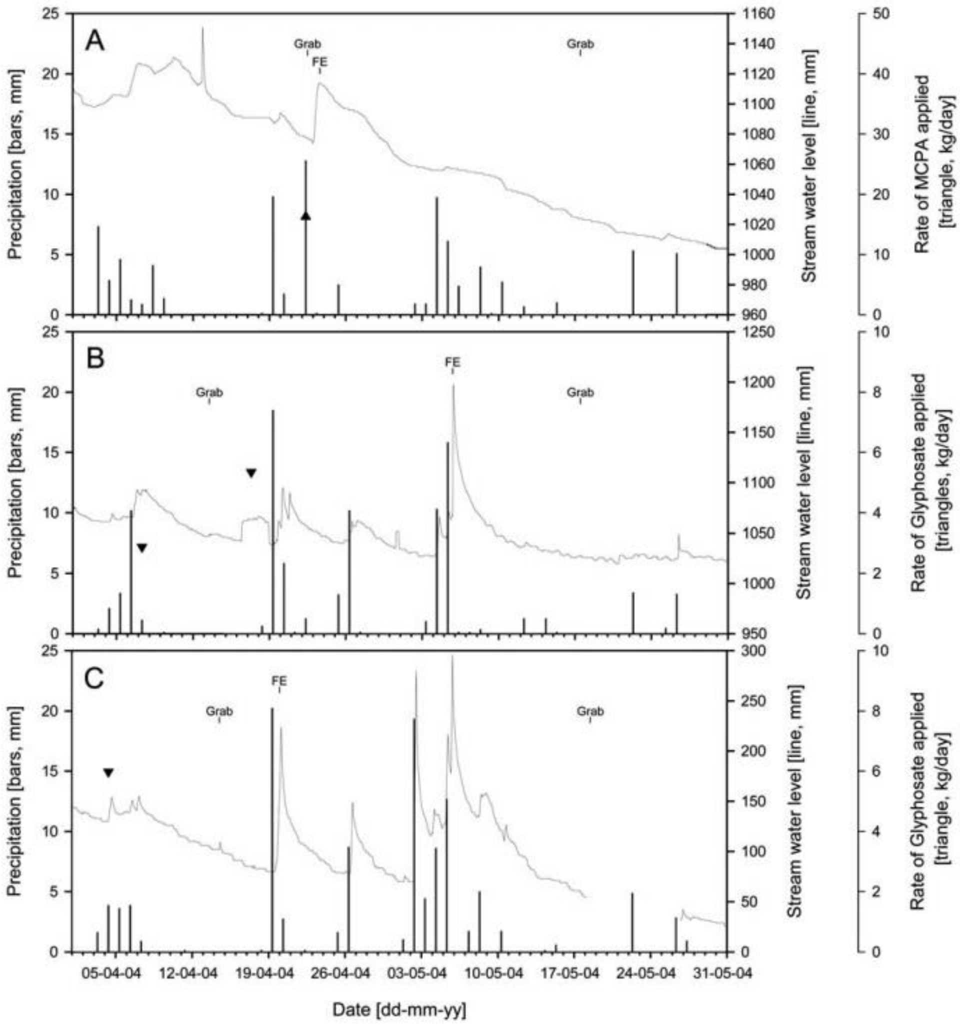


Flooding event	Catchment name	Latitude North	Longitude East	Altitude [m]	Size [ha]	Agriculture [%]	Forest/ nature [%]	Stream flow (average) [L s^{-1} km^{-2}]	Base flow index[a] [%]	Soil type (topsoil)[b]	Soil carbon (interval) [mg g^{-1} soil]
A	Højvads Rende	54°12′	11°16′	2–24	980	65[c]	31[f]	5.0	57	Loamy sand	11 (9–12)
B	Odderbaek	56°46′	9°32′	11–58	1140	86[d]	5	6.4	77	Sand	27 (15–41)
C	Horndrup Baek	56°7′	9°41′	41–171	550	72[e]	22	9.6	62	Loamy sand	13 (10–17)

[a] BFI calculated by Grant *et al.*[6] for the period 1989–99 according to the method described by Gustard *et al.*[11] [b] The clay content increased to 20–25% in the subsoil of the loamy sand soils. [c] More than 70% are tile drained. [d] About 10% are tile drained. [e] Naturally drained. [f] A large proportion is drained by ditches.

Standards based on Milli-Q water spiked with the respective analytes were processed and analysed in the same way as the samples, and the recovery of the standards was used to correct the concentrations in the samples. The detection limit was 0.01 µg/L with 15% relative standard deviation for all three methods.

Figure 8.5-154: Daily precipitation (bars), stream water level (line) and daily application of herbicides within the catchment (triangles). Dates of flood events (FE) and 2 L grab samplings under non-flood (Grab) are indicated



Method 1 (LC-MS/MS)

The samples were acidified to pH 4.5 by adding 6 mL 100% acetic acid and 5 mL 25% NaOH, and the compounds were concentrated by solid-phase extraction. The columns were dried under a flow of air and eluted using 2 x 5 mL methanol/acetonitrile. Subsequently, 50 µL 1,2-propanediol was added to the elute, which was then evaporated under N_2 flow at 35 °C. The evaporation residue was re-dissolved in 400 µL methanol–water (1 : 1). The analytical column for LC was a Hypersil BDS (Thermo Scientific, 2.1 x 250 mm, 5 µm particle size) and the mobile phase was 5mM ammonium acetate–methanol (Eluent A: 990/10 and B: 100/900, both containing 0.1% formic acid) in a gradient of: 0% B (1 min), linearly to 50% B (2 min), linearly to 100% B (24 min), 100% B (3 min), and linearly to 0% B (3 min). The column temperature was 30°C and the flow rate was 0.2 mL/min.

Method 2 (GC-SIM-MS)

The compounds were concentrated using a Chelex 100 resin column and eluted by 4 x 2 mL 6 M HCl. The elute passed directly into an AG 1-X8 resin column. A subsample of 2 mL was evaporated to dryness and re-dissolved. Trifluroacetic anhydride and 2,2,3,3,4,4,4-heptafluro-1-butanol were used for derivatisation at 90°C. After cooling, the sample was evaporated to dryness under N_2 flow and re-dissolved by 200 µL ethylacetate. The analytical column for GC was a HP-5 (crosslinked 5% PH ME siloxane, 30 m x 0.25 mm i.d. with a film thickness of 0.25 µm) and the carrier gas was He with a flow rate of 0.9 mL/min. A 2 µL sample was injected (splittless mode) at 280°C. The oven temperature was 65°C (2 min) followed by an increase of 20°C/min to 310 °C (1 min) with a post-run (4 min). The mass spectrometer (MS) was kept in Single Ion Monitoring (SIM) mode and the interface temperature was 275°C for detection of glyphosate and aminomethylphosphonic acid (AMPA) (Method M2275, Eurofins Denmark A/S).

Method 3 (GC-SIM-MS)
The samples were acidified to pH <0.5 by adding 7.5 mL concentrated sulphuric acid. Sodium sulphate was added and the samples were extracted with 50 mL methyl-tert-butylether (MTBE) for 30 min. The MTBE phase was re-extracted with MTBE, and the total extract was evaporated to 2 mL. Subsequently, 4 mL 10% sulphuric acid in methanol was added to the extract which was subsequently heated to 50 °C for 2 h. After cooling, 4 mL saturated sodiumbicarbonate was added and the MTBE phase was removed and evaporated to 200 µL under N_2 flow. The analytical column was a HP-5MS capillary column (30m x 0.25 mm i.d. with a film thickness of 0.25 µm) and the carrier gas was He with a flow rate of 1 mL/min. A 3 µL sample was injected (splittless mode) at 220 °C. The oven temperature was 45°C (1 min) followed by an increase of 12°C/min to 130°C and 30°C/min to 280°C with a post-run (5min). The mass spectrometer (MS) was kept in Single Ion Monitoring (SIM) mode and the interface temperature was 280°C for detection of trichloroacetate (TCA) (Method 2276, Eurofins Denmark A/S).

Catchments and use of herbicides
According to the Danish Agricultural Monitoring Programme, we extracted data on the use of the corresponding herbicides. The pulses and occurrence of herbicides and transformation products during flood events were related to (1) herbicides used in the spring season immediately prior to the sampling in 2004 (current season); (2) herbicides used in the previous 6 seasons of the farmer interview period (1998–2003) (average use in the seasons previous to the sampling season); (3) herbicides not used during the interview period but potentially applied before initiation of the farmer interview period in 1998.

Precipitation and stream water level
Meteorological and hydrological recordings were extracted from databases. Based on daily recordings, the Danish Meteorological Institute (DMI) calculates interpolated values for precipitation in 10 x 10 km^2 grids. From the Raingauge Network of The Water Pollution Committee of The Society of Danish Engineers at DMI, we obtained data on precipitation on an hourly basis. The nearest precipitation station was located 10, 31 and 21 km from the centre of catchments A, B and C, respectively. From the database on stream hydrology included in the National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environment, we obtained interpolated hourly values on the stream water level.

Two simple parameters were calculated. Firstly, the amplitude was calculated for each compound as the maximum–minimum concentration ratio during the flood events. Secondly, the recorded concentrations during pulses were normalised for each compound relative to the maximum concentration of the pulse.

Results
Two herbicides were used in the spring before sampling – MCPA in catchment A and glyphosate in catchments B and C. Pulses of glyphosate and AMPA were recorded 3–4 h after the start of the sampling during flood event C. The amplitudes of glyphosate and AMPA during flood event C were 90 and 9, respectively. In contrast, the pulses during flood event B were observed within 1–2 h, and the amplitude of both glyphosate and AMPA was 30. A pulse of MCPA was observed 3–7 h after a short and intensive precipitation event during flood event A, where the maximum concentration was 45 times the minimum concentration. However, agricultural use of glyphosate was not recorded in the current season prior to flood event A, but elevated concentrations were observed during the flood. The clear glyphosate pulse recorded at flood event A had a maximum concentration in the same order as for B and C, but the concentration of the transformation product aminomethylphosphonic acid (AMPA) was doubled–tripled compared with the grab sampling.

The maximum concentrations of glyphosate and AMPA are well below the non-lethal concentrations of 12 000 µg/L (acute 7 days EC value). Even though low concentrations were recorded during flood events, these compounds were often found (>0.1 mg/L) in drain pipe water and soil water extracted by suction cups installed at 1 m depth under Danish conditions. This means that a more or less constant and recurring contribution to streams may be expected at drainage events.

The physical/chemical properties indicate a fast degradation rate of glyphosate compared to the more persistent AMPA. However, detailed adsorption and degradation studies underpin that the transport of these compounds is complex due to the potential interaction with binding sites in the soil matrix, and the leakage of glyphosate and AMPA was recorded 1 and 2 years, respectively, after application. Thus, the slightly elevated concentrations of AMPA at flood event A (without recorded agricultural use of glyphosate in the current season) indicate leakage of residuals in consequence of former use, in particular the application of 86 kg glyphosate in August–October of the preceding season, illustrating the persistent character of AMPA ($DT_{50\text{-soil}}$ = 151 days).

Typical pulse shapes were recorded at all three flood events. The 10 times greater amplitude of glyphosate compared with the transformation product AMPA indicates a relatively direct leakage of glyphosate applied 2 weeks prior to sampling at C, avoiding adsorption in the soil matrix. The precipitation pattern shows that flood event C was caused by a first flush, whereas B was caused by a third flush. The two flushes preceding flood event B, which did not trigger the automatic samplers, may have facilitated some transportation of glyphosate from the soil phase to the water phase, potentially resulting in an intervening decomposition of glyphosate owing to a shorter ‘half-life’ of glyphosate in water than in soil ($DT_{50\text{-soil}}$ (typical) = 12 days, $DT_{50\text{-water phase}}$ = 3 days). Thus, the distribution in space and the difference in decomposition rates may explain the similarity in the amplitude of glyphosate and AMPA at event B compared to C. The distinct glyphosate pulse without a concurrent AMPA pulse at flood event A indicates a direct transport of glyphosate applied within a few days prior to the precipitation recorded on the 23 April. However, other sources may also be involved and the glyphosate pulse might be due to non-agricultural use, for instance in spraying of paved driveways and yards, including farm yards, as glyphosate is a very popular herbicide to control weeds in these areas. The distinct pulses (chemographs) of glyphosate and MCPA during floods (hydrographs) seem to be clearly related to their use in the current season.

The intention of this programme was to take into account the intra-annual dynamics of streams and occurrences of pesticides by using grab sampling for monitoring the long-term changes. However, our results indicate that the duration of concentration peaks is short (<2 h) and that peaks are most likely asynchronous. Therefore, it is very difficult to catch the peaks even when using the stratified sampling scheme for flood events, implicating that maximum concentrations may be underestimated.

Conclusion

A number of compounds occur within the same hydrograph when analysing stream water samples from small agricultural catchments under Danish conditions. Herbicides applied within the spring season prior to sampling lead to clear pulses (chemographs), but also herbicides applied in the past cause pulses or elevated concentrations compared with grab sampling under non-flood conditions. The recorded chemographs are not synchronous, except for pairs of a herbicide and its transformation product, and the chemographs are narrow with a typical duration of 1½–4 h. Elevated concentrations of herbicides not recently applied contribute to the total toxicity and are assumed to recur at repeated floods driven by precipitation events. In consequence, detailed studies on the occurrence, fate and transport of herbicides in streams require short sampling intervals, in particular when farmers’ use of herbicides is unknown, both in the past and in the future. It is very difficult to catch the short-lived chemograph peaks in long-term monitoring programmes, even when using a stratified grab sampling approach.

Assessment and conclusion by applicant:

The article describes an experiment in a Danish agricultural area, where glyphosate concentrations were measured during stream flood events. The development of concentrations levels after precipitation events were investigated. Different analytical methods were described. Maximum concentration of 2.8 µg/L for glyphosate and 0.54 µg/L for AMPA.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

The article describes an experiment in a Danish agricultural area. Intensive sampling of herbicide pulses (chemographs) in streams was planned for surface run-off events in the 2004 spring spraying season in Denmark (April–June).

The stream water sampling was carried out in three catchments (A, B and C) at a precipitation driven flood event as indicated.

Use of glyphosate within the 3 studied catchments is reported in the full text article: Average dose of 690 to 980 g/ha in 2004 or the preceding year. Glyphosate was used in the spring before sampling –in catchments B and C.

Spraying details on glyphosate and MCPA

Glyphosate	– Current season (2004)			
	– No. of sprayed fields (total area [ha])		2 (9.8)	1 (6.1)
	– Average dose [g ha^{-1}]		840	980
Glyphosate	– August–October of the preceding season (2003)			
	– No. of sprayed fields (total area [ha])	14 (88.9)	13 (55.8)	0 (0)
	– Average dose [g ha^{-1}]	970	690	—

Typical pulse shapes were recorded at all three flood events. Pulses of glyphosate and AMPA were recorded 3–4 h after the start of the sampling during flood event C. Maximum concentration of glyphosate in the 3 catchment A, B, C are respectively 2.8 µg/L, 1.8 µg/L and 2.0 µg/L.

The article is considered reliable.

Data point:	CA 7.5/060
Report author	Zgheib, S. *et al.*
Report year	2012
Report title	Priority pollutants in urban stormwater: Part 1 – Case of separate storm sewers
Document No	Water research 46 (2012) 6683-6692
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Organic and mineral pollutants have become part of today's urban environment. During a rain event, stormwater quality as well as the corresponding contaminant loads is affected by both atmospheric deposition and the various types of impervious surfaces (roads, rooftops, parking lots etc.) on which runoff occurs. This study provides results on stormwater pollution in Paris and its suburbs from three separate storm sewers (n = 20 samples). These results show that the stormwater had been contaminated by 55 chemical substances out of the 88 investigated. A particular attention was given to stormwater particle contamination. Concentrations are provided for: metals, PAHs, PCBs, organotins, alkylphenols, phthalates, pesticides, and VOCs. Our findings are among the first available in the literature since the relevant analyses were all conducted on both the particulate (P) and dissolved (D) phases. For most substances, particles from the three storm sewers were more heavily contaminated than dredged sediments and settleable particles from the Seine River. As a consequence of this finding, the release of untreated stormwater discharges may impact the receiving waters and contribute to sediment contamination.

Materials and Methods

Sampling site

Stormwater quality was monitored on three catchments, all located in Paris and its suburbs. The sites differed however in terms of land development and housing density. Sucy-en-Brie (SEB) is a residential area (with 90% of individual dwellings) with an impervious surface coefficient (ISC) of 0.27. Noisy-le-Grand (NLG) is an urbanized zone (ISC: 0.65), its catchment is typical of a dense urban area with a population of 59,000 inhabitants. ZAC Paris Rive Gauche (PRG) is a high density urbanized area with a mixed residential and commercial use area. These three watersheds are served by a separate sewer and storm drain. Polluted stormwater is discharged in an untreated state into local watercourses. Our sampling points were located at the storm sewer outlet of each watershed prior to discharge into the receiving waters.

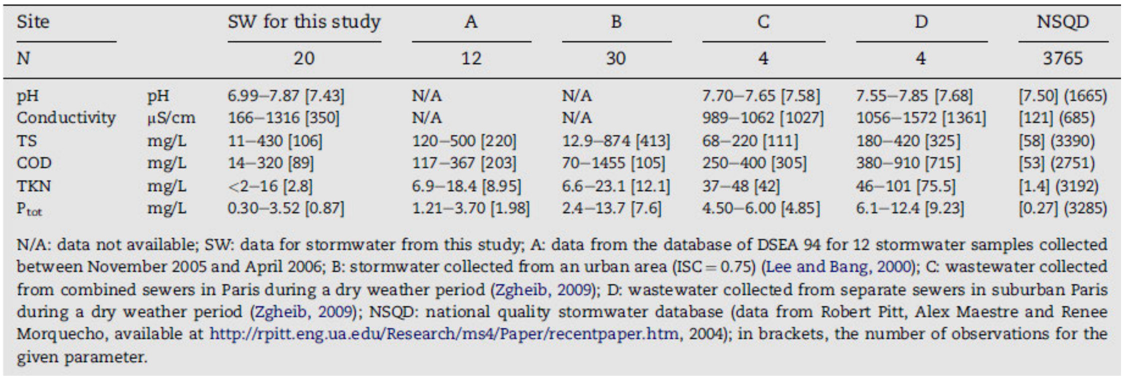
Sampling procedure

Twenty storms were followed between February 2008 and March 2009: 10 for SEB, 6 on NLG and 4 on PRG. However, due to technical problems, only 16 were analysed for stormwater priority substances. The entire sampling procedure has already been described in Zgheib *et al.* (2008). In brief, once collected, the samples were filtered to separate the dissolved phase (D) from the particulate phase (P). Analyses were carried out within 24 h for the dissolved phase, while the suspended particulate matter was deep-frozen then lyophilised and analysed after 48 h.

Experimental procedure

Routine water quality parameters - Each stormwater sample was analysed for routine water quality parameters (Table 8.5-192), such as pH, conductivity, suspended particulate matter (TS), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN) and total phosphorus (P_{tot}). These parameters were measured on the bulk water sample, or total phase (T), in accordance with French standards.

Table 8.5-192: Stormwater quality parameters (Minimum - Maximum [median])



Site		SW for this study	A	B	C	D	NSQD
N		20	12	30	4	4	3765
pH	pH	6.99–7.87 [7.43]	N/A	N/A	7.70–7.65 [7.58]	7.55–7.85 [7.68]	[7.50] (1665)
Conductivity	µS/cm	166–1316 [350]	N/A	N/A	989–1062 [1027]	1056–1572 [1361]	[121] (685)
TS	mg/L	11–430 [106]	120–500 [220]	12.9–874 [413]	68–220 [111]	180–420 [325]	[58] (3390)
COD	mg/L	14–320 [89]	117–367 [203]	70–1455 [105]	250–400 [305]	380–910 [715]	[53] (2751)
TKN	mg/L	<2–16 [2.8]	6.9–18.4 [8.95]	6.6–23.1 [12.1]	37–48 [42]	46–101 [75.5]	[1.4] (3192)
P_{tot}	mg/L	0.30–3.52 [0.87]	1.21–3.70 [1.98]	2.4–13.7 [7.6]	4.50–6.00 [4.85]	6.1–12.4 [9.23]	[0.27] (3285)

N/A: data not available; SW: data for stormwater from this study; A: data from the database of DSEA 94 for 12 stormwater samples collected between November 2005 and April 2006; B: stormwater collected from an urban area (ISC = 0.75) (Lee and Bang, 2000); C: wastewater collected from combined sewers in Paris during a dry weather period (Zgheib, 2009); D: wastewater collected from separate sewers in suburban Paris during a dry weather period (Zgheib, 2009); NSQD: national quality stormwater database (data from Robert Pitt, Alex Maestre and Renee Morquecho, available at http://rpitt.eng.ua.edu/Research/ms4/Paper/recentpaper.htm, 2004); in brackets, the number of observations for the given parameter.

Stormwater priority substances - The 88 stormwater priority substances (SPS) consisted of 3 organotins, 16 polycyclic aromatic hydrocarbons (PAHs), 8 polychlorobiphenyls (PCBs), 12 volatile organic compounds (VOCs), 5 chlorobenzenes, 2 chlorophenols, 5 alkylphenols (APs), 3 polybromodiphenyl ethers (PBDEs), 24 pesticides, chloroalkanes (sum of C10 - C13), Di(2-ethylhexyl) phthalate (DEHP), 8 metals (i.e., Cd, Cr, Cu, Hg, Ni, Pb, Pt and Zn). All SPS, except for metals and VOCs, were analysed on both the dissolved and particulate fractions for each sample. Metals were evaluated on the total and dissolved fractions, whereas VOCs were only analysed on the total fraction. When a substance provided concentrations below the limit of detection for the two phases, it was considered as not detected. Hence, the total concentration has been calculated as follows:

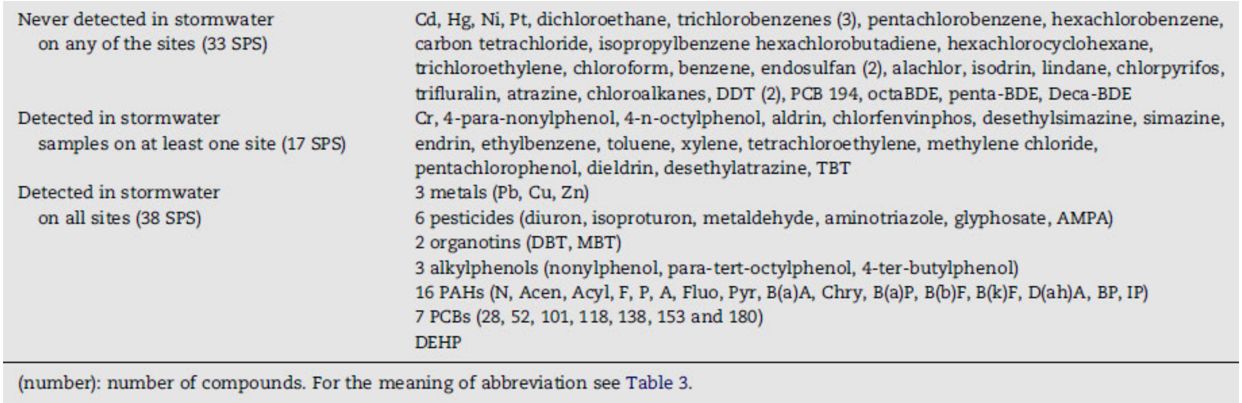
$$D + P\ (\mu g/L) = D\ (\mu g/L) + P\ (\mu g/L),\ \text{with}\ P\ (\mu g/L) = P^{*}(\mu g/g\ dw) \times TS\ (g/L)$$

When a substance was observed in just one of the two phases however, (D + P) was calculated in a way to maximize its concentration by substituting the concentration of the substance by its limit of quantification (LOQ) in the phase where the substance was observed to lie below this LOQ. Maximization referred to the fact that no null concentration was attributed to the phase where a substance was observed below LOQ. Moreover, maximization of the concentration was decided because 23 substances exhibited LOQs less than or equal to their EQS both for the dissolved and the particulate phases. When LOQs were greater than EQS, for all those substances excepted organotins the LOQ/EQS ratio was in the 1.5 - 10 range for the dissolved phase and in the 1.5 - 5 range for the particulate phase.

Results and Discussion

In a previous study, Zgheib *et al*. (2011a) investigated the relationships between land use and stormwater quality for these three catchments (on the basis of total concentrations). They reported that the statistical analysis of available SPS data did not reveal any significant differences for most substances in any of the three watersheds that could be explained by land use ($\alpha = 0.05$, $p > 95\%$). As a matter of fact, SPS concentrations were relatively homogeneous from one watershed to the next, thus suggesting that land use in these urban residential areas would not exert a predominant impact on the levels measured, especially when the land uses of the watersheds were contrasted much less than expected, being too close to Paris conurbation. In fact, the temporal variability was greater than the spatial variability. This finding was supported by previous results from the National Stormwater Quality Database (NSQD), which recorded some 3700 storms throughout the United States. The NSQD provided data for routine water quality parameters, a few metals, methylene chloride and DEHP.

Table 8.5-193: Detected and undetected substances in stormwater



Never detected in stormwater on any of the sites (33 SPS)	Cd, Hg, Ni, Pt, dichloroethane, trichlorobenzenes (3), pentachlorobenzene, hexachlorobenzene, carbon tetrachloride, isopropylbenzene hexachlorobutadiene, hexachlorocyclohexane, trichloroethylene, chloroform, benzene, endosulfan (2), alachlor, isodrin, lindane, chlorpyrifos, trifluralin, atrazine, chloroalkanes, DDT (2), PCB 194, octaBDE, penta-BDE, Deca-BDE
Detected in stormwater samples on at least one site (17 SPS)	Cr, 4-para-nonylphenol, 4-n-octylphenol, aldrin, chlorfenvinphos, desethylsimazine, simazine, endrin, ethylbenzene, toluene, xylene, tetrachloroethylene, methylene chloride, pentachlorophenol, dieldrin, desethylatrazine, TBT
Detected in stormwater on all sites (38 SPS)	3 metals (Pb, Cu, Zn) 6 pesticides (diuron, isoproturon, metaldehyde, aminotriazole, glyphosate, AMPA) 2 organotins (DBT, MBT) 3 alkylphenols (nonylphenol, para-tert-octylphenol, 4-ter-butylphenol) 16 PAHs (N, Acen, Acyl, F, P, A, Fluo, Pyr, B(a)A, Chry, B(a)P, B(b)F, B(k)F, D(ah)A, BP, IP) 7 PCBs (28, 52, 101, 118, 138, 153 and 180) DEHP

(number): number of compounds. For the meaning of abbreviation see Table 3.

Routine water quality parameters

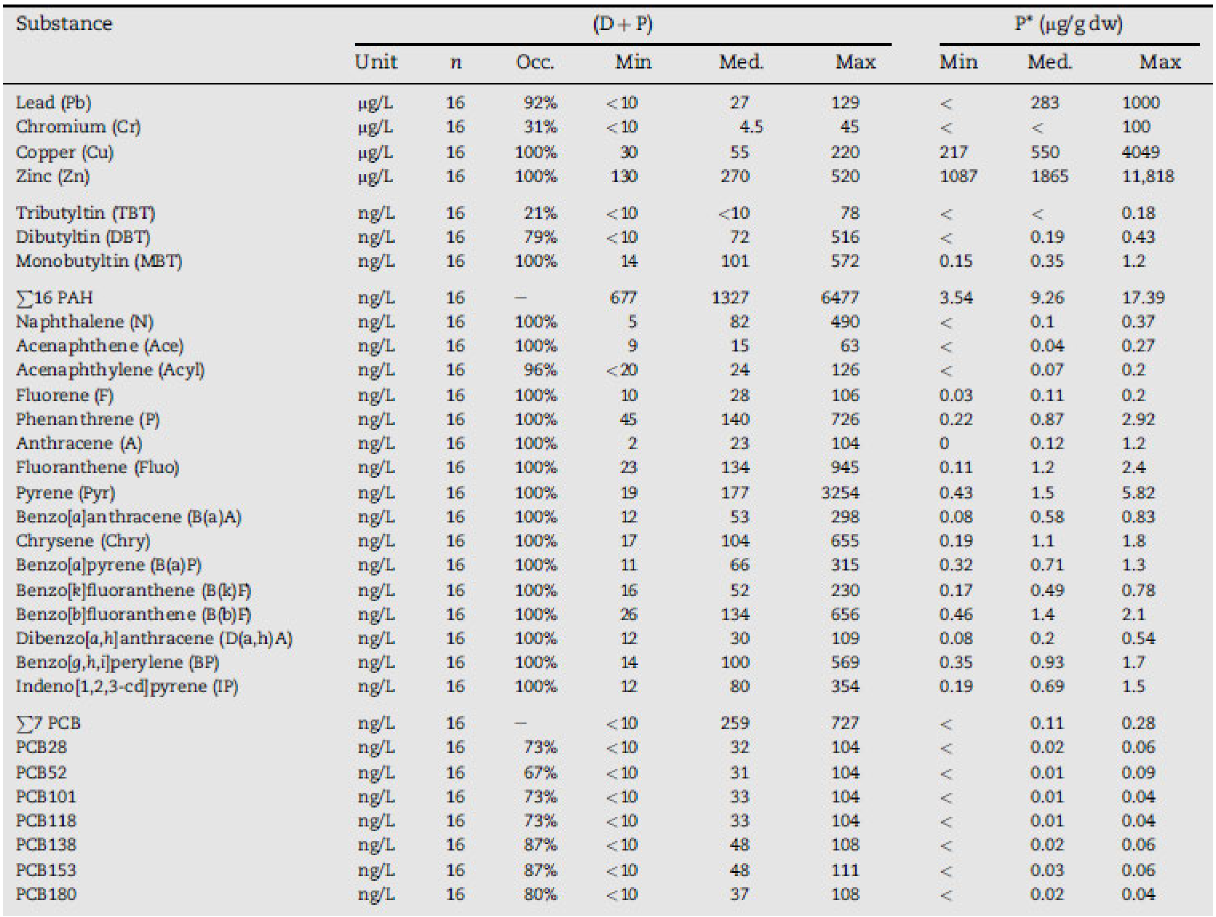
Table 8.5-192 presents the results obtained for routine water quality parameters. This table also provides data found in other databases, either (A) from stormwater networks used in a previous monitoring survey carried out on the residential watershed of Sucy-en-Brie between November 2005 and April 2006 (data provided by the watershed managing entity, DSEA 94) and (B) on an urban area with an ISC equal to 0.75, or from two types of sewer networks (i.e. the Parisian combined sewer (C) and separate sewers (D) in suburban Paris), both during dry weather. Data from NSQD are also given in Table 8.5-192. Routine water quality parameters provide key information on stormwater quality. In general, except for the data from NSQD, most of the routine parameters relative to the three investigated storm sewers exhibited the lowest concentrations: TS ranged from 11 to 430 mg/L, with a median of 106 mg/L. Conductivity varied between 166 and 1316 µS/cm (median: 350 µS/cm). COD ranged between 14 and 320 mg/L (median: 89mg/L), which is comparable to the quality of stormwater collected on the Marais urban catchment, although this represents half the value of wastewater from combined sewer networks. This latter finding suggests that the three storm sewers were not contaminated by infiltration from sewerage, a point reinforced by the fact that stormwater from the three watersheds all contained rather low concentrations of COD, TS, TKN and P_{tot} when compared either to discharge from combined sewer overflows in the Paris network or to wastewater during dry weather flow from a separate sewer and a combined sewer.

Stormwater priority substances

SPS occurrences

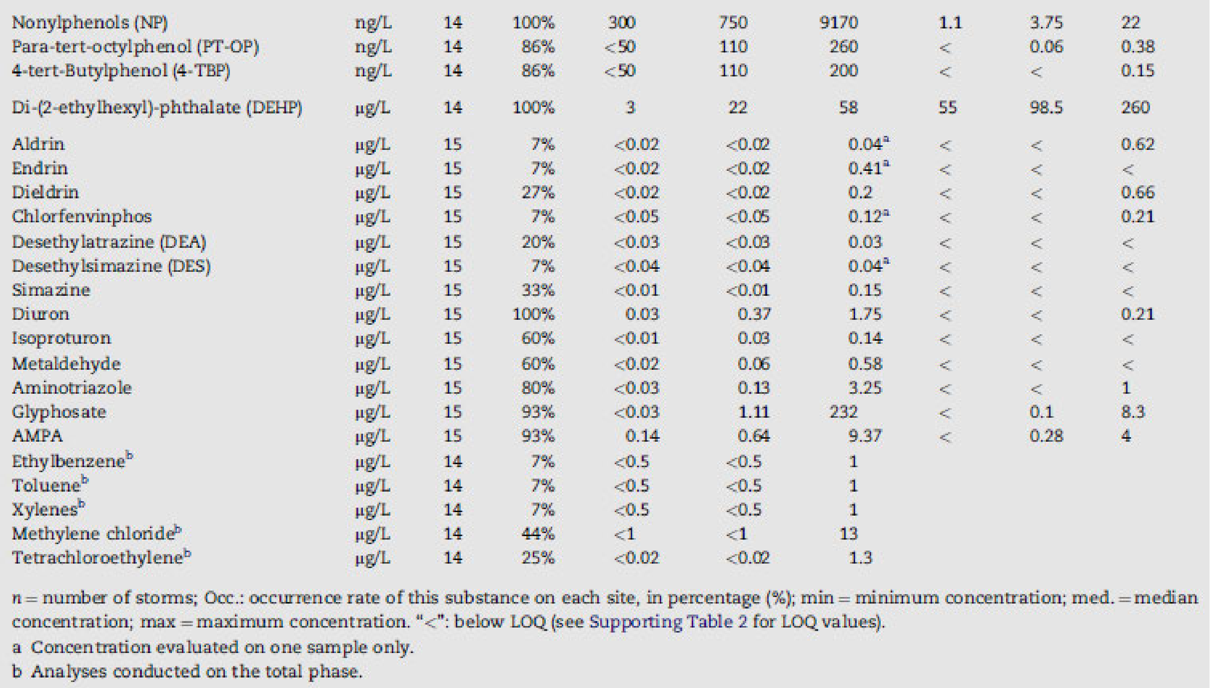
SPS occurrences have been already reported (Zgheib *et al*., 2010). Detailed examination of our results showed the total number of substances regardless of the site was comparable and that our samples of stormwater contained 55 different individual substances (Table 8.5-193). 21 SPS were observed across all samples: 15 PAHs, two metals (Cu, Zn), one pesticide (diuron), one organotin (MBT), DEHP, and nonylphenols. Some chlorophenols and VOCs were less commonly observed and seemed to show greater site dependence due to either a local source or a mix of sources that still need to be identified (Table 8.5-193). Besides, 33 substances were never quantified (see Table 8.5-193 for the entire list of these substances). Their concentrations always remained below the limit of detection (LOD) in both fractions. Several explanations for this finding can be forwarded. Samples were in fact only collected at the end of storm events, hence increasing the risk of losses. VOCs are known to be highly volatile, so they were sometimes observed because of the presence of numerous local sources, which compensated losses. For pesticides, many reasons are available to explain the non-detection of some of these products, though the main reason remains the cessation of their use. Most of these pesticides are in fact now banned from use in France. Furthermore, some LODs were set too high to quantify certain substances (i.e. Cd, Ni, PBDEs). This last consideration constitutes one of the main drawbacks to working with accredited laboratories. These LODs appeared to be too high for some substances, in comparison with levels generally determined by research centres. Since in many countries, however, regulation imposes sewer network managers to work with accredited laboratories, the managers must be able to face such constraints.

Table 8.5-194: Concentrations of stormwater priority substances at the outlets of the three storm sewers both in water (DDP) and in the particulate phase (P*)



Substance	(D + P)						P* (µg/g dw)		
	Unit	*n*	Occ.	Min	Med.	Max	Min	Med.	Max
Lead (Pb)	µg/L	16	92%	< 10	27	129	<	283	1000
Chromium (Cr)	µg/L	16	31%	< 10	4.5	45	<	<	100
Copper (Cu)	µg/L	16	100%	30	55	220	217	550	4049
Zinc (Zn)	µg/L	16	100%	130	270	520	1087	1865	11,818
Tributyltin (TBT)	ng/L	16	21%	< 10	<10	78	<	<	0.18
Dibutyltin (DBT)	ng/L	16	79%	< 10	72	516	<	0.19	0.43
Monobutyltin (MBT)	ng/L	16	100%	14	101	572	0.15	0.35	1.2
∑16 PAH	ng/L	16	–	677	1327	6477	3.54	9.26	17.39
Naphthalene (N)	ng/L	16	100%	5	82	490	<	0.1	0.37
Acenaphthene (Ace)	ng/L	16	100%	9	15	63	<	0.04	0.27
Acenaphthylene (Acyl)	ng/L	16	96%	< 20	24	126	<	0.07	0.2
Fluorene (F)	ng/L	16	100%	10	28	106	0.03	0.11	0.2
Phenanthrene (P)	ng/L	16	100%	45	140	726	0.22	0.87	2.92
Anthracene (A)	ng/L	16	100%	2	23	104	0	0.12	1.2
Fluoranthene (Fluo)	ng/L	16	100%	23	134	945	0.11	1.2	2.4
Pyrene (Pyr)	ng/L	16	100%	19	177	3254	0.43	1.5	5.82
Benzo[*a*]anthracene (B(a)A)	ng/L	16	100%	12	53	298	0.08	0.58	0.83
Chrysene (Chry)	ng/L	16	100%	17	104	655	0.19	1.1	1.8
Benzo[*a*]pyrene (B(a)P)	ng/L	16	100%	11	66	315	0.32	0.71	1.3
Benzo[*k*]fluoranthene (B(k)F)	ng/L	16	100%	16	52	230	0.17	0.49	0.78
Benzo[*b*]fluoranthene (B(b)F)	ng/L	16	100%	26	134	656	0.46	1.4	2.1
Dibenzo[*a,h*]anthracene (D(a,h)A)	ng/L	16	100%	12	30	109	0.08	0.2	0.54
Benzo[*g,h,i*]perylene (BP)	ng/L	16	100%	14	100	569	0.35	0.93	1.7
Indeno[1,2,3-cd]pyrene (IP)	ng/L	16	100%	12	80	354	0.19	0.69	1.5
∑7 PCB	ng/L	16	–	< 10	259	727	<	0.11	0.28
PCB28	ng/L	16	73%	< 10	32	104	<	0.02	0.06
PCB52	ng/L	16	67%	< 10	31	104	<	0.01	0.09
PCB101	ng/L	16	73%	< 10	33	104	<	0.01	0.04
PCB118	ng/L	16	73%	< 10	33	104	<	0.01	0.04
PCB138	ng/L	16	87%	< 10	48	108	<	0.02	0.06
PCB153	ng/L	16	87%	< 10	48	111	<	0.03	0.06
PCB180	ng/L	16	80%	< 10	37	108	<	0.02	0.04

Table 8.5-194 – continued



Nonylphenols (NP)	ng/L	14	100%	300	750	9170	1.1	3.75	22
Para-tert-octylphenol (PT-OP)	ng/L	14	86%	<50	110	260	<	0.06	0.38
4-tert-Butylphenol (4-TBP)	ng/L	14	86%	<50	110	200	<	<	0.15
Di-(2-ethylhexyl)-phthalate (DEHP)	µg/L	14	100%	3	22	58	55	98.5	260
Aldrin	µg/L	15	7%	<0.02	<0.02	0.04^{a}	<	<	0.62
Endrin	µg/L	15	7%	<0.02	<0.02	0.41^{a}	<	<	<
Dieldrin	µg/L	15	27%	<0.02	<0.02	0.2	<	<	0.66
Chlorfenvinphos	µg/L	15	7%	<0.05	<0.05	0.12^{a}	<	<	0.21
Desethylatrazine (DEA)	µg/L	15	20%	<0.03	<0.03	0.03	<	<	<
Desethylsimazine (DES)	µg/L	15	7%	<0.04	<0.04	0.04^{a}	<	<	<
Simazine	µg/L	15	33%	<0.01	<0.01	0.15	<	<	<
Diuron	µg/L	15	100%	0.03	0.37	1.75	<	<	0.21
Isoproturon	µg/L	15	60%	<0.01	0.03	0.14	<	<	<
Metaldehyde	µg/L	15	60%	<0.02	0.06	0.58	<	<	<
Aminotriazole	µg/L	15	80%	<0.03	0.13	3.25	<	<	1
Glyphosate	µg/L	15	93%	<0.03	1.11	232	<	0.1	8.3
AMPA	µg/L	15	93%	0.14	0.64	9.37	<	0.28	4
Ethylbenzene^{b}	µg/L	14	7%	<0.5	<0.5	1			
Toluene^{b}	µg/L	14	7%	<0.5	<0.5	1			
Xylenes^{b}	µg/L	14	7%	<0.5	<0.5	1			
Methylene chloride^{b}	µg/L	14	44%	<1	<1	13			
Tetrachloroethylene^{b}	µg/L	14	25%	<0.02	<0.02	1.3			

n = number of storms; Occ.: occurrence rate of this substance on each site, in percentage (%); min = minimum concentration; med. = median concentration; max = maximum concentration. "<": below LOQ (see Supporting Table 2 for LOQ values).

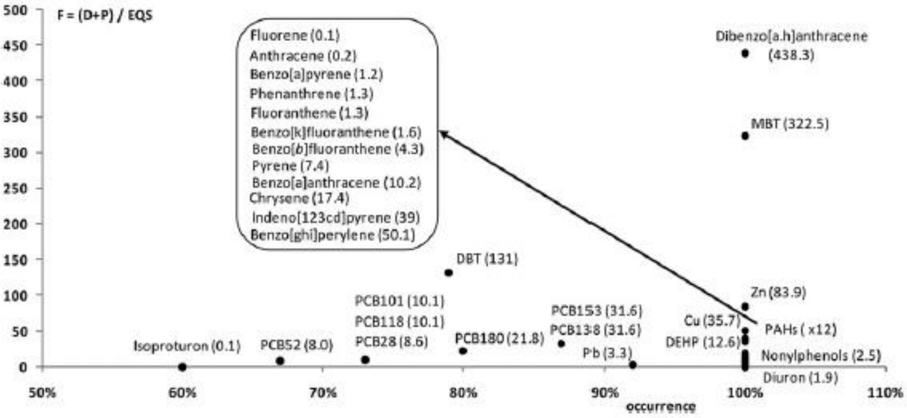
a Concentration evaluated on one sample only.

b Analyses conducted on the total phase.

SPS concentrations in stormwater particles

Table 8.5-194 presents, for all the 55 detected SPS, the (D + P) event mean concentrations (in µg/L), along with occurrence rates (in %) and particulate contamination levels (in µg/g dw). As previously mentioned, it was observed that (D + P) concentrations for the three watersheds were not significantly different, allowing the pooling of all data. The same observation held true for the particulate concentrations (P*), since statistical ANOVA did not find any significant differences for all tested substances ($\alpha = 0.05$, $p > 95\%$, data not shown). For this reason, results have been discussed by considering a global approach for interpretation, based on particle contamination followed by a comparison with sediments and settleable particles of the Seine River basin. To our knowledge, such a comparison has never been conducted so far.

Figure 8.5-155: Dilution factor (F), obtained by comparing total concentration (D + P) for stormwater with French EQS, expressed as a function of occurrence



Metals

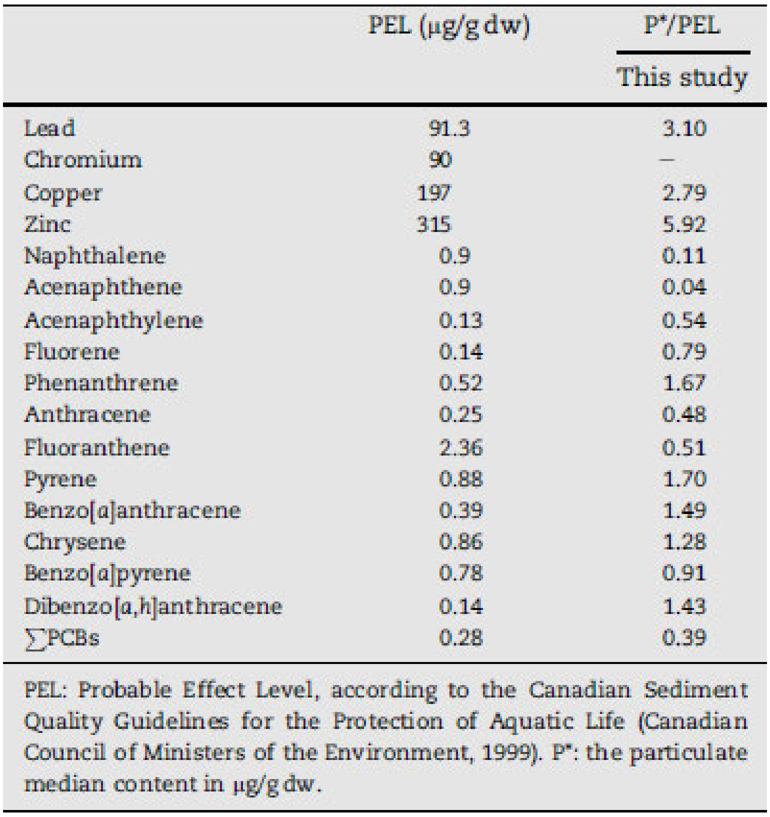
Metal contents were calculated from the results of the analysis carried out on the bulk sample and on the dissolved phase. The difference was then normalized to TS content. Metals were detected either above LOQ or below LOD, never in between. Stormwater was contaminated by Zn (270 µg/L, median concentration), Cu (55 µg/L), Pb (27 µg/L) and Cr (4.5 µg/L). These concentrations were twice as high as those for stormwater in London: Zn (82 µg/L), Cu (35 µg/L), Pb (10 µg/L), and Cr (3 µg/L). The presence of these metals in stormwater is caused by: i) vehicle brake emissions for Cu, ii) tire wear for Zn, and iii) atmospheric deposition for Cu and Pb.

Cu was observed at 550 µg/kg dw, with a range extending from 217 to 4049 µg/kg dw. These values are similar to the median concentrations typically reported in the literature. The value estimated for Cu in the NQSD equaled about 138 µg/g dw. This estimation was derived using the concentrations of total and filtered fractions, as well as the TS content provided by the database. Pb exhibited a different trend: Pb was evaluated at 283 µg/g dw, a level similar to our estimation in NSQD (241 µg/g dw). For Zn, we measured a level of 1865 µg/g dw (Zn-NQSD:1120 µg/g dw), which equalled the level reported in the QASTOR database, i.e. 1629 µg/g dw. The discharge of untreated stormwater may impact the receiving waters and contribute to sediment contamination with regards to metals.

Polycyclic aromatic hydrocarbons

As can be seen from the Table 8.5-194, the 16 PAHs were observed in almost 100% of the samples. Stormwater concentrations of the Σ16 PAHs ranged from 677 to 6477 ng/L (median: 1327 ng/L). The composition pattern of PAHs showed a distribution dominated by Pyrene, followed by Fluoranthene, Phenanthrene, and Chrysene. These high molecular-weight PAHs (containing between 4 and 6 aromatic rings) indicate inputs of pyrolytic origin tied to the high density of combustion sources within Paris and its suburbs, such as gasoline-powered vehicles and residential heating. Moreover, the PAH loads varied from 3.5 to 17.4 µg/g dw (median: 9.26 µg/g dw). In contrast, lift station sediments in Paris contained 23.5 µg/g dw (range:14 - 45 µg/g dw) for Σ16 PAHs. It is therefore likely that these findings resulted from the high traffic density in Paris compared to the densities of the three investigated watersheds. The comparison with dredged sediments (6.7 µg/g dw) and settleable particles from the Seine River (2.01-17.31 µg/g dw) has confirmed the severe contamination of stormwater particles in the Paris region by PAHs, which contribute during storm events to the contamination of watercourses.

Table 8.5-195: Comparison of median particulate contents for all three storm sewers with Canadian sediment guidelines



	PEL (µg/g dw)	P^*/PEL
		This study
Lead	91.3	3.10
Chromium	90	–
Copper	197	2.79
Zinc	315	5.92
Naphthalene	0.9	0.11
Acenaphthene	0.9	0.04
Acenaphthylene	0.13	0.54
Fluorene	0.14	0.79
Phenanthrene	0.52	1.67
Anthracene	0.25	0.48
Fluoranthene	2.36	0.51
Pyrene	0.88	1.70
Benzo[*a*]anthracene	0.39	1.49
Chrysene	0.86	1.28
Benzo[*a*]pyrene	0.78	0.91
Dibenzo[*a*,*h*]anthracene	0.14	1.43
∑PCBs	0.28	0.39

PEL: Probable Effect Level, according to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment, 1999). P^*: the particulate median content in µg/g dw.

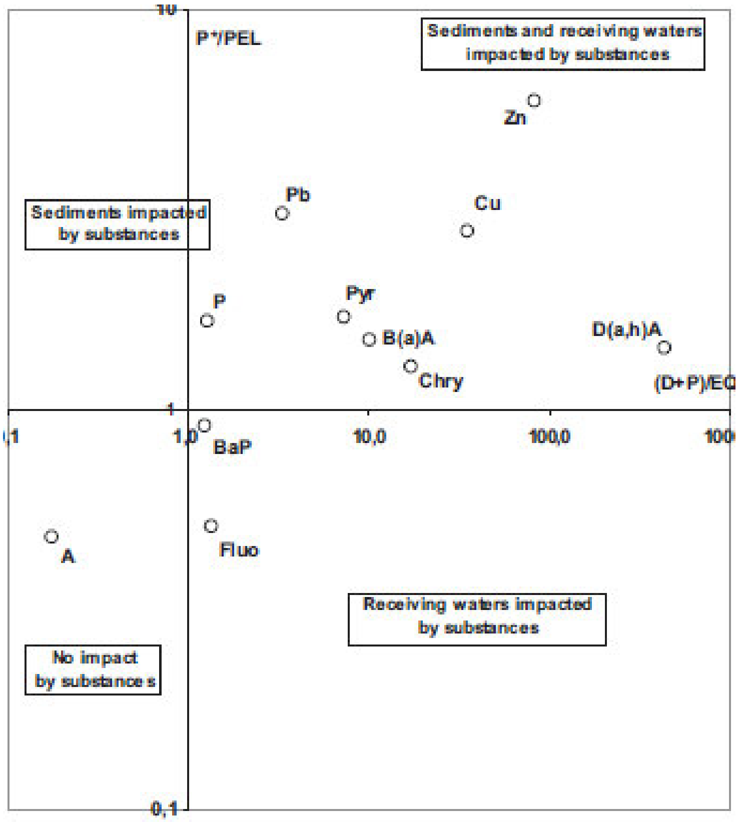
Polychlorinated biphenyls

Despite their ban in France since 1970, 7 congeners out the 8 investigated, namely PCB 28, 52, 101, 118, 138, 153 and 180, were detected (Table 8.5-194). The PCB distribution in stormwater revealed that 7-Cl (PCB 180) congener accounted for 14%, 6-Cl (PCB138 + PCB153) for 29%, 5-Cl (PCB101 + PCB118) for 27%, 4-Cl (PCB 52) for 11%, and 3-Cl (PCB 28) for 14%. This distribution, comparable to that observed for stormwater in Switzerland, is quite similar to that of the industrial mixture Arochlor but differs from that reported for total atmospheric deposition in Paris. The main sources of PCBs in water resources remain however atmospheric deposition and runoff on urban surfaces. PCBs were particle-bound at 100% and the ΣP7 PCBs ranged from <0.005 to 0.280 µg/g dw, with a median of 0.110 µg/g dw. These levels were comparable to those observed for a stormwater sediment trap in Norway: 0.0004 - 0.704 µg /g dw.

Organotins

Three organotin compounds, namely monobutyl (MBT), dibutyl (DBT) and tributyl (TBT), were monitored; they all presented contrasted behaviour, since MBT was observed in 100% of stormwater samples, while TBT and DBT were observed in just 21% and 79% of the samples, respectively. Observations were mainly recorded in the particulate phase at the following levels: <10 - 78 (median: <10), <10 – 516 (72) and 14 - 572 (101) ng/L for TBT, DBT and MBT, respectively. Similar ranges of concentrations in stormwater have been measured in two Norwegian harbours: 9 - 185, 8 -140 and 9 -85 ng/L for TBT, DBT and MBT, respectively. The organotin contents of stormwater particles were: 0.35 µg/g dw for MBT, 0.19 µg/g dw for DBT, and below the LOD for TBT. These levels were all higher than those measured in Norwegian stormwater, i.e. from 0.009 to 0.045 µg/g dw for MBT, 0.008 to 0.041 µg/g dw for DBT, with an exception for TBT, whose contents were similar (0.007 - 0.032 µg/g dw). On the other hand, contents were lower than those observed in stormwater particles from an industrial area in Norway (0.1 - 2.3 µg/g dw for DBT, 0.2 - 11 µg/g dw for TBT), except for MBT, whose levels were comparable (0.06 - 1.3 µg/g dw). It is generally agreed that the levels of MBT and DBT in stormwater exceed those of TBT. Since sediment did not accumulate in any of our three storm sewers, TBT degradation can be neglected and the levels of MBT and DBT may be due to their release from either organotin-stabilized PVC (e.g., in packaging material, piping, window frames.) or the local use of biocides).

Figure 8.5-156: Comparison of the environmental risk assessment for sediments, according to Canadian sediment quality guidelines (P*/PEL), with that for receiving waters, using environmental quality standards ((D+ P)/EQS)



Volatile organic compounds
Amongst the VOCs monitored, only methylene chloride (in 44% of samples, between <1 and 13 µg/L) and tetrachloroethylene (25% of samples, <0.02 - 1.3 µg/L) were observed in samples collected from the dense urban areas of PRG and NLG, while they were never detected in the residential area. As previously stated, our sampling strategy was not suitable for VOC analysis.

Pesticides
Data from Table 8.5-194 show that six pesticides were ubiquitous regardless of either the storm event or the watershed, meaning that they displayed an occurrence rate of at least 60%: diuron (100%), glyphosate (93%), amino methyl phosphonic acid or AMPA (93%), aminotriazole (80%), isoprotuon (60%), and metaldehyde (60%). All these pesticides except metaldehyde are herbicides. This finding was not surprising since herbicides represent 90% of all pesticides applied in urban areas. AMPA is the major metabolite of glyphosate; as would be expected therefore, the level of AMPA has increased along with that of glyphosate. Our findings are in good agreement with Botta *et al*. (2009), whose results suggested that contamination of the Orge River urban watershed by glyphosate was essentially of an urban origin (road and railway applications). The stormwater is thus contaminated by herbicides through the leaching of impervious urban surfaces. As a consequence, pesticides were able to reach receiving waters mainly through the storm sewer during a storm event. Moreover, the pesticide content in stormwater differed from one compound to another, lying between 0.04 and 0.92 µg/g dw. Among the pesticides listed as priority substances by the WFD, aldrin and chlorofenvinphos were quantified on a single sample with values at 0.62 and 0.21 µg/g dw, respectively. For aminotriazole, the maximum level equaled 1 µg/g dw, while the value for diuron was 0.21 µg/g dw and for dieldrin 0.66 µg/g dw. For glyphosate and AMPA, these levels were respectively 8.30

(median: 0.1) and 4 µg/g dw (median: 0.3). The data presented herein are original because the pesticide contents of particles are rarely reported in urban areas. For the remaining pesticides, particle contents were below LOD. Further research should be conducted to investigate a potential seasonal effect during urban pesticide application (looking closely at spring and fall).

Di(2-ethylhexyl) phthalate

DEHP was measured in all samples between 3 and 58 µg/L. Such levels were higher to those previously reported for stormwater in Sweden (5 µg/L) and in London (0.75 - 1.25 µg/L). The DEHP content in stormwater has ranged between 55 and 260 µg/g dw, with a median concentration of 99 µg/g dw. Surprisingly, Björklund *et al*. (2009) reported that DEHP was never detected in deposits from Norwegian storm sewers; however, their LOD was quite high (approx. 50 µg/g dw).

Alkylphenols

Overall, nonylphenols were ubiquitous in stormwater with a median concentration of 0.75 µg/L. These levels are average levels compared to previous results reported for stormwater. Their presence in stormwater is due to leaching from urban paint and cleaning products, as well as from pesticide residues. Data records for alkylphenols in stormwater particles are rare. For the three investigated watersheds, the levels of nonylphenol in stormwater lie in the range of 1.10 - 22 µg/g dw, with a median of 8.12 mg/g dw (Table 8.5-194). The SEB watershed, in the suburban area, and the NLG watershed, in the dense urban area, posted significantly higher levels for nonylphenols: 5.22 and 17.75 µg/g dw respectively, when compared to PRG watershed (2.85 µg/g dw). These levels exceed those measured in storm sewer deposits (0.72 - 1.5 µg/g dw) in Sweden and in urban stormwater: 3.7 µg/g dw. For the other alkylphenols, particulate contents were as follows: para-tert-octylphenol varied between <LOD and 0.38 µg/g dw, 4-tert-butylphenol between <LOD and 0.15 µg/g dw, and lastly 4-n-octylphenol between <LOD and 0.17 µg/g dw. For octylphenols, Bressy *et al*. (2011) observed a value of 0.27 µg/g dw for urban stormwater.

Environmental risk assessment

The European Commission has established environmental quality standards (EQS) so as to limit the quantity of certain chemical substances in receiving waters in the European Union. As stated in the Directive 2008/105/EC of the European Parliament, Member States must verify that the concentration of substances concerned does not increase significantly in sediments and/or the relevant biota. As a consequence, an environmental risk assessment was carried out according to Zgheib *et al*. (2011b), despite the simplicity of the method. For a given substance, its (D + P) concentration was compared to its corresponding EQS, as established by either the European Commission (Directive 2008/105/EC) or the French government (Circular 2007/23). This approach gave an indicative dilution factor for the stormwater discharge by the river flow to avoid the increase of the concentration of the priority substances in the watercourse beyond their EQS. As shown in Figure 8.5-155, many substances needed a dilution factor between 10 and 50 (the flow of the discharge should be the tenth or the fiftieth of the river flow to comply with regulation), whereas the dilution factor for 5 other substances had to exceed 50, i.e. dibenzo[a,h]anthracene (438), MBT (322), DBT (131), benzo [g,h,i]perylene (50) and Zn (84). This study produced results which corroborate the findings of the previous work on the watershed of Noisy-le-Grand. We have demonstrated for most substances that particles from the three storm sewers were more contaminated than dredged sediments and settleable particles from the Seine River. A consequence of the discharge of contaminated particles can result in sediment contamination. To evaluate to what extent this might occur, SPS particulate content (P*) was compared to the Canadian sediment quality guidelines (Canadian Council of Ministers of the Environment, 1999). According to these guidelines, the probable effect level (PEL) defines the level above which adverse effects are expected to occur frequently. As shown in Table 8.5-195, 8 substances (namely, Pb, Cu, Zn, phenanthrene, pyrene, benzo[a]anthracene, chrysene and dibenzo[a,h] anthracene) exceeded the guideline threshold, thus implying potential adverse biological effects on freshwater organisms. These results also point out that PAHs and metals in stormwater particles constitute a potential risk to the receiving waters. Finally, Figure 8.5-156 establishes a comparison of the trends observed for the environmental risk assessment using both approaches, for substances having thresholds defined both for sediments (PEL) and receiving waters (EQS). Though no mathematical correlation could be established between P*/PEL and (D + P)/EQS, it can be seen that the 8 substances exceeding the guideline threshold (i.e., P*/PEL > 1) displayed a dilution factor greater than one ((D + P)/EQS > 1). Therefore, this means that each approach led to the same result: these substances represent a threat to both media. As a consequence, they should be included into monitoring programs. For the remaining substances, two different situations were observed the substance impacts the receiving waters but not the sediments (i.e., benzo[a]pyrene and fluoranthene), or no impact was observed whatever the media (i.e., anthracene and fluorene). The remaining situation, namely the substance impacts the sediments but not the receiving waters, was not encountered.

Conclusion

The aim of this research has been to assess the potential presence of 88 stormwater priority substances in three watersheds located within the Paris metropolitan area with respect to particle contamination. A good number of findings have been derived from our results:

- Among the 55 substances observed at least once, 21 were present in all samples: 15 PAHs, two metals (Cu, Zn), one pesticide (diuron), one organotin (MBT), DEHP and nonylphenols.
- The levels of contamination of particles for the three watersheds were not significantly different.
- For most pollutants (metals, PAHs, PCBs, etc.), particles from the three storm sewers were more contaminated than dredged sediments and settleable particles from the Seine River. Consequently, the release of untreated stormwater discharge may impact receiving waters and contribute to sediment contamination. This point has been confirmed by comparing particulate concentrations with the Canadian Sediment Quality Guidelines, which have shown that metals and PAHs in stormwater particles constitute a potential risk to receiving waters.

A special effort should therefore be made to treat or remove as much of the particulate fraction of stormwater as possible, as this step will significantly reduce the impact on receiving waters given that most stormwater priority substances are particle-bound. To supplement our assessment of stormwater in the urban environment, a comparison of stormwater quality from separate storm sewers with the quality from combined sewer overflows is discussed in details in Gasperi *et al.* (2012).

Assessment and conclusion by applicant:

The article reports the contamination of stormwater with organic and mineral pollutants in the urban region of Paris. Among other substances, glyphosate and AMPA were measured and identified. The detected concentrations derive from atmospheric deposition and surface runoff from the urban environment, i.e. agricultural uses are not in the focus. Maximum glyphosate concentration of 232 µg/L in water (dissolved and particulate phases) and 8.3 µg/g dw (particulate phase). Maximum AMPA concentrations of 9.37 µg/L in water (dissolved and particulate phases) and 4 µg/g dw (particulate phase). The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

The aim of this research has been to assess the potential presence of 88 stormwater priority substances in three watersheds located within the Paris metropolitan area. Therefore agricultural uses are not in the scope of the study.

The study provides supportive information on the concentrations of glyphosate and AMPA in stormwater samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

RMS notes that the analytical method is not described within this study, but in another one (Zgheib, 2011) that is not submitted within this review. Concentration are given in dissolved + particulate phases, and particular phase.

Stormwater quality was monitored in 16 samples from three different catchments, all located in Paris and its suburbs. The sites differed in terms of land development and housing density. However, the concentration results of the pollutants are given as % occurrence, min & max concentrations, median of the 16 analysed samples. The results cannot be assigned to the respective sites.

Glyphosate has an occurrence of 93%. Maximum glyphosate concentration of 232 µg/L in water (dissolved and particulate phases) and 8.3 µg/g dw (particulate phase) were measured. Maximum AMPA concentrations of 9.37 µg/L in water (dissolved and particulate phases) and 4 µg/g dw (particulate phase) were measured.

The article is considered reliable with restrictions.

Data point:	CA 7.5/061
Report author	Birch H. *et al.*
Report year	2011
Report title	Micropollutants in stormwater runoff and combined sewer overflow in the Copenhagen area, Denmark
Document No	Water science and technology (2011) Vol. 64, No. 2, pp. 485-93.
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (Eurofins Miljø A/S)
Acceptability/Reliability:	Reliable with restrictions

Stormwater runoff contains a broad range of micropollutants. In Europe a number of these substances are regulated through the Water Framework Directive, which establishes Environmental Quality Standards (EQSs) for surface waters. Knowledge about discharge of these substances through stormwater runoff and combined sewer overflows (CSOs) is essential to ensure compliance with the EQSs. Results from a screening campaign including more than 50 substances at four stormwater discharge locations and one CSO in Copenhagen are reported in the paper. Glyphosate and AMPA were found in all samples at similar levels (glyphosate 0.043 – 1.3 µg/L; AMPA 0.06 – 1.3 µg/L). The highest concentrations were found in the combined sewer overflow; all these sources would result in direct input into streams without any form of treatment.

Materials and methods

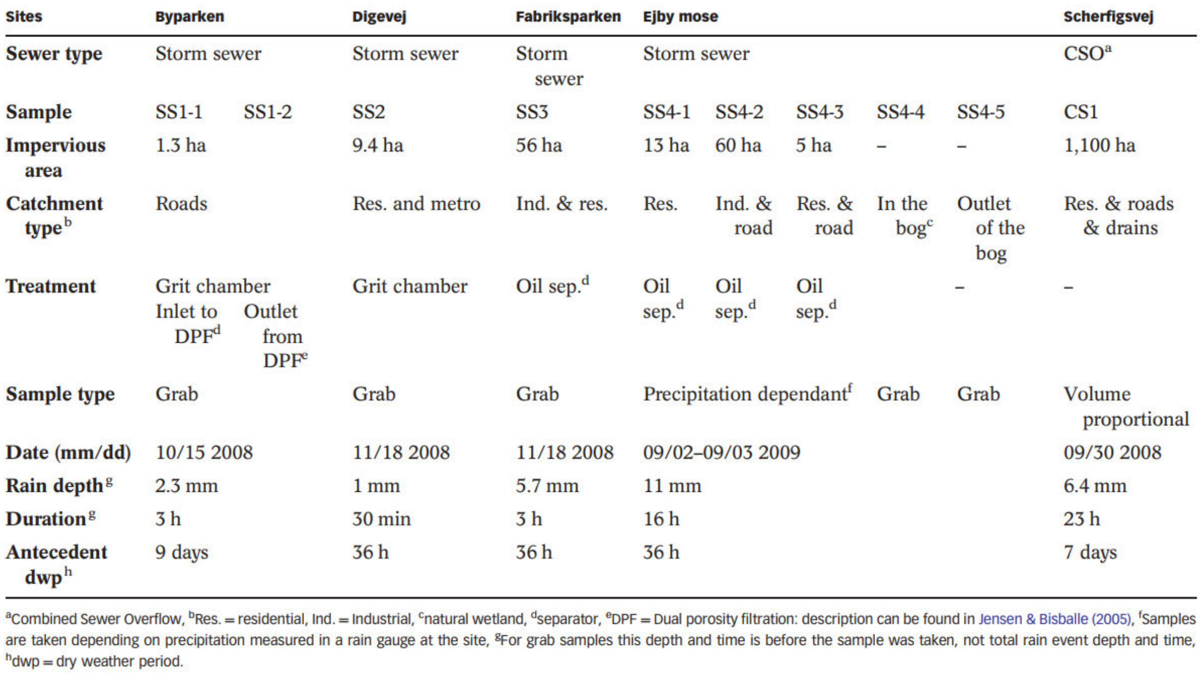
Sampling and sampling locations

Five sampling locations in the greater Copenhagen area were selected for this study and a total of 10 samples were analysed (see Table 8.5-196). Two of the sites (SS1 and SS2) were located in Tårnby, situated on the island Amager, and the remaining three (CS1, SS3 and SS4) were located in Gentofte, Albertslund and Glostrup, respectively. The sites varied in size, catchment type and treatment method and different events were sampled using different sampling methods. None of the rain events sampled were extreme rain events and all had return periods below 0.5 yr^{-1}. Samples were stored at 5°C and in darkness before analysis, which was started within 24 h of sampling.

Substances and sources

Substances for analysis were primarily selected from the WFD list, as illustrated in Figure 8.5-157, but earlier Danish runoff studies and a risk assessment for one of the catchment areas were also considered. Furthermore, industrial intermediates not used in Denmark, available analytical packages and prices affected the final choice of analysed substances.

Table 8.5-196: Description of the sites, samples and rain events

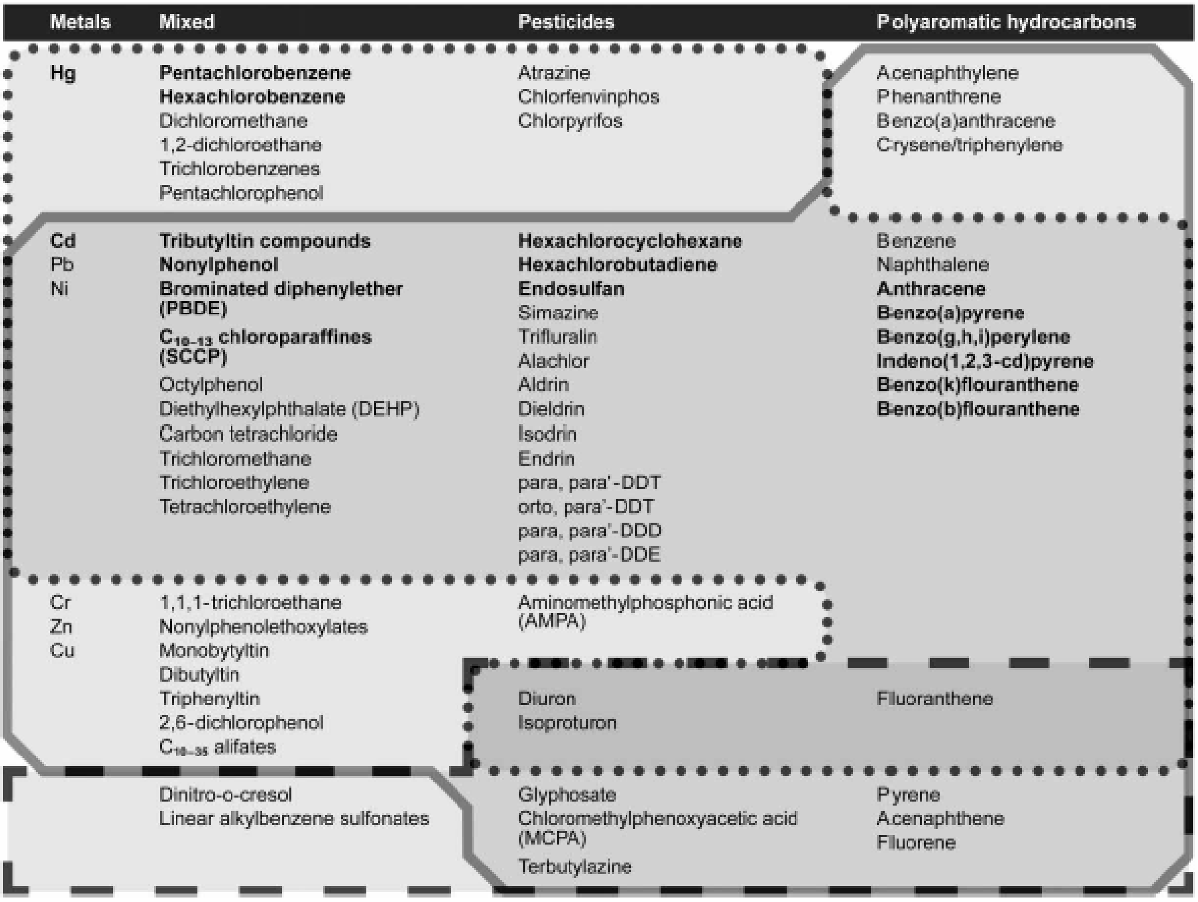


Sites	Byparken		Digevej	Fabriksparken	Ejby mose					Scherfigsvej
Sewer type	Storm sewer		Storm sewer	Storm sewer	Storm sewer					CSO[a]
Sample	SS1-1	SS1-2	SS2	SS3	SS4-1	SS4-2	SS4-3	SS4-4	SS4-5	CS1
Impervious area	1.3 ha		9.4 ha	56 ha	13 ha	60 ha	5 ha	–	–	1,100 ha
Catchment type[b]	Roads		Res. and metro	Ind. & res.	Res.	Ind. & road	Res. & road	In the bog[c]	Outlet of the bog	Res. & roads & drains
Treatment	Grit chamber Inlet to DPF[d]	Outlet from DPF[e]	Grit chamber	Oil sep.[d]	Oil sep.[d]	Oil sep.[d]	Oil sep.[d]		–	–
Sample type	Grab		Grab	Grab	Precipitation dependant[f]			Grab	Grab	Volume proportional
Date (mm/dd)	10/15 2008		11/18 2008	11/18 2008	09/02–09/03 2009					09/30 2008
Rain depth[g]	2.3 mm		1 mm	5.7 mm	11 mm					6.4 mm
Duration[g]	3 h		30 min	3 h	16 h					23 h
Antecedent dwp[h]	9 days		36 h	36 h	36 h					7 days

[a]Combined Sewer Overflow, [b]Res. = residential, Ind. = Industrial, [c]natural wetland, [d]separator, [e]DPF = Dual porosity filtration: description can be found in Jensen & Bisballe (2005), [f]Samples are taken depending on precipitation measured in a rain gauge at the site, [g]For grab samples this depth and time is before the sample was taken, not total rain event depth and time, [h]dwp = dry weather period.

Pesticides originate from public and private use as well as atmospheric deposition and leaching from building materials and paints during rain events.

Figure 8.5-157: **EU PS and PHS are shown in the dotted shape. Substances found in an earlier risk assessment of a catchment in Copenhagen are shown in the stippled shape. Substances selected in the present study are shown in the solid shape.**



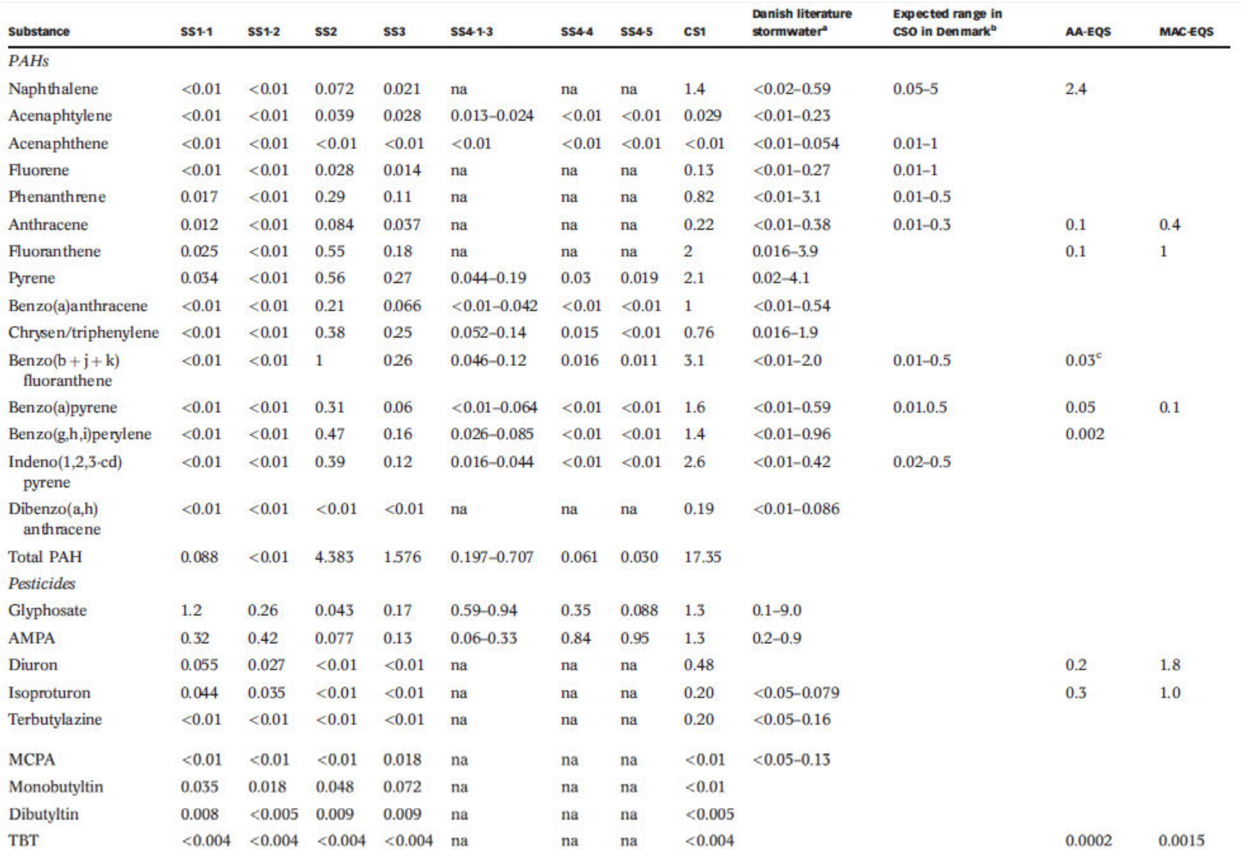
Analysis

Eurofins Miljø A/S (Denmark) performed all analyses of more than 50 micropollutants, except heavy metals in the samples from SS1, SS2, SS3 and CS1 which were analysed at DTU Environment's own laboratories. For all analyses total concentrations were measured.

Results

After a discussion of the sampling method, the following paragraphs present and discuss the findings for glyphosate and AMPA only (see Table 8.5-197).

Table 8.5-197: Presence in µg/L of the micropollutants found in water samples from the sampling locations SS1-SS4 and CS1



Substance	SS1-1	SS1-2	SS2	SS3	SS4-1-3	SS4-4	SS4-5	CS1	Danish literature stormwater[a]	Expected range in CSO in Denmark[b]	AA-EQS	MAC-EQS
PAHs												
Naphthalene	<0.01	<0.01	0.072	0.021	na	na	na	1.4	<0.02–0.59	0.05–5	2.4	
Acenaphtylene	<0.01	<0.01	0.039	0.028	0.013–0.024	<0.01	<0.01	0.029	<0.01–0.23			
Acenaphthene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01–0.054	0.01–1		
Fluorene	<0.01	<0.01	0.028	0.014	na	na	na	0.13	<0.01–0.27	0.01–1		
Phenanthrene	0.017	<0.01	0.29	0.11	na	na	na	0.82	<0.01–3.1	0.01–0.5		
Anthracene	0.012	<0.01	0.084	0.037	na	na	na	0.22	<0.01–0.38	0.01–0.3	0.1	0.4
Fluoranthene	0.025	<0.01	0.55	0.18	na	na	na	2	0.016–3.9		0.1	1
Pyrene	0.034	<0.01	0.56	0.27	0.044–0.19	0.03	0.019	2.1	0.02–4.1			
Benzo(a)anthracene	<0.01	<0.01	0.21	0.066	<0.01–0.042	<0.01	<0.01	1	<0.01–0.54			
Chrysen/triphenylene	<0.01	<0.01	0.38	0.25	0.052–0.14	0.015	<0.01	0.76	0.016–1.9			
Benzo(b + j + k) fluoranthene	<0.01	<0.01	1	0.26	0.046–0.12	0.016	0.011	3.1	<0.01–2.0	0.01–0.5	0.03[c]	
Benzo(a)pyrene	<0.01	<0.01	0.31	0.06	<0.01–0.064	<0.01	<0.01	1.6	<0.01–0.59	0.01.0.5	0.05	0.1
Benzo(g,h,i)perylene	<0.01	<0.01	0.47	0.16	0.026–0.085	<0.01	<0.01	1.4	<0.01–0.96		0.002	
Indeno(1,2,3-cd) pyrene	<0.01	<0.01	0.39	0.12	0.016–0.044	<0.01	<0.01	2.6	<0.01–0.42	0.02–0.5		
Dibenzo(a,h) anthracene	<0.01	<0.01	<0.01	<0.01	na	na	na	0.19	<0.01–0.086			
Total PAH	0.088	<0.01	4.383	1.576	0.197–0.707	0.061	0.030	17.35				
Pesticides												
Glyphosate	1.2	0.26	0.043	0.17	0.59–0.94	0.35	0.088	1.3	0.1–9.0			
AMPA	0.32	0.42	0.077	0.13	0.06–0.33	0.84	0.95	1.3	0.2–0.9			
Diuron	0.055	0.027	<0.01	<0.01	na	na	na	0.48			0.2	1.8
Isoproturon	0.044	0.035	<0.01	<0.01	na	na	na	0.20	<0.05–0.079		0.3	1.0
Terbutylazine	<0.01	<0.01	<0.01	<0.01	na	na	na	0.20	<0.05–0.16			
MCPA	<0.01	<0.01	<0.01	0.018	na	na	na	<0.01	<0.05–0.13			
Monobutyltin	0.035	0.018	0.048	0.072	na	na	na	<0.01				
Dibutyltin	0.008	<0.005	0.009	0.009	na	na	na	<0.005				
TBT	<0.004	<0.004	<0.004	<0.004	na	na	na	<0.004			0.0002	0.0015

AMPA: Aminomethylphosphonic acid; MCPA: Chloromethylphenoxy acetic acid; TBT: Tributyltin; NP: Nonylphenol; NPEs: Nonylphenol ethoxylates; NPE$_2$s: Nonylphenol diethoxylates; OPE$_n$s: Octylphenol polyethoxylates; DEHP: Diethylhexylphthalate; PBDE: Polybrominated diphenylether; na: no analysis; <: concentration below the LOD; CSO: combined seweroverflow; AA: annual average; MAC: maximum allowable concentration; –: not applicable; [a]Kjølholt et al. (1997) and Danish EPA (2006); [b]Arnbjerg-Nielsen et al. (2002); [c]EQS is only for b and k

Sampling methods

When sampling stormwater, the most representative sampling method is to use flow-proportional sampling or volume proportional sampling. Using these methods, event mean concentrations (EMCs) can be evaluated from each rain event. Another method, which is not as accurate as flow-and volume-proportional sampling, is the precipitation dependant sampling method where the input to the autosampler is determined by a rain gauge rather than flow measurements. Since the actual flow is not measured with this method, variation in rain intensity and varying runoff times over the catchment area are sources of uncertainty. Grab sampling is the least representative sampling method, but also the cheapest. The variability of pollutant concentrations in stormwater is very high, both between sites, between events and during events. This means that the variation of grab samples from different sites and events will be higher than the expected variation of EMCs from the same site or event.

In this study grab sampling was used where equipment for volume or precipitation proportional sampling was not available. Different sites were sampled during different events without specific attention to the duration and intensity of the event or the antecedent dry weather period. This means that the results cannot be considered statistically representative, be used to distinguish different pollution sources across sites or be used to calculate EMCs.

Nevertheless, the pattern of identified substances and their concentrations give a valuable first insight into the presence of a large number of micropollutants in stormwater runoff and CSO around Copenhagen and may be used as a starting point for more detailed monitoring studies targeting urban discharges of PSs in the context of the WFD.

Pesticides

Alachlor, aldrin, para,para'-DDT, orto,para'-DDT, para,para'-DDD, para,para'-DDE, dieldrin, endosulfan, endrin, hexachlorobutadiene, isodrin, lindane, simazin and trifluralin are all regulated under the WFD but were not found in this study. They are all prohibited in Denmark.

The CSO sample contained the highest concentrations of pesticides. Glyphosate and the degradation product aminomethylphosphonic acid (AMPA) were found in all samples. Glyphosate is currently included in the list of candidate substances for the WFD. From the inlet to the outlet of the treatment facility (SS1) as well as from the inlet to the outlet of the bog (SS4) the concentration of glyphosate decreased and the concentration of AMPA increased, indicating degradation throughout the two systems.

Pesticide concentrations in runoff are influenced more by local conditions and specific uses, than traffic related substances such as heavy metals and PAHs. For example, Weston *et al.* (2009) showed that pyrethroid pesticides in an urban creek came from residential runoff. Blanchoud *et al.* (2007) found a range of different pesticides in the Marne stream and showed that urban pesticide uses were important factors because of application on impervious areas resulting in rapid, unimpeded transport to the river during rain. An environmental risk assessment performed for a stream in the greater Copenhagen area, concluded that glyphosate, diuron, isoproturon, terbutylazine and MCPA all pose a risk to the stream's aquatic environment. This study confirms that these specific pesticides are being used in the greater Copenhagen area and that stormwater as well as CSOs contribute to the pesticide pollution load to the stream.

Monitoring

Whether stormwater discharges pose a risk to the aqueous environment depends on local conditions (water baseflow, amount and frequency of discharged water, etc.). Nevertheless, untreated stormwater discharges, especially CSOs, are a considerable source of pollution. For the Danish RBMPs, submitted for revision during spring 2010, the influence of micropollutants on the water quality was only included when monitoring data allowed doing so. There is however a severe lack of data on the presence of micropollutants in Danish surface waters, lakes and streams, for which reason it is difficult to exempt these substances from deteriorating water courses. In preliminary investigations on which Danish RBMPs are based, it is therefore 'anticipated that water courses receiving large amounts of stormwater discharges from roads and/or larger cities will be at risk'.

Conclusion

The present investigation shows that a broad range of EU WFD priority substances and other identified micropollutants including degradation products are found in various stormwater and combined sewage discharges around the greater Copenhagen area. Glyphosate and AMPA were found in all samples at similar levels (glyphosate 0.043 – 1.3 µg/L; AMPA 0.06 – 1.3 µg/L). The highest concentrations were found in the combined sewer overflow; all these sources would result in direct input into streams without any form of treatment.

Assessment and conclusion by applicant:

The article describes a monitoring experiment considering storm water from different catchments in the Copenhagen area. Glyphosate and AMPA were measured in the study, and the catchments are classified as mainly urban.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

The article is considered reliable with restrictions.

This study describes monitoring of storm water from five sampling locations in the greater Copenhagen area selected for this study. A total of 10 samples were analysed.

The study provides supportive information on the concentrations of glyphosate and AMPA in stormwater samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

Authors indicate that different sample methods were used. It is also indicated that different sites were sampled during different events without specific attention to the duration and intensity of the event or the antecedent dry weather period. This means that the results cannot be considered statistically representative.

Glyphosate and AMPA were found in all samples at similar levels (glyphosate 0.043 – 1.3 µg/L; AMPA 0.06 – 1.3 µg/L).

Data point:	CA 7.5/027
Report author	Bruchet, A. *et al.*
Report year	2011
Report title	Natural attenuation of priority and emerging contaminants during river bank filtration and artificial recharge
Document No	European Journal of Water Quality 42 (2011) 123-133
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at an officially recognised testing facilities
Acceptability/Reliability:	Reliable

The article was found relevant for multiple subchapters. The summary is provided in the groundwater monitoring subchapter of this document.

Assessment and conclusion by RMS:

This study describes monitoring experiment in the area of Paris, FR. The sampling points examined comprised Seine river water downstream of the Paris area, water from a primary well after bank filtration, water from a secondary well influenced by an artificial recharge process and water from the mixture of secondary wells after drinkingwater treatment.
More than 80 organic contaminants including glyphosate and AMPA, were monitored during five campaigns.

Grab samples were taken on five occasions during September and October 2008
In the river, glyphosate was found at <0.1 – 0.12 µg/L, and AMPA at 0.25 – 0.65 µg/L.

The aticle is considered reliable for surface water concentrations.

Data point:	CA 7.5/062
Report author	Lamprea, K., Ruban, V.
Report year	2011
Report title	Pollutant concentrations and fluxes in both stormwater and wastewater at the outlet of two urban watersheds in Nantes (France)
Document No	Urban Water Journal (2011), Vol. 8, no. 4, pp. 219-231
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (IDAC and IANESCO-CHIMIE Laboratory)
Acceptability/Reliability:	Reliable with restrictions

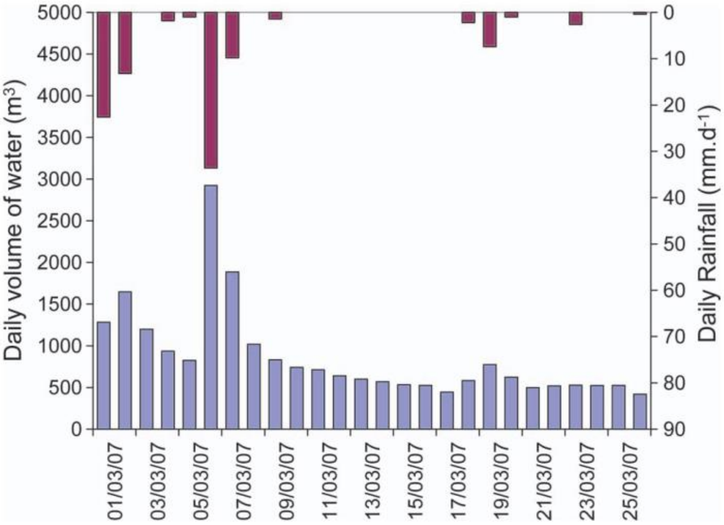
A two-year study of pollutants in both the stormwater and wastewater of urban watersheds was conducted in Nantes (France). The present paper discusses the characteristics of pollutants transported by stormwater and wastewater collection networks in two urban watersheds. A physicochemical characterisation of the effluents was performed, along with an estimation of pollutant fluxes discharged into the Gohards River. Suspended solids (SS), trace metals, polycyclic aromatic hydrocarbons (PAHs) and pesticides were studied. SS, Zn, Cu and glyphosate were the main pollutants in stormwater and wastewater.. Despite a reduction in the use of pesticides in Nantes Metropolitan area, herbicides containing glyphosate were still detected in stormwater. It should be noted that this herbicide is widely used by homeowners, a fact that may explain its occurrence in stormwater.

Materials and methods

Study sites

This study was conducted in the Pin Sec and Gohards watersheds located to the east of the city of Nantes (western France), between the Loire and Erdre rivers. In this area, the urban network was a separate sewer system. Stormwater was collected separately and discharged directly to Gohards River, whereas the wastewater network connected to the combined sewer system of Nantes city centre. The Pin Sec watershed comprised a surface area of 31 ha and encompassed 2500 residents. The type of housing was primarily composed of single-family dwellings and multi-family units. Impervious surfaces accounted for 49% of the area, mainly roofs, streets, pavements and parking lots. Roof surfaces represented 18% of the total watershed surface area. The mean watershed slope was approx. 1.1%. The stormwater network had a total length of 4 km and the diameter pipe at the outlet is was 1200 mm. The total length of wastewater network was 7.3 km and the diameter at the outlet pipe was 600 mm. The Gohards watershed contained a total surface area of 174 ha; land use was mixed, with both residential and commercial zones. This watershed was located between thoroughfares carrying moderate traffic loads (9300 vehicles per day) and crossed by a highway with an average traffic load of 44,200 vehicles per day. The impervious surfaces, which represented 38% of this watershed, consist mainly of: roofs, streets, pavements and parking lots. Roof surfaces accounted for 14% of the total surface area, while streets and parking lots made up 24% of the total. The total length of the stormwater network was 14.3 km and the diameter at the outlet pipe was 1600 mm. Although separate sewer systems were conceived to be selective, extraneous water inflow was observed. Extraneous water includes groundwater infiltrations and inappropriate connections (stormwater directly introduced to the wastewater network or wastewater collected by stormwater pipes). In the stormwater network of Pin Sec watershed, it was reported elsewhere that there was a strong relation between dry periods base flow and seasonal variation of the groundwater level. These authors report leaks as the main cause of infiltration. In the wastewater network, the inflow of stormwater has been observed in this study (Figure 8.5-158). These observations are in good agreement with other studies conducted in separate sewer systems and show that the networks are were not perfectly water tight. The behaviour of this separate wastewater network during wet periods is was similar to those observed in combined sewer systems.

Figure 8.5-158: Evolution of water volume in the wastewater sewer during wet weather



Sampling campaigns

So as to characterize quality and pollutant substances transported by stormwater, dry and wet weather conditions were studied in both stormwater and wastewater networks. The campaigns were carried out from September 2007 to October 2008 for stormwater, and from April 2007 to December 2008 for wastewater. During wet periods, sampling was flow dependent. The flow was monitored continuously and measured by ISCO or SIGMA flowmeters associating water level and velocity sensors. The base flow was used as reference to start sampling. Samples were collected by automatic samplers and stored in polyethylene bottles of 1L capacity. In dry periods, samples collected in stormwater networks were performed by instantaneous samples taken manually. Samples of 4.5 L were collected and stored in glass or polyethylene bottles depending on the type of analysis. In waste-water sewer system, samples of 120 mL were collected each 10 minutes over 24 hour periods. 24 mean hourly samples were collected for each campaign. In the laboratory, a mean daily flow-proportional sample was then prepared.

Stormwater

In order to characterise dry weather conditions, six sampling campaigns were carried out in the Pin Sec watershed and four in Gohards. Recordings were collected for 11 rainfall events at the Pin Sec watershed outlet and for nine events at the Gohards outlet.

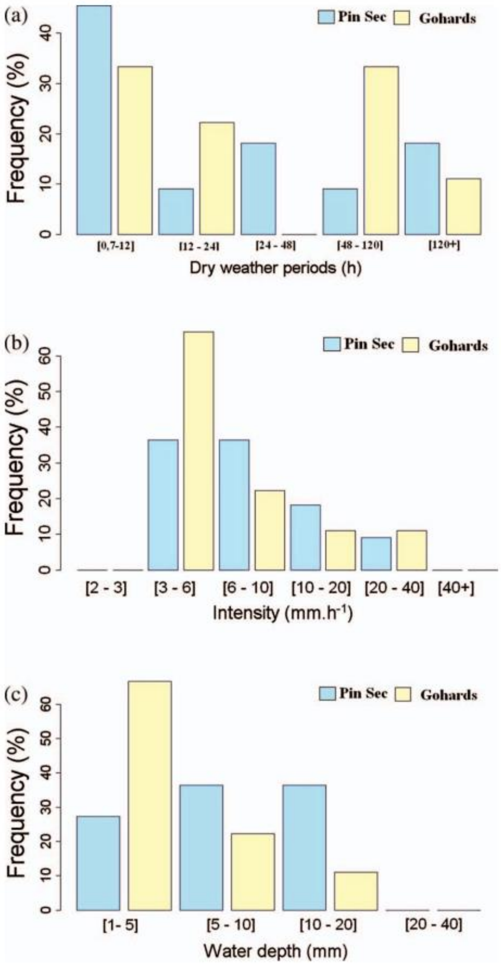
Wastewater

Eight dry weather campaigns were conducted at the Pin Sec wastewater network outlet. In order to determine the variation in pollutant concentration throughout the day, five of the eight days sampled were selected and analysed. In each case, 24 mean hourly samples were analysed for suspended solids (SS) and chemical oxygen demand (COD). Individual hourly time segments were also determined according to the variations in daily water flow, as well as in SS, VM (volatile matter) and COD concentrations. From these results, the day was divided into four time segments: 7 am–1 pm, 1 pm–7 pm, 7 pm–1 am, and 1 am–7 am. In addition, eight wet weather samples were collected, with sampling once again being flow-dependent.

Characteristics of rainfall events

Figure 8.5-159 presents the characteristics of these sampled rainfall events. In the Gohards watershed, 63% of events displayed low intensity (3–6 mm/h), with 56% of the events producing a rainfall depth ranging from 1 mm to 5 mm. Dry weather periods lasting less than 24 hours were observed 56% of the time. For the Pin Sec watershed, rainfall event characteristics were more diverse, with 27% of events producing a rainfall depth (H) lying between 1 mm and 5 mm, 36% with a depth of 5 mm < H < 10 mm and 36% with 10 mm < H < 20 mm. The maximum intensity (I_m) was moderate, i.e. 36% of precipitation within the interval of 3 mm/h < I_m < 6 mm/h. For 54% of events, the antecedent dry period (ADP) lasted less than 24 hours. The return period of these events, as well as the comparison of characteristics between sampled events and all events recorded in Nantes over the 2007–2008 period, shows that the sampled events were frequent and representative of Nantes rainfall in the Pin Sec and Gohards watersheds.

Figure 8.5-159: Characteristics of sampled rain events in the Pin Sec and Gohards watersheds. (a) Dry weather periods. (b) Intensity. (c) Water depth

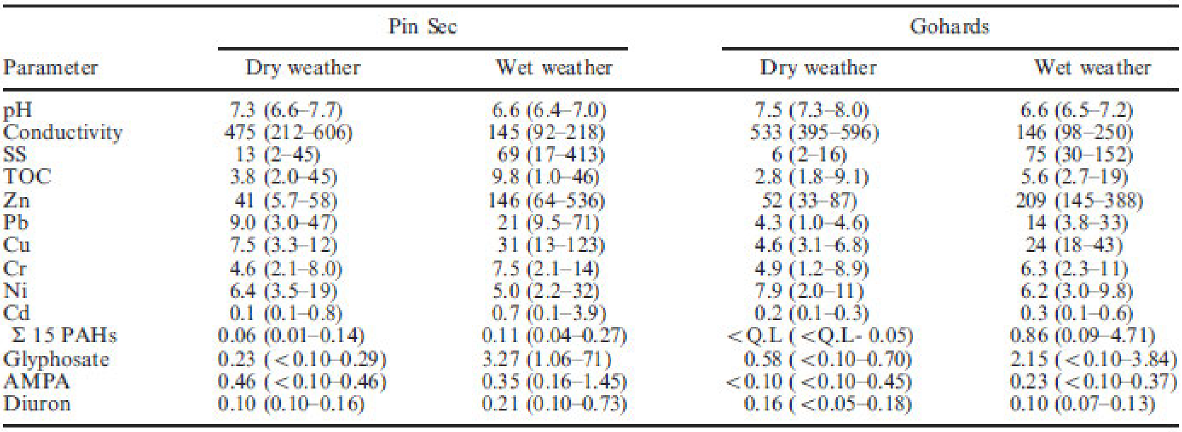


Analyses

pH and conductivity were measured in situ and in the laboratory. Before analysis, samples were sieved through a 2 mm mesh and analysed to obtain the concentrations of suspended solids (SS) according to French and European NF EN 872 standards. Bulk parameters and trace metals were analysed 24 h after the campaigns. Polycyclic aromatic hydrocarbons (PAHs) and pesticides were analysed by IDAC and IANESCO-CHIMIE Laboratory, respectively. For these analyses, the samples were stored in glass bottles in the dark at 4°C until analyses. pH, conductivity, suspended solids (SS) and total organic carbon (TOC) were all determined according to the French standards for water analysis. Chemical oxygen demand (COD), biological oxygen demand (BOD_5), volatile matter (VM), total Kjeldahl nitrogen (TKN) and total phosphorus (TP) were only measured in the wastewater samples, in accordance with French analytical standards. 15 of the 16 polycyclic aromatic hydrocarbons (PAHs) recommended by the Environmental Protection Agency (US EPA), i.e. naphthalene (Np), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Py), benzo(a)anthracene (B[a]An), chrysene (Chry), benzo(b)fluoranthene (B[b]Fl), benzo(k)fluoranthene (B[k]Fl), benzo(a)pyrene (B(a)Py), indeno(1,2,3-

c,d)pyrene (I[1,2,3-c,d]Py), dibenzo(a,h)anthracene (D(ah)An) and benzo(g,h,i)perylene (B[g,h,i]Pe), were analysed by the IDAC Laboratory as per the NF EN ISO 17993 protocol. The quantification limits for PAHs was 2.0 ng/L, with the exception of Np, Fl, Phe and An (10 ng/L). Pesticide analyses were performed by the IANES-CO-CHIMIE Laboratory in Poitiers. Glyphosate and aminomethyl phosphonic acid (AMPA) were evaluated using HPLC with a fluorimetric detection. Prior to analysis, the homogenised sample was derived with 9-fluorenyl methyl chloroformate (FMO-Cl) at pH 9. For diuron, 250 mL of the sample were extracted (liquid/solid extraction). The extract was then analysed using HPLC coupled with a double mass spectrometer (GC/MS/MS). Quantification limits were 0.05 ug/L for glyphosate and AMPA, and 0.1 ug/L for diuron. Trace metals (Zn, Ni, Cd, Cr, Cu, Pb) were studied at the LCPC Environmental and Chemical Laboratory by means of atomic absorption spectrometry, according to Standard NF EN ISO 15586. The quantification limits used for this analysis were: 0.10 ug/L for Cd, 1.0 ug/L for Pb, 2.0 ug/L for Cu, 0.5 ug/L for Cr, 8.0 ug/L for Zn, and 1.0 ug/L for Ni.

Table 8.5-198: Median, maximum and minimum values of pH, conductivity (µs/cm), suspended solids (SS, mg/L), total organic carbon (TOC, mg/L), trace metals (µg/L), PAHs (µg/L) and pesticides (µg/L) in stormwater at the Pin Sec and Gohards watersheds (Nantes, France)



	Pin Sec		Gohards	
Parameter	Dry weather	Wet weather	Dry weather	Wet weather
pH	7.3 (6.6–7.7)	6.6 (6.4–7.0)	7.5 (7.3–8.0)	6.6 (6.5–7.2)
Conductivity	475 (212–606)	145 (92–218)	533 (395–596)	146 (98–250)
SS	13 (2–45)	69 (17–413)	6 (2–16)	75 (30–152)
TOC	3.8 (2.0–45)	9.8 (1.0–46)	2.8 (1.8–9.1)	5.6 (2.7–19)
Zn	41 (5.7–58)	146 (64–536)	52 (33–87)	209 (145–388)
Pb	9.0 (3.0–47)	21 (9.5–71)	4.3 (1.0–4.6)	14 (3.8–33)
Cu	7.5 (3.3–12)	31 (13–123)	4.6 (3.1–6.8)	24 (18–43)
Cr	4.6 (2.1–8.0)	7.5 (2.1–14)	4.9 (1.2–8.9)	6.3 (2.3–11)
Ni	6.4 (3.5–19)	5.0 (2.2–32)	7.9 (2.0–11)	6.2 (3.0–9.8)
Cd	0.1 (0.1–0.8)	0.7 (0.1–3.9)	0.2 (0.1–0.3)	0.3 (0.1–0.6)
Σ 15 PAHs	0.06 (0.01–0.14)	0.11 (0.04–0.27)	<Q.L (<Q.L- 0.05)	0.86 (0.09–4.71)
Glyphosate	0.23 (<0.10–0.29)	3.27 (1.06–71)	0.58 (<0.10–0.70)	2.15 (<0.10–3.84)
AMPA	0.46 (<0.10–0.46)	0.35 (0.16–1.45)	<0.10 (<0.10–0.45)	0.23 (<0.10–0.37)
Diuron	0.10 (0.10–0.16)	0.21 (0.10–0.73)	0.16 (<0.05–0.18)	0.10 (0.07–0.13)

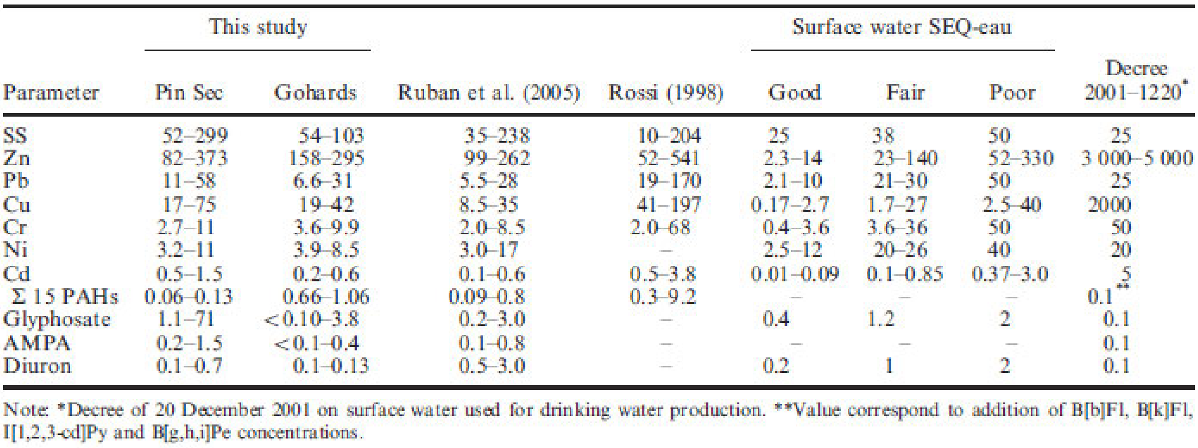
Results and Discussion

Stormwater quality

Bulk parameters

The bulk parameters concentrations are listed in Table 8.5-198. Stormwater pH and conductivity values measured in situ and in the laboratory were similar. pH ranged from 6.4 to 7.2; these values lie close to those measured in the collector during dry weather periods. Conductivity values were similar in the Pin Sec and Gohards watersheds, ranging between 92 µs/cm and 250 µs/cm. These values were three to four times less than those recorded during dry weather periods, a finding that can be explained by lower ion concentrations in runoff water as well as by a dilution during rainfall events. Regarding SS, 90% of the concentrations exceeded the maximum value of 35 mg/L set by the European directive on urban wastewater Directive 91/271/EEC. Median concentrations equal 69 mg/L at Pin Sec and 75 mg/L at Gohards; in both cases, these values were well above those measured during dry weather periods (Table 8.5-199). It needs to be pointed out that two values recorded for Pin Sec are exceptionally high (315 mg/L and 413 mg/L), most likely due to an accidental pollution incident that occurred in September and October 2008 related to the civil engineering works taking place upstream of the network. SS concentrations remained similar in both watersheds (Wilcoxon test with α = 0.05). On the other hand, total organic carbon (TOC) concentrations were twice as high as those measured during dry weather, with median concentrations of 9.8 mg/L for Pin Sec and 5.6 mg/L for Gohards. High concentrations of TOC in stormwater reflected urban runoff impact.

Table 8.5-199: **Comparison of pollutant concentrations in stormwater - (suspended solids (SS) in mg/L, trace metals, PAHs and pesticides in µg/L). Concentrations used for this comparison were 10th and 90th percentiles for metals and PAHs, min and max values for pesticides.**



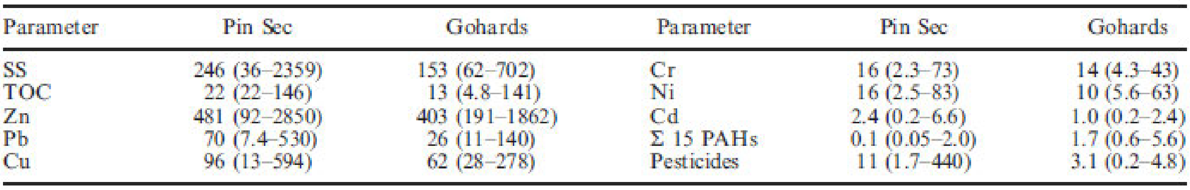
Parameter	This study		Ruban et al. (2005)	Rossi (1998)	Surface water SEQ-eau			Decree 2001–1220*
	Pin Sec	Gohards			Good	Fair	Poor	
SS	52–299	54–103	35–238	10–204	25	38	50	25
Zn	82–373	158–295	99–262	52–541	2.3–14	23–140	52–330	3 000–5 000
Pb	11–58	6.6–31	5.5–28	19–170	2.1–10	21–30	50	25
Cu	17–75	19–42	8.5–35	41–197	0.17–2.7	1.7–27	2.5–40	2000
Cr	2.7–11	3.6–9.9	2.0–8.5	2.0–68	0.4–3.6	3.6–36	50	50
Ni	3.2–11	3.9–8.5	3.0–17	–	2.5–12	20–26	40	20
Cd	0.5–1.5	0.2–0.6	0.1–0.6	0.5–3.8	0.01–0.09	0.1–0.85	0.37–3.0	5
Σ 15 PAHs	0.06–0.13	0.66–1.06	0.09–0.8	0.3–9.2	–	–	–	0.1**
Glyphosate	1.1–71	<0.10–3.8	0.2–3.0	–	0.4	1.2	2	0.1
AMPA	0.2–1.5	<0.1–0.4	0.1–0.8	–	–	–	–	0.1
Diuron	0.1–0.7	0.1–0.13	0.5–3.0	–	0.2	1	2	0.1

Note: *Decree of 20 December 2001 on surface water used for drinking water production. **Value correspond to addition of B[b]Fl, B[k]Fl, I[1,2,3-cd]Py and B[g,h,i]Pe concentrations.

Pesticides

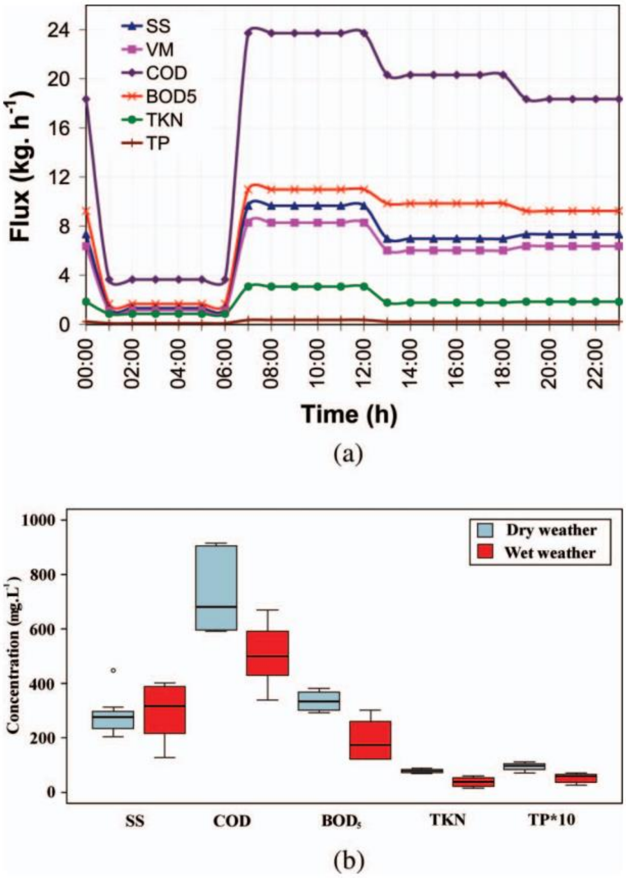
During wet weather periods, diuron and AMPA concentrations in the Gohards watershed wereclose to the quantification limits and similar to dry weather measurements. For glyphosate, wet weather concentrations were three times higher than the dry weather values (Table 8.5-199). In Pin Sec, most wet weather diuron and AMPA concentrations were similar to the dry weather values, with a maximum of 0.73 µg/L and 1.45 µg/L for diuron and AMPA, respectively. As regards glyphosate, stormwater concentrations were always higher than the dry weather values, with a median concentration of 3.27 µg/L and a maximum of 71 µg/L. The occurrence of these pesticides in stormwater can be explained by their application for cleaning unwanted grass and weeds from impervious surfaces and open spaces. The use of glyphosate has been reported by the Nantes municipality; this herbicide was also being widely used by homeowners.

Table 8.5-200: **Median, minimum and maximum values of pollutant masses generated per active surface in the Pin Sec and Gohards watersheds - suspended solids (SS) in mg/m^2, trace metals, PAHs and pesticides (Σ glyphosate + AMPA + diuron) in µg/m^2**



Parameter	Pin Sec	Gohards	Parameter	Pin Sec	Gohards
SS	246 (36–2359)	153 (62–702)	Cr	16 (2.3–73)	14 (4.3–43)
TOC	22 (22–146)	13 (4.8–141)	Ni	16 (2.5–83)	10 (5.6–63)
Zn	481 (92–2850)	403 (191–1862)	Cd	2.4 (0.2–6.6)	1.0 (0.2–2.4)
Pb	70 (7.4–530)	26 (11–140)	Σ 15 PAHs	0.1 (0.05–2.0)	1.7 (0.6–5.6)
Cu	96 (13–594)	62 (28–278)	Pesticides	11 (1.7–440)	3.1 (0.2–4.8)

Figure 8.5-160: **Daily flux variations (a) and mean daily concentrations (b) for global parameters measured at the outlet of Pin Sec wastewater network. (Suspended solids (SS), volatile matter (VM), chemical oxygen demand (COD), biological oxygen demand (BOD5), total kjeldahl nitrogen (TKN) and total phosphorus (TP)).**



Influence of rainfall characteristics

The influence of rainfall characteristics on pollutant concentrations in stormwater was studied by introducing Pearson correlation coefficients. The targeted variables were: SS, Cd, Cr, Cu, Ni, Pb, Zn, the sum of PAH concentrations, rainfall depth (H), total antecedent dry period (ADP), and maximum 5 min intensity of rainfall (Imax - 5 min). The Pearson coefficients however did not display any significant linear correlation between rainfall characteristics and pollutant concentrations.

Stormwater quality and comparison with other studies

The stormwater concentrations measured in the Pin Sec and Gohards watersheds were also compared to both the SEQ-Eau regulatory values (i.e., the French standard for surface water quality) and Decree 2001–1220 (2001) relative to the quality of surface water used for drinking water production. Concentration values used for this comparison were 10th and 90th percentiles for metals and PAHs, min and max values for pesticides (Table 8.5-199). In the two watersheds, nickel concentrations are in the range of ‘good quality’ water, as defined by SEQ-Eau. Chromium and PAH concentrations lie in the ‘fair quality’ category, while cadmium, copper and zinc concentrations vary from ‘fair’ to ‘very poor’ quality. Cadmium, chromium, copper, nickel and zinc concentrations are all below the reference values set for drinking water production (Table 8.5-199). In contrast, lead, pesticide and PAH (B[b]Fl, B[k]Fl, I[1,2,3-c,d]Py and B[g,h,i]Pe) concentrations often exceed the corresponding threshold values. Such is the case for Pb in 36% of the samples; also, 50% (Pin Sec) and 83% (Gohards) of PAH concentrations surpass the maximum value of 0.1 µg L^{-1}. Pesticide concentrations also lie above the threshold; it should be noted that such is the case for dry weather concentrations as well. Based on these results, it would appear that stormwater quality in the studied watersheds is poor. Our results have been compared to those of analyses carried out in residential areas equipped with separate sewer systems (Table 8.5-199). Furthermore, most references relative to stormwater systems are old; we then choose to present the most recent and relevant references. This comparison is not straightforward since many factors vary from one study to the other (site, meteorological conditions, sampling techniques, analysis, etc.). With results from the St. Joseph watershed located north-east of the two monitored herein and the Swiss study, the 10th and 90th percentile values were also used.

- SS, Cd, Cr and Ni concentrations are similar in the watersheds studied;
- Cu, Pb and Zn concentrations are higher in the Pin Sec and Gohards watersheds, likely as a result of higher traffic density;
- PAH concentrations in Pin Sec and St. Joseph are similar, while at Gohards they prove to be higher, again due to traffic density;
- Diuron concentrations are 4–23 times lower than those measured at St. Joseph, a finding that can be explained by a reduction in the use of this herbicide. Glyphosate and AMPA concentrations are comparable in Gohards and St. Joseph, whereas glyphosate is much more heavily con-centrated in Pin Sec than in St. Joseph. Glyphosate is widely used as a herbicide in the Pin Sec watershed area, which underscores this difference.

With regard to the Swiss study, SS, heavy metals and PAHs concentrations are similar to those measured at Pin Sec and Gohards watersheds.

Pollutant fluxes

For each watershed, the mass of pollutants released via active surfaces for each rainfall event along with the corresponding fluxes were examined. The objective of this estimation was to compare, for a given rainfall event, the pollution generated in each watershed and then derive an annual estimation of the pollutant flux likely to be discharged into the Gohards River, which is the watercourse that receives effluent from both the Pin Sec and Gohards watersheds. The following equation was used to calculate the pollutant mass generated during rainfall events:

$$M_{ac} = \frac{C\ x\ V}{S_{ac}}$$

with:

M_{ac} = mass per active surface (in mg/m^2 or µg/m^2)
C = concentration measured for each sampling campaign (mg/L or µm/L)
V = total water flow in the collector (L)
S_{ac} = active surface area of the watershed (m^2).

As mentioned above, no correlation was observed between metal concentrations and either rainfall depth, max I_{5min} or ADP. Each rainfall event selected in 2009 was thus multiplied by the experimental runoff coefficient determined for Pin Sec (0.25) and Gohards (0.29) and by one of the concentration values obtained during the sampling period and then chosen at random. The sum of all masses corresponds to the mean annual flux; this operation was repeated 1000 times in order to yield the mean annual flux and its confidence interval (the ‘‘bootstrap method’’). For organic micro-pollutants, this estimation proved impossible due to the correlations observed between PAHs concentrations and ADP, as well as to the seasonal occurrence of pesticides. Only the per-event masses were therefore calculated for PAHs and pesticides.

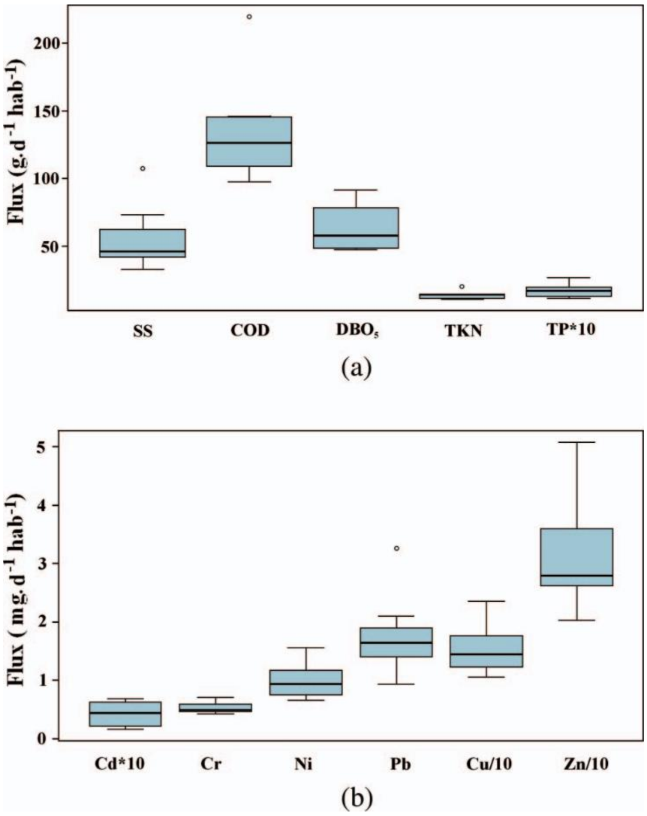
Masses generated for a rainfall event:

Table 8.5-200 gives the pollutant masses generated at the rainfall event scale for all events collected on the two studied watersheds. Metal, SS and TOC concentrations are similar in both watersheds, although total precipitation is higher in Pin Sec; consequently, pollutant masses are greater in this watershed. When the common rainfall events are considered, however, the masses observed at Gohards turn out to be higher, which can be explained by the more intensive commercial traffic activity and the prevalence of zinc roofs found in this watershed. The PAH mass generated at Gohards is greater, as already observed for concentrations and explained by the heavier vehicle traffic loads. Due to the higher pesticide concentrations measured in Pin Sec, the mass measurements there are 3.5 to 100 times greater than those in Gohards.

Wastewater quality

Global parameters
In the Pin Sec watershed, dry weather pH values range from 7.3 to 8 (median: 7.6) and conductivity is between 960 µs/cm and 1150 µs/cm (median: 1096 µs/cm). During wet weather periods, median pH values drop slightly to 7.1; conductivity is also lower, with a median of 589 µs/cm. This difference can be explained by a dilution of effluents during rainfall events. The ion concentration of stormwater is indeed less than that of wastewater. Daily variations in SS, VM, COD, BOD_5, TKN and TP are similar to the flow variations. Figure 8.5-160a shows daily flux variations. Minimum values are observed during the early morning hours (1 am to 7 pm), whereas maximum values appear between 7 am and 1 pm, which corresponds with a daily time segment of greater human activity. The 1 pm-to-7 pm and 7 pm-to-1 am concentrations remain roughly the same. Similar observations have been reported in other studies. From these values, mean daily concentrations were estimated. Concentrations are presented in Figure 8.5-160b. The median values of mean daily SS, VM, COD, BOD_5, TKN and TP concentrations are 275, 241, 681, 333, 78 and 9.6 mg/L, respectively. The high concentrations of COD, BOD_5 and TKN attest to the rich organic matter content of these effluents, which may be explained by the upstream location of the sampling station; at this site, the degradation in organic matter is negligible, as demonstrated by the presence of toilet paper, faeces and food residue. It should be noted that the biodegradability of effluents evaluated as COD/BOD_5 displays a median of 2.04. Median SS, COD and TKN concentrations are similar to those reported for the St. Joseph watershed (220 mg/L (SS), 518 mg/L (COD) and 72 mg/L (TKN)). SS concentrations are also similar to measurement results down-stream of the Nantes combined sewer system during dry weather periods (200–400 mg/L). These values exceed those cited in other studies also conducted in dry periods but in combined sewer systems (100–243 mg/L for SS, 231–535 mg/L for COD and 31–73 mg/L for TKN). As previously mentioned for the high organic matter content, this finding could be explained by the upstream location of the Pin Sec outlet. Except for COD, the variability of wet weather concentrations is greater than that observed for dry weather values (Figure 8.5-160b). Moreover, in all cases, the wet weather COD, BOD_5, TKN and TP concentrations are lower than the dry weather recordings, with median values of 500/681 mg/L for COD and 37/ 78 mg/L for TKN. Effluent dilution during wet weather periods offers a possible reason for this difference.

Figure 8.5-161: **Daily fluxes per inhabitant in global parameters (a) and heavy metals (b) estimated for Pin Sec watershed wastewater**



Organic micropollutants
Glyphosate was not detected in any of the dry weather samples, and AMPA could not be analysed due to interference. The presence of AMPA in wastewater has been reported in the literature as a result of degradation of phosphonic acids present in detergents such as EDTMP (Ethylene Diamine Tetra Methylene Phosphonic acid) and DTPMP (Diethylene Triamine Penta Methylene Phosphonic acid). Glyphosate and AMPA were detected in both spring and summer wet weather samples; concentrations varied between 0.3–49 µg/L, with a maximum observed in June 2008. The presence of glyphosate in wastewater probably indicates storm-water infiltration into the collector, which corroborates our results on stormwater effluent, given that a concentration of 71 µg/L was measured over the same period. These observations are in agreement with other works conducted in separate sewer networks.

Influence of meteorological conditions
The influence of meteorological conditions on SS, metal and PAHs concentrations was studied through the use of Pearson coefficients. As was the case for stormwater, no significant linear correlation could be observed.

Pollutant fluxes
Under dry weather conditions, the daily pollutant mass generated per inhabitant is considered to be the flux. Such fluxes are shown for global parameters and trace metals in Figure 8.5-161a and b. As previously highlighted for pollutant concentrations, dry and wet weather pollutant fluxes are highly variable, especially during wet weather periods. The median dry weather fluxes (in g/inhabitant/day) are: 46 (SS), 127 (COD), 58 (BOD_5), 14 (TKN), and 1.8 (TP). During wet weather, the median global parameter masses (in g/m^2) are: 0.36 (SS), 0.57 (COD), 0.21 (BOD_5), 0.05 (TKN), and 0.01 (TP).

Comparison between stormwater and wastewater
A detailed study of dry and wet weather concentrations and fluxes within the stormwater and wastewater of both the Pin Sec and Gohards watersheds yields the following observations (see Table 8.5-201); Median

stormwater concentrations for glyphosate varied from 0.2 µg/L in dry weather, to 3.3 µg/L in wet weather (<0.1 and 0.4 µg/L for AMPA). In wastewater, glyphosate was not detected during dry weather (and AMPA could not be determined because of interference), while during wet weather median glyphosate concentrations reached 49 µg/L and AMPA 2 µg/L:

- The median glyphosate concentration in stormwater and wastewater was higher during wet weather periods.;
- Higher glyphosate concentrations during wet weather (in both stormwater and wastewater) can be attributed to the washout of impervious surfaces; this situation also enhances stormwater infiltration into wastewater pipes;

Table 8.5-201: Comparison of pollutant median concentrations obtained in stormwater (Pin Sec and Gohards watersheds) and wastewater (Pin Sec watershed). Suspended solids (SS) in mg/L, trace metals, PAHs and pesticides in µg/L.

	Dry weather			Wet weather		
	Stormwater			Stormwater		
Parameter Wastewater	Pin Sec	Gohards	Wastewater Pin Sec	Pin Sec	Gohards	Wastewater Pin Sec
SS	13	6	275	69	75	317
Zn	41	52	150	146	209	280
Pb	9.0	4.3	7.9	21	14	14
Cu	7.5	4.6	79	31	24	72
Cr	4.6	4.9	3	7.5	6.3	2.3
Ni	6.4	7.9	5	5.0	6.2	4.8
Cd	0.1	0.2	0.3	0.7	0.3	0.4
Σ 15 PAHs	0.06	< QL	0.2	0.1	0.9	0.3
Glyphosate	0.2	0.6	–	3.3	2.2	0.3 – 49
AMPA	0.5	< 0.1	–	0.4	0.2	0.3–2.0
Diuron	0.1	0.2	–	0.2	0.1	–

Conclusion

The study of the quality of effluents transported by separate stormwater and wastewater networks in the Pin Sec and Gohards watersheds reveals that during wet weather periods the concentrations of suspended solids, organic matter, metals, PAH and pesticides are higher than those measured in dry weather. These results are in agreement with the literature and reflect the impact of urban runoff on stormwater and wastewater quality. Most of the time during wet weather, high variations of pollutant concentrations and fluxes are observed in stormwater and wastewater samples. This variability cannot be explained by any of the rain characteristics taken into account in this study. The use of pesticides in these watersheds (homeowners and municipality) appear to be the main sources of those organic pollutants during wet weather periods. High concentrations of glyphosate are still detected in stormwater and wastewater samples despite the reduction in the use of pesticides by Nantes metropolitan authorities. Our results demonstrate that pollutant transport via separate sewer system effluent is far from being negligible, therefore effluent from both the Pin Sec and Gohards watersheds discharged directly to Gohards River can contribute to the deterioration of this river.

Assessment and conclusion by applicant:

The article describes a monitoring campaign in an urban area in the region of Nantes / France. Among others, glyphosate is measured. However, agricultural land use does not contribute significantly to the measured concentrations as the study area is described as an urban area. Median stormwater concentrations for glyphosate varied from 0.2 µg/L in dry weather, to 3.3 µg/L in wet weather (<0.1 and 0.4 µg/L for AMPA). In wastewater, glyphosate was not detected during dry weather (and AMPA could not be determined because of interference), while during wet weather median glyphosate concentrations reached 49 µg/L and AMPA 2 µg/L. Hence, urban use of glyphosate can generate significant residues in both stormwater and wastewater.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:
A two-year study of pollutants in both the stormwater and wastewater of urban watersheds has been conducted in Nantes (France). So as to characterize quality and pollutant substances transported by stormwater, dry and wet weather conditions were studied in both stormwater and wastewater networks. The campaigns were carried out from September 2007 to October 2008 for stormwater, and from April 2007 to December 2008 for wastewater. Samples were analyzed for Glyphosate and AMPA, LOQ = 0.05 µg/L.

The study provides supportive information on the concentrations of glyphosate and AMPA in stormwater and wastewater samples, but does not provide concentrations in water bodies, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

A physicochemical characterisation of the effluents was performed, along with an estimation of pollutant fluxes discharged into the Gohards River. Median stormwater concentrations for glyphosate varied from 0.2 µg/L in dry weather, to 3.3 µg/L in wet weather (<0.1 and 0.4 µg/L for AMPA). In wastewater, glyphosate was not detected during dry weather (and AMPA could not be determined because of interference), while during wet weather median glyphosate concentrations reached 49 µg/L and AMPA 2 µg/L. Hence, urban use of glyphosate can generate significant residues in both stormwater and wastewater.

The results can however be considered outdated and considered less representative of the current use of glyphosate.

The article is considered reliable with restrictions.

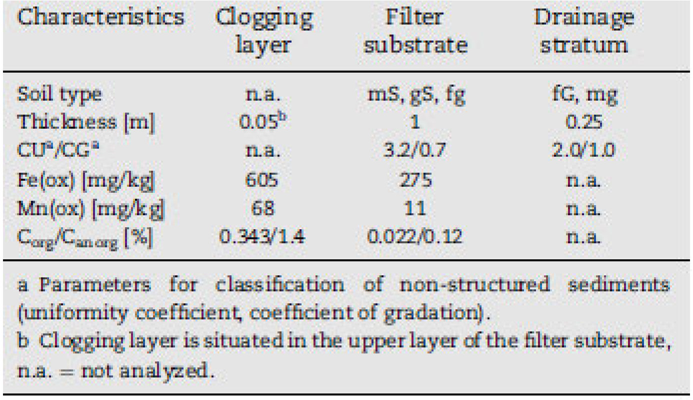
Data point:	CA 7.5/063
Report author	Litz, N.T. *et al.*
Report year	2011
Report title	Comparative studies on the retardation and reduction of glyphosate during subsurface passage
Document No	Water research (2011), Vol. 45, No. 10, pp. 3047-54
Guidelines followed in study	None (for filter experiments)
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities (German UBA, German KompetenzZentrum Wasser)
Acceptability/Reliability:	Reliable with restrictions

The herbicide Glyphosate was detected in River Havel (Berlin, Germany) in concentrations between 0.1 and 2 µg/L (single maximum outlier: 5 µg/L). As the river indirectly acts as drinking water source for the city's 3.4 million inhabitants' potential risks for drinking water production needed to be assessed. For this reason laboratory (sorption and degradation studies) and technical scale investigations (bank filtration and slow sand filter experiments) were carried out. Batch adsorption experiments with glyphosate yielded a low K_F of 1.89 (1/n = 0.48) for concentrations between 0.1 and 100 mg/L. Degradation experiments at 8°C with oxygen limitation resulted in a decrease of glyphosate concentrations in the liquid phase probably due to slow adsorption (half life: 30 days). During technical scale slow sand filter (SSF) experiments glyphosate attenuation was 70-80% for constant inlet concentrations of 0.7, 3.5 and 11.6 µg/L, respectively. Relevant retardation of glyphosate breakthrough was observed despite the low adsorption potential of the sandy filter substrate and the relatively high flow velocity. The VisualCXTFit model was applied with data from typical Berlin bank filtration sites to extrapolate the results to a realistic field setting and yielded sufficient attenuation within a few days of travel time. Experiments on an SSF planted with *Phragmites australis* and an unplanted SSF with mainly vertical flow conditions to which glyphosate was continuously dosed showed that in the planted SSF glyphosate retardation exceeds 54% compared to 14% retardation in the unplanted SSF. The results show that saturated subsurface passage has the potential to efficiently attenuate glyphosate, favourably with aerobic conditions, long travel times and the presence of planted riparian boundary buffer strips.

Materials and methods

In all experimental settings – laboratory batch, enclosure and SSF tests- the same filter material was used. The texture of the applied sandy substrate can be characterized as follows: on average 2% fine sand (0.1-0.2 mm), 43% medium sand (>0.2-0.5 mm), 49% coarse sand (>0.5-2.0 mm) and 6% fine gravel (>2 mm), no clay or silt with only traces of organic matter and an effective porosity of 0.38-0.4% (Table 8.5-202). The pH value of the percolated water was ~7.7. Solid glyphosate produced by Sigma-Aldrich with a purity degree of 98.7%, dissolved in a 0.01 M $CaCl_2$-solution, was used for the experiments. Glyphosate concentrations were analyzed according to the German Standard DIN 38407-22 (2001). The quantitative determination of AMPA and glyphosate was done using a Waters HPLC system with a fluorescence detector and two Knauer 64 as reagent pumps. The analytical column for glyphosate was a Supelco SAX column (25 x 4 mm), for the quantification of AMPA a cation exchange column (Pickering) was applied (15 x 4 mm), because in field samples the AMPA peak was interfered by matrix peaks. The run conditions were: 0.4 mL/min, isocratic, phosphate buffer pH 2.05 ± 0.1 at 50°C. Retention time for glyphosate was 13.6 min on the anion exchange column and for AMPA 13.9 min on the cation exchange column. The detection limits were 0.02 µg/L and 0.005 µg/L, the quantification limit 0.07 µg/L and 0.02 µg/L for glyphosate, for AMPA, respectively. The two analytes AMPA and glyphosate were detected after a 2-step post-column derivatization. The first step was an oxidation with a phosphate buffer containing sodium hypochlorite (0.4 mL/min) in a 10 m reaction coil of PEEK tubing (i. d. 0.25 mm, volume 500 µL) at 50°C, the second a transformation into fluorescing compounds by reaction with phthaldialdehyde and 2-mercaptoethanol in an alkaline borate buffer (0.3 mL/min) in a 2 m reaction coil of PEEK tubing (i.d. 0.25 mm, volume 100 µL) at ambient temperature. The excitation wavelength of the resulting compounds was 390 nm and the emission wavelength 450 nm. All solutions were degassed and filtered through 0.45 µm prior to use. Samples of the filter substrate were extracted according to methodology reported elsewhere: 10 g of the sample were brought into contact for 30 min with 25 mL of 1 M NaOH. Subsequently the mixture was centrifuged for 15 min at 3000 rpm. The supernatant was abstracted with a pipette and the extraction was repeated. 4.2 mL concentrated HCl was added to the combined supernatants. After dilution of the sample with deionized water to a volume of 200 mL the analytes glyphosate and AMPA were determined as described above. The cleanup of the water samples was also performed according to the abovementioned German standard method DIN 38407-22. Water samples obtained from laboratory-, and enclosure experiments (typically 100-500 mL) were filtrated through glass fiber filters and adjusted with hydrochloric acid to pH 2 ± 0.1. The filtrate was applied to a column filled with a cation exchange resin which had been loaded with Fe^{3+} ions. Subsequently the column was rinsed with 20 mL water and 40 mL 0.02 M HCl. The analyte-iron complex was eluted with 10 mL 6 M HCl and 4 mL 32% HCl were added to the eluate. This solution was applied to an anion exchange column. By elution of the column with 6 M HCl the iron was retained on the column.

Table 8.5-202: Characterisation of the enclosure filling material



Characteristics	Clogging layer	Filter substrate	Drainage stratum
Soil type	n.a.	mS, gS, fg	fG, mg
Thickness [m]	0.05[b]	1	0.25
CU[a]/CG[a]	n.a.	3.2/0.7	2.0/1.0
Fe(ox) [mg/kg]	605	275	n.a.
Mn(ox) [mg/kg]	68	11	n.a.
$C_{org}/C_{an\,org}$ [%]	0.343/1.4	0.022/0.12	n.a.

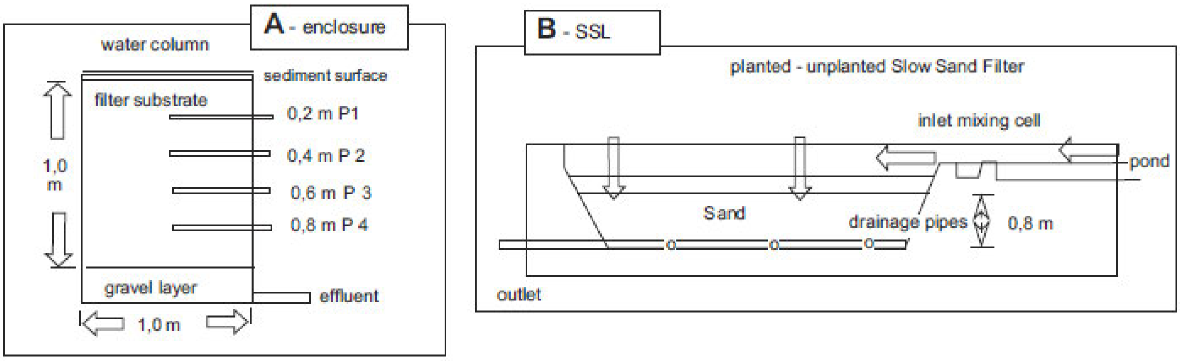
a Parameters for classification of non-structured sediments (uniformity coefficient, coefficient of gradation).
b Clogging layer is situated in the upper layer of the filter substrate, n.a. = not analyzed.

Laboratory experiments

Batch experiments
The batch experiments were conducted according to OECD 106 using the filter substrate and deionized water with glyphosate concentrations of 0.1 mg/L, 1 mg/L, 10 mg/L and 100 mg/L and a soil/water-ratio of 1:2, shaking the mixture for 4 h to establish an equilibrium. The chosen concentrations were applied in three parallels. After centrifugation the supernatant was carefully extracted and prepared for measurement. The Freundlich adsorption isothermal model was used to describe the nonlinear water/sediment distribution relations (K_F) over the total concentration range. The equation's first differentiation was used to describe also the linear distribution coefficient (K_D) and to estimate retardation factors (R_F).

Degradation experiment
Degradation studies were carried out by taking a defined sediment sample of 450 g wet material and mixing it with 10 mg glyphosate per kg filter substrate. The vessels were stored in the dark at a temperature of around 8°C for a period of up to 73 days to allow for biological degradation processes to take place. The airtight stoppers of the vessels sealed the sample from the atmosphere. During the experiment the vessels were left undisturbed. The redox potential, oxygen content, pH value and the temperature in the supernatant were determined after the respective vessels were opened and sampled. At intervals (7, 14, 21, 28 and 73 days) two experiment vessels were opened at a time. This experimental arrangement was intended to simulate naturally deposited filter substrate under partly reducing conditions, as it would be expected in slowly flowing groundwater.

Figure 8.5-162: Schematic cross section and location of sampling ports in enclosures (A) and slow sand filter - infiltration site with inlet and outlet device (B)



Technical scale experiments

Enclosure experiments

Water production pre-treatment via bank filtration or/and slow sand filtration is commonly used if drinking water is produced from surface water. In enclosure experiments the attenuation of compounds can be determined simulating conditions that occur during slow sand filtration or within the first meter of infiltration. The enclosures are three metal cylinders with an area of 1 m^2 and a height of 1.85 m (filtration length 1.00 m) (see Figure 8.5-162A). They are situated within an infiltration pond (area: 90 m^2) in order to be exposed to natural environmental conditions. Three different concentration levels of glyphosate were continuously dosed to the supernatant of the enclosures over a time period of 14 d from 20 October to 6 November 2007, yielding average inlet concentrations of 0.7, 3.5 and 11.6 µg/L. Water samples for glyphosate and AMPA analysis were taken for 34 days from the supernatant, from sampling points within the filter material and from the filter effluent. The flow rate was set at 50 cm/d and was controlled by adjustable pumps connected to the enclosure outlets. The depth of the supernatant was kept constant by siphoning the water out of the infiltration pond into the enclosure without additional pumping. The water in the infiltration pond originates from a large storage pond (volume of 7000 m^3) with relatively high mineralization (average electrical conductivity: 1000 µS/m) but low nutrient status (nitrate < 1 mg/L, orthophosphate < 1 mg/L, DOC 3-4 mg/L) thus representing oligotrophic surface water.

Slow and filter (SSF) experiments

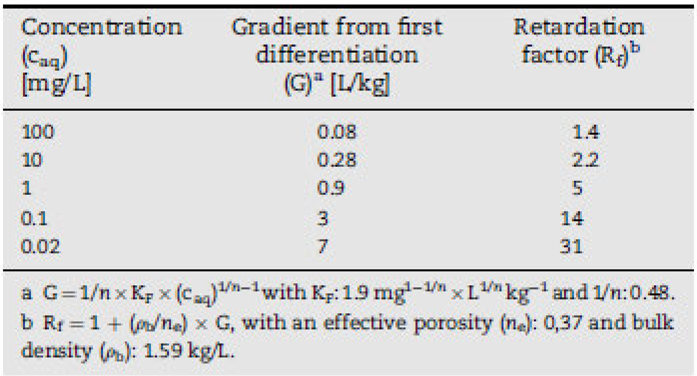
The SSF experiments were conducted at two vertical-flow experimental SSFs: (Figure 8.5-162B) one without vegetation cover (average area 60 m^2, filter depth 0.8 m, filter volume 48 m^3) and the other with a 3 year old vegetation cover of *Phragmites australis* (average area 68 m^2, filter depth 1.2 m, filter volume 81.6 m^3) to simulate processes in grown planted bank filtration sites along rivers or surface water lakes. Due to the arrangement of inflow, water reservoir and drainage pipes, water flow through the SSFs was assumed to be predominantly vertical simulating conditions that occur during the first meter of bank filtration. The water fluxes of the unplanted and the planted SSF were regulated at the outlet and were regularly controlled by discharge measurements. Their yield amounted in average to approximately 0.41 and 0.45 m^3/h, respectively (corresponding to a filtration velocity of 0.16 and 0.18 m/d). Physico-chemical parameters of the water (pH, redox potential, and temperature) as well as DOC, PO_4^{3-} and NO_3^- concentrations were also monitored to gain insights into controlling processes. After an equilibration phase of 1 month during which nitrate and phosphate were dosed to target 10 mg/L N and 1 mg/L PO_4^{3-} in the supernatant, glyphosate was additionally applied for 22 days with a target concentration of 20 µg/L.

Results and Discussion

Batch experiments

Glyphosate exhibits under different site conditions a complex adsorption behavior in the environment which is influenced by pH and by variation of soil constituents and the chemical glyphosate species. In order to determine the distribution coefficient of glyphosate, degree of adsorption in the filter substrate batch experiments were conducted. The resulting linear regression with a Freundlich sorption coefficient (K_F) of 1.90 and a Freundlich exponential of 0.48 confirms the poor adsorptive characteristics of the sandy material and indicates beginning saturation at higher concentrations (Table 8.5-203). With sorption data from different concentration ranges a calculation of the adsorption coefficients (K_D-value) was carried out for different concentration ranges. Due to lower adsorption at high concentrations the K_D-values decrease by 3 orders of magnitude when regarding the complete range of concentrations from 0.1 to 100 mg/L. This is in agreement with comparable experiments of with sandy material reported elsewhere, which is comparable to the one used in this study, where a K_D-range of 1.5-2.9 L/kg was determined. Compared to other studies on glyphosate adsorption with soils showing K_D values that range from 62 to 410 L/kg these values are quite low. This is most probably due to the low content of clay, iron and aluminum oxide or organic matter content in the filter material. Only some iron and organic matter content may have influenced the sorption in the filter material and should be responsible for slightly elevated adsorption coefficients (5.4 L/kg) at least with low glyphosate concentrations (0.1-1 mg/L).

Table 8.5-203: Estimated retardation of glyphosate in the filter substrate on the basis of Freundlich distribution equation



Concentration (c_{aq}) [mg/L]	Gradient from first differentiation (G)[a] [L/kg]	Retardation factor (R_f)[b]
100	0.08	1.4
10	0.28	2.2
1	0.9	5
0.1	3	14
0.02	7	31

a $G = 1/n \times K_F \times (c_{aq})^{1/n-1}$ with K_F: 1.9 $mg^{1-1/n} \times L^{1/n} kg^{-1}$ and $1/n$: 0.48.

b $R_f = 1 + (\rho_b/n_e) \times G$, with an effective porosity (n_e): 0,37 and bulk density (ρ_b): 1.59 kg/L.

Degradation experiment

It is well known that glyphosate degrades more easily under aerobic conditions compared to anaerobic conditions. Figure 8.5-163 shows the residual glyphosate concentrations, obtained from the analysis of the solvent samples in the batch degradation experiment under anaerobic conditions. As it is not clear, if the reduction of concentrations was due to degradation or adsorption, the term dissipation will be used in the following. The development of the redox potential and oxygen content during the degradation experiment showed that oxygen-free conditions were partially achieved. The oxygen in the supernatant was almost completely consumed (data not shown) whereas the pH value remained constant at around 7.7. Dissipation of 50% (DT_{50}) of the glyphosate in the supernatant was calculated to be achieved after 30.5 days yielding a rate of dissipation of 0.0227/d. A mass balance approach was carried out taking into account the initially applied amount of glyphosate, the concentrations measured in solution and the adsorbed fraction. During the first 30 days the decrease in dissolved concentration is due to a continuous adsorption in this time (data not shown). Degradation must therefore be initially negligible. Similar findings in anoxic substrate have been reported elsewhere. The results of laboratory degradation studies differed from the findings in the outside enclosure experiments, which were carried out under more aerobic and temperate conditions.

Enclosure experiments

By simulating slow sand filter conditions, enclosure experiments can help to verify the risk for groundwater pollution by contaminants entering from surface waters. Glyphosate and AMPA concentrations in enclosures II and III for the time of the experiment (34 days) are given in Figure 8.5-164 and Figure 8.5-165. Glyphosate was continuously dosed for 14 days to both enclosures reaching average concentrations of 3.5 and 11.6 µg/L, respectively, with a standard deviation of 20%. The two concentrations reflect medium and maximum levels generally observed in surface water. In enclosure II the glyphosate concentrations at the outlet reached a maximum value of 0.7 µg/L towards the end of the experiment (after 34 days). Since the experiment was terminated before the concentrations decreased again the point in time for the peak value could only be estimated. A break-through curve was observed in enclosure III, to which the highest glyphosate concentration was applied. The maximum outlet concentration for glyphosate of 2.7 µg/L occurred after 23 days. After 8 days (enclosure III) and after 17 days (enclosure II) nearly all observed glyphosate concentrations exceeded the European limit for pesticides in drinking water of 0.1 µg/L. AMPA concentrations above 0.1 µg/L were observed since day 6 in enclosure III and since day 12 in enclosure II. An example vertical concentration profile is illustrated for enclosure III in Figure 8.5-166. This shows sthat retardation and degradation processes are distributed almost linearly along the filtration depth as this was also observed in experiments elsewhere. Tracer and glyphosate concentrations at the outlets of enclosures II and III were modeled using the computer program VisualCXTFit. On the basis of the hydrodynamic properties of the filter substrate obtained from the tracer experiment (R^2 = 0.95 and 0.93 for enclosures II and III, respectively (data not shown)), it was possible to assess the retardation and degradation capacity of the enclosures for glyphosate. The modeled results of the glyphosate concentrations in enclosures II and III corresponds well compared to the observed breakthrough curves. Based on the recovered concentrations at the outlet the applied glyphosate was reduced by 78-80%. Modeling yielded a retardation factor of 25 and 18 and a degradation rate of 0.0069/d and 0.092/d in enclosures II and III, respectively. The half-lives derived from the modeled degradation rates, amounted to 10 d (enclosure II) and 7.5 d (enclosure III), respectively, and correspond well to the values mentioned in literature with 2-14 d for aerobic conditions. The slightly higher degradation in enclosure III could be related to the higher glyphosate concentrations in the liquid phase and a resulting better access of microorganisms to glyphosate. With the obtained parameters data it was attempted to predict the necessary depth of filter substrate to ensure an attenuation of glyphosate to values below the European threshold for drinking water starting from source water concentrations of 3.5 µg/L (enclosure II) and 11.6 µg/L (enclosure III). The modeled filtration length for a sufficient attenuation in enclosure II and III would be about 2.75 m and 3.75 m, respectively (Figure 8.5-167). Model calculations assuming conditions occurring at existing bank filtration well fields yielded in all cases no contamination risk for the water used in drinking water production. Similar findings have been published elsewhere.

Figure 8.5-163: Glyphosate partitioning between solid and aqueous phases during degradation batch experiments (points represent samples from 2 replicates for each sampling date)

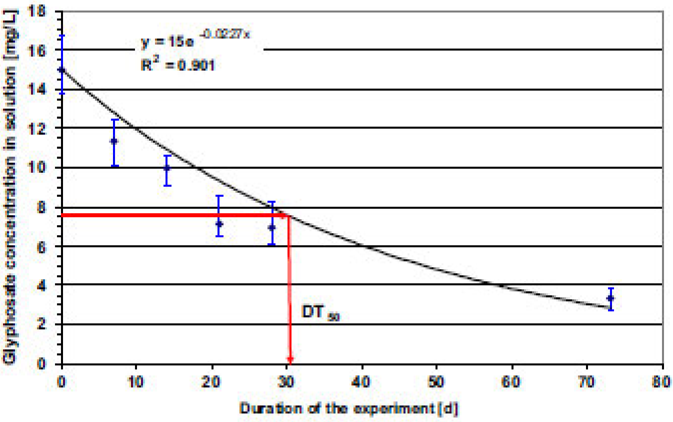


Figure 8.5-164: Glyphosate and AMPA concentrations in the outlet of enclosure II (with an average inlet glyphosate concentration of 3.5 µg/L)

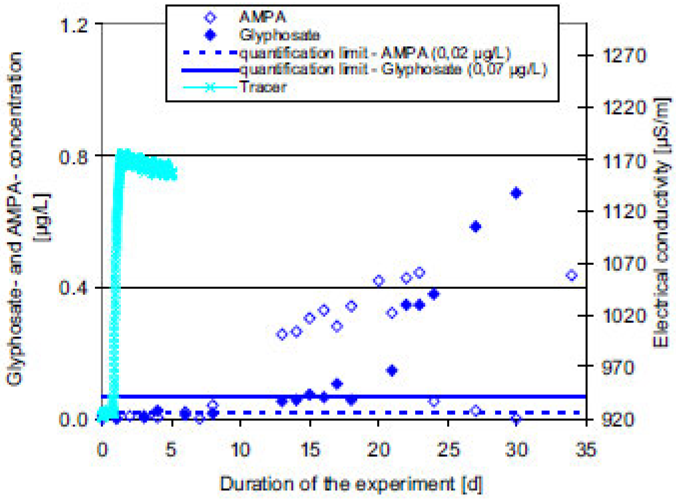


Figure 8.5-165: Glyphosate and AMPA concentrations in the outlet of enclosure III (with an average inlet glyphosate concentration of 11.6 µg/L)

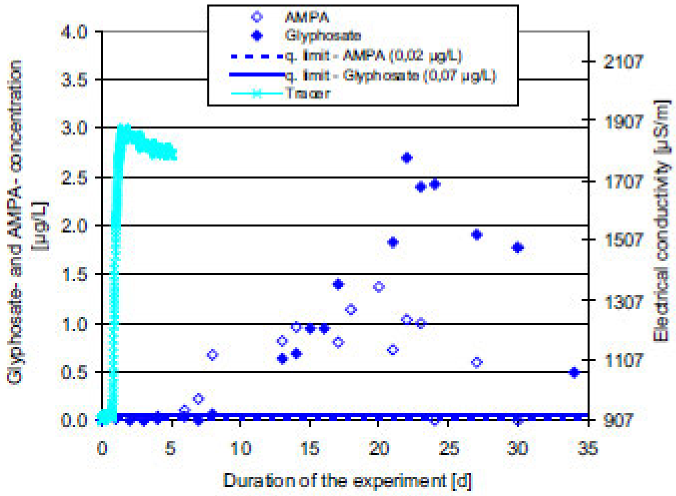
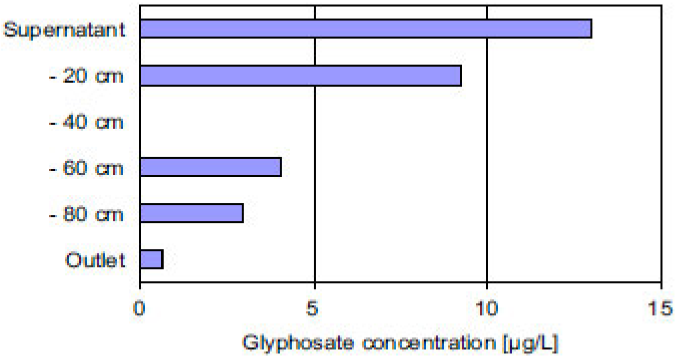


Figure 8.5-166: Vertical distribution of glyphosate concentrations in enclosure III on 05.11.2007 (16 days after dosing commenced)



Slow sand filter experiments
For simulating glyphosate attenuation in a riparian zone, studies with an adapted planted SSF and unplanted SSF were conducted. The hydro-chemical analyses (tracer tests, break-through curves of nitrate) indicated that the planted SSF does not show a homogeneous vertical flow pattern. Thus the planted SSF was divided into two zones (right and left) with different hydraulic and subsequently hydro-chemical characteristics and an estimation of the hydraulically effective surface area was carried out. These estimations showed a reduction in average surface area of the planted SSF to around 67% of the unplanted SSF, confirming that the flux in the planted SSF seems to be partly inhibited. The lowering to around 67% of the average surface area could be explained by collimation due to high production of biomass which at constant hydraulic head results in a decrease of pore velocities or even blocking of pore volume. The concentrations of glyphosate measured in the mixing cell, in the supernatant, in 40 cm depth and in the outlet of the planted SSF (left site) are given in Figure 8.5-168. In the mixing cell of the planted SSF the average glyphosate concentration of 21.2 µg/L was slightly higher than the targeted level of 20 µg/L. In the left zone of the planted SSF only little reduction was observed in the water reservoir above the SSF surface (19 µg/L in average). In 40 cm depth the maximum concentration of glyphosate was retarded by 11 days and reduced to approximately 7 µg/L (63% of the average concentration in the supernatant). In the right zone (data not shown) the concentrations decreased by more than 50% between mixing cell and surface water of the SSF. Glyphosate was completely removed from solution in 40 cm depth, which seems to be due to lower inlet concentrations, higher residence times and therefore higher efficiency of reduction. In the combined outlet (left and right zone) the fluxes of all sampling sites rejoined and resulted in a maximum concentration of 1.4 µg/L. The final measurements at the end of the experiment showed a reduction of about 93% of the applied glyphosate compared to the inlet concentration. While the planted SSF had to be divided into two zones the unplanted SSF can be regarded as homogenous (Figure 8.5-169). The inlet concentrations of the unplanted SSF did not reach the targeted level of 20 µg/L. In average it was lower and characterized by strong fluctuations probably due to degradation processes in the stock solution (17.6 µg/L in average). The concentration gradient between the level of glyphosate in the mixing cell corresponds well to the concentrations measured in the supernatant. In contrast to the planted SSF where an increase in 40 cm depth was found only after 10 days, low concentrations of glyphosate were observed here from the very beginning in the unplanted SSF. This is clearly a result of enhanced attenuation and could be interpreted as retardation by the biomass of the root zone. Maximum glyphosate concentrations decreased to 9 µg/L after 40 cm of the filter passage (49% reduction of average supernatant concentration). The concentration in the outlet did not reach the climax of the breakthrough curve. The maximum concentration detected here was 4.5 µg/L. Comparing the concentrations in 40 cm depth and in the effluent of the unplanted SSF with those of the left zone as representative for the planted SSF there was slightly higher glyphosate reduction in the planted SSF (63% in 40 cm depth, compared to 49% in the unplanted filter), although the inlet concentrations were slightly higher and the residence time was lower. The higher reduction rate of glyphosate in the planted SSF could be due to the strong biological activity, which was concluded from the lower oxygen contents. The redox potential at 40 cm depth varied strongly in both SSFs and amounted to an average of -200 eV in the left zone as representative for the planted and +235 eV in the unplanted SSF. The decisive factor seems to be the availability of organic carbon, due to vegetal growth. The influence of *phragmites* buffer strips along surface water on glyphosate retardation has not been not studied by other experts before. Studies elsewhere on glyphosate attenuation during artificial recharge bank filtration have been carried out. Comparison of the results, demonstrated a high natural variability of subsurface mobility for glyphosate depending on site characteristics.

Figure 8.5-167: **Modeled length of the filter substrate (from left to right: 1.25; 2.0; 3.0; 3.5 and 3.75 m) in order to ensure a reduction of the glyphosate concentrations below the European threshold for drinking water of 0.1 µg/L (enclosure III)**

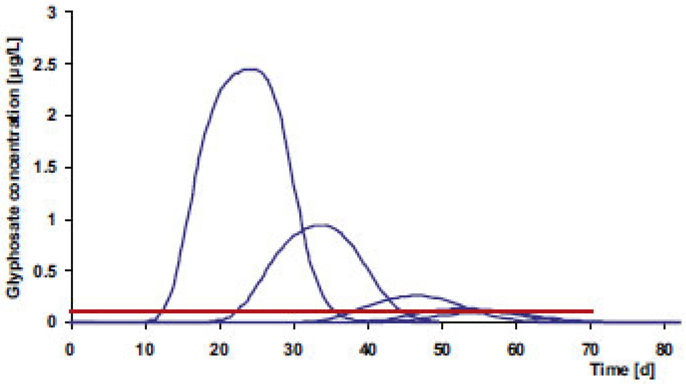


Figure 8.5-168: **Glyphosate distribution in the left zone of the vegetated SSF**

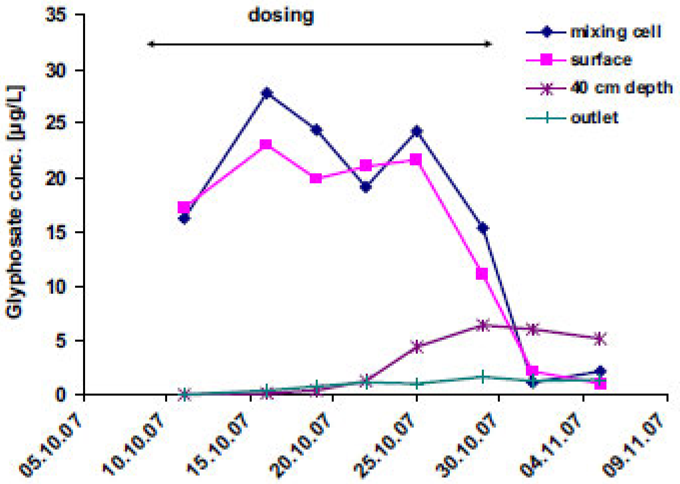
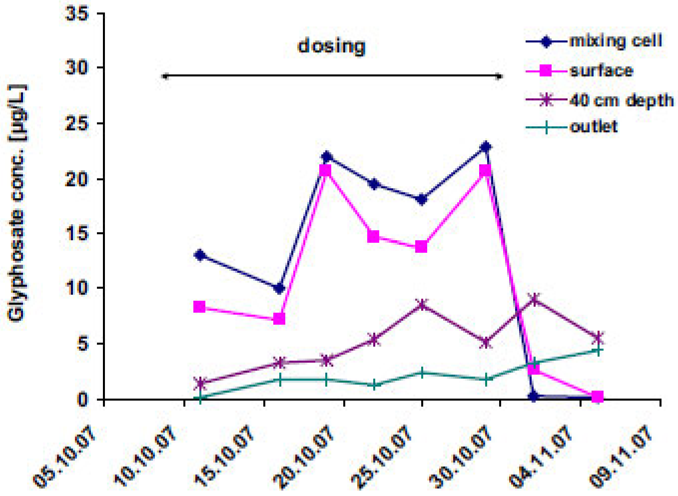


Figure 8.5-169: Glyphosate distribution in the unplanted SSF



Conclusion

Laboratory studies were conducted to characterize the substrate of the enclosures and the slow sand filters with regard to glyphosate removal processes. Batch adsorption studies yielded a very low adsorption capacity for glyphosate with a K_F of 1.9 in the sandy material. This is presumably due to the low organic matter content compared to studies carried out with soils, especially with those of a higher iron and aluminum oxide content. Anaerobic dissipation studies under laboratory conditions at 10°C resulted in a half-life of 30.5 d with dissipation rate of 0.023/d in the solvent phase. However, it could not be proven, that degradation is the main removal process for short subsurface passage as complete recovery was achieved from the solid phase after 30 d. In the further course of the experiment, however, significant degradation was observed. In the enclosure experiments a rapid degradation was observed due to the aerobic conditions and higher temperatures with a half-life of 7.5-10.5/d, with lower initial concentrations (3.5-12 µg/L) compared to the lab experiments. The enclosure experiments showed that between 78 and 80% of continuously applied glyphosate (3.5 µg/L or 11.6 µg/L in average) can be attenuated despite of low adsorption capacity of the filter substrate and high filtration velocity. The necessary length of the filter substrate in order to ensure a reduction of the glyphosate concentrations below the European threshold for drinking water of 0.1 µg/L was modeled with VisualCXTfit and must exceed 2.75 or 3.75 m for an initial glyphosate concentration of 3.5 µg/L (enclosure II) or 11.6 µg/L (enclosure III), respectively. In the SSF experiments the SSF covered with *P. australis* showed a 2-5 times higher removal capacity (57%) for glyphosate than the one without reed cover (14%). Thus, the following conclusions can be drawn for the attenuation of glyphosate during subsurface passage: At low concentrations adsorption may play an important role, however, degradation needs to be considered as the main process for glyphosate attenuation. Favourable for glyphosate removal at bank filtration sites are oxic conditions, planted sediment surfaces and travel times of more than 10 days.

Assessment and conclusion by applicant:

The article describes experiments on subsurface passage of river water using so-called enclosures and semi-technical scale vertical slow sand filters (SSFs) to investigate the behavior of glyphosate and AMPA during bank filtration for drinking water supply. The filter experiments were supported by batch adsorption and degradation experiments with the filter material. Overall, the results showed that saturated subsurface passage has the potential to efficiently attenuate glyphosate, with aerobic conditions, long travel times and the presence of riparian boundary buffer strips. The main filter experiments and the analytical methods are well described and reported with sufficient details.

The article is considered reliable.

Assessment and conclusion by RMS:

The article is considered reliable with restrictions. It mainly gives supportive information regarding potential mitigation measures.

The herbicide Glyphosate was detected in River Havel (Berlin, Germany) in concentrations between 0.1 and 2 mg/L. Laboratory (sorption and degradation studies) and technical scale investigations (bank filtration and slow sand filter experiments) were carried out.

Batch adsorption experiments with Glyphosate yielded a low K_f of 1.89 ($1/n = 0.48$) for concentrations between 0.1 and 100 mg/L. Degradation experiments at 8°C with oxygen limitation resulted in a decrease of Glyphosate concentrations in the liquid phase probably due to slow adsorption (half life: 30 days). During technical scale slow sand filter (SSF) experiments Glyphosate attenuation was 70-80% for constant inlet concentrations of 0.7, 3.5 and 11.6 mg/L, respectively. Relevant retardation of Glyphosate breakthrough was observed despite the low adsorption potential of the sandy filter substrate and the relatively high flow velocity. The VisualCXTFit model was applied with data from typical Berlin bank filtration sites to extrapolate the results to a realistic field setting and yielded sufficient attenuation within a few days of travel time. Experiments on an SSF planted with Phragmites australis and an unplanted SSF with mainly vertical flow conditions to which Glyphosate was continuously dosed showed that in the planted SSF Glyphosate retardation exceeds 54% compared to 14% retardation in the unplanted SSF. The results show that saturated subsurface passage has the potential to efficiently attenuate glyphosate, favourably with aerobic conditions, long travel times and the presence of planted riparian boundary buffer strips.

Data point:	CA 7.5/064
Report author	Maillard, E. *et al*.
Report year	2011
Report title	Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment
Document No	The Science of the total environment (2011), Vol. 409, No. 11, pp. 2317-24
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (Pasteur Institute of Lille (France))
Acceptability/Reliability:	Reliable (but concentration in surface runoff and not surface water)

Wetlands can collect contaminated runoff from agricultural catchments and retain dissolved and particle-laden pesticides. However, knowledge about the capacity and functioning of wetland systems with respect to the removal of pesticides is very limited. Here we show that stormwater wetlands can efficiently remove pesticides in runoff from vineyard catchments during the period of pesticide application, although flow and hydrochemical conditions of the wetland largely vary over time. During the entire agricultural season, the inflowing load of nine fungicides, six herbicides, one insecticide and four degradation products was 8.039 g whereas the outflowing load was 2.181 g. Removal rates of dissolved loads by the wetland ranged from 39% (simazine) to 100% (cymoxanil, gluphosinate, kresoxim methyl and terbuthylazine). Dimethomorph, diuron, glyphosate, metalaxyl and tetraconazole were more efficiently removed in spring than in summer. More than 88% of the input mass of suspended solids was retained, underscoring the capability of the wetland to trap pesticide-laden particles via sedimentation. Only the insecticide flufenoxuron was frequently detected in the wetland sediments. Our results demonstrate that stormwater wetlands can efficiently remove pesticide mixtures in agricultural runoff during critical periods of pesticide application, although fluctuations in the runoff regime and hydrochemical characteristics can affect the removal rates of individual pesticides.

Materials and methods

Description of the vineyard catchment and stormwater wetland

The studied wetland is located at the outlet of a 42.7 ha vineyard catchment in Rouffach (Alsace, France; 47°57′9 N, 07°17′3 E). The characteristics of the catchment and agricultural practices have already been described (Gregoire et al., 2010). Application of pesticides typically takes place from mid-April (bud breaking of grapevine) until August (grapevine maturity). Nine fungicides, six herbicides, one insecticide and four degradation products were selected for the present study because of their widespread use as well as their high frequency of application and detection revealed in previous studies (Gregoire et al., 2010). The studied compounds belong to 12 different chemical groups and largely differ with respect to their physico-chemical properties. Rainfall–runoff events do not generate permanent streams in the catchment and statistically occur every week through the year. Runoff converges at the outlet of the catchment and is collected by the stormwater wetland, which is sized for a 100-year return period of rainfall.

The stormwater wetland has a surface area of 319 m^2 and a total volume of 1500 m^3 and was initially constructed to control flooding in the downstream urban area (Figure 8.5-170). The wetland is composed of two main zones in series. The first zone is a sediment deposition pond (234 m^2) that collects suspended solids. The water storage capacity of the sediment deposition zone was 40 m^3. Hence, runoff water mixes with water stored during quiescent period. Water depth in the sediment deposition zone varied from 0.05 to 0.5 m from April to September. Physico-chemical characteristics of wetland sediments were (%): clay 44, fine silt 33, coarse silt 10, fine sand 5, coarse sand 8; organic carbon 14.8; SiO_2 50, Al_2O_3 9.5, MgO 2.2, CaO 11.6, Fe_2O_3 4.1, MnO 0.1, Na_2O 0.7, K_2O 2.5 and pH 8.1 (in water) (n= 5). A gabion barrier is used to enhance the dispersion of water ahead of the gravel filter. The second zone is a 13 m long, 8 m wide and 0.6 m deep gravel filter (saturated hydraulic conductivity, $K=10^{-3}$ m/s) that increases the hydraulic retention time in the wetland, and thus the capacity of contaminant removal. Detailed characteristics and hydraulic functioning of the wetland and gravel filter have been studied previously (Wanko et al., 2009) and detailed hydrological characteristics of the wetland that correspond to the investigation period are provided in Table 8.5-204. Due to the clay liner on the wetland bed ($K_s < 10^{-10}$ m/s) and based on the water balance, water losses by vertical subsurface infiltration between the sediment/gravel and the clay liner were negligible. The bottom slope of the stormwater wetland was 2.8%. The vegetation cover in the sediment deposition zone, mainly formed of *Phragmites australis, Schoenoplectus lacustris* and *Typha latifolia*, was <1% of the area in April, 5% in May, 25% in June, 60% in July, 70% in August and 85% in September. *Phragmites australis* ranged between 70% and 80%of the total vegetation cover through the investigation period. The vegetation in the gravel filter, mainly formed by *Lolium perenne* and *P. austalis*, varied, respectively, from 20 to 30% and from 5 to 15% of the area throughout the investigation period. Algae, mainly *Chara vulgaris*, appeared in the sediment deposition zone since August and covered more than 70% of the area in September.

Figure 8.5-170: **Schematic of the storm water wetland (Rouffach, Alsace, France) and sampling locations (●) in the sediment deposition zone (SDZ), the gabion barrier (G) and the gravel filter (GF)**

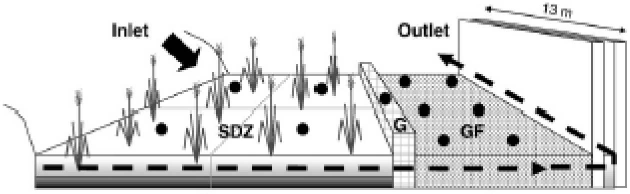
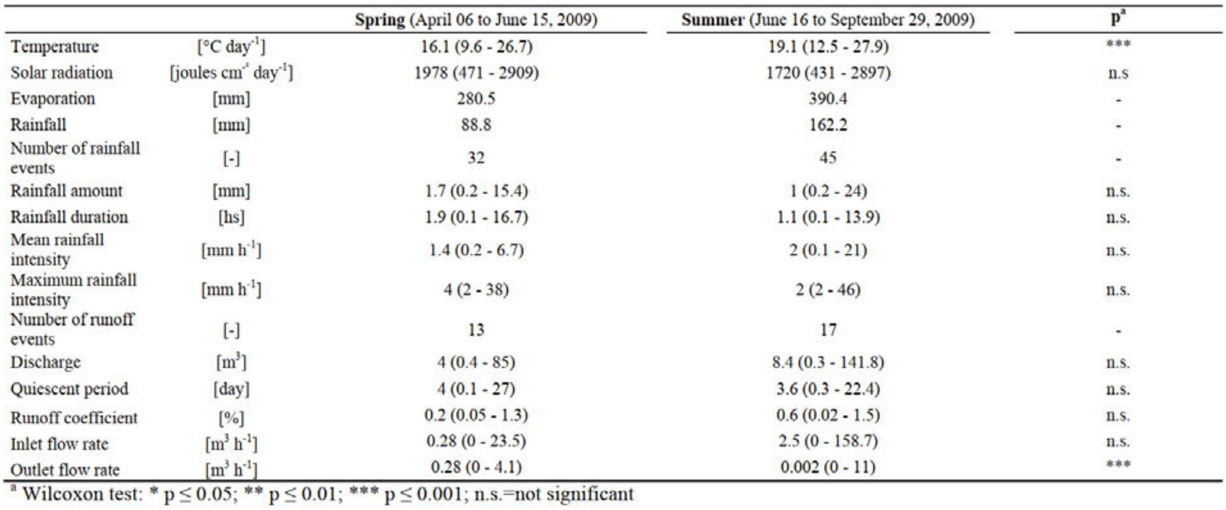


Table 8.5-204: Climatic and hydrological conditions in the vineyard catchment (Rouffach, Haut-Rhin, France) and the stormwater wetland in spring (06 April to 15 June 2009) and in summer (15 June to 29 September 2009). Values are provided as the median and ranges.



		Spring (April 06 to June 15, 2009)	**Summer** (June 16 to September 29, 2009)	p[a]
Temperature	[°C day^{-1}]	16.1 (9.6 - 26.7)	19.1 (12.5 - 27.9)	***
Solar radiation	[joules cm^{-2} day^{-1}]	1978 (471 - 2909)	1720 (431 - 2897)	n.s
Evaporation	[mm]	280.5	390.4	-
Rainfall	[mm]	88.8	162.2	-
Number of rainfall events	[-]	32	45	-
Rainfall amount	[mm]	1.7 (0.2 - 15.4)	1 (0.2 - 24)	n.s.
Rainfall duration	[hs]	1.9 (0.1 - 16.7)	1.1 (0.1 - 13.9)	n.s.
Mean rainfall intensity	[mm h^{-1}]	1.4 (0.2 - 6.7)	2 (0.1 - 21)	n.s.
Maximum rainfall intensity	[mm h^{-1}]	4 (2 - 38)	2 (2 - 46)	n.s.
Number of runoff events	[-]	13	17	-
Discharge	[m^3]	4 (0.4 - 85)	8.4 (0.3 - 141.8)	n.s.
Quiescent period	[day]	4 (0.1 - 27)	3.6 (0.3 - 22.4)	n.s.
Runoff coefficient	[%]	0.2 (0.05 - 1.3)	0.6 (0.02 - 1.5)	n.s.
Inlet flow rate	[m^3 h^{-1}]	0.28 (0 - 23.5)	2.5 (0 - 158.7)	n.s.
Outlet flow rate	[m^3 h^{-1}]	0.28 (0 - 4.1)	0.002 (0 - 11)	***

[a] Wilcoxon test: * $p \leq 0.05$; ** $p \leq 0.01$; *** $p \leq 0.001$; n.s.=not significant

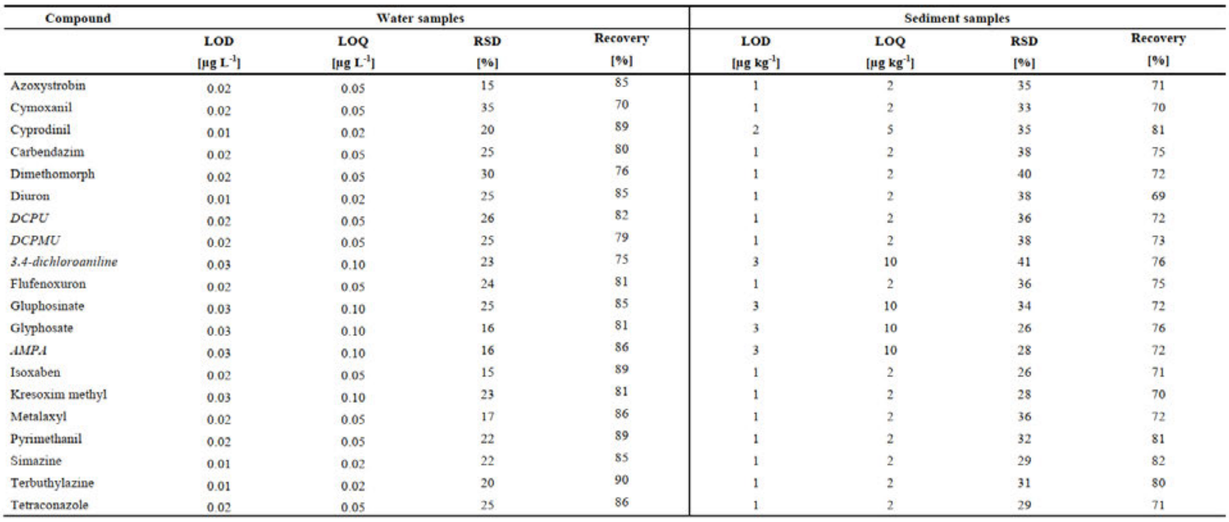
Sampling procedure

Daily rainfall and evapotranspiration were measured at a weather station located on the catchment (Meteo France, station no. 68287003). Samples were collected from the inlet, the sediment deposition zone, the gravel filter, and the outlet of the wetland (Figure 8.5-170) from 01 April through 29 September 2009, corresponding to the period of pesticide application. Runoff discharges were continuously monitored by measurements of water depth using bubbler flow modules (Hydrologic, Sainte-Foy, Québec, Canada) combined with a Venturi channel at the inlet and a V-notch weir at the outlet. Water samples were collected every 6 m^3 at the inlet of the wetland using a 4010 Hydrologic automatic sampler (Hydrologic, Sainte-Foy, Québec, Canada) and at the outlet using a 6712FR ISCO Teledyne automatic sampler (Lincoln, Nebraska, US). The detailed procedure of sample collection and storage ensuring reliable pesticide measurements was previously tested and discussed (Domange and Gregoire, 2006). Briefly, water samples (100 mL) were collected in glass jars, stored in the dark at 4 °C until collection after each runoff event, and placed on ice during transportation to the laboratory. A series of discrete water samples taken over a runoff event were combined in a single composite sample. Suspended solids were obtained from continuously operating samplers consisting of 2 mm and 50 µm sieves in series and installed at the inlet and outlet of the wetland. The samplers were emptied every week throughout the investigation period. In order to ensure representative and reliable measurements, pesticide concentrations in suspended-solids were measured only when the mass of collected material reached 20 g or more. In parallel, 10 sampling campaigns were performed every two weeks during quiescent period (i.e. in the period between two runoff events) on day 21 (21 April 2009), 35, 49, 63, 76, 91, 111, 128, 141 and, after harvesting grapevine, on day 182 (29 September 2009) to collect water and sediment samples within the wetland. At each sampling campaign, grid-cell sampling was performed in the sediment deposition zone by dividing the zone in four equal rectangular cells (9 × 6 m) (Figure 8.5-170). Four water samples (collected from 0 to 10 cm depth from the water surface) and four surface sediment grab samples (collected from 0 to 5 cm depth from the sediment surface) were separately collected at the center of each cell. Pore water samples were also collected in the gabion barrier from one PVC well and in the gravel filter from six PVC wells (Figure 8.5-170). To ensure representative sampling, the wells were purged using a pump to replace the equivalent of one volume of the tube. Dissolved oxygen, pH, conductivity, redox potential and temperature were directly measured in the field using WTW multi 350i portable sensors (WTW, Weilheim, Germany). Water samples were dispensed into 100 ml glass and plastic vials for pesticide analysis (headspace free) and 1 L acid washed HDPE bottles (10% HCl and rinsed with distilled water) for hydrochemical analysis. Water and sediment samples were placed on ice and directly transported to the laboratory for chemical analysis. A chemical analysis of water samples was performed within 2 days of collection. Sediment samples were kept at −20°C until chemical analysis, for a maximum of 30 days.

Analysis of water and sediment samples

Eighteen hydrochemical parameters (TIC, DIC, NPOC, DOC, TKN, PO_4^{2-}, P_{tot}, NO_3^-, NO_2^-, NH_4^+, Mn_2^+, Fe_2^+, Fe_{tot}, SO_4^-, Mg_2^+, Na^+, Cl^-, and K^+) were determined by FR EN ISO standards and laboratory procedures. Pesticide analysis was performed according to the NF XPT 90–210 French standards at the Pasteur Institute of Lille (France), which is a service of pesticide residues analysis accredited by the French National Accreditation Authority (COFRAC). For international quality control purposes, the COFRAC calibration certificate is recognized by other European calibration services (EA — European Cooperation for Accreditation). Briefly, water samples were filtered through 1 µm glass fiber filters, solid–liquid extracted before analyzing the subsequent extracts. The 16 pesticides and four degradation products were quantified using liquid chromatography coupled to tandem mass spectrometry (LC–MS–MS). Quantification of glyphosate, AMPA and gluphosinate was performed after derivatization with fluorenemethoxycarbonyle (FMOC). Limits of pesticide quantification in water samples ranged from 0.02 to 0.1 µg/L. Quantification of pesticide residues in sediment samples was performed by LC–MS–MS measurements following ultrasonic and methanol extraction. Limits of quantification ranged from 2 to 10 µg/kg. Extraction efficiencies of pesticides from water and sediment samples were estimated for each sample set by spiking with surrogates. Surrogate recovery for water samples ranged from 70 to 89% and those of sediment from 68 to 85%. Further quality control was achieved by using a blank for each set of samples. Detection and quantification limits, relative standard deviation (RSD) and recovery efficiencies for each studied pesticide are provided for both water and sediment samples in Table 8.5-205.

Table 8.5-205: Detection and quantification limits, as well as relative standard deviation (RSD) and recovery efficiency for the investigated pesticide in both water and sediment samples. Values are provided as the median and ranges.



Compound	Water samples				Sediment samples			
	LOD [µg L^{-1}]	LOQ [µg L^{-1}]	RSD [%]	Recovery [%]	LOD [µg kg^{-1}]	LOQ [µg kg^{-1}]	RSD [%]	Recovery [%]
Azoxystrobin	0.02	0.05	15	85	1	2	35	71
Cymoxanil	0.02	0.05	35	70	1	2	33	70
Cyprodinil	0.01	0.02	20	89	2	5	35	81
Carbendazim	0.02	0.05	25	80	1	2	38	75
Dimethomorph	0.02	0.05	30	76	1	2	40	72
Diuron	0.01	0.02	25	85	1	2	38	69
DCPU	0.02	0.05	26	82	1	2	36	72
DCPMU	0.02	0.05	25	79	1	2	38	73
3.4-dichloroaniline	0.03	0.10	23	75	3	10	41	76
Flufenoxuron	0.02	0.05	24	81	1	2	36	75
Gluphosinate	0.03	0.10	25	85	3	10	34	72
Glyphosate	0.03	0.10	16	81	3	10	26	76
AMPA	0.03	0.10	16	86	3	10	28	72
Isoxaben	0.02	0.05	15	89	1	2	26	71
Kresoxim methyl	0.03	0.10	23	81	1	2	28	70
Metalaxyl	0.02	0.05	17	86	1	2	36	72
Pyrimethanil	0.02	0.05	22	89	1	2	32	81
Simazine	0.01	0.02	22	85	1	2	29	82
Terbuthylazine	0.01	0.02	20	90	1	2	31	80
Tetraconazole	0.02	0.05	25	86	1	2	29	71

Data analysis

Dissolved pesticide concentrations found at the inlet and outlet of the wetland were compared using the paired nonparametric Wilcoxon Signed Rank test. Correlations between hydrological variables and pesticide metrics were tested by the rank-based Spearman's test. Hydrochemical data were subjected to principal component analysis (PCA), which were performed on the basis of the correlation matrix. In turn, the numerical data matrices were converted using the program R (R: Copyright 2005, The R Foundation for Statistical Computing, Version 2.1.1). Principal component analysis (PCA) is an ordination method that allows summarizing large data sets and exploring the spatial and temporal trends in the data. Reduction of pesticide concentration, RC (%), was calculated for each runoff event as the reduction of mean concentrations at the outlet relatively to the mean concentrations at the inlet of the wetland. A nondetect (n.d.) was treated as zero. The RC (%) in a given period was the average of all runoff event RC (%) values for this period. Pesticide event loads at the inlet and the outlet of the wetland were obtained by multiplying the mean pesticide concentrations by the corresponding runoff volume. Removal rates of pesticide load RL (%) were calculated for each runoff event as the reduction of the load at the outlet relatively to the load at the inlet of the wetland using Eq. (1).

$$R_L(\%) = \left[1 - \frac{M_{out}}{M_{in}}\right] \times 100 = \left[1 - \frac{C_{out}V_{out}}{C_{in}V_{in}}\right] \times 100 \qquad (1)$$

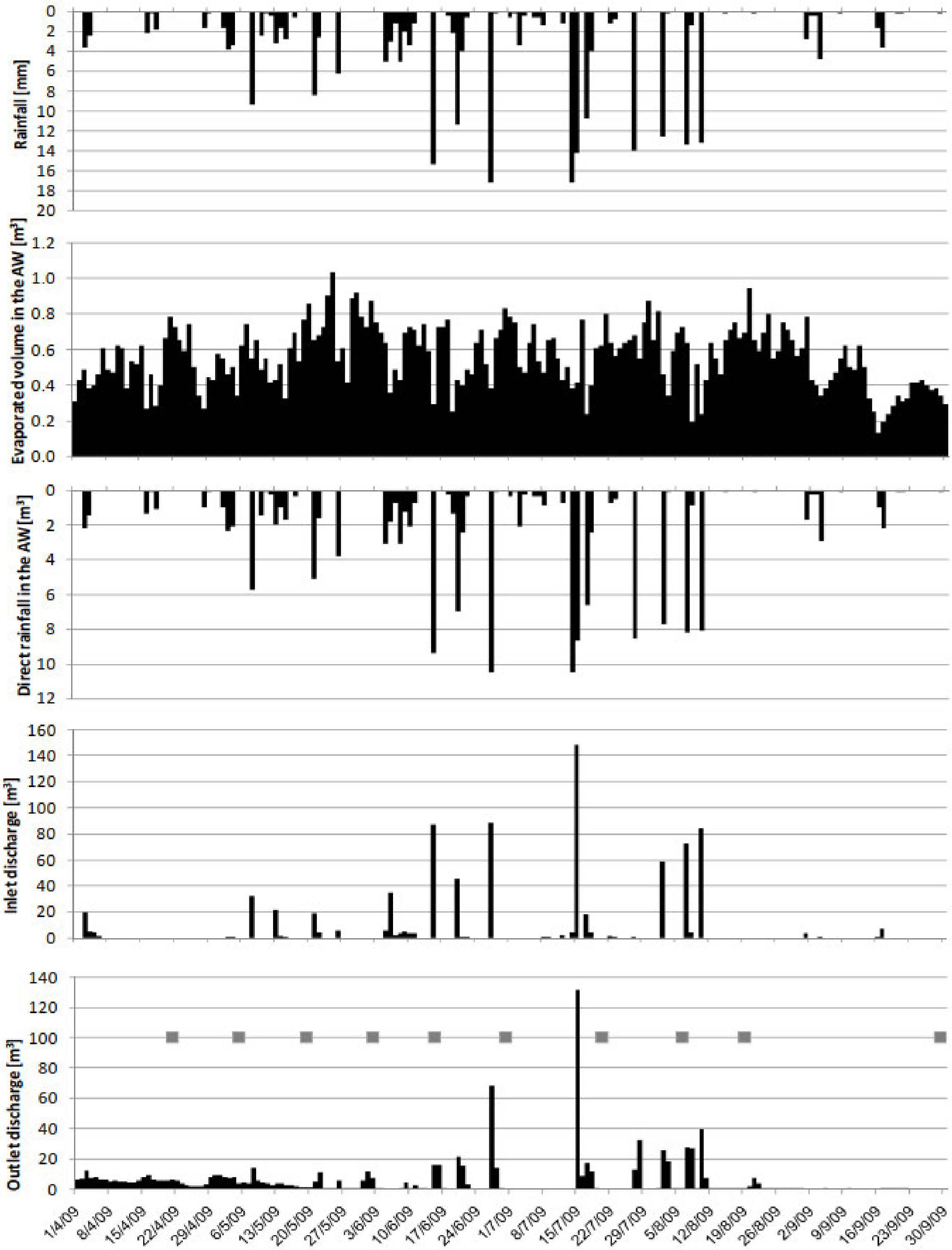
where M_{in} and M_{out} are the influent and effluent pesticide loadings, V_{in} and V_{out} are the influent and effluent volumes, and C_{in} and C_{out} the inlet and outlet mean concentrations, respectively. Load (mg) at the inlet or outlet of the wetland was calculated from the integral sum of all event loads in a given period (i.e., between 2 sampling campaigns or in a season).

Results

Hydrological and hydrochemical characteristics of the wetland

Detailed climatic and hydraulic data from 01 April through 29 September is provided in Figure 8.5-171 and in Table 8.5-204. Rainfall amount, duration, mean and maximal intensities, as well as the duration of the period between two rainfall events did not significantly differ between spring and summer ($p > 0.37$). Rainfall on the vineyard catchment amounted to 251 mm between 06 April and 29 September, and the direct rainfall input on the wetland was 153 m^3. Waterloss resulting from evaporation was 99 m^3. Thirty runoff events ranging from 0.3 to 141.8 m^3 occurred during the investigation period, generating a total volume of 730 m^3. The mean quiescent period between two runoff events ranged from 2.4 h to 27 days during the investigation period and did not significantly differ between spring and summer ($p > 0.61$). The budget of water volumes inflowing and outflowing the wetland was balanced when direct rainfall and evapotranspiration volumes were included. Flow rates at the wetland inlet ranged from 0 to 158.7 m^3/h (mean±SE: 6.3 ± 9.6 m^3/h) during the investigation period. Inlet flow rates in spring (2.1 ± 2.7 m^3/h) and summer (12.2 ± 11.8 m^3/h) did not significantly differ ($p > 0.09$), although larger and more variable flow rates were observed in summer. In contrast, outlet flow rates significantly differed between spring (0.3 ± 0.8 m^3/h) and summer (0.2 ± 1.0 m^3/h) ($p < 0.001$), which strongly suggests that larger vegetation cover in summer reduced the flow rate. During the investigation period, the hydraulic retention time (HRT) of the wetland ranged between 6.7 and 14 h (mean±SE: 10.8 ± 2.6 h) for runoff events exceeding 40 m^3, whereas smaller runoff events could be stored in the wetland. The duration of runoff events ranged between 0.78 and 15 h. However, only one runoff event lasts longer than 12 h and likely completely flushed the stormwater wetland. The PCA ordination plot (Figure 8.5-172) shows for each of the 10 sampling campaigns the replicate samples collected from the sediment deposition zone and the gravel filter as well as the hydrochemical variables. Symbols in the plot lying close together display similar hydrochemical patterns. The principal component analysis of hydro-chemical data revealed that hydrochemical conditions changed in the wetland over time. Water samples collected from the first (21 April) to the fifth sampling campaigns (15 June) clustered together and were clearly separated from those collected from the sixth (30 June) to the tenth sampling campaign (29 September), which indicates distinct hydrochemical profiles between the two periods corresponding to spring and summer. On the variables plot (Figure 8.5-172), scores of PC1 correlated positively to cations (Ca^{2+}, Mg^{2+}, and Na^+), anions (Cl^-, NO_2^-, and NO_3^-), redox potential, as well as organic (DOC and NPOC) and inorganic carbon (TIC and DIC). In addition, they correlated negatively to temperature, showing that these hydrochemical variables considerably changed in the wetland between spring and summer. Samples corresponding to the tenth sampling campaign (29 September) were associated with higher concentrations of ferrous iron, manganese and ammonium, indicating the prevalence of reducing conditions in the wetland. Mean water temperature and pH across all sampling points and campaigns was 19.0 ± 4.3 °C and 7.6 ± 0.3, respectively. In spring, oxic conditions prevailed in the wetland, as inferred from mean values of redox potential larger than 50 mV, concentrations of ferrous iron lower than 1 mg/L, and concentrations of dissolved oxygen higher than 2.9 mg/L in the sediment deposition zone. In summer, lower concentrations of dissolved oxygen and negative values of redox potential indicated the prevalence of an anoxic milieu. In spring, Fe^{2+} concentrations were one order of magnitude lower than those of total iron, suggesting the prevalence of the ferric form. In contrast, larger Fe^{2+} concentrations (up to 6.0 mg/L) attested the occurrence of anoxic conditions in summer. The analysis of both hydrological and hydrochemical data revealed that conditions in the wetland differed between spring and summer. Therefore, pesticide removal by the wetland in spring and summer is compared.

Figure 8.5-171: **Daily rainfall [mm] in the catchment area, evaporated volume (m^3), direct rainfall in the wetland [mm], and daily discharges (m^3) at the inlet and outlet of the stormwater wetland (Rouffach, Haut-Rhin, France) during the investigation period (06 April to 29 September 2009) that corresponded to the wine growing season and the period of pesticide. Grey squares indicate water and sediment sampling in the wetland.**



Occurrence and concentration reduction of pesticides in the wetland
Detailed data of pesticide concentrations in water, in suspended solids and wetland sediments as well as reduction of pesticides based on inlet and outlet concentrations are provided in Table 8.5-206. Mean concentrations of dissolved pesticides generally decreased between the inlet, the sediment deposition zone, the gravel filter and the outlet of the wetland (Figure 8.5-173A and B). Temporal variation of pesticide concentrations in runoff reflects both timing of pesticide applications in the catchment and changes in rainfall–runoff patterns over time, as previously shown (Gregoire et al., 2010). Degradation products of diuron (DCPU, DCPMU and 1,3-dichloroaniline) were systematically below the detection limit, suggesting that diuron was not subject to aerobic degradation or that degradation products were readily degraded in the wetland. In spring, reduction in mean concentrations from inlet to outlet ranged from 71 (AMPA) to 100% (cymoxanil, dimethomorph, gluphosinate, kresoxim methyl, terbuthylazine and tetraconazole). In summer, concentration reductions were lower compared to those observed in spring, and ranged from 0 (tetraconazole) to 100% (azoxystrobin, cyprodinil, isoxaben, kresoxim methyl and terbuthylazine). Concentrations from inlet to outlet significantly differed for cymoxanil, diuron, glyphosate, AMPA, isoxaben, metalaxyl, simazine, terbuthylazin and tetraconazol in spring and for glyphosate in summer ($p < 0.05$). Pesticide concentrations in water from the sediment deposition zone and the gravel filter were smaller in spring compared to those measured in summer, although concentrations found in the inflowing runoff were similar. Altogether, the results indicate lower efficacy of the wetland in reducing pesticide concentrations in summer. Patterns of pesticide concentrations associated with suspended solids and the wetland sediments also differed between spring and summer (Figure 8.5-173C). Flufenoxuron, dimethomorph, and cyprodinil concentrations associated with suspended solids in inlet samples increased over time and then decreased. However, mean concentrations of pesticides and degradation products in the wetland sediments were close to or below the detection limits, except for flufenoxuron. The results indicate no significant transfer of dissolved or particle-laden pesticides from the water column to the bed sediments, and thus no accumulation or persistence of pesticides in the wetland sediments.

Figure 8.5-172: **PCA ordination plots of hydrochemical characteristics of water samples collected in the storm water wetland (Rouffach, Alsace, France) between day 0 (06 April 2009) and day 182 (29 September 2009).**

Values on the axes indicate the % of the total variation explanation by the corresponding axis (PC 1, principal component axis 1; PC 2, principal component axis 2). The first and second principal components accounted for 52.7% of the variance in the data set. Objects are labeled according to the section of the wetland they were collected from (▲, sediment deposition zone; ◊, gabion barrier and gravel filter) and numbered according to their sampling date: day 0 (06 April 2009), 21, 35, 49, 63, 76, 91, 111, 128, 141 and 182 (29 September 2009). Description vectors correspond to: T °C, temperature; P_{tot}, total phosphorus; Fe^{2+}, ferrous iron; Mn^{2+}, manganese; Fe_{tot}, total iron; NH_4^+, ammonium; TKN, total kjeldahl nitrogen; TIC, total inorganic carbon; DIC, dissolved inorganic carbon; NPOC, non-purgeable organic carbon; DOC, dissolved organic carbon; EC, electric conductivity; Ca^{2+}, calcium; NO_2^-, nitrite; Mg^{2+}, magnesium; Cl^-, chlorine; SO_4^-, sulfate; Eh, redox potential; Na^+, sodium; NO_3, nitrate; PO_4^{3-}, orthophosphate; K^+, potassium.

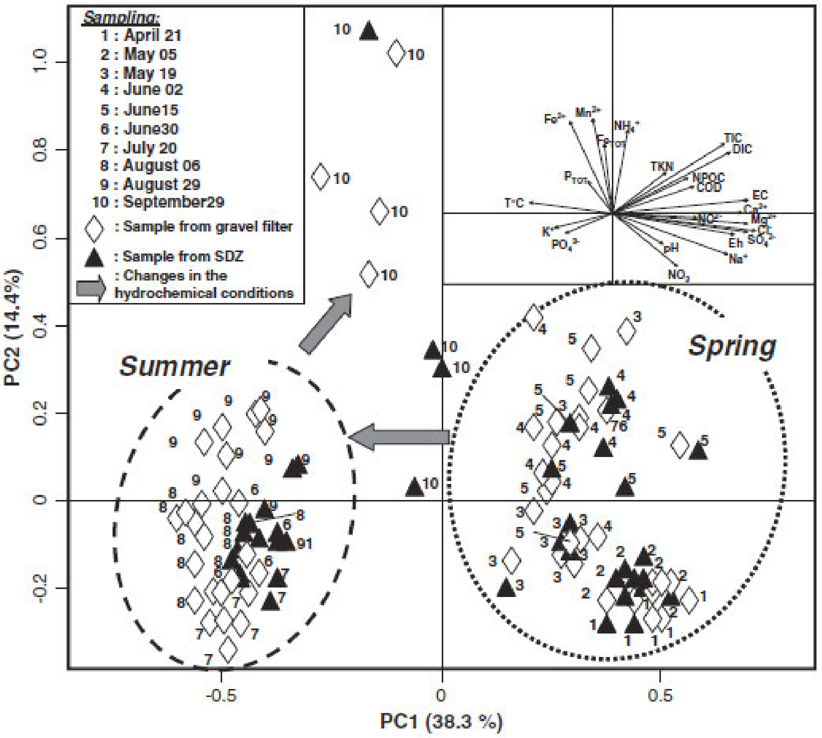
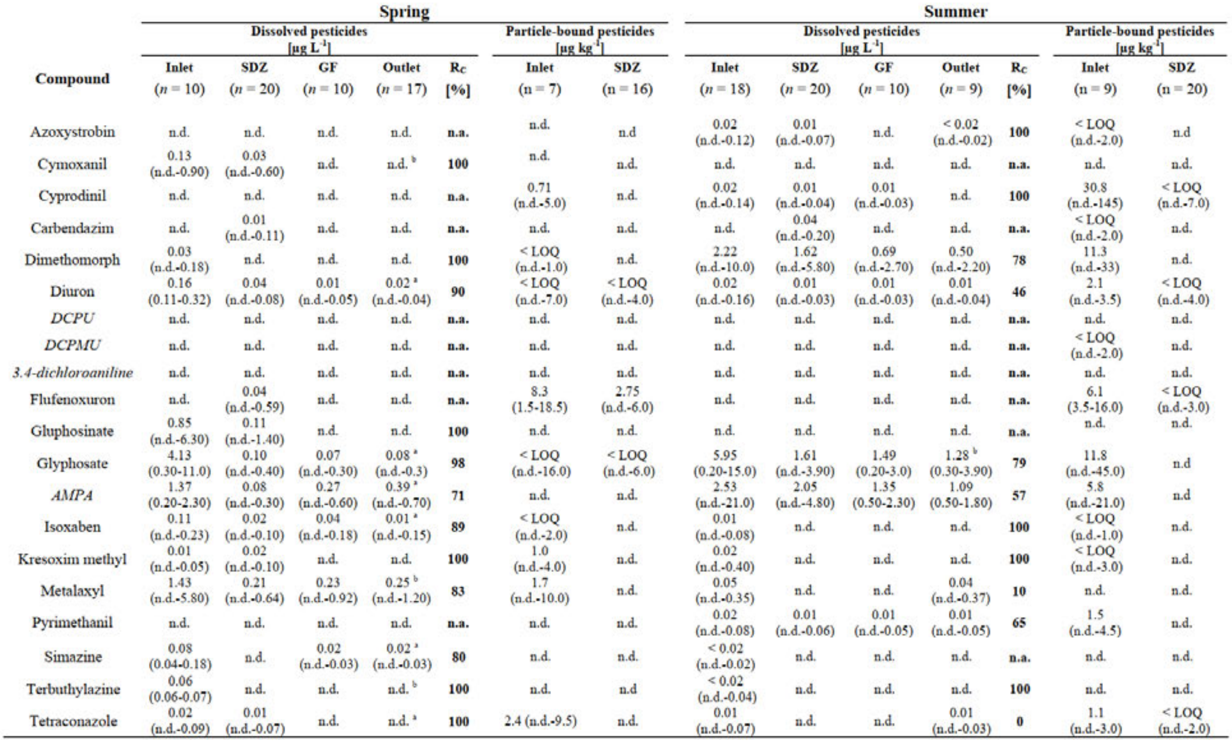


Table 8.5-206: Mean concentrations and ranges of dissolved and particle-bound pesticides in the inlet, the sediment deposition zone (SDZ), the gravel filter (GF) and the outlet of the storm water wetland (Rouffach, Haut-Rhin, France) in spring (06 April to 15 June 2009) and in summer (15 June to 29 September 2009). Reduction in mean concentrations from inlet to outlet are given in percent (RC %). n.d.: not detected.

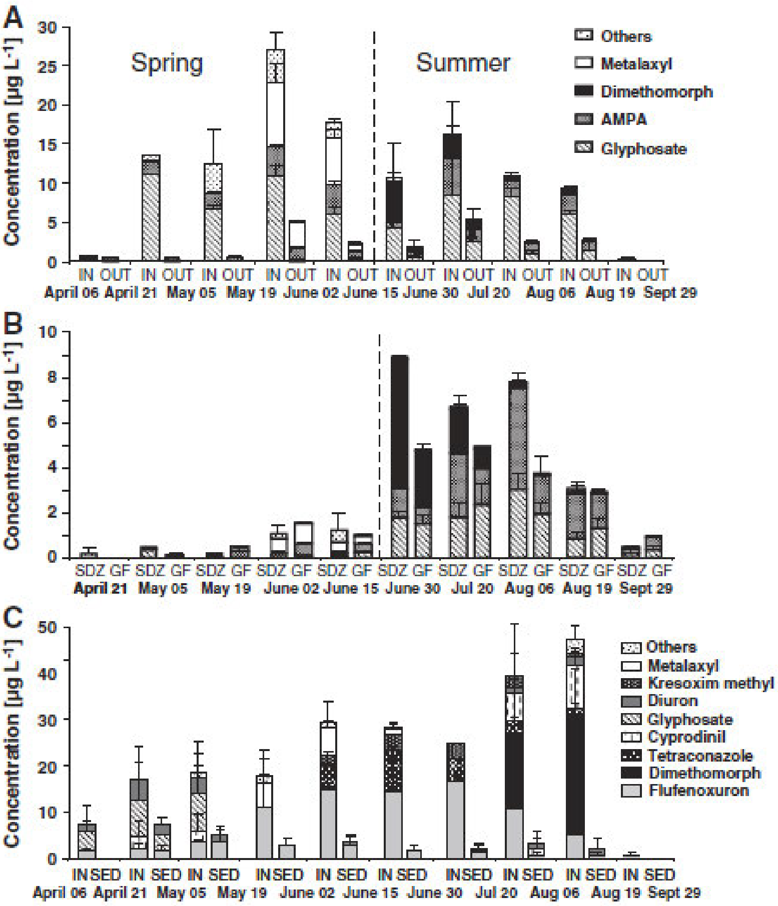


Compound	Spring							Summer						
	Dissolved pesticides [µg L⁻¹]					Particle-bound pesticides [µg kg⁻¹]		Dissolved pesticides [µg L⁻¹]					Particle-bound pesticides [µg kg⁻¹]	
	Inlet ($n = 10$)	SDZ ($n = 20$)	GF ($n = 10$)	Outlet ($n = 17$)	R_C [%]	Inlet (n = 7)	SDZ (n = 16)	Inlet ($n = 18$)	SDZ ($n = 20$)	GF ($n = 10$)	Outlet ($n = 9$)	R_C [%]	Inlet (n = 9)	SDZ (n = 20)
Azoxystrobin	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d	0.02 (n.d.-0.12)	0.01 (n.d.-0.07)	n.d.	< 0.02 (n.d.-0.02)	**100**	< LOQ (n.d.-2.0)	n.d
Cymoxanil	0.13 (n.d.-0.90)	0.03 (n.d.-0.60)	n.d.	n.d. ^{b}	**100**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.
Cyprodinil	n.d.	n.d.	n.d.	n.d.	**n.a.**	0.71 (n.d.-5.0)	n.d.	0.02 (n.d.-0.14)	0.01 (n.d.-0.04)	0.01 (n.d.-0.03)	n.d.	**100**	30.8 (n.d.-145)	< LOQ (n.d.-7.0)
Carbendazim	n.d.	0.01 (n.d.-0.11)	n.d.	n.d.	**n.a.**	n.d.	n.d.	n.d.	0.04 (n.d.-0.20)	n.d.	n.d.	**n.a.**	< LOQ (n.d.-2.0)	n.d.
Dimethomorph	0.03 (n.d.-0.18)	n.d.	n.d.	n.d.	**100**	< LOQ (n.d.-1.0)	n.d.	2.22 (n.d.-10.0)	1.62 (n.d.-5.80)	0.69 (n.d.-2.70)	0.50 (n.d.-2.20)	**78**	11.3 (n.d.-33)	n.d.
Diuron	0.16 (0.11-0.32)	0.04 (n.d.-0.08)	0.01 (n.d.-0.05)	0.02 ^{a} (n.d.-0.04)	**90**	< LOQ (n.d.-7.0)	< LOQ (n.d.-4.0)	0.02 (n.d.-0.16)	0.01 (n.d.-0.03)	0.01 (n.d.-0.03)	0.01 (n.d.-0.04)	**46**	2.1 (n.d.-3.5)	< LOQ (n.d.-4.0)
DCPU	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.
DCPMU	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.a.**	< LOQ (n.d.-2.0)	n.d.
3.4-dichloroaniline	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.
Flufenoxuron	n.d.	0.04 (n.d.-0.59)	n.d.	n.d.	**n.a.**	8.3 (1.5-18.5)	2.75 (n.d.-6.0)	n.d.	n.d.	n.d.	n.d.	**n.a.**	6.1 (3.5-16.0)	< LOQ (n.d.-3.0)
Gluphosinate	0.85 (n.d.-6.30)	0.11 (n.d.-1.40)	n.d.	n.d.	**100**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.
Glyphosate	4.13 (0.30-11.0)	0.10 (n.d.-0.40)	0.07 (n.d.-0.30)	0.08 ^{a} (n.d.-0.3)	**98**	< LOQ (n.d.-16.0)	< LOQ (n.d.-6.0)	5.95 (0.20-15.0)	1.61 (n.d.-3.90)	1.49 (0.20-3.0)	1.28 ^{b} (0.30-3.90)	**79**	11.8 (n.d.-45.0)	n.d
AMPA	1.37 (0.20-2.30)	0.08 (n.d.-0.30)	0.27 (n.d.-0.60)	0.39 ^{a} (n.d.-0.70)	**71**	n.d.	n.d.	2.53 (n.d.-21.0)	2.05 (n.d.-4.80)	1.35 (0.50-2.30)	1.09 (0.50-1.80)	**57**	5.8 (n.d.-21.0)	n.d
Isoxaben	0.11 (n.d.-0.23)	0.02 (n.d.-0.10)	0.04 (n.d.-0.18)	0.01 ^{a} (n.d.-0.15)	**89**	< LOQ (n.d.-2.0)	n.d.	0.01 (n.d.-0.08)	n.d.	n.d.	n.d.	**100**	< LOQ (n.d.-1.0)	n.d.
Kresoxim methyl	0.01 (n.d.-0.05)	0.02 (n.d.-0.10)	n.d.	n.d.	**100**	1.0 (n.d.-4.0)	n.d.	0.02 (n.d.-0.40)	n.d.	n.d.	n.d.	**100**	< LOQ (n.d.-3.0)	n.d.
Metalaxyl	1.43 (n.d.-5.80)	0.21 (n.d.-0.64)	0.23 (n.d.-0.92)	0.25 ^{b} (n.d.-1.20)	**83**	1.7 (n.d.-10.0)	n.d.	0.05 (n.d.-0.35)	n.d.	n.d.	0.04 (n.d.-0.37)	**10**	n.d.	n.d.
Pyrimethanil	n.d.	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.	0.02 (n.d.-0.08)	0.01 (n.d.-0.06)	0.01 (n.d.-0.05)	0.01 (n.d.-0.05)	**65**	1.5 (n.d.-4.5)	n.d.
Simazine	0.08 (0.04-0.18)	n.d.	0.02 (n.d.-0.03)	0.02 ^{a} (n.d.-0.03)	**80**	n.d.	n.d.	< 0.02 (n.d.-0.02)	n.d.	n.d.	n.d.	**n.a.**	n.d.	n.d.
Terbuthylazine	0.06 (0.06-0.07)	n.d.	n.d.	n.d. ^{b}	**100**	n.d.	n.d	< 0.02 (n.d.-0.04)	n.d.	n.d.	n.d.	**100**	n.d.	n.d.
Tetraconazole	0.02 (n.d.-0.09)	0.01 (n.d.-0.07)	n.d.	n.d. ^{a}	**100**	2.4 (n.d.-9.5)	n.d.	0.01 (n.d.-0.07)	n.d.	n.d.	0.01 (n.d.-0.03)	**0**	1.1 (n.d.-3.0)	< LOQ (n.d.-2.0)

Removal of dissolved pesticides by the wetland

During the investigation period, the load of the 20 pesticides and degradation products entering the wetland was 8.039 g whereas 2.181 g passed through the wetland (Table 8.5-204). Inflowing load in summer (6.819 g, i.e. 85% of the total dissolved load) was larger compared to that of spring (1.219 g, i.e. 15% of the total dissolved load). This reflects both the seasonal change of runoff regime as underscored in Section *Hydrological and hydrochemical characteristics of the wetland* and pesticide applications in the vineyard catchment (31%of the total applications occurred in spring and 69% in summer, data not shown). Glyphosate, AMPA, dimethomorph and the other compounds accounted for, respectively, 51.7, 20.4, 21.1, and 6.8% of the total inflowing load. According to the removal rates calculated from the difference between loads at the outlet and the inlet of the wetland during the entire period of investigation, pesticides can be classified as (i) efficiently retained (removal rates between 80 and 100%; i.e. azoxystrobin, cymoxanil, gluphosinate, kresoxim methyl and terbuthylazine); (ii) moderately retained (removal rates between 50 and 80%; i.e. cyprodinil, dimethomorph, diuron, glyphosate, AMPA, isoxaben, metalaxyl, pyrimethanil and tetraconazole); and (iii) poorly retained (removal rates lower than 50%; i.e. simazine). Summing seasonal loads of all compounds, very similar removal rates were found for spring and summer (i.e. 72 and 73%, respectively), indicating that seasonal changes of pesticide loadings did not affect the removal capacity of the wetland. This was supported by the absence of significant correlation between pesticide loadings in runoff and pesticide removal rates ($p > 0.1$) throughout the investigation period, suggesting no threshold at which pesticide removal would decrease at larger loads. However, removal rates of individual compounds largely varied between spring and summer (Table 8.5-204).

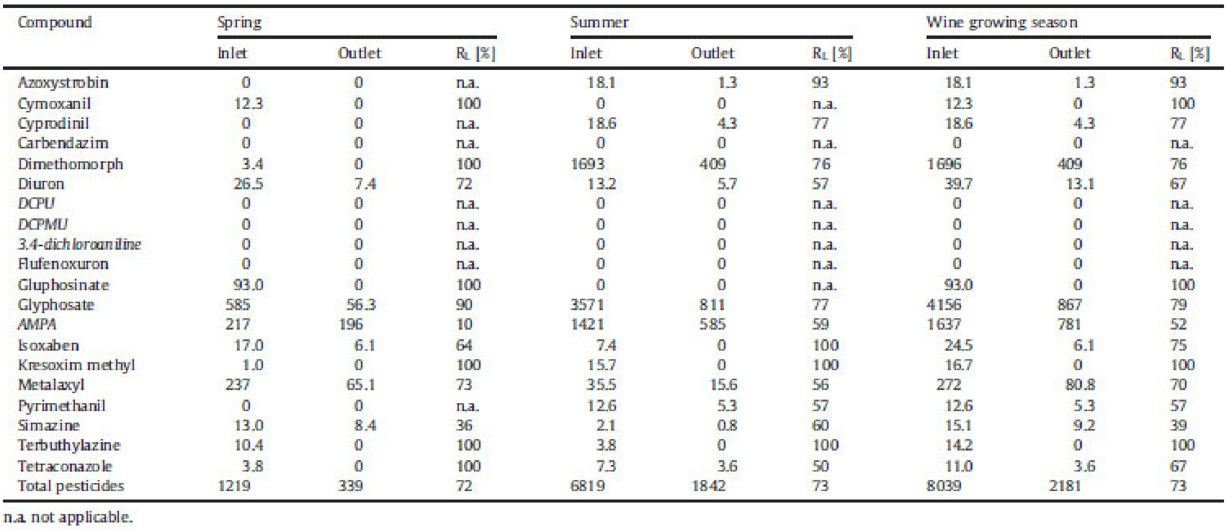
Figure 8.5-173: **Mean concentrations of pesticides (A) in the inflowing runoff (IN) and the outlet (OUT), (B) within the sediment deposition zone (SDZ) and the gravel filter (GF), and (C) associated with inflowing suspended solids (IN) and sediment (SED) of the stormwater wetland (Rouffach, Alsace, France). Error bars show the standard deviation.**



Retention of particle-laden pesticides

The role of sedimentation in pesticide removal was evaluated based on analysis of total suspended solids (TSS) and dissolved organic carbon (DOC). Detailed loads of pesticide associated with suspended-solids entering the wetland are provided in Table 8.5-208. The pesticide load associated with suspended solids in inflowing runoff was 198 mg for the entire investigation period, which represents 2.4% of the total load. The trifling contribution of the solid load to the total load of pesticides is due to low fractions (<1%) of glyphosate, AMPA and dimethomorph associated with suspended solids, while these compounds accounted for 93% of the total dissolved pesticide load. Nevertheless, partition coefficient K_d in inflowing runoff ranged between −4.22 (glyphosate) and 1.07 (diuron), reflecting large variations of the partitioning patterns among pesticides and seasons (see Table 8.5-208 for detailed values of K_d). Pesticide concentrations in suspended solids at the outlet of the wetland could not be obtained on a runoff-event basis because the amount of material collected in the sieve of the suspended solid samplers was too low (<5 g of sediment) to enable reliable measurements. Therefore, rates of pesticide removal attributable to retention by the wetland of pesticides associated with suspended solids could not be calculated using a mass balance approach. Nevertheless, average sedimentation rates estimated from discharge measurements and TSS values were 2.7 kg/day (99% of the input mass) in spring and 7.0 kg/day (88% of the input mass) in summer, indicating that the wetland can act as a sink for particle-laden pesticides. Since the pore size of the filter paper used for separating TSS from DOC was 0.45 µm, only finer particles were included in the DOC mass balance analysis. Mass balance of DOC between the inlet and the outlet showed that the output mass (12.9 kg) exceeded by 34% the input mass. This indicates that pesticide removal cannot be attributed to the retention of the DOC-bound fraction in the wetland. Additionally, re-suspension of particles from the wetland bed to the water column during higher flow regime and plant material, as well as sediment re-suspension by the aquatic fauna and proliferation of algae likely reduced the removal of pesticides associated with TSS and DOC by the wetland.

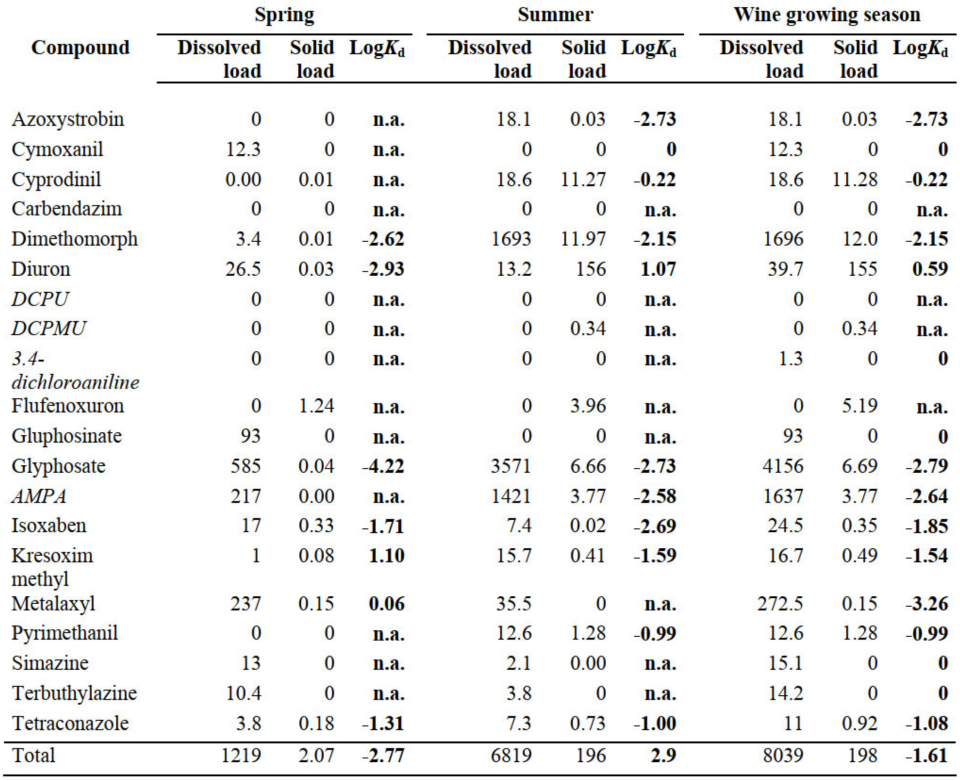
Table 8.5-207: Load estimates (mg) of dissolved pesticides and load reduction, RL (%) by the storm water wetland (Rouffach, Alsace, France) in spring (06 April to 15 June 2009), in summer (15 June to 29 September 2009) and during the wine growing season (06 April to 29 September 2009). Degradation products are shown in italics.



Compound	Spring			Summer			Wine growing season		
	Inlet	Outlet	R_L [%]	Inlet	Outlet	R_L [%]	Inlet	Outlet	R_L [%]
Azoxystrobin	0	0	n.a.	18.1	1.3	93	18.1	1.3	93
Cymoxanil	12.3	0	100	0	0	n.a.	12.3	0	100
Cyprodinil	0	0	n.a.	18.6	4.3	77	18.6	4.3	77
Carbendazim	0	0	n.a.	0	0	n.a.	0	0	n.a.
Dimethomorph	3.4	0	100	1693	409	76	1696	409	76
Diuron	26.5	7.4	72	13.2	5.7	57	39.7	13.1	67
DCPU	0	0	n.a.	0	0	n.a.	0	0	n.a.
DCPMU	0	0	n.a.	0	0	n.a.	0	0	n.a.
3,4-dichloroaniline	0	0	n.a.	0	0	n.a.	0	0	n.a.
Flufenoxuron	0	0	n.a.	0	0	n.a.	0	0	n.a.
Gluphosinate	93.0	0	100	0	0	n.a.	93.0	0	100
Glyphosate	585	56.3	90	3571	811	77	4156	867	79
AMPA	217	196	10	1421	585	59	1637	781	52
Isoxaben	17.0	6.1	64	7.4	0	100	24.5	6.1	75
Kresoxim methyl	1.0	0	100	15.7	0	100	16.7	0	100
Metalaxyl	237	65.1	73	35.5	15.6	56	272	80.8	70
Pyrimethanil	0	0	n.a.	12.6	5.3	57	12.6	5.3	57
Simazine	13.0	8.4	36	2.1	0.8	60	15.1	9.2	39
Terbuthylazine	10.4	0	100	3.8	0	100	14.2	0	100
Tetraconazole	3.8	0	100	7.3	3.6	50	11.0	3.6	67
Total pesticides	1219	339	72	6819	1842	73	8039	2181	73

n.a. not applicable.

Table 8.5-208: Load estimates [mg] of dissolved pesticides and suspended-solid associated pesticides entering the storm water wetland in spring (06 April to 15 June 2009), in summer (15 June to 29 September 2009) and during the entire investigation period (06 April to 29 September 2009). Solid to dissolved load ratio [%] are also provide. Degradation products are shown in italics.

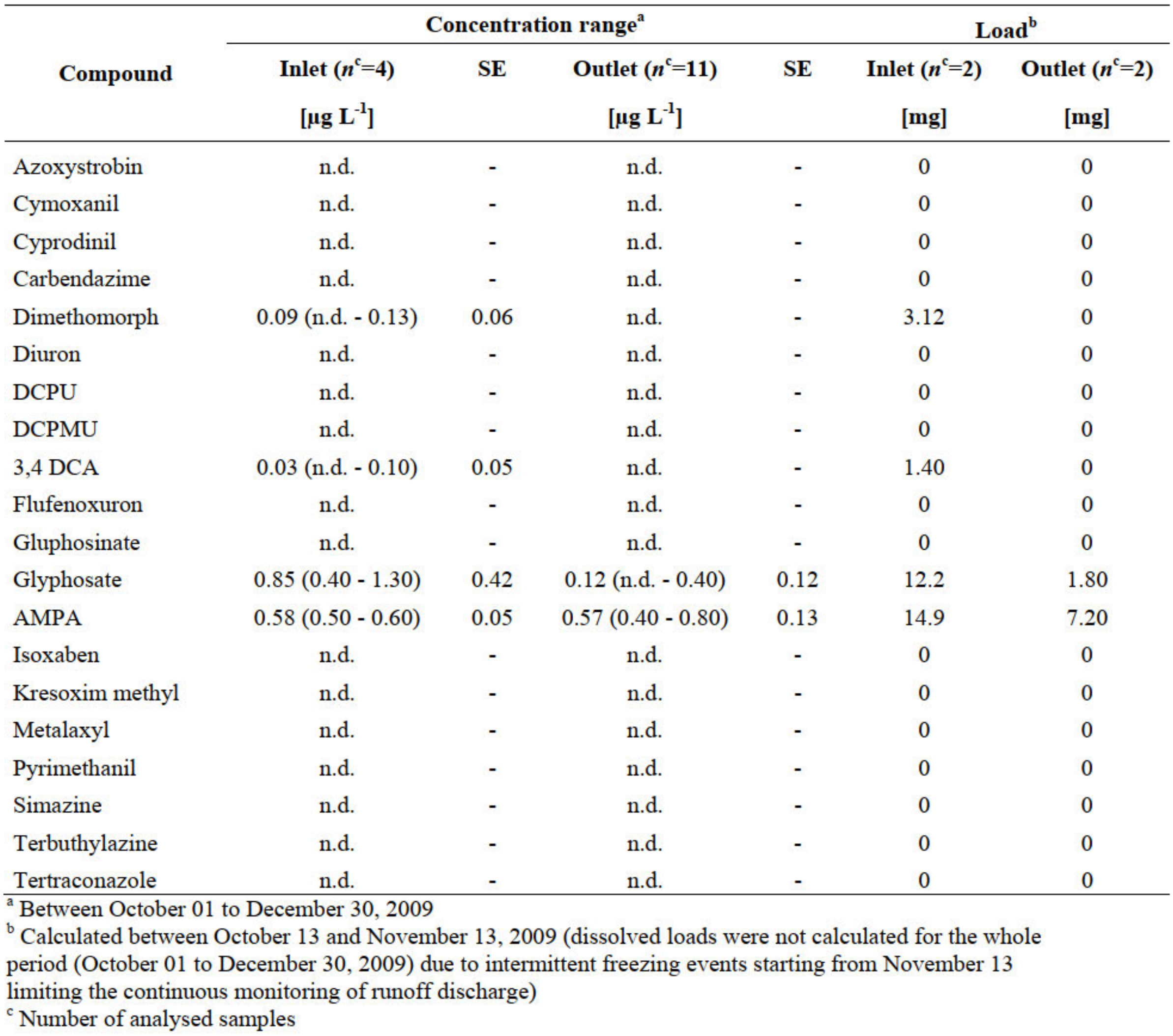


Compound	Spring			Summer			Wine growing season		
	Dissolved load	Solid load	LogK_d	Dissolved load	Solid load	LogK_d	Dissolved load	Solid load	LogK_d
Azoxystrobin	0	0	**n.a.**	18.1	0.03	**-2.73**	18.1	0.03	**-2.73**
Cymoxanil	12.3	0	**n.a.**	0	0	**0**	12.3	0	**0**
Cyprodinil	0.00	0.01	**n.a.**	18.6	11.27	**-0.22**	18.6	11.28	**-0.22**
Carbendazim	0	0	**n.a.**	0	0	**n.a.**	0	0	**n.a.**
Dimethomorph	3.4	0.01	**-2.62**	1693	11.97	**-2.15**	1696	12.0	**-2.15**
Diuron	26.5	0.03	**-2.93**	13.2	156	**1.07**	39.7	155	**0.59**
DCPU	0	0	**n.a.**	0	0	**n.a.**	0	0	**n.a.**
DCPMU	0	0	**n.a.**	0	0.34	**n.a.**	0	0.34	**n.a.**
3.4-dichloroaniline	0	0	**n.a.**	0	0	**n.a.**	1.3	0	**0**
Flufenoxuron	0	1.24	**n.a.**	0	3.96	**n.a.**	0	5.19	**n.a.**
Gluphosinate	93	0	**n.a.**	0	0	**n.a.**	93	0	**0**
Glyphosate	585	0.04	**-4.22**	3571	6.66	**-2.73**	4156	6.69	**-2.79**
AMPA	217	0.00	**n.a.**	1421	3.77	**-2.58**	1637	3.77	**-2.64**
Isoxaben	17	0.33	**-1.71**	7.4	0.02	**-2.69**	24.5	0.35	**-1.85**
Kresoxim methyl	1	0.08	**1.10**	15.7	0.41	**-1.59**	16.7	0.49	**-1.54**
Metalaxyl	237	0.15	**0.06**	35.5	0	**n.a.**	272.5	0.15	**-3.26**
Pyrimethanil	0	0	**n.a.**	12.6	1.28	**-0.99**	12.6	1.28	**-0.99**
Simazine	13	0	**n.a.**	2.1	0.00	**n.a.**	15.1	0	**0**
Terbuthylazine	10.4	0	**n.a.**	3.8	0	**n.a.**	14.2	0	**0**
Tetraconazole	3.8	0.18	**-1.31**	7.3	0.73	**-1.00**	11	0.92	**-1.08**
Total	1219	2.07	**-2.77**	6819	196	**2.9**	8039	198	**-1.61**

Discussion

Pesticides in runoff from agricultural catchments typically occur in mixtures. Therefore studies on pesticide mixtures are necessary to understand how mitigation capacities in wetland systems develop over time and can be used for reducing impacts on receiving aquatic ecosystems. Lizotte et al. (2009) observed in a 700 m long backwater wetland in summer a larger concentration reduction (N90%) for individual pesticides of a mixture of atrazine, S-metolachlor and fipronil than those observed in our study, although no pesticide load removal estimates was provided. The same authors emphasized that factors such as wetland size, sediment characteristics, type and density of vegetation and hydrochemical conditions that prevailed at a particular stage of the wetland lifespan can largely influence the ability to mitigate pesticide mixtures. In stormwater wetlands, removal processes of dissolved and particle-laden pesticides such as sedimentation, photolysis, hydrolysis and degradation are intimately linked with both the prevailing hydrochemistry and the rapid changes of runoff regime. Moreover, their respective contribution strongly depends on the properties of the molecules. Smaller logK_{ow} pesticides (with logK_{ow}< 3) result in loading being predominantly associated with runoff and wetland water, lower partitioning to suspended solids or DOC, and a potentially faster degradation in the dissolved phase owing to higher availability of molecules in abiotic or biotic transformation processes. For less-hydrophobic pesticides included in this study (e.i. azoxystrobin, cymoxanil, carbendazim, dimethomorph, diuron, gluphosinate, glyphosate, AMPA, metalaxyl, pyrimethanil, and simazine) an important hydrochemical characteristic in constructed wetlands is their pH. Azoxystrobin, 3.4-dichloroaniline, and simazine were expected to dissipate through aqueous photolysis that prevailed in the wetland during the entire investigation period, given that their half-life was lower than 6 days. Cymoxanil can be degraded by aqueous hydrolysis at pH 7 which is supported by the complete removal of cymoxanil by the wetland. In contrast, degradation of carbendazim, dimethomorph, diuron, glyphosate and pyrimethanil via photolysis or hydrolysis was not a dominant removal process (half-life > 40 days). Nevertheless, mean quiescent period (±SD) between runoff events were 5.1 ± 7.3 and 5.2 ± 5.7 days for spring and summer respectively, indicating sufficient time for both biotic and abiotic degradation reactions to occur in the wetland. In spring, runoff events were lower than 40 m^3 and thus could be stored in the wetland and treated until the next runoff event. Moreover, average inlet flow rates were smaller in spring compared to those observed in summer, although the difference was not statistically significant, and outlet flow rate were significantly larger in spring. Small runoff volumes entering the wetland, low flow rates and longer quiescent periods can increase the contact time between runoff water and wetland compartments. In contrast, larger runoff volumes and inlet flow rates, such as those observed in summer, are expected to limit the occurrence of removal processes. Nevertheless, larger vegetation cover in summer compared to that observed in spring can largely enhance pesticide removal efficiencies by increasing both sorption sites and contact time, thus compensating shorter times of contact and degradative reactions during high flow conditions. Further-more, incomplete flushing of the wetland during low to moderate flow conditions (<40 m^3) can also cause longer retention of stable and less-sorptive substances. For instance, Lange et al. (in press) used uranine (DT_{50}-photolysis=11 days) as a reference to mimic photolysis, and sulforhodamine B ($LogK_{ow}$=−2.02) as one to mimic moderate sorption of contaminants in various wetland systems, including our stormwater wetland. Their study simulated a 37.5 m^3 runoff event and indicated favourable conditions for photocatalytic decay (removal of uranine by 57%) and high sorption capacities (removal of sulforhodamine B by 82%) in our stormwater wetland. In contrast, shorter circuiting and contact time with sediment and vegetation under high flow or flood conditions is expected to decrease removal of dissolved contaminant via sorption and degradation processes, as previously described (Lange et al., in press; Holland et al., 2004). Besides sorption, larger plant cover and density can also directly affect the removal of pesticides in wetlands. Under anaerobic conditions (prevalent in summer), it is likely that the elimination of chlorinated pesticides (i.e. simazine and terbuthylazine) via reductive dechlorination was also favored by the occurrence of biofilm, sediment, root complexes as well as potential sources of electron donors provided by roots and organic matter in the wetland. Besides, plant uptake cannot be excluded for compounds with a log K_{ow} ranging between 1 and 3. However, due to large variations of the vegetal biomass and type in our wetland on both spatial and temporal scales, the contribution of vegetation and vegetal material to pesticide removal could not be quantified in the present study. Though the comprehensive sampling highlighted major hydro-chemical changes in the wetland during quiescent period between runoff events, transient changes during runoff events may also occur. Intermittent flow regime in stormwater wetland is presumed to enhance the mixing of anaerobic zones in sediments with the adjacent aerobic and anoxic micro-sites in the rhizosphere, leading to temporal variations of hydrochemical conditions. Oxic conditions that prevailed in spring can be related to higher removal of dimethomorph, diuron, glyphosate, metalaxyl and tetraconazole, whereas higher temperatures and anaerobic conditions in summer can be related to the removal of AMPA, isoxaben and simazine. Seasonal changes of the duration and frequency of rainfall–runoff events, vegetal covering and ecotypes, as well as hydrochemical and climate conditions very likely determined the dominant microbial populations present in the wetland, as well as the metabolic pathway that pesticides and their degradation products took. In summer, higher plant density slowed water flows and allowed for particle settling to occur and may have increased degradation rates by favoring oxidative transformation pathways in the rhizosphere. Glyphosate and AMPA that accounted for 72.1% of the contaminant load entering the wetland are major compounds in our study. Biodegradation of glyphosate in the environment takes place under both aerobic and anaerobic conditions, although biodegradation under anaerobic conditions is normally less than under aerobic conditions. Biodegradation of AMPA is generally slower than that of glyphosate possibly because of AMPA transient capacity to be strongly sorbed through the phosphonate group and thus protected against further biodegradation. Among the compounds studied, glyphosate and AMPA are strongly sorbed by soil minerals, and have been previously observed to rapidly adsorb to wetland sediments, before being gradually removed within 5 to 15 days. This is in agreement with our results showing no accumulation of glyphosate and AMPA in the wetland sediments and efficient degradation of glyphosate into AMPA in the dissolved phase. This was underscored by a larger AMPA to glyphosate ratio at the outlet (3.5) compared to that found at the inlet (0.4) in spring. In summer, AMPA to glyphosate ratio at the outlet was 0.9, which indicates a more effective removal of AMPA in the dissolved phase. Since glyphosate and AMPA were not detected in sediments and the occurrence of abiotic degradation mechanisms is unlikely for these compounds, the results indicate that glyphosate was microbially degraded into AMPA, which in turn was gradually degraded in the water column of the wetland. Though variable-charge minerals, such as aluminum or iron oxides, can adsorb large amounts of glyphosate and AMPA, competitive adsorption with phosphorus may occur, explaining the absence of significant sorption onto wetland sediments. Ratios of dissolved inorganic phosphorus to glyphosate (µmol/µmol) ranging between 20 and 21,040 indicate that competitive adsorption can hinder the partitioning of glyphosate and AMPA into the wetland sediment. Several studies have shown that a large portion of the removal of hydrophobic chemicals with $\log K_{ow}$ values > 3 in aquatic environments is due to the sedimentation of pesticide-laden solids. However, concentrations in the wetland sediments of flufenoxuron, cyprodinil, isoxaben, kresoxim methyl, tetraconazole and terbuthylazine could not be detected or were one order of magnitude lower than concentrations at the wetland inlet. Although aqueous photolysis of isoxaben and flufenoxuron cannot be excluded (DT_{50} = 6 days, at pH= 7), significant degradation of hydrophobic compounds in the wetland is not expected due to reduced bioavailability. Therefore, a large fraction of these contaminants passed through the stormwater wetland in association with suspended particles. Transport of pesticides-laden sediment through the wetland under high flow regime has been previously suggested to decrease the removal of hydrophobic pesticides by affecting the degree of bottom scouring and re-suspension of settled solids. However, no significant correlation was found between runoff volumes and removal rates of dissolved pesticides (i.e. DOC-laden pesticides and pesticides in the aqueous phase) observed in our study, suggesting no threshold at which removal of dissolved pesticides would be reduced at greater runoff inflow. Nevertheless, positive correlations between runoff volumes and both TSS and DOC loads at the inlet ($p < 0.001$) indicate larger particle mass transport through the wetland during large flow events. This is also under-scored by moderate load removal of cyprodinil and isoxaben, suggesting that hydrophobic compounds associated with DOC, which are taken into account in the mass balance of dissolved pesticides, were transferred through the wetland. It also has to be noted that pesticide concentrations in fall (from 01 October to 30 December 2009) ranged from not detected to 0.85 ± 0.42 µg/L (glyphosate) at the inlet, and from not detected to 0.57 ± 0.13 µg/L (AMPA) at the outlet. No significant release of pesticides with $\log K_{ow}$ value and no release of hydrophobic pesticides could be observed during fall which indicates that the most of the pesticides mass (>99.6%) entered the wetland and passed from April to September, which correspond to the period of pesticide application (see also Table 8.5-209).

Table 8.5-209: Mean concentrations and ranges and loads estimates of dissolved pesticides at the inlet and the outlet of the stormwater wetland (Rouffach, Haut-Rhin, France) during fall



Compound	Concentration range[a]				Load[b]	
	Inlet (n^c=4) [µg L^{-1}]	SE	Outlet (n^c=11) [µg L^{-1}]	SE	Inlet (n^c=2) [mg]	Outlet (n^c=2) [mg]
Azoxystrobin	n.d.	-	n.d.	-	0	0
Cymoxanil	n.d.	-	n.d.	-	0	0
Cyprodinil	n.d.	-	n.d.	-	0	0
Carbendazime	n.d.	-	n.d.	-	0	0
Dimethomorph	0.09 (n.d. - 0.13)	0.06	n.d.	-	3.12	0
Diuron	n.d.	-	n.d.	-	0	0
DCPU	n.d.	-	n.d.	-	0	0
DCPMU	n.d.	-	n.d.	-	0	0
3,4 DCA	0.03 (n.d. - 0.10)	0.05	n.d.	-	1.40	0
Flufenoxuron	n.d.	-	n.d.	-	0	0
Gluphosinate	n.d.	-	n.d.	-	0	0
Glyphosate	0.85 (0.40 - 1.30)	0.42	0.12 (n.d. - 0.40)	0.12	12.2	1.80
AMPA	0.58 (0.50 - 0.60)	0.05	0.57 (0.40 - 0.80)	0.13	14.9	7.20
Isoxaben	n.d.	-	n.d.	-	0	0
Kresoxim methyl	n.d.	-	n.d.	-	0	0
Metalaxyl	n.d.	-	n.d.	-	0	0
Pyrimethanil	n.d.	-	n.d.	-	0	0
Simazine	n.d.	-	n.d.	-	0	0
Terbuthylazine	n.d.	-	n.d.	-	0	0
Tertraconazole	n.d.	-	n.d.	-	0	0

[a] Between October 01 to December 30, 2009

[b] Calculated between October 13 and November 13, 2009 (dissolved loads were not calculated for the whole period (October 01 to December 30, 2009) due to intermittent freezing events starting from November 13 limiting the continuous monitoring of runoff discharge)

[c] Number of analysed samples

Conclusion

Our results provide quantitative field data of pesticide mixtures in runoff and stormwater wetlands, in both the particulate and dissolved phases, that often fail to completely evaluate the potential of best management practices (BMPs) for agricultural stormwater. To the best of our knowledge, this paper is the first investigation that reports detailed concentrations and mass balances of pesticides mixtures in a stormwater wetland collecting agricultural runoff during an entire agricultural season. The results for pesticides and some of their degradation products in this study indicate that stormwater wetlands collecting agricultural runoff have good capacities for retaining, at various flow conditions and loadings, mixtures of pesticides with different physico-chemical properties. Seasonal removal rates of dissolved loads by the wetland ranged from below 60% (simazine, AMPA and pyrimethanil) to 100% (cymoxanil, gluphosinate, kresosxim methyl and terbuthylazine). Our findings also underscore the crucial role of vegetation characteristics for retaining pesticides and of dissolved organic carbon for transporting hydrophobic pesticides in stormwater wetlands. Accompanied with careful guidance and planning, stormwater wetlands have the potential to serve as a tool for urban and agricultural stormwater management practices, thus contributing to the improvement of water quality for receiving aquatic ecosystems. However, the use of stormwater wetlands as a management practice targeting pesticide mitigation should not be utilized as a unique solution to treat pesticide runoff, but should rather integrate in the design of holistic approaches to stormwater management. The present study demonstrates that the runoff regime works in concert with hydrochemical characteristics to mitigate pesticide in runoff, which should be included into design considerations of stormwater wetlands. However, further knowledge about hydrological and biogeochemical processes that alter stormwater wetlands during their lifespan is necessary to improve removal of pesticides in runoff.

Assessment and conclusion by applicant:
The article describes a runoff experiment in a vineyard of the Alsatian area in France. The results demonstrate that storm water wetlands can efficiently remove pesticide mixtures in agricultural runoff during critical periods of pesticide application, although fluctuations in the runoff regime and hydrochemical characteristics can affect the removal rates of individual pesticides. Maximum concentrations of glyphosate and its main metabolite AMPA measured at the inlet of the catchment were 15 µg/L and 21 µg/L, respectively.
The article is considered reliable.

Assessment and conclusion by RMS:
The study is considered reliable but provides measured concentration in runoff water and not in surface water, and as such cannot be considered as monitoring study in surface water as defined in Regulation 1107/2009.

The main objective of the present study was to assess the ability of a stormwater wetland to remove pesticides in runoff from a vineyard catchment during an entire period of pesticide application.

Note that results from this experimental site are reported in several articles for different times. The characteristics of the catchment and agricultural practices have already been described and commented in Imfeld et al., 2013 (CA7.5/055) or Gregoire et al., 2010, (CA7.5/068).

This article reports results from 2009.

Maximum concentrations of glyphosate and its main metabolite AMPA measured at the inlet of the catchment were 15 µg/L and 21 µg/L, respectively. These occurred in summer. Maximum concentration at spring period are 11 and 2.30 µg/L respectively for glyphosate and AMPA and at fall are 1.30 and 0.60 µg/L respectively.

Reduction of pesticide concentration, RC (%), was calculated for each runoff event as the reduction of mean concentrations at the outlet relatively to the mean concentrations at the inlet of the wetland. Removal rates of pesticide load RL (%) were calculated for each runoff event as the reduction of the load at the outlet relatively to the load at the inlet of the wetland.

The use amount of glyphosate is not given within this study. The study of Imfeld, 2013 (CA7.5/055) on the same catchment reports a cumulated amount of used glyphosate of 3.8 kg in 2009 on the catchment. However the results in Imfeld et al. (2013) focus on the spring period while the present article of Maillard last from spring to autum. It is not know whether additional application of glyphosate occurred at summer and autumn 2009.

Data point:	CA 7.5/065
Report author	Meyer, B. *et al.*
Report year	2011
Report title	Concentrations of dissolved herbicides and pharmaceuticals in a small river in Luxembourg
Document No	Environmental Monitoring and Assessment, (2011) Vol. 180, No. 1-4, pp. 127-146

Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facility (Department of Environmentand Agro-Biotechnologies (EVA))
Acceptability/Reliability:	Reliable

Urban and agricultural areas affect the hydraulic patterns as well as the water quality of receiving drainage systems, especially of catchments smaller than 50 km^2. Urban runoff is prone to contamination due to pollutants like pesticides or pharmaceuticals. Agricultural areas are possible sources of nutrient and herbicide contamination for receiving water bodies. The pollution is derived from leaching by subsurface flow, as well as wash-off and erosion caused by surface runoff. In the Luxembourgish Mess River catchment, the pharmaceutical and pesticide concentrations are comparable with those detected by other authors in different river systems worldwide. Some investigated pesticide concentrations infringe current regulations. The maximum allowable concentration for diuron of 1.8 µg/L is exceeded fourfold by measured 7.41 µg/L in a flood event. The load of dissolved pesticides reaching the stream gauge is primarily determined by the amount applied to the surfaces within the catchment area. Storm water runoff from urban areas causes short-lived but high-pollutant concentrations and moderate loads, whereas moderate concentrations and high loads are representative for agricultural inputs to the drainage system. Dissolved herbicides, sulfonamides, tetracyclines, analgesics and hormones can be used as indicators to investigate runoff generation processes, including inputs from anthropogenic sources. The measurements prove that the influence of kinematic wave effects on the relationship between hydrograph and chemographs should not be neglected in smaller basins. The time lag shows that it is not possible to connect analysed substances of defined samples to the corresponding section of the hydrograph.

Materials and methods

Area under investigation

Luxembourg is divided into two natural regions, the Oesling in the north (225–559 m above sea level) and the Gutland in the south (140–440 m above sea level). Hydrological measurements are conducted in the small Mess catchment in the southwestern part of Luxembourg. It is located in the Gutland region, which is characterised by a cuesta landscape where large gentile sloped valleys occur on marly substrates, contrasting with the deeply cut Luxembourg sandstone. The basin has a total surface area of 32.5 km^2 at the stream gauge. Marls and sandy marls of the sedimentary Paris basin dominate the lithology (93% Lias bedrock, 7% alluvials near the stream network). The marly bedrock is considered as being mostly impermeable. Luvisoils, pelosoils, planosoils, fluvisoils and gleysoils are dominating, with a silty–clayey to clayey texture. The land use in the basin consists of grassland (58%) and arable land (22.7%); forest is about 9.7%, urban and industrial areas amount to 8.7%, 2.3% contain the road and rail network. The most widespread crops are maize, colza and winter wheat. Runoff from several roads, effluents from small industries and untreated wastewaters from solitary farms and storm drainages of the combined sewer system influence river water quality. A mechanical–biological sewage water treatment plant is located in the small village of Reckange. This purification plant is connected with 3,500 inhabitants (340,000 m^3 sewage per year). Housing areas are drained by a combined sewage water system with several storm-control reservoirs. By passing above the Ardennes massif, the dominating westerly atmospheric fluxes cause annual rainfall totals in Luxembourg exceeding 900 mm. December, January and February are the wettest months (more than 100 mm), while April, August and September are the driest months (less than 70 mm) on average. January is the coldest month (0°C) and July the warmest month (16.9°C). Monthly potential evapotranspiration values vary from 81.8 mm in July to 13.5 mm in December (Local station, 1971–2000). The runoff regime is of pluvial oceanic unimodal type, with high runoff occurring during winter (maximum runoff in February) and low runoff occurring in summer (minimum runoff in September). A meteorological station of the ‘Administration des services techniques de l’Agriculture’ (Agriculture Administration) is recording the most important hydro-climatological parameters, such as air temperature and humidity (both in 2 m above ground). Rainfall (1 m above ground) is measured in ten minutes intervals with a heated tipping bucket rain gauge (Lambrecht 15188). This station is located about three kilometres north of our stream gauge in the center of the catchment area. The stream gauge (ISCO 4120 flow logger, pressure probe) in the village of Pontpierre registers 15-minute average water levels. Discharge is obtained with level-to-flow conversions applying the Manning equation. In parallel, conductivity is automatically registered in 10-min intervals (WTW 3310). The mean discharge of the Mess was of 261 L/s in the year 2008, with a specific runoff of 8 L/(s km^2). During the same year a total of 253 of 804 mm rainfall had been transformed into discharge. In summer, multi-peaked flood waves, which can be traced to consecutive contributions of tributaries and the rainfall patterns, are characteristic in the catchment. Especially thunderstorms produce runoff events characteristic of a steep gradient and a relatively short outlet. Precipitation events of very small intensities and amount are indicated by small discharge peaks, which result predominantly from the runoff from impervious surface areas. The long-lasting, low intensity winter precipitation events cause singular broad discharge maxima, which are primarily composed of laterally flowing soil water and groundwater. In the Mess basin, during winter runoff events, the largest dilution mostly occurs some hours before the discharge maximum. This dilution is mainly induced by rainwater runoff from paved surface areas like streets or roofage. Furthermore, the spillways of the sewage system storm water retention basins and the sewage water treatment plant deliver larger volumes of rainwater and high quantities of diluted sewerage water.

Sampling

Two ISCO autosamplers with 2-l glass bottles (24 bottles, non-cooled) were connected to the flow logger in order to trigger the sampling after a fixed water level is reached. Subsequently, sampling is performed at different intervals through-out the duration of the investigated events. Every sample is a spot sample and not a composite one, collected during a certain time span. A representative selection of samples has been chosen for analysis selected according to discharge and electrical conductivity (WTW 197i conductivity meter) or water colour. In total, between October 2006 and January 2010, 29 flood events were analysed with respect to nitrate–nitrogen (NO_3–N), nitrite–nitrogen (NO_2–N), chloride (Cl^-) and sulphate (SO_4^{2-}). Fourteen of these floods were additionally investigated concerning dissolved pharmaceuticals or pesticides. During base-flow conditions, grab samples were taken by hand in brown glass bottles to investigate low flow conditions before and after the flood events under investigation. In addition to the sampling described above, during March 2007 and January 2010, 36 samples were taken from the outflow of the local sewage water treatment plant of Reckange. All samples were stored at 4°C in the dark and processed immediately as described below. Concentrations of Cl^-, NO_2–N, SO_4^{2-} and NO_3–N were determined by ion chromatography (Dionex DX-500).

This investigation focuses on the analysis of four classes of veterinary and human pharmaceuticals (sulfonamides, tetracyclines, analgesics and hormones). The 12 selected pharmaceuticals include four sulfonamides (sulfathiazole, sulfamethoxazole, sulfadimethoxine and sulfamethazine), three tetracyclines (chlortetracycline, tetracycline and oxytetracycline), two analgesics (ibuprofen and diclofenac) and three hormones (estrone, ß-estradiol and 17-α-ethinylestradiol). In addition, the two degradation compounds sulfamethazine-N4-acetyl and 4′-hydroxy-diclofenac are under investigation. Furthermore, 19 herbicides belonging to various chemical classes (phenylureas, chlorotriazines, triazinones, organophosphorus and chloroacetanilides) were analysed. The phenylureas are isoproturon, diuron, linuron, metoxuron, chlorotoluron, monolinuron, metabenzthiazuron and metobromuron. From the triazines group atrazine, simazine, desethylatrazine (DEA), terbutylazine, cyanazine and sebutylazine were investigated. Considered organophosphorus herbicides are glyphosate and its main metabolite aminomethylphosphonic acid (AMPA). Metazachlor and metolachlor were chosen from the chloroacetanilide herbicide group.

Sample preparation and extraction

Surface water and wastewater were successively filtered through 3- and 1-µm glass fibre filters (Pall Corporation, Ann Arbor, USA) to eliminate the coarse suspended matter and then filtered through 0.45 µm cellulose acetate filters (Sartorius, Göttingen, Germany). For the extraction of the pharmaceuticals, the 2 l samples were acidified to pH 4 with diluted sulphuric acid solution (25%). Afterwards, 3 ml of Na_2-EDTA 0.5 M were added per liter of water and extracted in the following 24 to 48 h to minimise degradation. All target compounds were concentrated by Solid-Phase Extraction (SPE) on polymeric cartridges (Waters Oasis® HLB, 200 mg, 6 mL) using an automated SPE workstation (Caliper Autotrace, Teralfene, Belgium). One liter of the samples was loaded on 200 mg–6 ml HLB at 10 ml/min. The sorbents were previously conditioned using 5 ml of methanol and 5 ml of Milli-Q water at pH 4. After sample loading, the cartridges were rinsed with 5% of methanol in water (5 ml) and dried with a stream of N_2 for 15 min. The selected compounds were eluted using methanol (2 × 5ml). Extracts were concentrated with a gentle stream of N_2 and redissolved in 1 ml of a water/acetonitrile 75/25 (*v/v*) mixtures before HPLC injection.

Due to their specific chemical properties, glyphosate and its main metabolite AMPA were analysed by derivatisation with Fluorenylmethyloxycarbonyl chloride (FMOC-Cl), off-line SPE and LC-MS/MS. The derivatisation was obtained by adding 5 ml of Borate buffer (120 mM) and 7 ml of FMOC-Cl solution (2.5 mM in acetonitrile) to 50 ml of filtered sample in a 100-ml glass bottle. The mixture was left to react overnight at room temperature, then the derivatisation was stopped by adding 0.5 ml of concentrated phosphoric acid. After a dilution with DI-water, the derivatised analytes were extracted by automated off-line SPE on Waters Oasis HLB cartridges, using the above-mentioned Caliper Autotrace SPE Workstation.

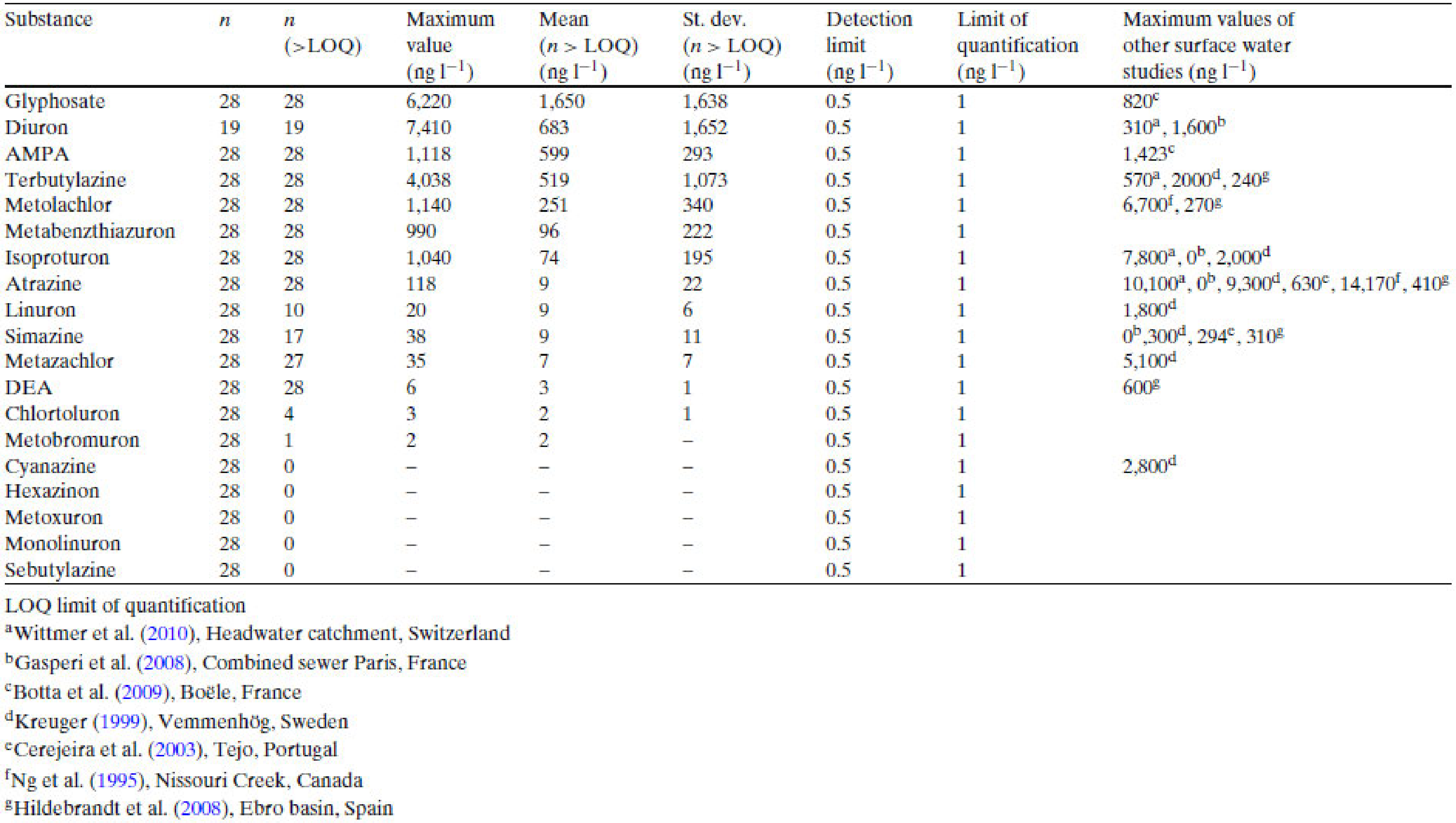
LC/MS–MS analysis
The chromatographic system consisted of an Ultimate 3000 Intelligent LC system (Dionex, Sunnyvale, USA) with a binary high-pressure gradient pump HPG-3200, an automatic injector WPS-3000 and a column oven TCC-3100. For the analysis of the pharmaceuticals and hormones, the chromatographic column was a NUCLEODUR C18 GRAVITY column, 125 × 2 mm internal diameter, 3 µm particle size (Macherey Nagel, Düren, Germany). The MS–MS analyser consisted of a triple quadrupole mass spectrometer API 3200 (Applied Biosystem/MDS Sciex, Rotterdam, The Netherlands) equipped with a Turbo Ion Spray interface (Electrospray). N_2 was used as nebuliser, curtain and collision gas. Sulfonamides, tetracyclines and diclofenac were analysed in positive electrospray ionisation mode (+ESI) while estrogens and ibuprofen were analysed separately in negative electrospray ionisation mode (−ESI). The API 3200 triple quadrupole mass spectrometer was running under Multiple Reaction Monitoring mode (MRM) for increased sensitivity, with two MRM transitions for each molecule for improved selectivity. Optimal conditions were chosen in each mode. Each compound was analysed separately by flow injection analysis, in positive and negative mode, to find the optimum parameters (voltages and gas flows) for maximum intensities. Calibration curves ranging from 1 to 100 ng/ml were used to quantify the xenobiotics. After the final calculation the majority of the substances were successfully quantified at 1 ng/L except for E2 (3 ng/L) and EE2 (6 ng/L). The choice of a single extraction method on HLB cartridges was a compromise between recovery of extraction and the ease of the method. Our method led to efficient recoveries for sulfonamides (75–85%), analgesics (80–95%) and hormones (80–90%). The recovery of tetracycline group was sufficient. For the pesticides, the analytical column was a Dionex Acclaim C18 (2 × 100 mm, 3 µm particle size) and the mobile phase was a gradient of water and acetonitrile, both containing 0.1% formic acid. The column temperature was 40°C and the flow rate was 250 µL/min. The detection and quantification were achieved by positive electrospray MS/MS in Multiple Reaction Monitoring (MRM) mode. Each compound was detected and confirmed by two MRM transitions. The FMOC derivatives were quantified by reverse-phase chromatography coupled to a triple quadrupole. The analytical column was a Macherey-Nagel Nucleodur Gravity C18 and the mobile phase was a gradient of ACN and 10 mM ammonium acetate. The oven temperature was set at 40°C, and the flow rate was 250 µL/min. The detection was achieved in negative electrospray mode, using two transitions for each compound. For the pesticides, the limit of quantification is 1 ng/L.

Results

Concentrations of dissolved pharmaceuticals and herbicides
Despite usage restrictions and the banishment of different toxic compounds, pesticides still represent an issue in water pollution. For the EU-wide banned atrazine, the measured maximum is 118 ng/L (Table 8.5-210). All samples had atrazine concentrations well above the LOQ of 1 ng/L indicating recent use of this herbicide. Due to their broad application fields, determining the main origin of pesticides found in water streams is not always easy. Glyphosate (6,220 ng/L), AMPA (1,118 ng/L), diuron (7,410 ng/L), terbutylazine (4,038 ng/L) and metolachlor (1,140 ng/L) were the pesticides found in the highest concentrations during flood events in the Mess River. Metoxuron, cyanazine, hexazinone, sebutylazine and monolinuron have not been detected in the investigated flood events. According to Skark et al. (2004) the occurrence of herbicides such as chlortoluron, isoproturon and terbutylazine in surface water is due to agricultural application. In Luxembourg, terbutylazine and metolachlor are used in the production of maize, rape, turnip and cabbage. Isoproturon is mainly applied in the cultivation of grain. The occurrence of diuron

(house paint and antifouling) and glyphosate (fruit, vegetable, not cultivated land, private gardens, parks and public areas) primarily results from their use in settlement areas. A snapshot sampling in different catchments all over the country supports these assumptions (results not shown). Corresponding distribution patterns appeared to be significantly different depending on the land-use of the river catchments. Glyphosate and AMPA were found in higher concentrations in urban basins, whereas terbutylazine, metolachlor, atrazine and DEA were prominent in rural zones. In addition, Table 8.5-210 illustrates that the pesticide concentrations in the Mess are in the same range than those detected in other river systems.

Table 8.5-210: Measured concentrations of selected dissolved herbicides in three flood events from May/June 2008 in comparison to other studies, detection limits and limits of quantification



Substance	*n*	*n* (>LOQ)	Maximum value (ng l^{-1})	Mean (*n* > LOQ) (ng l^{-1})	St. dev. (*n* > LOQ) (ng l^{-1})	Detection limit (ng l^{-1})	Limit of quantification (ng l^{-1})	Maximum values of other surface water studies (ng l^{-1})
Glyphosate	28	28	6,220	1,650	1,638	0.5	1	820^{c}
Diuron	19	19	7,410	683	1,652	0.5	1	310^{a}, $1{,}600^{b}$
AMPA	28	28	1,118	599	293	0.5	1	$1{,}423^{c}$
Terbutylazine	28	28	4,038	519	1,073	0.5	1	570^{a}, 2000^{d}, 240^{g}
Metolachlor	28	28	1,140	251	340	0.5	1	$6{,}700^{f}$, 270^{g}
Metabenzthiazuron	28	28	990	96	222	0.5	1	
Isoproturon	28	28	1,040	74	195	0.5	1	$7{,}800^{a}$, 0^{b}, $2{,}000^{d}$
Atrazine	28	28	118	9	22	0.5	1	$10{,}100^{a}$, 0^{b}, $9{,}300^{d}$, 630^{e}, $14{,}170^{f}$, 410^{g}
Linuron	28	10	20	9	6	0.5	1	$1{,}800^{d}$
Simazine	28	17	38	9	11	0.5	1	0^{b},300^{d}, 294^{e}, 310^{g}
Metazachlor	28	27	35	7	7	0.5	1	$5{,}100^{d}$
DEA	28	28	6	3	1	0.5	1	600^{g}
Chlortoluron	28	4	3	2	1	0.5	1	
Metobromuron	28	1	2	2	–	0.5	1	
Cyanazine	28	0	–	–	–	0.5	1	$2{,}800^{d}$
Hexazinon	28	0	–	–	–	0.5	1	
Metoxuron	28	0	–	–	–	0.5	1	
Monolinuron	28	0	–	–	–	0.5	1	
Sebutylazine	28	0	–	–	–	0.5	1	

LOQ limit of quantification

[a] Wittmer et al. (2010), Headwater catchment, Switzerland

[b] Gasperi et al. (2008), Combined sewer Paris, France

[c] Botta et al. (2009), Boële, France

[d] Kreuger (1999), Vemmenhög, Sweden

[e] Cerejeira et al. (2003), Tejo, Portugal

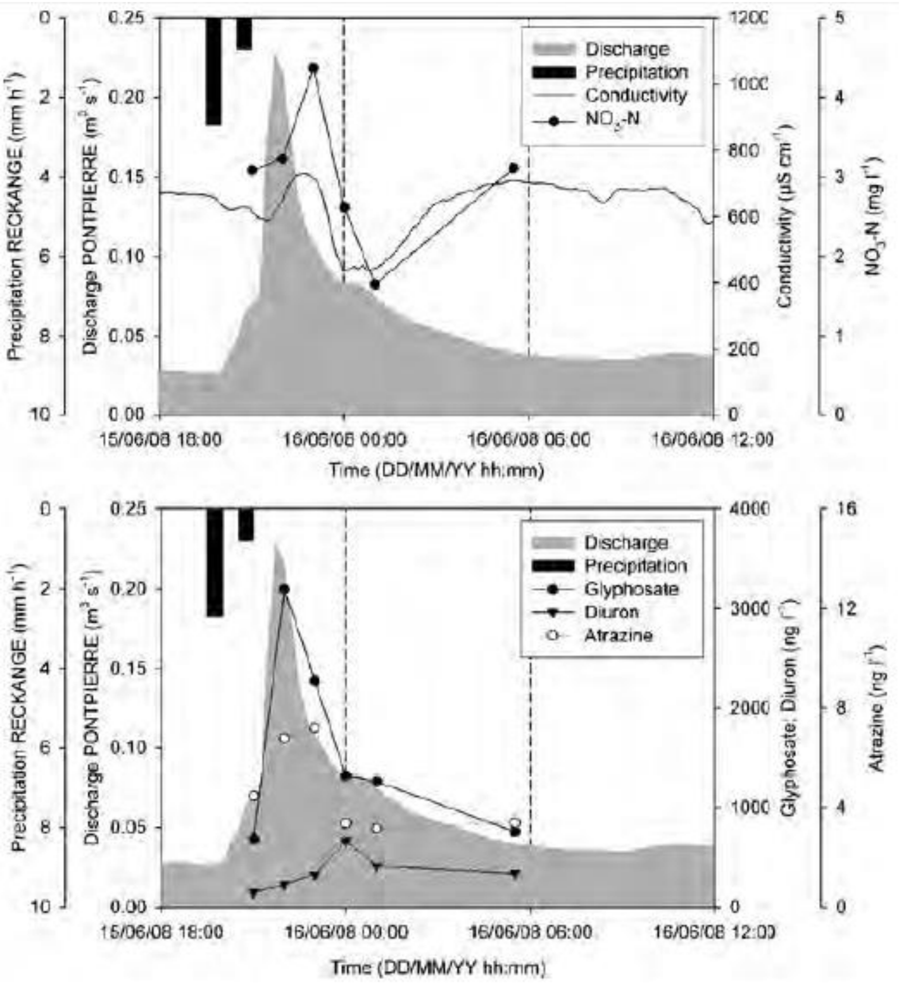
[f] Ng et al. (1995), Nissouri Creek, Canada

[g] Hildebrandt et al. (2008), Ebro basin, Spain

Chemographs of dissolved herbicides during flood events
Several flood waves with different precipitation intensities and runoff ratios have been investigated and sampled in early summer 2008, a main application period of herbicides in the area under investigation. Three events have been selected according to different precipitation intensities for a further thorough analysis. The following results in Figures 7.5-169, 7.5-170 and 7.5-171 are presented in the order of increasing flood intensity.

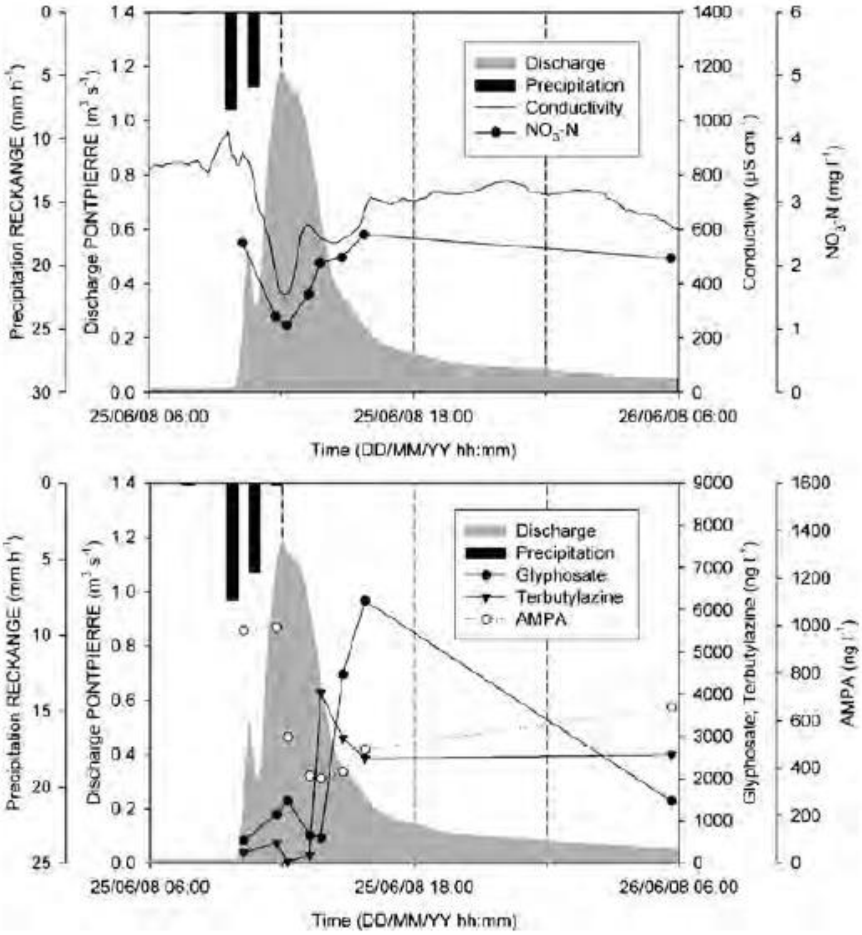
The flood event of 15 June 2008 is characterised by low rainfall (3.5 mm), low precipitation intensities (max. 1.2 mm/10 min) and a small runoff ratio (2.4%; Figure 8.5-174). At 10 p.m., a single peak of dissolved glyphosate (3,000 ng/L) is observed, originating from the vicinity of the gauging station, including the motorway crossing the Mess River approximately 150 m upstream and the village of Pontpierre. The local department of highways, the municipal administrations and private house owners apply this herbicide for weed removal at roadsides. A peak of atrazine (8 ng/L) is registered 1 h later together with increasing NO_3–N (4.5 mg/L) and the maximum of a small conductivity peak. This runoff component from agricultural sources is followed by peaking diuron concentrations (700 ng/L) originating from runoff from the settlement area of Reckange. This peak goes in parallel with declining conductivity, indicating dilution with low mineralised rainwater, which is supposed to be flushed from impervious surfaces in the relevant village.

Figure 8.5-174: **Dissolved NO_3–N, glyphosate, diuron, atrazine and conductivity measured during the flood event in the Mess River catchment on 15 June 2008**



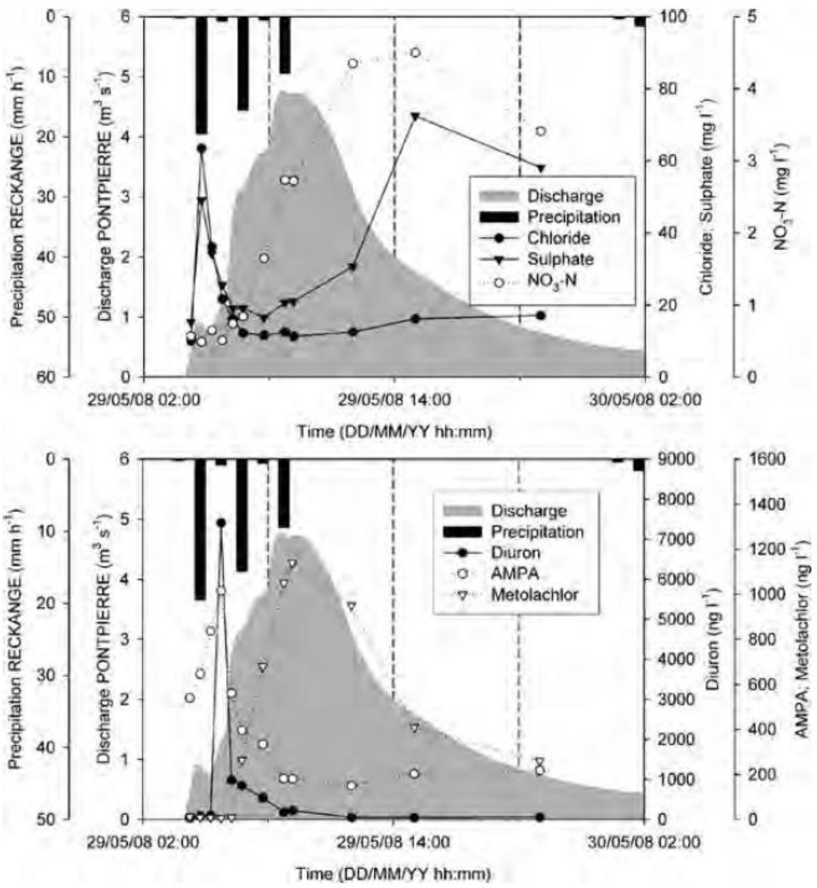
The flood event of 25 June 2008 (Figure 8.5-175) is characterised by a higher rainfall (13.7 mm), higher precipitation intensities (4.3 mm/10 min) and a higher runoff ratio (3.7%) than the first flood event on 15 June 2008. The first concentration peak of glyphosate (1,500 ng/L) at 12 a.m. originates from the vicinity of the stream gauge mainly from the town of Ehlange. Between the flood events on 15 June (Figure 8.5-174) and 25 June (Figure 8.5-175), pesticides have again been applied in the catchment area, which is indicated by a late distinct glyphosate peak (6,000 ng/L) in the falling limb (3 p.m.). AMPA shows a dilution curve in parallel to peaking discharge, but this concentration decrease is shifted 2 h after the discharge peak. The highest concentrations of terbutylazine (4,000 ng/L) are measured when AMPA exhibits the biggest dilution; this water mainly originates from the agricultural surroundings of Reckange.

Figure 8.5-175: **Dissolved NO_3–N, glyphosate, terbuthylazine, AMPA and conductivity measured during the flood event in the Mess River catchment on 25 June 2008**



The flood event of 29 May 2008 (Figure 8.5-176) is characterised by the highest rainfall intensities (10.1 mm/10 min) and the highest runoff ratio (9.6%) from the selected flood events. It shows a clear succession of different runoff components. The first discharge originates from impervious areas near the stream gauge, shown by a first small discharge peak with high concentrations of dissolved chloride (flushed atmospheric deposition material), sulphate (weathering material) and glyphosate (5,075 ng/L, not shown). In the following rising limb, the sewer overflows of Reckange leads to high AMPA (1,100 ng/L) and diuron (7,000 ng/L) concentration peaks, which are diluted afterward by the main discharge peak. Simultaneously, isoproturon (1,040 ng/L) and atrazine (118 ng/L) concentrations rise. Some hours later, a further runoff component contains surface runoff from arable land highlighted by an increase of the metolachlor concentration up to 1,200 ng/L. A distinct NO_3–N curve indicates the soil water component followed by a late peak of dissolved sulphate representing the final groundwater component. Sulphate originates from gypsum layers and gypsum pockets incorporated in the local bedrock.

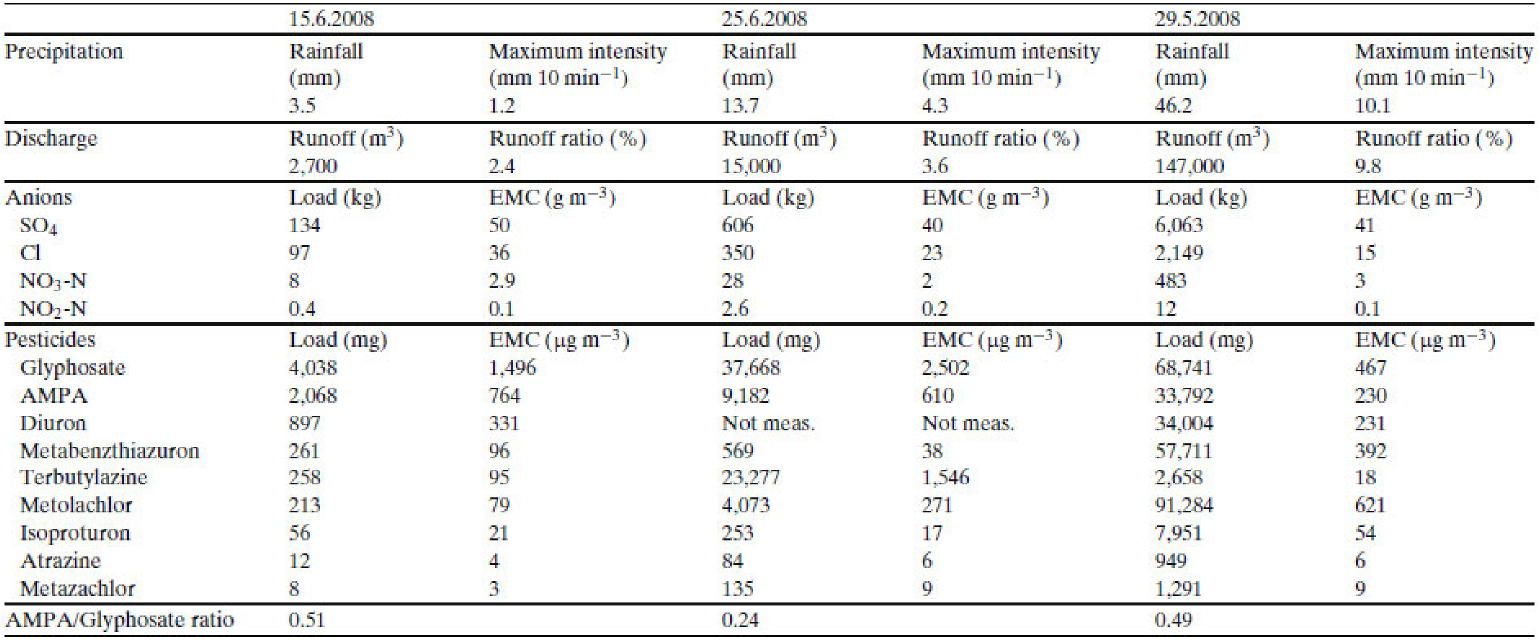
Figure 8.5-176: **Dissolved chloride, sulphate, NO_3–N, diuron, AMPA and metolachlor measured during a flood event in the Mess River catchment on 29 May 2008**



Substance loads and event mean concentrations

The load of different substances has been calculated by multiplying substance concentrations with corresponding discharge values. The load of a single flood is the total of these products and equals the area of the time series plotted against the multiplication results between discharge and substance concentration. The Event Mean Concentration (EMC) is a flow-weighted average of the constituent concentration. For an individual storm runoff event, it is defined as the total pollutant load divided by total runoff volume. Table 8.5-211 shows the loads and the EMC of different compounds calculated for the three flood events. With increasing precipitation amount and intensity, the runoff ratio increases (2.4%, 3.6%, 9.8%). Nutrient loads and loads of sulphate and chloride exhibit a strong relationship to discharged volume. The EMC of chloride decreases with rising runoff ratios, which is an indication of the lower importance of surface runoff from paved areas like rooftops or streets in stronger rainfall runoff events. On the contrary, NO_3–N exhibits the highest EMC in the biggest flood just as the EMC of metolachlor or isoproturon. This indicates a higher proportion of surface runoff from arable land and higher proportions of soil water in general. The EMCs for glyphosate and AMPA are elevated in smaller floods originating mainly from urban storm water runoff, running directly into the brook. High EMC values in this flood event of 25 June are caused by repeated applications of terbutylazine and glyphosate before the event. Furthermore, a smaller AMPA/glyphosate ratio is an indication for "fresh glyphosate sources" with only a small amount of AMPA as the relevant degradation compound. However, the study of Botta *et al.* (2009) suggests that sewage from domestic activities with cleaning agents are likely to be another source of AMPA. Here, further investigations are necessary. In total, the herbicide loads confirm the outcome of investigations by Skark et al. (2004) who concluded that non-agricultural pesticide use contributed more than two thirds of the whole observed pesticide load in the tributaries and at least one third in the River Ruhr.

Table 8.5-211: Hydro-climatological characterisation, chemical loads and corresponding event-mean concentrations of three flood events in the Mess River catchment from May/June 2008

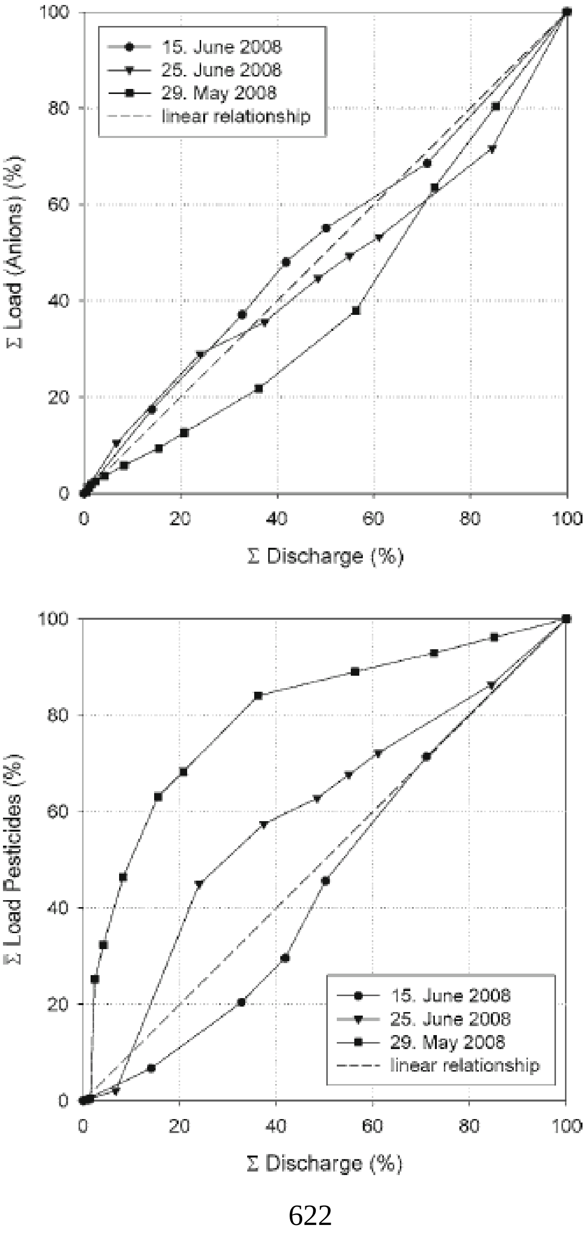


	15.6.2008		25.6.2008		29.5.2008	
Precipitation	Rainfall (mm)	Maximum intensity (mm 10 min^{-1})	Rainfall (mm)	Maximum intensity (mm 10 min^{-1})	Rainfall (mm)	Maximum intensity (mm 10 min^{-1})
	3.5	1.2	13.7	4.3	46.2	10.1
Discharge	Runoff (m^3)	Runoff ratio (%)	Runoff (m^3)	Runoff ratio (%)	Runoff (m^3)	Runoff ratio (%)
	2,700	2.4	15,000	3.6	147,000	9.8
Anions	Load (kg)	EMC (g m^{-3})	Load (kg)	EMC (g m^{-3})	Load (kg)	EMC (g m^{-3})
SO_4	134	50	606	40	6,063	41
Cl	97	36	350	23	2,149	15
NO_3-N	8	2.9	28	2	483	3
NO_2-N	0.4	0.1	2.6	0.2	12	0.1
Pesticides	Load (mg)	EMC (µg m^{-3})	Load (mg)	EMC (µg m^{-3})	Load (mg)	EMC (µg m^{-3})
Glyphosate	4,038	1,496	37,668	2,502	68,741	467
AMPA	2,068	764	9,182	610	33,792	230
Diuron	897	331	Not meas.	Not meas.	34,004	231
Metabenzthiazuron	261	96	569	38	57,711	392
Terbutylazine	258	95	23,277	1,546	2,658	18
Metolachlor	213	79	4,073	271	91,284	621
Isoproturon	56	21	253	17	7,951	54
Atrazine	12	4	84	6	949	6
Metazachlor	8	3	135	9	1,291	9
AMPA/Glyphosate ratio	0.51		0.24		0.49	

Discussion

The results show that comparable to other studies (Wittmer *et al.* 2010; Pailler *et al.* 2009a), a distinct relationship between discharge and pollutant concentrations does not exist for pharmaceuticals or for pesticides. The variable dependence of xenobiotic concentrations to event specific conditions and processes is discussed in the following sections. Many studies have described the first flush phenomenon as a relatively high load of pollutants in the first part of runoff events. In contrast, the kinematic wave effect results in a postponement of pollutant loads in comparison to associated discharge. Lee and Bang (2000) concluded that the pollutant concentration peak occurs before the flow peak in watersheds with areas smaller than 100 ha, and the pollutant concentration peak is followed by the flow peak in the watersheds with areas larger than 100 ha. The investigation of first flush effects and kinematic wave effects is done by drawing the curve (Figure 8.5-177) that gives the variation of the cumulative pollutant mass divided by the total pollutant mass (dimensionless cumulative pollutant mass) in relation to the cumulative volume divided by the total volume (dimensionless cumulative runoff volume).

Figure 8.5-177: **Dimensionless cumulative runoff volume and runoff mass curves for measured anions (Chloride, NO_3–N, NO_2–N, Sulphate) and selected pesticides (isoproturon, atrazine and diuron) supposed to be flushed from impervious surfaces**



If the concentration remains constant during the storm event, the pollutant mass is proportional to the volume and the double frequency cumulating curve follows the line of origin with a gradient of one (Line of Identity). If the data for a particular storm lies above this, a first flush is suggested. If the curve falls below the Line of Identity, the main substance load is observed coming after the discharge peak. This can be caused by the kinematic wave effect, the later arrival of compounds originating farer away from the gauging station or a late reaction of deeper soil or groundwater components. Figure 8.5-177 highlights that in the flood event with the lowest precipitation intensity, measured anions are not important and the curve goes along the Line of Identity. In the bigger events, the late soil water component with measured anions is more important. Therefore, this line lies under the Line of Identity. In contrast, the cumulative load curves of the selected pesticides lay about this line. The maximum divergence was used as a measure of the magnitude of the first flush. A significant first flush was considered to have occurred in the biggest event on 29 May 2008. The presence of accumulated materials on the surfaces tends to be responsible for the first flush phenomenon of herbicides.

The results confirm the investigations by Skark *et al.* (2004), who concluded that pathways for pesticide input to the receiving waters were related to both, surface runoff and underground passage. Two thirds of the observed diuron load in the surface water resulted from an input by direct runoff. The corresponding spills cause high but short-lived concentration peaks. The authors interpreted this as a result of total pesticide application to impervious surfaces. As a consequence, the high corresponding concentrations in the tributary infringe current regulations and recommendations. The directive 2008/105/EC of the European Parliament and of the Council on Environmental Quality Standards in the field of water policy contains environmental quality standard parameters. The maximum allowable concentration for diuron of 1.8 µg/L is exceeded fourfold by measured 7.41 µg/L in the flood event of 29 May 2008. The determination of the impact of storm water runoff from settlement areas can greatly increase the predictive power of models of urban effects on water quality. In addition, the results show that like Hatt *et al.* (2004) demonstrated, very small proportions of impervious area are capable of increasing pollutant concentrations, as long as there is a direct connection between the impervious area and the corresponding stream. Consequently, the aim must be to break the direct linkage between the impervious areas and the receiving water.

Furthermore, it seems that for some compounds the antecedent conditions before flood events, such as precipitation quantities, results in an exhaustion of potential sources, so that less material is available to be washed off in subsequent events. Kim *et al.* (2006) and Krein and Schorer (2000) show similar results for dissolved and particle bound pollutants. An example is the short succession of the three thunderstorms with high precipitation amounts, which induced the flood event in the Mess River on 29 May 2008 (Figure 8.5-176). Areas directly connected to the Mess River are flushed by the first event and the second and the third thunderstorms do not mobilise further dissolved diuron, AMPA or chloride. These com-pounds show distinct peaks after the first rainfall event and no reaction thereafter.

Conclusion

Overall, the pharmaceutical and pesticide concentrations in the Mess are comparable with those detected by other authors in different river systems. Some investigated pesticide concentrations in the tributary temporarily infringe current regulations. The analysis of flood events using rainfall pattern, hydrograph and dissolved xenobiotic chemographs can provide a detailed insight into the temporal structure of flood events. However, the corresponding anthropogenic sources show a temporal and spatial variability, caused by different rainfall patterns and distributions as well as different characteristics (e.g. retention capacities) of the sewer systems. The discharge increase from anthropogenic sources is mainly brought about by overlandflow, the influx of surface water from the road network, as well as from residential areas. It is difficult to postulate that recurring characteristics of the processes control the xenobiotics chemographs, due to highly variable anthropogenic factors. These are the changing amount of pharmaceutical consumption, sewage water treatment plant control programs, pesticide application dates and amounts, or the heterogeneous urban storm water runoff generation. Furthermore, hydraulic processes within current flood waves like kinematic wave effects influence the event structure e.g. time lags between discharge and dis-solved loads. The load of dissolved pesticides reaching the stream gauge is primarily determined by the amount applied to the surfaces within the catchment area. In the Mess River catchment, a characteristic difference between urban and agricultural induced pollution by pesticides exists in the concentration/load relationship. Storm water runoff from urban areas causes short-lived but high-pollutant concentrations and moderate loads in the Mess River, whereas moderate concentrations and high loads are representative for agricultural inputs to the drainage system. Non-agricultural pesticides contribute to a large part to the observed pesticide loads in the Mess.

Generally, kinematic wave effect, accumulation, exchange, dilution and mixture processes modify the flood wave and its composition within the watercourse. The measurements prove that the influence of kinematic wave effects on the relationship between hydrograph and chemographs should not be neglected in smaller basins. The time lag shows that it is not always possible to connect analysed substances of defined samples to the corresponding section of the hydrograph. The different velocities indicate that after the substances have been transported over several hundred meters, there is no relationship between those parameters. Consequently, classification be-tween discharge component and dissolved substances at the sampling points is impeded. These results highlight that simple rating curves between discharge and pollutant loads intended to calculate the total load by hydrographs are overly simple. At the Mess River, even the position of the gauging station is important, because the time lag between chemical signal and discharge increases over distance.

However, every flood event is unique due to variable rainfall characteristics, changing catchment conditions, as well as anthropogenic activities. The next step is the investigation of long lasting, low intensity winter precipitation events that cause singular broad discharge maxima, which are primarily composed of laterally flowing soil water and groundwater.

Assessment and conclusion by applicant:
The article describes a monitoring study in an agricultural area in Luxembourg. The study design and the analytical methods are well described. The highest concentration of glyphosate was 6.22 µg/L and for AMPA was 1.118 µg/L.
The article is considered reliable.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions, the study design and analytical method are well described.

The following information can be retained:
The study area is at the small Mess catchment in the southwestern part of Luxembourg. The basin has a total surface area of 32.5 km^2 at the stream gauge. The land use in the basin consists of grassland (58%) and arable land (22.7%); forest is about 9.7%, urban and industrial areas amount to 8.7%, 2.3% contain the road and rail network. The most widespread crops are maize, rapeseed oil and winter wheat. Runoff from several roads, effluents from small industries and untreated wastewaters from solitary farms and storm drainages of the combined sewer system influence river water quality.

Study reports maximum concentration throughout the study period of 6.22 µg/L for glyphosate and 1.118 µg/L for AMPA.

Is also decribed the runoff dynamics of pesticide during selected flood events of different intensities, and characterized the origine of the peak concentration of glyphosate:

- One flood event (15 June 2008) characterised by low rainfall (3.5 mm), low precipitation intensities (max. 1.2 mm/10 min) and a small runoff ratio (2.4%). A single peak of dissolved glyphosate (3,000 ng/L) is observed, originating from the vicinity of the gauging station, including the motorway crossing the Mess River approximately 150 m upstream and the village of Pontpierre.
- One flood event (25 June 2008) characterised by a higher rainfall (13.7 mm), higher precipitation intensities (4.3 mm/10 min) and a higher runoff ratio (3.7%): a first concentration peak of glyphosate (1,500 ng/L) originates from the vicinity of the stream gauge mainly from the town of Ehlange
- One flood event (29 May 2008) characterised by the highest rainfall intensities (10.1 mm/10 min) and the highest runoff ratio (9.6%): It shows a clear succession of different runoff components. The first discharge originates from impervious areas near the stream gauge, shown by a first small discharge peak with high concentrations of dissolved glyphosate (5,075 ng/L) among others.

Study authors concludes that "anthropogenic sources show a temporal and spatial variability, caused by different rainfall patterns and distributions as well as different characteristics (e.g. retention capacities) of the sewer systems. The discharge increase from anthropogenic sources is mainly brought about by overlandflow, the influx of surface water from the road network, as well as from residential areas".
"However, every flood event is unique due to variable rainfall characteristics, changing catchment conditions, as well as anthropogenic activities"

The article is considered reliable.

Data point:	CA 7.5/066 CA 7.5/067 (Translation)
Report author	Busetto, M. *et al*.
Report year	2010
Report title	Survey of herbicide glyphosate and degradation product aminomethyl phosphonic acid in waterways of Monza-Brionza province
Document No	Il bolletino 2010/4
Guidelines followed in study	None
Deviations from current test guideline	Not applicable

GLP/Officially recognised testing facilities	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Reliable

During the period 2006-2009 ARPA (the Lombardy Regional Environmental Agency) has been collecting analytical data concerning the presence and concentration of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) in the water of the Lambro, Seveso and Terrò rivers in the Brianza region. River flow-rate, COD, BOD_5 and conductivity have also been measured in each sample.

Both AMPA and glyphosate have been found in every sample, with AMPA concentrations always higher than glyphosate concentrations. Larger amounts of herbicide have been detected in water sampled in autumn, with concentrations decreasing in the following months. Our data are consistent with the available information about the use and release of the herbicide during the year.

Materials and Methods

Monitoring in the Lombardy Region and Purpose of the Study

In pursuing the objective envisaged in the "National Plan for the Control of Environmental Effects of Plant Protection Products" to adjust controls on the basis of substances actually used in its territory, the Lombardy Region has included glyphosate and AMPA among the compounds to be periodically monitored in its waters. The ARPA Department of Monza was entrusted with the task of monitoring the possible presence of glyphosate and ammonium methylphosphonic acid in the Lambro and Seveso waterways, in the area around the capital of the province of Monza-Brianza, by relying on measuring and sampling stations assigned as follows:

- Lambro river (Stations of Lesmo and Cologno Monzese);
- Seveso creek (Stations of Lentate sul Seveso and Bresso).

Samples were collected at periodic intervals, in the months of March, June, September and December during the 2007-2009 three-year period. An additional sampling point was added in 2009 along the Terrò creek, near Cesano Maderno, in the proximity of the confluence into the Seveso river. The results obtained are detailed in this article. The concentrations of glyphosate and AMPA, as well as their trends recorded during the three-year observation period detected on the samples analyzed were compared with some parameters (Flow, Conductivity, COD and BOD_5) characteristic of the watercourses under study. In March 2010, the data relating to glyphosate and AMPA became available also for the three waterways relating to the collection points of Lesmo, Lentate and Cesano Maderno.

The Lambro River and the Seveso and Terrò Creeks

The Lambro river originates in the territory of the municipality of Magreglio (Como), continues towards Vallassina and feeds the lake of Pusiano. It reaches Brianza by flowing at the foot of morainic hills, where it collects the waters of numerous streams, irrigation ditches and small lakes of the Brianza area.

It quickly reaches the city of Monza through the homonymous park. It continues its course east of Milan, in the low Lombard plain, until it enters the Po river. In the stretch of river between Lesmo and Cologno Monzese, the Lambro river has relatively constant average flow values between 3 m^3/s (Lesmo) and 5-10 m^3/s (Cologno Monzese); however, frequent flood phenomena related to rainfall may bring about notable flow fluctuations. The analytical findings relating to macro-descriptors, which represent the state of health of stream waters, point to a marked deterioration of the river waters downstream of the city of Monza, with a transition of the environmental quality from sufficient (Lesmo station) to poor (Cologno Monzese station). However, it should be noted that the parameters measured in the latter station are influenced by the water contributions of the purification plant of the Consorzio di Bonifica dell'Alto Lambro, which discharges treated water a few tens of meters upstream of the Cologno Monzese sample collection point.

The Seveso creek originates at the foot of Mount Pallanza (province of Como), near the Swiss border, and dumps into the Naviglio della Martesana within the urban circle of the city of Milan. In the first section of its course, the creek flows through a hilly area, passing through inhabited places of modest size and relatively distant from each other. In the valley area, the Seveso creek seamlessly crosses broad urban centers, consequently behaving much like a sewer. The control stations of Lentate and Bresso are located, respectively, at the end of the mountainous stretch and downstream of the main industrial areas and urban settlements in the western sector of Brianza (Cesano Maderno and Varedo). In this stretch, the flow rates observed are modest, even with respect to the measured values of the Lambro, with average values between 0.5-1.0 m^3/s, and peaks up of about 9.0 m^3/s in periods of swells, without remarkable differences between the stations of Lentate and Bresso. The state of health of the creek is quite compromised: macro-descriptors show a change in the environmental quality from poor (Lentate station) to bad (Bresso station).

The Terrò creek is indebted to the union of several streams in the area of the morainic hills between Cascina Inchigollo and Cascina Cassinazza, collecting rainwater and some springs. After a journey of about 20 kilometers, it flows into Seveso creek. In its terminal part, crossing markedly anthropized and industrialized areas (Mariano Comense and Meda), it undergoes a marked deterioration as it pertains to water quality, which practically becomes sewage. The flow rates are minimal in dry periods, in the absence of rainfall.

AMPA and Glyphosate were determined by HPLC equipped with a fluorescence detector, in accordance with the MTMI604 Rev.0 method.

Results

Table 8.5-212 shows the Flow, COD, BOD_5 and Conductivity values detected in water samples of the Lambro river, collected from the Lesmo and Cologno Monzese stations.

The values obtained do not differ, in terms of average and maximum values, from those published in previous years concerning the health of rivers north of Milan.

Table 8.5-212: Flow rate, COD, BOD_5 and Conductivity values detected in Lambro river at the Lesmo and Cologno Monzese stations, during 2007-2009

Date of sampling	Flow Capacity (m^3/s)		COD (mg/L)		BOD_5[1] (mg/L)		Conductivity (µS/cm)	
	Lesmo	**Cologno Monzese**	**Lesmo**	**Cologno Monzese**	**Lesmo**	**Cologno Monzese**	**Lesmo**	**Cologno Monzese**
Mar-07	5.2	16.3	70	74	8	6	--	--
Jun-07	5.9	14.4	29	37	<2	12	400	--
Sep-07	0.9	3.8	10	31	8	5	552	975
Dec-07	2.8	5.0	18	42	<2	5	536	869
May-08	3.0	5.3	17	31	<2	3	478	810
Jun-08	13.7	13.9	14	28	2	2	390	468
Sep-08	--	--	16	27	<2	3	509	852
Dec-08	6.5	12.0	15	74	2	8	448	765
Mar-09	4.8	7.5	11	16	<2	2	446	630
Jun-09	2.6	6.5	18	41	2	7	448	665
Sep-09	0.4	4.1	15	75	<2	3	492	924
Dec-09	2.3	6.3	13	48	<2	9	485	731
Value avg	**4.4**	**8.6**	**21**	**44**	**3**	**5**	**471**	**767**

[1] A value of 2 was assumed in calculating the average value where the measured concentration was <2

The increase in COD and BOD_5 values show the deterioration of the environmental quality of the river as it passes through the city of Monza, as a result of the discharge of civil waste, which determines the organic pollution of waters. The increase in conductivity is also remarkable and testifies to a significant contribution of ionic products in the deterioration of water quality. For example, a significant increase in the concentration of nitrates had previously been reported at the point the river transits between the Stations of Lesmo and Cologno Monzese, and had been related to the purification processes that take place upstream of the latter station, in the of Treatment Plant of Upper Lambro.

Taking into consideration the data relating to the individual stations, variances over time of the different parameters do not seem to be influenced by the seasons; in fact, the same months in subsequent years yield differing values. In particular, variances in flow rates are probably not so much related to season effects, which occur with a certain periodicity, but rather by the extent of rainfall recorded during the sampling period.

Likewise, Table 8.5-213 shows the values yielded on the samples of the waters of the Seveso creek collected from the Lentate and Bresso stations. The high concentrations of COD and BOD_5 confirm the poor water quality, with values comparable to each other throughout the course of the stream monitored by the ARPA of Monza. As regards conductivity, similar parameter values are observed in water samples collected from the Lentate and Bresso stations. This trend testifies to considerable pollution, due to ionic substances, which is greater not only than the values yielded by samples of the Lambro river collected at the Lesmo station, but also than those measured at the Cologno Monzese station. Just like the Lambro, for the Seveso too changes in values with respect to the monitored parameters do not seem to show trends over time linked to seasonal phenomena. The flow rates are much lower than those recorded for the Lambro. Only on particular occasions are the maximum values observed at the Lentate Station comparable to the average values calculated for the Lambro.

Table 8.5-213: Flow rate, COD, BOD_5 and Conductivity values detected in the Seveso river at Lentate and Bresso stations, during 2007-2009

Date of sampling	**Flow Capacity (m^3/s)**		**COD (mg/L)**		**BOD_5[1] (mg/L)**		**Conductivity (µS/cm)**	
	Lentate	**Bresso**	**Lentate**	**Bresso**	**Lentate**	**Bresso**	**Lentate**	**Bresso**
Mar-07	0.6	1.0	55	57	<2	5	--	--
Jun-07	2.1	2.3	31	28	6	9	--	--
Sep-07	0.5	1.1	50	37	11	11	1250	894
Dec-07	0.5	1.0	45	33	<2	<2	1151	1082
May-08	0.7	1.2	57	59	2	2	1089	1123
Jun-08	--	1.6	26	26	<2	<2	712	643
Sep-08	0.5	0.5	40	31	<2	5	1559	762
Dec-08	4.0	1.1	24	37	5	8	437	349
Mar-09	1.5	1.4	30	30	3	6	783	769
Jun-09	1.2	--	28	28	7	6	742	492
Sep-09	0.5	0.9	22	31	<2	3	1165	1053
Dec-09	4.5	1.0	22	25	<2	4	924	904
Value avg	**1.5**	**1.1**	**36**	**35**	**4**	**5**	**981**	**807**

[1] A value of 2 was assumed in calculating the average value where the measured concentration was <2

Table 8.5-214 shows the Flow, COD, BOD_5 and Conductivity values found on the samples collected from the Terrò creek, in the proximity of Cesano Maderno in 2009 only, the period in which the ARPA of Monza began its monitoring activities. The values yielded show a relatively constant trend of the parameters over the months in which monitoring was conducted, highlighting a high degree of pollution of organic nature, pertaining to ionic products. The flow rates are very limited, with values at almost zero in the winter months. Regarding the presence of glyphosate herbicide and the AMPA degradation product, the relevant data are detailed in Tables 7.5-199, 7.5-200 and 7.5-201. All the three waterways sampled show average values of concentrations higher than 0.1 µg/L, which are comparable with data relating to the presence of these pollutants reported in the relevant literature.

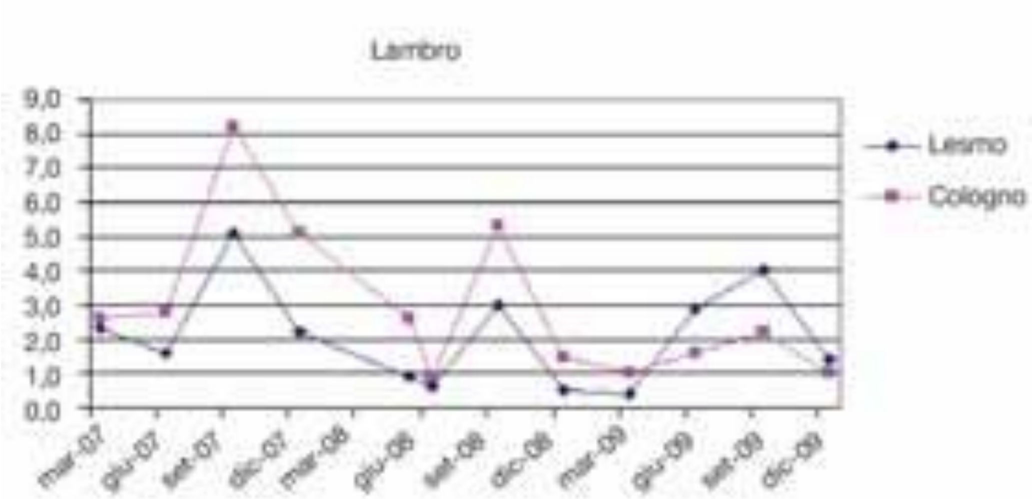
The AMPA/Glyphosate ratio in all the cases under study is skewed in favor of the degradation product, in accordance with the half-life times of the two compounds. Hence the accumulation of aminomethylphosphonic acid in the environment. Figure 8.5-178 shows trends relating to the sum of the concentrations of aminomethylphosphonic acid and the parental product measured on water samples collected from the Lambro river, in the Lesmo and Cologno Monzese stations. Unlike what has emerged for COD, BOD_5 and Conductivity, the trend of concentrations is dependent on the period in which sampling was performed.

Table 8.5-214: Flow rate, COD, BOD_5 and Conductivity values detected in the Terrò creek near Cesano Moderno during 2009

Date of sampling	Flow Capacity (m^3/s)	COD (mg/L)	BOD_5 [1] (mg/L)	Conductivity (µS/cm)
	Cesano Maderno	**Cesano Maderno**	**Cesano Maderno**	**Cesano Maderno**
Mar-09	0.2	25	3	788
Jun-09	0.3	34	4	750
Sep-09	0.2	25	<2	859
Dec-09	0.1	35	2	1002
Value avg	**0.2**	**30**	**3**	**850**

[1] A value of 2 was assumed in calculating the average value where the measured concentration was <2

Figure 8.5-178: Variations in the sum of AMPA and glyphosate concentrations observed on samples of water of the Lambro river, collected from the Lesmo and Cologno Monzese stations, during the 2007-2009 three-year period.



During the three-year monitoring period, maximum values were observed in September, with a subsequent decrease in values in the winter period. Data yielded are consistent with the methods of use and release of the herbicide during the course of the year. Glyphosate is applied to foliage during the growth period of the plant (spring and summer); subsequently, it is released and accumulates in the ground, where it undergoes partial degradation into AMPA. The two compounds are therefore washed out and transported to the waterways by the abundant rainfall that generally occurs in late summer and early autumn.

Sampling also shows greater concentrations of AMPA in samples collected at the Cologno Monzese station, downstream of the city of Monza. This phenomenon could be explained on the basis of a greater use of the herbicide in the area of the homonymous park, which is crossed by the river, and attributed to the purification processes that take place upstream of the Cologno Monzese station, in the Consortium Purification plant of the Upper Lambro (use of phosphonate-based additives). The values measured in September 2009 seem to counter this trend, highlighting an inversion between the concentrations of Lesmo and those of Cologno. The presence of the consortium plant could also be responsible for this anomaly, being the plant able to perform the dual function of removing polluting compounds from waste water, by adsorption by the treatment sludge, and to promote the formation of AMPA from additives used during the cleaning processes.

Depending on the operating mode of the plant, one of the two processes may conceivably prevail, thus altering the concentration trends. Figure 8.5-179 shows trends yielded by the sum of the concentrations of aminomethylphosphonic acid and the parental product measured on water samples collected from the Seveso creek, at the Lentate and Bresso stations. Similarly to the results yielded by the Lambro river, during the three-year monitoring period, maximum concentration values were observed in the months of September, with subsequent decrease in the winter and spring period. In this case too, there are no correspondences among COD, BOD_5 and Conductivity values. The concentration values are comparable for the entire stretch of the stream monitored by the ARPA of Monza. Pollution by AMPA and glyphosate due to the path of the stream in the hilly area richest in vegetation (upstream of the Lentate station) are not subject to significant changes at the point in which the Seveso creek transits through an area of high urban density and numerous industrial sites (stretch between the Lentate and Bresso Stations). The comparison between the concentrations monitored on the samples of the Lambro river with respect to those collected from the Seveso creek highlights a more marked degree of pollution of the latter. The average values for the sum of the concentrations of the two products are 9.1 µg/L and 7.1 µg/L, respectively in the Lentate and Bresso samples, compared to 2.1 µg/L and 2.9 µg/L for samples collected at the Lesmo and Cologno Monzese stations. The maximum values observed in the months of September fluctuate between 16.2-14.1 µg/L (Lentate) and 15.1-6.1 µg/L (Bresso), against 5.1-3.0 µg/L (Lesmo) and 8.2-2.2 µg/L (Cologno Monzese). Even the minimum values of the concentrations, which for both watercourses are those measured on samples collected at the end of winter or in the spring, are higher for the Seveso Station than for those of the Lambro point of collection. Although the Terrò creek was sampled only during 2009, it can be said that the trends observed (Figure 8.5-180) follow the same evolution as those recorded on the two main waterways: also in this case, the maximum concentrations of the two products are recorded at the end of summer and early autumn, at the end of the period of application of the herbicide.

Figure 8.5-179: **Variations in the sum of AMPA and glyphosate concentrations observed in water samples of the Seveso creek, collected at the Lentate and Bresso stations, during the 2007-2009 three-year period**

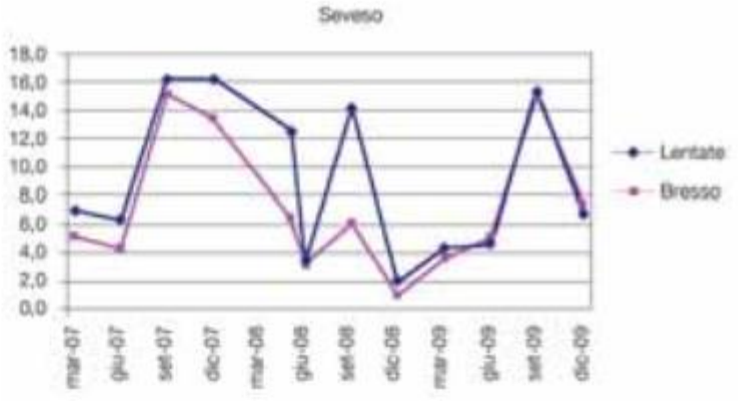


Figure 8.5-180: **Variations in the sum of AMPA and glyphosate concentrations detected in the water samples of the Terrò creek, collected near Cesano Maderno during 2009**

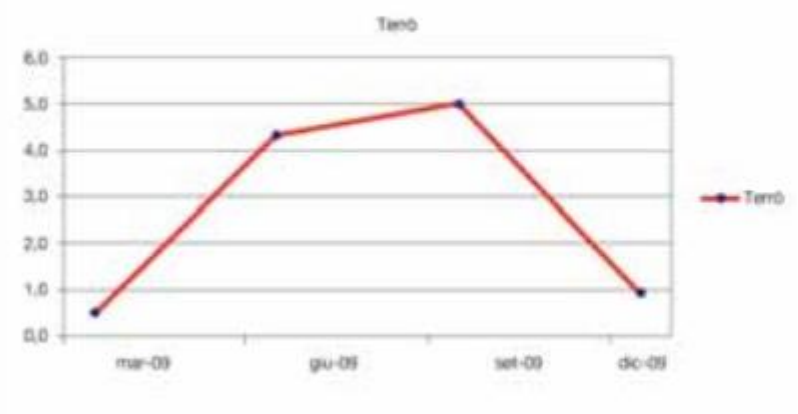


Table 8.5-215: **Values relating to the concentrations of AMPA and glyphosate found in the Lambro, at the Lesmo and Cologno Monzese Stations during 2007-2009**

LESMO STATION[1]			
Date of sampling	AMPA (µg/L)	Glyphosate (µg/L)	Sum (µg/L)
Mar-07	2.2	0.1	2.3
Jun-07	1.1	0.5	1.6
Sep-07	5.0	<0.1	5.1
Dec-07	1.7	0.5	2.2
May-08	0.7	0.2	0.9
Jun-08	0.5	<0.1	0.6
Sep-08	2.9	0.1	3.0
Dec-08	0.4	<0.1	0.5
Mar-09	0.3	<0.1	0.4
Jun-09	1.7	1.2	2.9
Sep-09	3.3	0.7	4.0
Dec-09	1.3	<0.1	1.4
Value avg	1.8	0.3	2.1
AMPA/Glyphosate ratio		6.0	
COLOGNO MONZESE STATION[a)]			
Date of sampling	AMPA (µg/L)	Glyphosate (µg/L)	Sum (µg/L)
Mar-07	2.4	0.2	2.6
Jun-07	2.3	0.5	2.8
Sep-07	7.7	0.5	8.2
Dec-07	4.7	0.4	5.1
May-08	2.1	0.5	2.6
Jun-08	0.7	0.2	0.9
Sep-08	4.9	0.4	5.3
Dec-08	1.3	0.2	1.5
Mar-09	0.9	<0.1	1.0
Jun-09	1.0	0.6	1.6
Sep-09	1.7	0.5	2.2
Dec-09	0.7	0.3	1.0
Value avg	2.5	0.4	2.9
AMPA/Glyphosate ratio		6.2	

[1] A value of 1 was assumed in calculating the average value and the sums of AMPA and glyphosate concentrations where the measured concentration was <1.

Table 8.5-216: Values relating to the concentrations of AMPA and glyphosate found in the Seveso creek, at the Lentate and Bresso Stations during 2007-2009

LENTATE STATION[1]			
Date of sampling	AMPA (μg/L)	Glyphosate (μg/L)	Sum (μg/L)
Mar-07	6.1	0.9	7.0
Jun-07	6.1	0.2	6.3
Sep-07	16.0	0.2	16.2
Dec-07	16.0	0.3	16.9
May-08	12.0	0.6	12.6
Jun-08	3.3	0.2	3.5
Sep-08	14.0	<0.1	14.1
Dec-08	1.2	0.9	2.1
Mar-09	4.2	0.1	4.3
Jun-09	4.0	0.6	4.6
Sep-09	13.2	2.2	15.4
Dec-09	6.4	0.3	6.7
Value avg	8.5	0.6	9.1
AMPA/Glyphosate ratio		14.2	
BRESSO STATION			
Date of sampling	AMPA (μg/L)	Glyphosate (μg/L)	Sum (μg/L)
Mar-07	4.1	1.0	5.1
Jun-07	3.8	0.5	4.3
Sep-07	14.9	0.2	15.1
Dec-07	13.3	0.1	13.4
May-08	6.2	0.2	6.4
Jun-08	2.9	0.2	3.1
Sep-08	6.0	<0.1	6.1
Dec-08	0.7	0.2	0.9
Mar-09	3.4	0.2	3.6
Jun-09	4.0	1.0	5.0
Sep-09	13.3	1.6	14.9
Dec-09	7.2	0.2	7.4
Value avg	6.7	0.5	7.1
AMPA/Glyphosate ratio		13.4	

[1] A value of 1 was assumed in calculating the average value and the sums of AMPA and glyphosate concentrations where the measured concentration was <1.

Table 8.5-217: Values relating to the concentrations of AMPA and glyphosate found in the Terrò creek, at the Cesane Maderno station in 2009

CESANO MADERNO[1]			
Date of sampling	AMPA (μg/L)	Glyphosate (μg/L)	Sum (μg/L)
Mar-09	0.5	<0.1	0.6
Jun-09	3.0	1.3	4.3
Sep-09	4.0	1.0	5.0
Dec-09	0.9	<0.1	1.0
Value avg	2.1	1.2	2.7
AMPA/Glyphosate ratio		1.7	

[1] A value of 1 was assumed in calculating the average value and the sums of AMPA and glyphosate concentrations where the measured concentration was <1.

Conclusions

The analyses carried out in the 2007-2009 three-year period have confirmed the broad presence of AMPA and lesser quantities of glyphosate in all the waterways monitored. The highest concentrations were detected on samples taken at the start of the autumn season, at the end of the period of application of the herbicide, carried out in the previous months during plant growth. The winter and early spring season show decreasing concentration trends. These trends occurred periodically over the three years of observation.

Among the three waterways monitored, the Seveso creek shows the highest degree of pollution, both as an average value of the sum of concentrations of the two compounds and with respect to the maximum values found for this sum, 16.3 µg/L for the Seveso creek on samples collected from the control station downstream of the hilly area with most vegetation, compared to 8.2 µg/L on the Lambro waters sampled at the point where the river has just traversed the center of Monza, and 4.3 µg/L measured for the water samples of the Terrò creek. Data relating to the sampling carried out downstream of the city of Monza seem to be influenced by water contributions from the water purification plant of the Alto Lambro Reclamation Consortium, which dumps treated water near the sampling point. It has been hypothesized that the plant fulfills at once the role of filtering out glyphosate and AMPA contained in treated waters, and of being one of the sources of pollution by AMPA due to the degradation of phosphonate additives used in cleaning processes.

Assessment and conclusion by applicant:
The article describes the monitoring results for glyphosate and AMPA from the Lombardy region in Italy. The information relies on official monitoring data of the authorities. The maximum measured concentrations for glyphosate and AMPA in river samples were 2.2 µg/L and 16.0 µg/L, respectively. The article is considered reliable.

Assessment and conclusion by RMS:
This article provides results from the ARPA Lombardia monitoring program from the period 2006-2009. It is likely that these data are included in the monitoring raw data review of [redacted], 2020 (CA 7.5/002) at least for the glyphosate concentration.

It brings further detailed information that for all 3 years monitored, the maximum values were observed in autumn, with a decrease in concentration during fall and winter. Article authors indicated that the "data yielded are consistent with the methods of use and release of the herbicide during the course of the year". However no details on use pressure of glyphosate is given in the article.

The article is considered reliable.

Data point:	CA 7.5/068
Report author	Gregoire, C. *et al*.
Report year	2010
Report title	Use and fate of 17 pesticides applied on a vineyard catchment
Document No	International Journal of Environmental Analytical Chemistry (2010), Volume 90, Number 3/6, pp. 406-420
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, analyses of samples conducted by officially recognised testing facility (Pasteur Institute of Lille (France))
Acceptability/Reliability:	Reliable

Non point source (NPS) pollution may degrade water quality and is of concern to water quality managers and environmental risk regulators whose responsibility it is to monitor the status of water bodies. There are many methods of evaluating the impact on a water body from NPS pollution, but one of the most important, effective, and unfortunately expensive methods is to monitor the quality of water flowing from a particular catchment. The flux of 17 pesticides from a small (42.7 ha) agricultural (vineyard) catchment in the Alsatian piemont (France) was systematically monitored over 4 years (2003–2006) from June to September. A metrological station is located within the catchment area and run-off of 58 run-off events was monitored throughout. A water sample for pesticide analyses was collected every 8 m^3 of run-off. Detailed information regarding pesticide application was obtained from voluntary surveys submitted annually to active farmers of the studied catchment. There was considerable climatic variation among years. However, variability of the total load of pesticides exported yearly from the catchment was low. Some 78% of the total pesticide applications in the catchment were herbicides and glyphosate was the most used herbicide with annual application ranging from 18 to 61 kg. The run-off coefficient was low (less than 2%), but the frequency of determination was high for some pesticides such as the fungicide dimetomorph (72%) and the herbicides diuron (98%) and glyphosate (100%). The pesticide export coefficients were below 1% of the applied amount, and often below 0.1%. Every water sample exceeded the EU drinking water limit of 0.1 ug/L.

Materials and methods

Study site

The studied Hohrain catchment area is located in the Alsatian vineyard (Eastern part of France, latitude 47°57′9 N; longitude 007°17′3 E; altitude 284 m). The area of the catchment is 42 hectares. The minimum and maximum annual precipitation for the period of record was 361 mm (1953) and 867 mm (1999), respectively. The average annual rainfall calculated since 1946 is 600 mm. The mean slope of the catchment is 15%. Geologically, Würm loamy loess and Oligocene clayey conglomerates and marls, as well as compact calcareous substrate, largely dominate in the upper and lower parts of the catchment, respectively. The main soil type is mostly calcareous clay loams with medium infiltration capacity. Sixty-eight per cent of the hydraulic catchment is covered by vineyards. The land use shows a gradient from mostly forested areas and partly orchard at the upstream of the basin to agricultural and vineyard areas nearer to the outlet. With more than 120 farming plots, it should be noted that the road network is dense, mostly impervious and represents about 6% of the area of catchment. The catchment can be qualified as ‘dry’ catchment with no permanent flow. The hydrological functioning can be summarised in three steps: (1) no discharge occurs without rainfall, (2) then, from >0 to 4 mm of rainfall per event only the road network contributes to the discharge, (3) finally, rainfall greater than 4 mm, the number of fields contributing to the discharge increases with both intensity and total rainfall depth (unpublished results).

Sampling and sample collection

The catchment area is equipped with a meteorological station and the outlet of the catchment has been instrumented for 4 years to monitor water, only observed during rainfall-run-off events, and pesticide concentrations. The measurement of the water level was carried out with a Venturi channel (ENDRESS and HAUSER, Huninge, France) and was performed with a surface water level sensor. Flow proportional water samples of 0.9 L were systematically collected every 8 m^3 for measurement of pesticide concentrations by a cooled automatic sampler (Hydrologic, Sainte-Foy, Québec, Canada). Samples were transferred via a polyethylene pipe to glass bottles and stored in the dark at 4°C. Twice a week, samples were collected and subsampled into plastic and glass bottles and analysed for glyphosate and aminomethyl phosponic acid (AMPA) and for the other pesticides.

Then, the samples were frozen until their analysis. According to the quality assurance procedures performed during this work, volatilisation, degradation and adsorption between the sampling and the analysis of the samples is negligible. Water sampling was conducted from 2003 to 2006, during the active wine growing season that corresponds to the major period of pesticide application and where the risk of offsite movement is large, i.e. March to October. Fifty-eight storm events were measured, which include a total of 280 collected water samples for pesticide concentration analyses and transfer quantification.

The variability of pesticide concentration was analysed over the targeted run-off events. Hydrograms and chemograms were available for each storm event from April 2003 to September 2006. Corresponding hyetograms were provided by the Meteo France station.

Estimation of applied pesticides and selection of monitored pesticides

Surveys were sent annually to the 28 farmers active in the Hohrain catchment in order to record the type and amount of pesticides applied. The survey includes the chemical species, their quantities, and their application date. No farmyard or urban area is located within the Hohrain catchment, which minimises the potential for pesticide point source pollution.

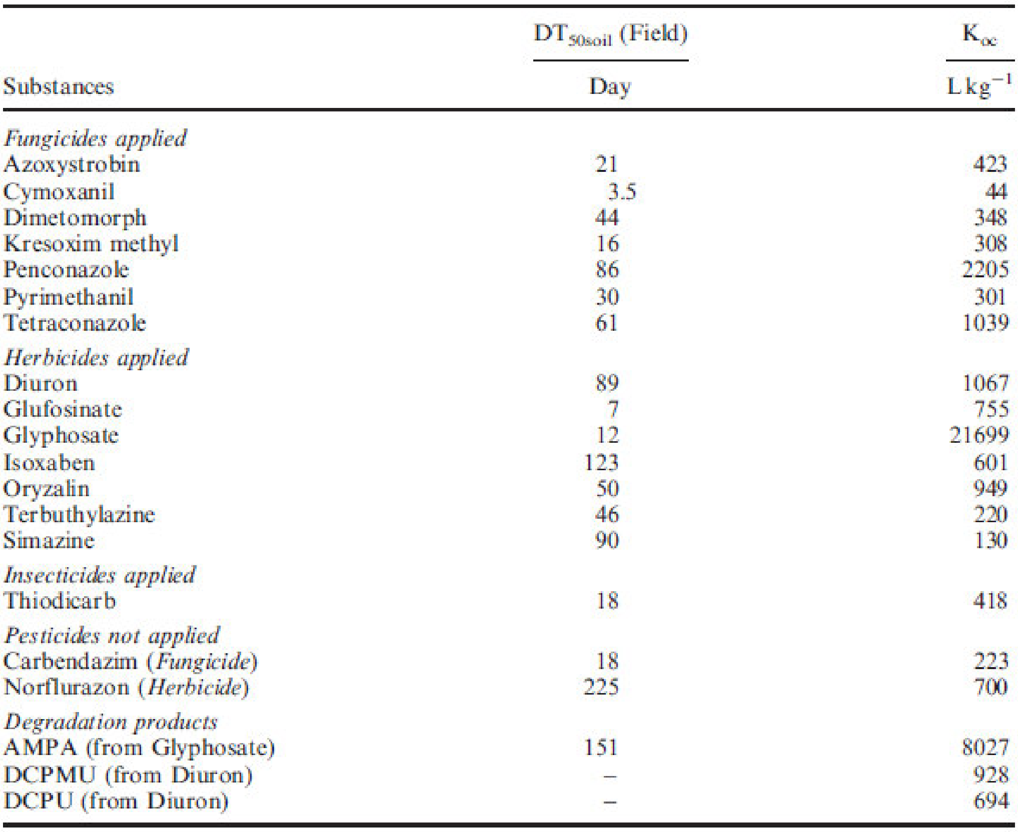
The goal of this study is to assess a broad spectrum of pesticides that display various physico-chemical characteristics in order to allow a thorough estimation of contaminant transfer at the catchment scale. The selection of compounds analysed at each sample series was based on preliminary knowledge regarding annual pesticide applications on the Hohrain catchment and on the physico-chemical properties of compounds most likely to move from their application site. According to the monitoring studies of the pesticide fate at the catchment scale, the sorption coefficient normalised to soil organic carbon content (K_{oc}) and the time for 50% decline of the initial pesticide concentration in soil, i.e. dissipation half-time (DT_{50soil}) are the important physico-chemical properties to explain pesticide fate.

The full list includes 17 molecules (8 herbicides, 8 fungicides and 1 insecticide) and 3 degradation products. The K_{oc} and $DT_{50,soil}$ values of the 17 molecules and the three metabolites are summarised in Table 8.5-218.

Pesticides such as diuron, the triazines, e.g. atrazine, simazine and terbuthylazine, have had their environmental behaviour studied for years; oryzalin and others such as glyphosate and glufosinate (Table 8.5-218) have been studied fewer times. Carbendazim and norflurazon belong to the priority list for groundwater survey in the Alsace area (France) and were included in the list of analyses because of their persistence, even if they are no longer applied (Table 8.5-218). The three degradation products investigated are AMPA (aminomethyl phosphonic acid), glyphosate's degradation product, DCPMU (3,4-Dichlorophenyl-N-methyl urea) and DCPU (3,4-Dichlorophenyl urea), both degrades of diuron.

The application method, i.e. directly onto the soil for herbicides or on the leaves for fungicides and insecticides, represent a key-information to assess the fate of pesticides at the catchment scale. The herbicides, applied directly onto the soil, were *a priori* more available during the run-off process whereas the fungicides and insecticides can be also mobilised by foliar wash-off during rainfall event.

Table 8.5-218: Half-life of pesticide in soil (DT_{50soil}) and sorption coefficient normalised to soil organic carbon content (K_{oc}) for 17 pesticides and 3 degradation products (AMPA: aminomethyl phosphonic acid; DCPMU: 3,4-Dichlorophenyl-N-methyl urea and DCPU: 3,4-Dichlorophenyl urea).



	DT_{50soil} (Field)	K_{oc}
Substances	Day	$L\,kg^{-1}$
Fungicides applied		
Azoxystrobin	21	423
Cymoxanil	3.5	44
Dimetomorph	44	348
Kresoxim methyl	16	308
Penconazole	86	2205
Pyrimethanil	30	301
Tetraconazole	61	1039
Herbicides applied		
Diuron	89	1067
Glufosinate	7	755
Glyphosate	12	21699
Isoxaben	123	601
Oryzalin	50	949
Terbuthylazine	46	220
Simazine	90	130
Insecticides applied		
Thiodicarb	18	418
Pesticides not applied		
Carbendazim (*Fungicide*)	18	223
Norflurazon (*Herbicide*)	225	700
Degradation products		
AMPA (from Glyphosate)	151	8027
DCPMU (from Diuron)	–	928
DCPU (from Diuron)	–	694

Pesticide analyses

Suspended sediment was separated from the water phase by filtration through 1 mm glass fibre filters. Aqueous samples were solid-liquid extracted and extracts were analysed. The fungicides azoxystrobin, cymoxanil, dimethomorph, kresoxim methyl, penconazole, pyrimethanil, tetraconazole, carbendazim, the herbicides diuron and its degradation products DCPMU and DCPU, as well as isoxaben, oryzalin, simazine, terbuthylazine, norflurazon, and the insecticide thiodicarb were analysed by liquid chromatography coupled to tandem mass spectrometry (LC-MS-MS), according to the French standard. For glyphosate, AMPA, its degradation product and glufosinate-ammonium, the method of analysis consists of a derivatisation with 9-fluorenylmethyl chloroformate (FMOC-Cl) and detection by LC-MS-MS. The recovery rates ranged between 70% and 88% depending on the compound. All the analyses were carried out by the Pasteur Institute of Lille (France) certified by the French Ministries of Health and Environment. Due to this externalisation, no replicates were managed during the study. Therefore, duplicate frozen samples were stored in case of analytical problems with the original sample.

Pesticide use and fate metrics

Various pesticide metrics have been developed to evaluate the transfer of pesticides at the catchment scale. Metrics defined in the following equations (1 to 5), have been calculated and include the estimated values of pesticide use, as well as rainfall, run-off and the concentration of pesticides in water samples collected during each storm event. The selection of these metrics has been based on the balance between the required and available data, the environmental relevance of the information provided by these metrics and the possibility of performing a mass balance between the annual pesticide inputs applied to the fields and the loads detected at the outlet of the catchment.

The run-off coefficient (%) provides essential information about the hydrological behaviour during a rainfall event. Knowledge on the run-off to infiltration ratio is required to assess the potential vulnerability of surface water and groundwater. The run-off coefficient RC is calculated for each event by normalising the total run-off generated during a rainfall event (V_{run},m^3) by the total rainfall amount over a rainfall event (V_{rain},m^3) (Equation (1)).

$$\mathrm{RC} = \frac{V_{\mathrm{run}}}{V_{\mathrm{rain}}} \qquad [1]$$

To assess the occurrence of pesticides in the various environment compartments, a widely used metric is the detection rate. This metric is usually performed with the limit of detection (LOD), but it can also be performed with the limit of quantification (LOQ). A frequency of determination (FOD) is calculated by Equation (2):

$$\mathrm{FOD} = \frac{n_{\mathrm{sloq}}}{n_i} \qquad [2]$$

where n_{sloq} is the number of samples during an event *i* for which the pesticides were detected at a concentration higher than the limit of quantification (LOQ) and n_i is the total number of samples collected during an event i. The frequency of determination (FOD) is mathematically lower or equal to the limit of detection.

Assuming that the water sample is flow proportional, the calculation of the mean concentration for an event is Equation (3):

$$\mathrm{C}_{\mathrm{mean}\,j} = \frac{\sum_{s=1}^{n_j} \mathrm{C}_{js}}{n_j} \qquad [3]$$

where n_j is the total number of instantaneous concentrations available for a pesticide *j*, C_{js} is the instantaneous concentration of the pesticide *j*.

Because of analytical difficulties in analysing the fraction of pesticides sorbed on sediments, several studies on the fate and transport of pesticide only examine pesticides in the dissolved phase. Unless the pesticide has a very high partitioning coefficient, most of the flux of pesticide will be the dissolved phase. The sampling devices in the Hohrain catchment allow only monitoring pesticide in the dissolved phase.

Furthermore, the pesticide loads in the dissolved phase were calculated with the run-off and the pesticide concentration data. We have assumed a linear change between two successive analysed concentrations and monitored run-off data. We assumed a linear concentration between a null value of concentration at the beginning of discharge and the concentration of the first sample and between the concentration of the last sample and a null value at the end of the discharge. The exported quantities LPj out are calculated with one minute time step according to Equation (4):

$$\mathrm{LP}_{j\,\mathrm{out}} = \sum_{t=1}^{n} \mathrm{C}_{jt} \times \mathrm{Q}_t \qquad [4]$$

where C_{jt} is the instantaneous concentration of the pesticide *j*, *n* the duration of run-off event expressed in minutes and Q_t is the instantaneous run-off. To perform a mass balance between applied pesticide amount and pesticide loads, the estimation of the pesticide sorbed both in bedload and suspended matter would be also required. This pesticide amount can either be directly monitored or derived from the pesticide amount in the dissolved phase according to empirical equations. In the Hohrain catchment, the sampling device does not allow to collect enough suspended matter to perform pesticide analyses on the sorbed phase. The empirical equations cannot be applied without calibration in the Hohrain catchment. Therefore, the exported pesticide load (Equation (4)) should be considered lower than the total pesticide loads at the catchment outlet.

A yearly overall export coefficient Ec (%) for each compound by Equation (5) based on the estimates of pesticide application and the pesticides outputs calculated according to the Equation (4). Ec is calculated by comparing $LP_{j\,out}$ (g) the load of the pesticide *j* exported at the outlet of the catchment with $LP_{j\,in}$ (g), the cumulated load of each pesticide applied each year:

$$Ec = \frac{LP_{j\,out}}{LP_{j\,in}} \qquad [5]$$

Focusing on the removal rates calculated by comparing the pesticide inputs and the loads detected at the outlet of a hydro-system, this metric seems to be the most relevant to assess the export of active substances.

These 5 metrics were calculated for the 58 monitored run-off events to analyse the pesticide fate on vineyards in the Hohrain catchment.

Results and Discussion

Hydrology
Over the study period of 4 years, there was a large variability in rainfall amounts ranging between 359 and 730 mm per year (Table 8.5-219). There is no correlation between annual rainfall and the number of events analysed. All the rainfall events which generated a run-off volume higher than 8 m^3 were monitored and the associated pesticide concentrations were analysed according to the sampling method. The main run-off events, i.e. with more than 8 m^3, represented each year only 29% of the total rainfall amount between March and October (Table 8.5-219). No samples were collected for the run-off events generating less than 8 m^3. The threshold of 8 m^3 had the advantage to focus on the main run-off events with a contribution of vineyard fields on which the pesticides were applied but introduced a bias in the total annual pesticide loads. The mean run-off per event is stable (mean: 4 L/s; standard deviation: 0.9 L/s). The maximum run-off value observed each year is quite variable between 19 and 127 L/s. The run-off coefficients calculated (Equation (1)) are less than 2% for the 4 years. This low value from an agricultural area can be explained by (1) the medium infiltration capacity of the soil, (2) the vineyard management involving grass cover, which was initially adopted for soil conservation and induces a decrease of surface run-off and (3) the fact that the effective area contributing to run-off is limited with respect to the total catchment area. Therefore, the mean volume generated during rainfall events is relatively low and ranged between 31 m^3 in 2004 and 95 m^3 in 2006 with a maximum value observed in 2006 (250 m^3) (Table 8.5-219). The infiltration process is predominant during the rainfall events. However, the pesticides in the surface water represent the main threat both for surface water and groundwater regionally. Indeed, the run-off produced from the vineyard catchment rapidly flows into downstream water bodies, which are closely linked to the Rhenan aquifer.

Table 8.5-219: Hydrological metrics: Number of monitored events; total yearly rainfall; rainfall from March to October; rainfall of monitored events; proportion of monitored rainfall/rainfall from March to October; mean and maximum discharge observed during events; minimum, maximum and mean volume generated during events; and the mean Run-off Coefficient (RC) for water associated with run-off events.

	Number of monitored events	Yearly rainfall (mm)	Rainfall from March to October** (mm)	Rainfall of *m* monitored events** (mm)	Proportion of monitored rainfall/rainfall from March to October (%)	Discharge		Volume			RC* (%)
						Mean (l/s)	Max (l/s)	Min (m^3)	Max (m^3)	Mean (m^3)	
2003	12	359	265	101	38	4.8	127	1.2	198	62	1.6
2004	29	669	487	159	33	2.9	65	1	131	31	1.4
2005	8	470	407	105	26	3.6	19	6.7	117	64	1.1
2006	9	730	649	115	18	4.6	30	10.3	250	95	1.8
Mean		557	452	120	29	*4.0*	*60.3*	*4.8*	*174*	*63*	*1.475*
SD		172	160	27	8.9	*0.9*	*48.6*	*4.5*	*61.8*	*26.1*	*0.3*

*RC: Run-off coefficient.
**This period corresponds to the crop growing season.

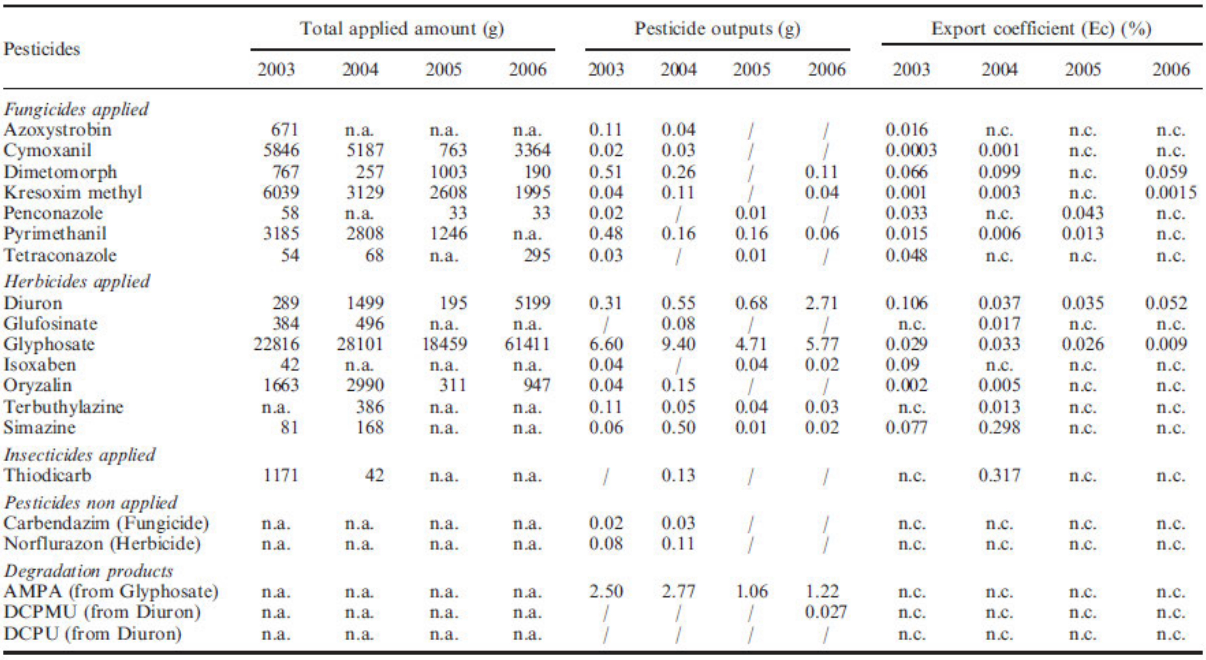
Pesticide inputs

The survey response rates, expressed in proportion of the total vineyard catchment’s area, are 75%, 83%, 57% and 61%, respectively, for 2003, 2004, 2005 and 2006. To take into account the missing information, a correcting ratio, i.e. ratio of investigated to total vineyard area, has been applied to estimate the total pesticide applied amount.

The difference of the total quantities of pesticides for 2003 and 2004 was low, i.e. 5% (Table 8.5-220) in spite of marked climatic variations (Table 8.5-219). This variation was higher for 2005 and 2006. For 2005, the total input decreased by 44% in comparison with the mean value calculated for 2003–2004. For 2006, we observed an increase of 66% compared to the mean values for the period 2003–2004, owing to the used of diuron and glyphosate by the Agricultural and Viticultural College of Rouffach (50% of the vineyard areas). Herbicides are the most used category of pesticides with 78% of the total amount applied (Table 8.5-220). Glyphosate was the most used herbicide and the yearly applied amount ranged from 18 to 61 kg. The highest input (61.4 kg for 2006) was associated with a very rainy year (730 mm, i.e. 22% more than the average inter-annual rainfall). In contrast, quantities of insecticides applied are marginal with nearly 1 kg annually. These quantities will continue to decrease due to the use of pheromones. Two hypotheses can be formulated to explain the frequency of determination of simazine banned since 2002: first, simazine was applied illegally on fields after 2002; secondly, the fraction of simazine sorbed on field soil particles has progressively desorbed and transferred during run-off events. The survey results have confirmed the first hypothesis as simazine was been applied until 2004. However, in 2008 on the Hohrain catchment, simazine was systematically detected during the run-off events monitored (non published data). Consequently, the second hypothesis of desorption associated with low degradation kinetics in soil, cannot be excluded, in agreement with previous observations.

Figure 8.5-181 illustrates pesticide used in 2004. These results underline the diversity of compounds applied in 2004 (20 fungicides, 8 herbicides and 6 insecticides). However, three pesticides analysed between 2003 and 2006 were not applied in 2004. Carbendazim and norflurazon were not applied during the studied period (2003–2006), according to the survey results, but analysed in 2003 and 2004. Indeed, these two pesticides belong to the priority list for groundwater survey and they had been applied in the past. The last year of their application was unknown.

Table 8.5-220: **Use and fate pesticide metrics with input data from farmer surveys; output flux for 17 pesticides and 3 compounds of degradation (AMPA: aminomethyl phosphonic acid; DCPMU: 3,4-Dichlorophenyl-N-methyl urea and DCPU: 3,4-Dichlorophenyl urea) and the export coefficient (Ec)(‘‘/’’pesticide was not analysed; “n.a.” the pesticide was not applied; and “n.c.” the export coefficient could not be calculated.**



Pesticides	Total applied amount (g)				Pesticide outputs (g)				Export coefficient (Ec) (%)			
	2003	2004	2005	2006	2003	2004	2005	2006	2003	2004	2005	2006
Fungicides applied												
Azoxystrobin	671	n.a.	n.a.	n.a.	0.11	0.04	/	/	0.016	n.c.	n.c.	n.c.
Cymoxanil	5846	5187	763	3364	0.02	0.03	/	/	0.0003	0.001	n.c.	n.c.
Dimetomorph	767	257	1003	190	0.51	0.26	/	0.11	0.066	0.099	n.c.	0.059
Kresoxim methyl	6039	3129	2608	1995	0.04	0.11	/	0.04	0.001	0.003	n.c.	0.0015
Penconazole	58	n.a.	33	33	0.02	/	0.01	/	0.033	n.c.	0.043	n.c.
Pyrimethanil	3185	2808	1246	n.a.	0.48	0.16	0.16	0.06	0.015	0.006	0.013	n.c.
Tetraconazole	54	68	n.a.	295	0.03	/	0.01	/	0.048	n.c.	n.c.	n.c.
Herbicides applied												
Diuron	289	1499	195	5199	0.31	0.55	0.68	2.71	0.106	0.037	0.035	0.052
Glufosinate	384	496	n.a.	n.a.	/	0.08	/	/	n.c.	0.017	n.c.	n.c.
Glyphosate	22816	28101	18459	61411	6.60	9.40	4.71	5.77	0.029	0.033	0.026	0.009
Isoxaben	42	n.a.	n.a.	n.a.	0.04	/	0.04	0.02	0.09	n.c.	n.c.	n.c.
Oryzalin	1663	2990	311	947	0.04	0.15	/	/	0.002	0.005	n.c.	n.c.
Terbuthylazine	n.a.	386	n.a.	n.a.	0.11	0.05	0.04	0.03	n.c.	0.013	n.c.	n.c.
Simazine	81	168	n.a.	n.a.	0.06	0.50	0.01	0.02	0.077	0.298	n.c.	n.c.
Insecticides applied												
Thiodicarb	1171	42	n.a.	n.a.	/	0.13	/	/	n.c.	0.317	n.c.	n.c.
Pesticides non applied												
Carbendazim (Fungicide)	n.a.	n.a.	n.a.	n.a.	0.02	0.03	/	/	n.c.	n.c.	n.c.	n.c.
Norflurazon (Herbicide)	n.a.	n.a.	n.a.	n.a.	0.08	0.11	/	/	n.c.	n.c.	n.c.	n.c.
Degradation products												
AMPA (from Glyphosate)	n.a.	n.a.	n.a.	n.a.	2.50	2.77	1.06	1.22	n.c.	n.c.	n.c.	n.c.
DCPMU (from Diuron)	n.a.	n.a.	n.a.	n.a.	/	/	/	0.027	n.c.	n.c.	n.c.	n.c.
DCPU (from Diuron)	n.a.	n.a.	n.a.	n.a.	/	/	/	/	n.c.	n.c.	n.c.	n.c.

Frequency of determination

Table 8.5-221 synthesises the results of pesticide fate metrics, i.e. the frequency of determination (FOD) and the maximum C_{max} and mean C_{mean} concentrations calculated for the 58 events between 2003 and 2006. The number of samples analysed is not the same for the different molecules in a same year. Indeed, owing to different technical constraints and timing of application, the numbers of sample for each pesticide can vary from one year to another.

The frequency of determination (FOD) (Equation (2)) was higher for herbicides (62%) than fungicides (30%). The rate is very low for the sole insecticide monitored (2%). The highest FOD have been observed for dimethomorph (74% on average for 2003–2006), pyrimethanil (67%), terbuthylazine (97.5%), diuron (98.5%) and glyphosate (99.75%) (Table 8.5-221). AMPA and DCPMU, degradation products of glyphosate and diuron, respectively, were always detected (100%) (Table 8.5-221). DCPU produced by the degradation of DCPMU could not be detected during the events of 2006.

Figure 8.5-181: **Total of pesticide amounts applied in 2004 (per kg) by distinguishing the pesticides (fungicides, herbicides and insecticides) analysed (black asterisk) or not during run-off events**

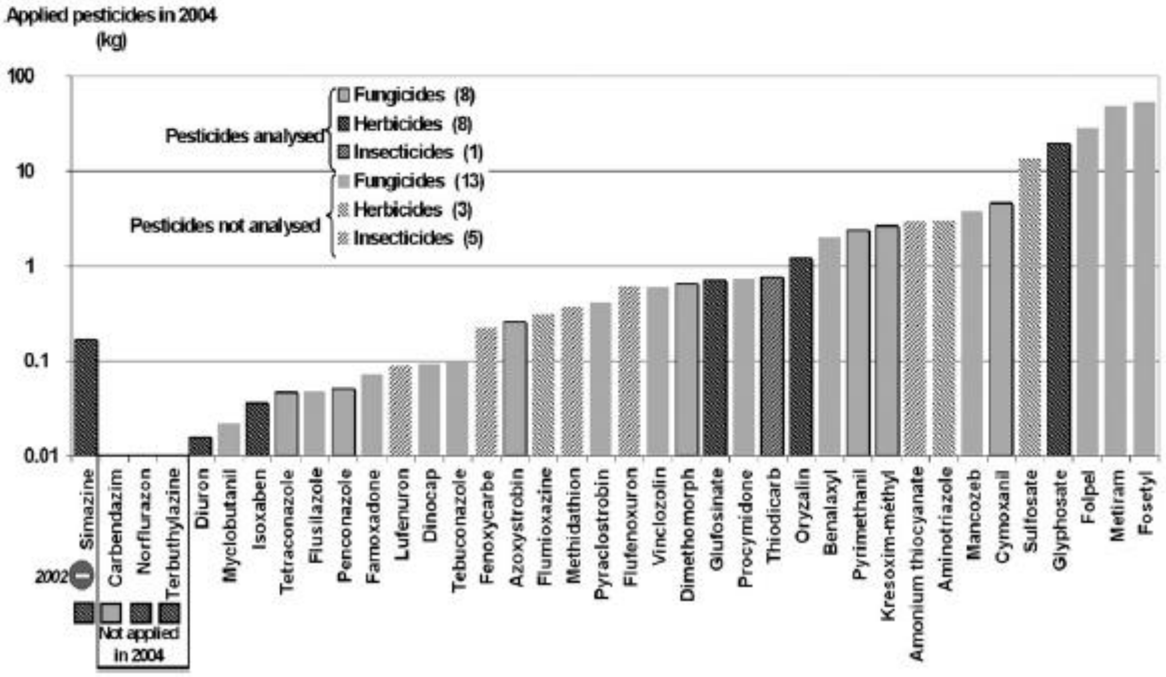


Table 8.5-221: **Pesticide fate metrics for 17 pesticides and 3 degradation products (AMPA: aminomethyl phosphonic acid; DCPMU: 3,4-Dichlorophenyl-N-methyl urea and DCPU: 3,4-Dichlorophenyl urea) for 58 run-off events between 2003 and 2006: limit of quantification (LOQ); number of samples analysed by year; the annual frequency of determination (FOD); maximum concentrations C_{max} and mean concentrations C_{mean}; ("/" the pesticide was not analysed).**

Pesticides	LOQ ($\mu g L^{-1}$)	Number of samples analysed				Frequency of determination (FOD) (%)				C_{max} ($\mu g L^{-1}$)				C_{mean} ($\mu g L^{-1}$)			
		2003	2004	2005	2006	2003	2004	2005	2006	2003	2004	2005	2006	2003	2004	2005	2006
Fungicides applied																	
Azoxystrobin	0.05	82	98	0	0	30	41	/	/	3.4	0.36	/	/	0.28	0.06	/	/
Cymoxanil	0.05	82	98	0	58	12	21	/	0	0.3	0.34	/	/	0.08	0.05	/	/
Dimetomorph	0.05	82	98	0	86	98	66	/	57	4.4	5.7	/	0.66	0.68	0.3	/	0.16
Kresoxim methyl	0.1	82	98	0	86	12	12	/	1	0.17	2.2	/	0.07	0.04	0.09	/	0.004
Penconazole	0.05	82	98	37	58	1	0	5	0	0.22	/	0.16	/	0.01	/	0.02	/
Pyrimethanil	0.1	82	98	37	86	48	80	100	39	5.8	1.5	1.8	0.39	0.45	0.2	0.23	0.1
Tetraconazole	0.05	82	98	37	58	21	0	9	0	0.14	/	0.09	/	0.05	/	0.01	/
Herbicides applied																	
Diuron	0.02	82	98	37	86	100	97	100	97	11	14	8.8	32	0.84	0.54	1.2	3.7
Glufosinate	0.1	82	98	0	0	0	16	/	/	/	1.3	/	/	/	0.26	/	/
Glyphosate	0.1	82	98	37	86	100	100	100	99	86	70	63	40	6.76	10.4	7.4	5.6
Isoxaben	0.1	82	98	37	86	4	0	8	2	0.28	/	1.9	0.07	0.04	/	0.15	0.001
Oryzalin	0.1	82	98	0	0	11	14	/	/	2.6	4.4	/	/	0.3	0.17	/	/
Terbuthylazine	0.025	82	98	37	86	100	99	100	91	5.6	0.27	0.22	0.12	0.44	0.05	0.07	0.04
Simazine	0.02	82	98	37	86	100	79	24	42	2.7	10.2	0.05	0.09	0.2	0.22	0.006	0.02
Insecticides applied																	
Thiodicarb	0.05	82	98	0	0	0	4	/	/	/	60	/	/	/	15	/	/
Pesticides not applied																	
Carbendazim (Fungicide)	0.05	82	98	0	0	10	19	/	/	0.19	0.18	/	/	0.03	0.03	/	/
Norflurazon (Herbicide)	0.1	82	98	0	0	24	49	/	/	1.6	4	/	/	0.32	0.2	/	/
Degradation products																	
AMPA (from Glyphosate)	0.1	82	98	37	86	100	100	100	100	23	44	8,5	5.5	2.76	2.9	1.9	1.4
DCPMU (from Diuron)	0.05	0	0	0	28	/	/	/	100	/	/	/	0.31	/	/	/	0.13
DCPU (from Diuron)	0.05	0	0	0	28	/	/	/	0	/	/	/	/	/	/	/	/

The pesticides studied involved a diverse group of chemical substances. Some older types in use, such as simazine, banned in France in 2002, persisted, with FODs of 100, 79, 24 and 42%, respectively, over the four years.

These frequencies of determination are relatively high with respect to the low run-off coefficient calculated. This could be explained by the hydrological connection of some areas within the catchment. Some vineyard fields located near the outlet may be directly connected to the impervious road network. Consequently, for all the run-off events, they would always contribute to both the discharge and to the pesticide loads.

The mean frequency of determination value for fungicide was about 50% lower than the herbicides with 28.4% (standard deviation: 32.3%) and 61.8% (standard deviation: 43.9%), respectively. These values were in agreement with the *a priori* higher availability of herbicides applied directly on soil compared to fungicides directly sprayed on the leaves. With only one export coefficient value (Table 8.5-220), it was not possible to compare the behaviour of insecticide with the one of herbicides and fungicides.

Pesticide concentration

Mean concentration values of herbicides was generally larger (1.7 µg/L on average for the 2003–2006 period) than fungicides concentrations (0.15 µg/L). The largest concentrations were obtained for the herbicide glyphosate (7.5 µg/L mean and 86 µg/L max), the insecticide thiodicarb (15 µg/L mean and 60 µg/L max) and the glyphosate degradation product AMPA (2.9 µg/L mean and 44 µ/gL max).

Concentrations detected in filtrated surface waters were one to three orders of magnitude larger than the drinking water limit (0.1 µg/L) (Table 8.5-221). Although water from the Hohrain catchment is not used directly for drinking water supply, such high pesticide concentrations could cause problems downstream.

Schulz (2004) reported a negative correlation (with a significance of p = 0.0025) between the log-transformed maximum insecticide concentration and the catchment size. The high pesticide concentration values obtained in the Hohrain catchment, 42 ha, are in agreement with this correlation. The Koc values of the monitored pesticides range from 44 L/kg (cymoxanil, fungicide) to 21 699 L/kg (glyphosate, herbicide). It may be noted that this range is similar to those mentioned by Schulz, suggesting similar fate processes. These results are of particular importance with regard to the European Water Framework Directive, which currently only covers catchment areas over 10 km^2. As discussed by Schulz, this directive thus excludes aquatic habitats that are potentially at the highest risk of being negatively affected by high pesticide concentrations.

Export coefficient

Knowledge of both pesticide input and output is used to calculate an export coefficient Ec (Equation (4)). The export coefficients calculated at the catchment scale were always less than 1% and often less than 0.1% (Table 8.5-221). The pesticides with higher export coefficients were thiodicarb and simazine (0.31%). The lower ratio is observed for fungicides such as cymoxanil (0.0003%). Despite these low export coefficients, all water samples were above the drinking water limit (0.1 µg/L). A comparison between the 4 years shows a relative constant export coefficient. No significant relationship can be determined between the export coefficient and (1) the characteristics of rainfall calculated yearly, or (2) the physico-chemical properties of each pesticide.

The export coefficients calculated for the Hohrain catchment were lower than the values obtained in similar studies, e.g. between 0.09% and 0.87% for Poissan *et al.*; between 0.2% and 17.5% for Blanchoud *et al.* and between 0.26% and 0.57% for Baran *et al.*

Considering mean and standard deviation values of export coefficient, no difference of availability can be determined at the catchment scale between fungicides (mean: 0.027%; standard deviation: 0.03%) and herbicides (mean: 0.055%; standard deviation: 0.074%).

As discussed in the hydrology results Section, the main run-off events, i.e. with more than 8 m^3, represented each year only 29% of the total rainfall amount between March and October (Table 8.5-219) and so the export coefficient values likely underestimate the total annual pesticide loads.

Conclusion

More than 80 kg of pesticides can be applied annually to the Hohrain vineyard catchment during a growing season. Pesticides studied were a diverse group of chemical substances. Some compounds were frequently detected at the outlet of the catchment for the 2003–2006 period (dimethomorph: 74%, pyrimethanil: 67%, diuron: 98.5% and glyphosate: 99%). AMPA and DCPMU, degradation products of glyphosate and diuron, respectively, were detected in every sample.

Glyphosate and diuron are the most extensively used pesticides on the Hohrain catchment. Overall, pesticides losses from Hohrain catchment were systematically less than 0.1%. Surprisingly, considering the high variability of applied amounts and weather conditions, this value (0.1%) seems to be stable over the study period.

Pesticides and their degradation products were present in the Hohrain catchment with maximum concentrations of 86 µg/L for the herbicide glyphosate and 44 µg/L for its degradation product AMPA.

The results from this 4 year study underscore that pesticide behaviour at the catchment scale varies both over time and according to the type of pesticide considered. Assessing the fate of pesticide in agro-ecosystems based on land use patterns is not a straightforward exercise. Indeed, the quantification of the export coefficient, expressing a mass balance requires also significant investment both to collect information on pesticides application amount and timing as well as to calculate the pesticides loads at the catchment scale.

Because a broad spectrum of pesticides has been detected in natural water, the effect of mixtures should also be taken into account; because the overall toxicity could be higher than the sum of toxicities caused by the concentrations of the individual pesticides.

Assessment and conclusion by applicant:

The article describes a monitoring study in a French vineyard catchment where glyphosate and AMPA among other pesticides were measured at the outlet flow of the catchment in water only observed during rainfall runoff events. Information on pesticide application amounts are provided as well as mean and max values of the measured concentrations on a yearly basis. The measured maximum concentration of glyphosate was 86 µg/L. Also, the measured maximum concentration of AMPA was 44 µg/L.
The article is considered reliable.

Assessment and conclusion by RMS:

The study is considered reliable. It provides concentration measurements at the outlet of a wetland in a vineyard area. It is the same site as already presented in several studies (CA7.5/051, CA7.5/055, CA7.5/064) with the exception that the concentrations reported here are measured at the outlet of the wetland and not in the surface runoff flow.

The following information can be retained:
The studied Hohrain catchment area is located in the Alsacian vineyard. The area of the catchment is 42 hectares. It is equipped with a meteorological station and the outlet of the catchment has been instrumented for 4 years to monitor water, only observed during rainfall-run-off events, and pesticide concentrations. The sampling devices allow only monitoring pesticide in the dissolved phase.

Only rainfall events that generated a runoff volume greater than 8 m^3 were monitored. The threshold of 8 m^3 had the advantage to focus on the main run-off events with a contribution of vineyard fields on which the pesticides were applied but introduced a bias in the total annual pesticide loads.
Moreover, the cathment area is characterised by great slope, with average slope indicated to be about 150 m/km. These are therefore considered worst-case conditions for pesticide run-off.

Over the study period of 4 years (2003-2006), there was a large variability in rainfall amounts ranging between 359 and 730 mm per year.

Fifty-eight runoff events from March to September 2003–2006 were sampled, and 303 samples were collected from the Rouffach basin. All but one sample had concentrations of glyphosate above the reporting level of 0.1 µg/L. Every sample had detectable levels of AMPA with maximum concentrations of glyphosate and AMPA of 86 and 44 µg/L (median concentrations: 4.7 and 1.9 µg/L).

The study also reports export coefficient which shows the pesticide loss from the catchment (to the inlet of the wetland) was quite stable through study time and less than 0.033% of the applied amount for glyphosate. This loss is however based only on the collected run-off events which represent 29% of the flow during the study period (which itself does not cover the all year (March-Oct)).

Data point:	CA 7.5/069
Report author	Hanke I. *et al*.
Report year	2010
Report title	Relevance of urban glyphosate use for surface water quality
Document No	Chemosphere (2010), Vol. 81, No. 3, pp. 422-9.
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facility (Eawag, Swiss Federal Institute of Aquatic Science and Technology)
Acceptability/Reliability:	Reliable

Relative contributions of agricultural and urban uses to the glyphosate contamination of surface waters were studied in a small catchment (25 km^2) in Switzerland. Monitoring in four sub-catchments with differing land use allowed comparing load and input dynamics from different sources. Agricultural as well as urban use was surveyed in all sub-catchments allowing for a detailed interpretation of the monitoring results. Water samples from the river system and from the urban drainage system (combined sewer overflow, storm sewer and outflow of wastewater treatment plant) were investigated. The concentrations at peak discharge during storm events were elevated throughout the year with maximum concentrations of 4.15

µg/L. Glyphosate concentrations mostly exceeded those of other commonly used herbicides such as atrazine or mecoprop. Fast runoff from hard surfaces led to a fast increase of the glyphosate concentration shortly after the beginning of rainfall not coinciding with the concentration peak normally observed from agricultural fields. The comparison of the agricultural application and the seasonal concentration and load pattern in the main creek from March to November revealed that the occurrence of glyphosate cannot be explained by agricultural use only. Extrapolations from agricultural loss rates and from concentrations found in the urban drainage system showed that more than half of the load during selected rain events originates from urban areas. The inputs from the effluent of the wastewater treatment plant, the overflow of the combined sewer system and of the separate sewer system summed up to 60% of the total load.

Materials and methods

The study catchment is located in the North-East of Switzerland and part of the Lake Greifen catchment where pesticide behavior has been studied in the past. In 2007, the significance of agriculture and urban uses of biocides and pesticides was studied in a small part of the catchment. Based on this study, the behavior of the herbicide glyphosate was examined. The study catchment (Figure 8.5-182) covers 25 km^2, of which 75% is used for agriculture, whereas 470 ha of the agricultural area are used for arable farming. Climate, soil, and land use are representative for the Swiss Plateau. There are two villages with 10 000 and 2000 inhabitants respectively. The urban sewer system is a mixture of a combined and a separate system (Figure 8.5-182c). In the combined sewer system, wastewater from households and the urban storm water are collected in the same sewer and discharged to the WWTP. In case of intense rainfall these combined sewer systems route excess water via overflows to surface waters. In the separate sewer systems, the urban storm water is collected separately and discharged directly to surface waters. The municipal waste water system lies completely within the hydrological boundaries. To differentiate the sources, the catchment was divided into four hydrological sub-catchments with different land use. The river water at each catchment outlet was sampled separately. The sub-catchments were characterized as follows:

Sub-catchment URB$_{north}$ is highly influenced by water from urban origin since the larger city is situated in this area (site 2). There are two combined sewer overflows (CSO) active during heavy rain events and several storm sewers (StS) discharging into the small creek. The total catchment size of the CSOs is 120 ha, whereas that of the StSs sums up to 46 ha. The wastewater treatment plant (WWTP), which collects wastewater from the whole catchment, is a conventional treatment plant and discharges into this creek as well. Additionally, to the river water the effluents of the WWTP (site 5) and of one StS with a catchment of 5.7 ha were monitored (site 6).

Sub-catchment AGR is dominated by agricultural uses (site 3). There are no CSO or StS discharging into this creek.

The land use in sub-catchment DRAI is dominated by agriculture. There is also one CSO with a catchment size of 28 ha discharging storm water into the creek; however, this CSO is hardly ever active. At the sampling site at the outlet of this sub-catchment, water from the entire catchment was collected (site 1).

Use in agricultural and non-agricultural applications

In total 100 farmers in the study catchment were interviewed about the application date and amount of pesticides (including products containing glyphosate). The survey covered 85% of the agricultural area. On the basis of land use data, the authors assumed that the remaining 15% of the agricultural area which were not considered in the survey received no further glyphosate applications. In order to evaluate the use of pesticides by private garden owners, 61 households out of approximately 1800 households with a garden in the two villages were interviewed to determine their pesticide use (reported elsewhere). Furthermore, other urban sources (e.g. road maintenance) were assessed by inquiries in the catchment. Use data for professional gardening were derived from a nationwide survey of gardeners and market gardens in Switzerland. Glyphosate is also important for weed control on railways; however, in the catchment there was no railway system.

Discharge and precipitation measurements

Discharge was measured at every sampling site. Precipitation was determined by three rain gauges (WWTP, two in sub-catchment URB$_{south}$). The data procedure is described in detail in Wittmer *et al.* (2010a). The uncertainties of the discharge and the precipitation measurements were in the range of 10–20%.

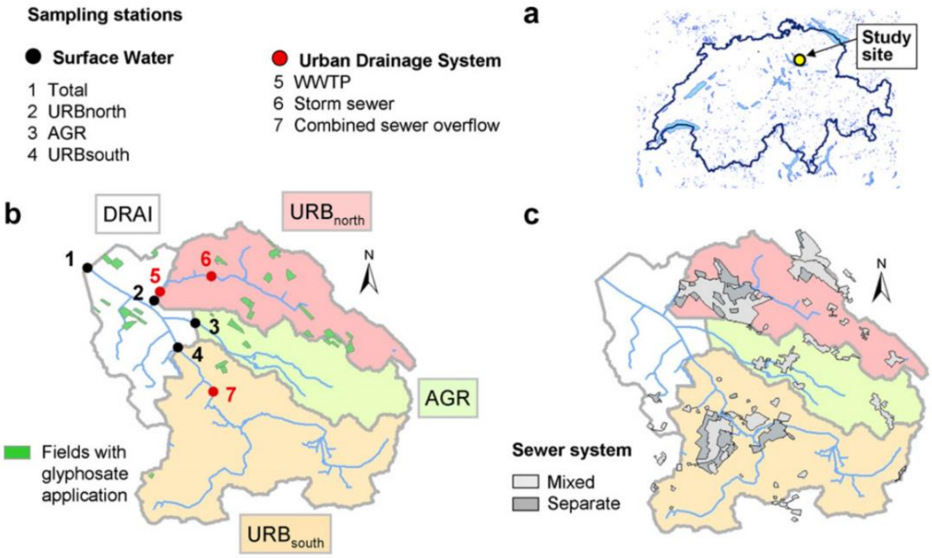
Sampling

Surface water and water from the urban drainage system were sampled by automatic devices at every sampling site except for the WWTP, where daily flow proportional composites were used. Samples were taken at high temporal resolution during 16 out of 35 rain events from March to November 2007. The event based sampling was done as follows: Time-proportional 15-min composite samples (three aliquots every 5 min) were collected during the first 6 h of an event, followed by a reduced sampling frequency of one composite sample per hour (four aliquots every 15 min). During dry periods base flow grab samples were taken. In total, 1600 samples were taken and stored in 250 mL glass bottles in the dark at -20°C. For glyphosate and AMPA no significant losses were detected during sampling and storage. To compare the situation in the study catchment to the situation in Switzerland, grab samples of the river Rhine at the monitoring station at Basel were taken in May, July, and August 2006. The average discharge during this time period was 1250 m^3/s. Based on Swiss agricultural use data, the estimated agricultural use of glyphosate within the catchment of the river Rhine was approximately 50 t.

Analytical procedure

The samples were analyzed according to the method described in elsewhere which is based on a derivatization with 9-fluorenylmethyl chloroformate (FMOC-Cl) followed by solid phase extraction (SPE) of the derivatized and filtered sample (0.45 μm regenerated cellulose membrane filter) and detection by liquid chromatography and tandem mass spectrometry (LC-MS/MS). Using this method, dissolved glyphosate and complexes of glyphosate with cations can be assessed. Samples with expected high concentrations were diluted with nanopure water. The overflow and WWTP samples were all diluted 1:4. To compensate analyte losses during sample preparation isotope labeled glyphosate and AMPA were spiked to the water samples. The calibration curve was linear over the entire range of 0.02–1.0 µg/L. The limit of quantification (LOQ) was defined by the lowest standard of 0.02 µg/L. A blank (without analytes, but with internal standard) and a double blank (nanopure water) were used to monitor background concentrations. For glyphosate, no significant background contamination was found. The background concentrations of AMPA were considerably lower than LOQ and could therefore be neglected. The precision was routinely determined by analyzing aliquots of a sample from sampling site 1 and from the outflow of the WWTP, which had been filtrated and spiked with 0.20 µg/L glyphosate and AMPA. The relative standard deviations (RSDs) for the surface water sample were 12% for glyphosate and 14% for AMPA (N = 6). The RSDs of the WWTP samples were 5% for glyphosate and 13% for AMPA (N = 6). The accuracy was determined by the recovery of a spiked analyte amount in environmental samples (at a level of 0.20 µg/L). The recoveries were in the range of 80–121% for glyphosate and 90 to 118% for AMPA. Due to the time-consuming and elaborate analytical method only selected samples could be analyzed (75 samples in total).

Figure 8.5-182: **(a) Location of the study catchment in Switzerland. (b) Study catchment separated into the four sub-catchments (DRAI, URB$_{north}$,, AGR, and URB$_{south}$) with sampling sites in the river (black, 1–4) and in the urban drainage system (red, 5–7). Furthermore, agricultural fields, which were treated with glyphosate in 2007 are shown in green. (1c) Urban areas with mixed or separate sewer system.**



Results and Discussion

Weather conditions and discharge

2007 was the fifth warmest year in Switzerland since 1864. Especially April and October were warmer, sunnier and drier than normal. The annual precipitation was 1112 mm, slightly more than the mean annual precipitation of the last 12 years (1073 mm). However, July and August were very rainy. At the beginning of August (8th and 9th), heavy continuing rainfall (120 mm in 2 d) caused the largest flood event during the study season. The discharge peak at the outlet of the study area reached 28 m^3/s compared to the mean base flow of 0.2 m^3/s (Figure 8.5-183b).

Use of glyphosate

In Switzerland, glyphosate is the pesticide with the highest sales volume, although the cultivation of genetically modified crops is not allowed in Switzerland. On agricultural areas, glyphosate is mainly used on conservation tillage acres to kill weeds or residues of intermediate crop before the main crop is sown. In 2005, 191 t were sold, which was over four times more than the Swiss sales volume of isoproturon (41 t) or atrazine (38 t). However, it is not known which fraction was used in agriculture or for urban weed control, respectively.

In the catchment area, the survey with around 100 farmers showed that glyphosate was, with a total of 88 kg, the second most used pesticide after isoproturon (107 kg) in agriculture. The third and fourth most used pesticides were atrazine with 74 kg and terbuthylazine with 42 kg. In total, 370 fields (470 ha) were used for arable farming. Glyphosate was applied on 32 fields with a total area of 53 ha (Figure 8.5-182b). There were two application periods. In spring, around 25% (21.5 kg) of the total yearly amount was mainly applied on corn fields for no-tillage farming. The rest (66.5 kg) was used in August and September for preparing the fields for new crop. In urban areas, the applied amounts were more challenging to estimate, since glyphosate was used in different applications and by a variety of people. To determine the total use by owners of private gardens, the results of the survey considering 61 households was extrapolated to all households with a garden in the catchment (approximately 1800). The evaluation of the questionnaires completed by the owners of private gardens in the study area revealed that up to 90% of them use plant protection products to control weed. Every fifth of the questioned house-holds admitted to spray paved forecourts and streets too, which is not allowed in Switzerland. Based on this survey, the total extrapolated glyphosate amount used in private gardens in the two villages was approximately 0.4 kg. Since the 61 households used 46 different substances, the uncertainty of the extrapolation was high. Based on Monte Carlo simulations, the applied amount was in the range of 0.04–1.3 kg. However, the used amount was considerably lower than the agricultural application amount of 88 kg. More important than the use of glyphosate by private persons was the use by professional gardeners. In 2005/2006, the non-agricultural use of glyphosate in horticulture and by professional gardeners in Switzerland was assessed on a national scale with information based on 10% of all registered private and public companies in this sector. Total use of glyphosate was found to be 14 t per year which accounted for around 7% of the total sales volume in Switzerland. The extrapolation of the Swiss use to our catchment revealed that around 18 kg were used in professional gardening. The maintenance of roads and roadsides often requires the use of pesticides. However, the public services and the street maintenance authority did not use glyphosate in the catchment according to interviews with the responsible persons. The amount of glyphosate used in agriculture could thus be determined accurately regarding the application date as well as the spatial distribution of treated fields. However, knowledge about urban use was scarce and no detailed information about the date of urban glyphosate applications was known.

Seasonal pattern at the outlet of the catchment

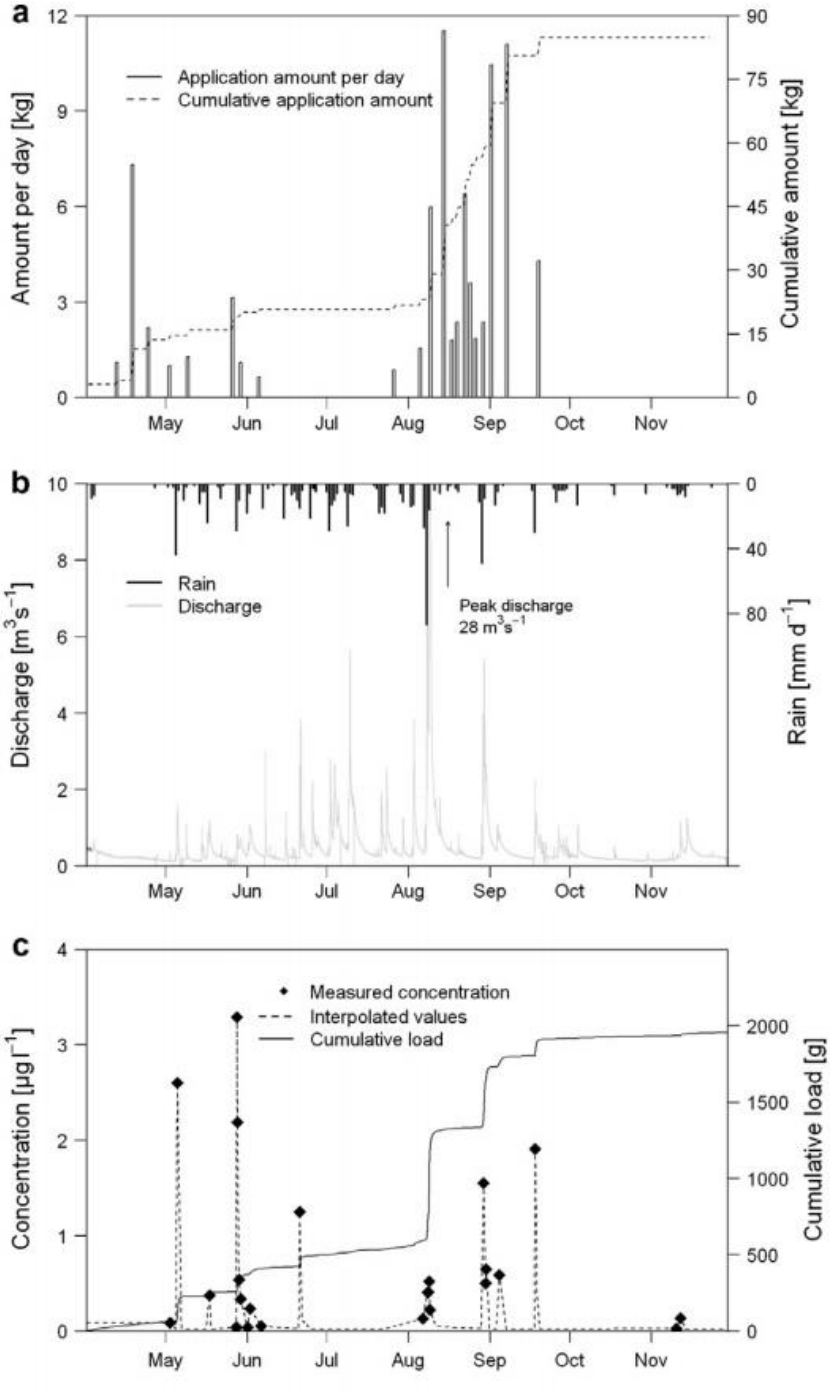
Concentration Dynamics

The occurrence of glyphosate in the creek at the outlet of the whole catchment (site 1, Figure 8.5-182b) was studied for ten rain events throughout the entire study period. As expected, peak discharge concentrations were much higher than the concentrations during base flow (Figure 8.5-183c). Between April and October, peak concentrations up to 3.30 µg/L were measured, whereas base flow concentrations were between 0.024 µg/L and 0.13 µg/L. The base flow concentrations fluctuated irregularly during the year and no clear trend could be observed. Peak concentrations were higher in spring than in late summer and they were significantly above those of other measured herbicides, although these had comparable application volumes and were supposed to be more mobile. Even during the flood situation in August, while the discharge reached 28 m^3/s, glyphosate was detected with a peak concentration of 0.52 µg/L. In November, glyphosate peak concentrations were still above 0.10 µg/L, although the last agricultural application was carried out 2 months before.

Minimum total load

We calculated a minimum load for the whole catchment based on the known concentrations measured at the outlet of the catchment. For this purpose, the measured peak concentrations were interpolated considering the discharge dynamics. For rain events without glyphosate measurements and for base flow periods, the lowest base flow concentration of 0.024 µg/L was assumed (see Figure 8.5-183c). In total, a load of 1.9 kg glyphosate was found in surface water from end of April to end of November (Figure 8.5-183c). If the whole load was assigned to agricultural use and compared to the agricultural application amount of 88 kg, the resulting agricultural loss rate would be 2.2%. This value is considerably higher than the calculated agricultural loss rates of atrazine (0.8%) or isoproturon (<0.5%) in the catchment in the investigated period. Atrazine is known as an herbicide with a relatively high mobility (K_d of 0.2–18 L/kg, Field DT_{50} of 16–77 d). In contrast, glyphosate is not supposed to be mobile in soil due to its sorption to soil particles (K_d of 13.2–427 L/kg) and its degradation to AMPA (Field DT_{50} of 7–63 d). Annual agricultural loss rates found in field studies were in the range of 0.1%. Furthermore, the agricultural application amount of atrazine until the end of May was three times higher than the one of glyphosate. However, the atrazine load in surface water was less than half the load of glyphosate. Even though minimum assumptions were used, the overall glyphosate load in surface water strongly indicated that diffuse agricultural inputs are not the only source.

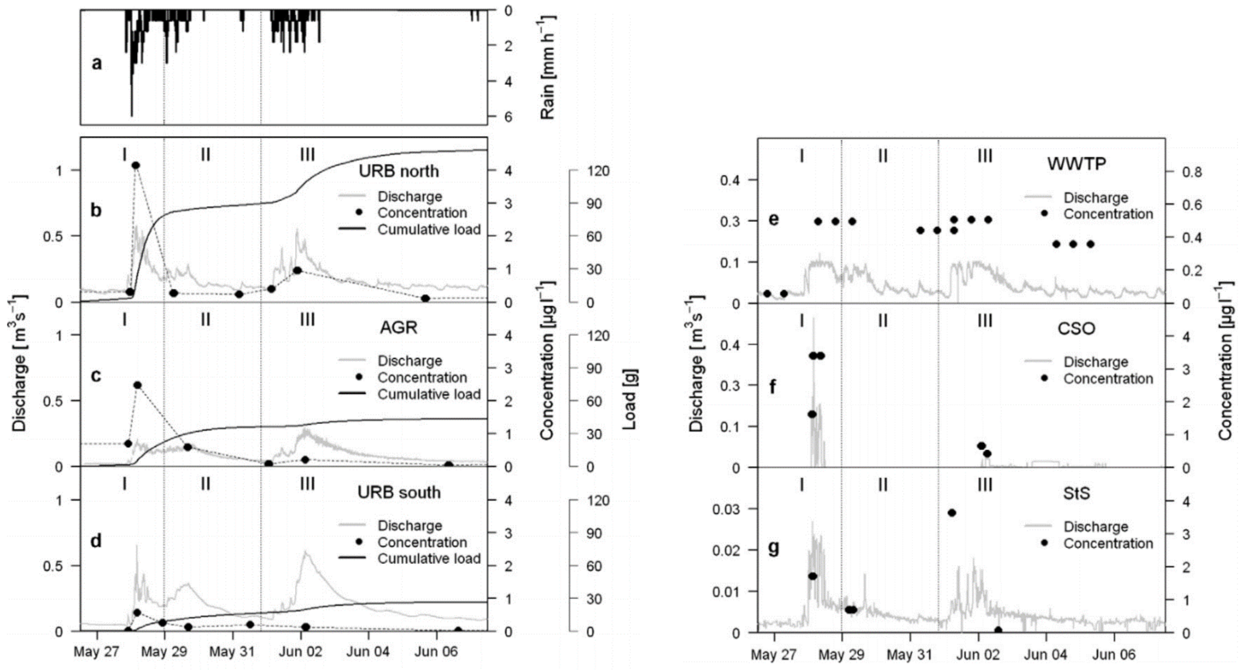
Figure 8.5-183: **(a) Agricultural application amount (per day and cumulative), (b) precipitation and discharge at the outlet of the catchment (site 1), (c) glyphosate concentration dynamics (site 1) and cumulative load of the total catchment from March to November 2007.**



Event dynamics

Thanks to the partitioning of the study catchment into four sub-catchments with various land use, the contribution of the agricultural and urban sources could be assigned more distinctively. In addition to the seasonal dynamics at the outlet of the total catchment event-based investigations on the sub-catchment scale were carried out.

Figure 8.5-184: **May/June event: rain intensity (a), discharge, concentration and cumulative load dynamics in surface water (b–d): URB$_{north}$ (b), AGR (c), URB$_{south}$ (d), discharge and concentration dynamics in the urban drainage system (e–g): wastewater treatment plant (e), combined sewer overflow (f), storm sewer (g).**



Characteristics of the selected rain event

One rain event at the end of May and beginning of June 2007 (hereafter called ‘‘May/June event”) was examined in detail. The event was chosen due to elevated glyphosate concentration at the outlet of the catchment. Furthermore, in previous studies the hydrographs during this event had been studied in more detail to investigate the hydrological response of the sub-catchments and the urban drainage system and to determine the origin of the water. These observations were supplemented with knowledge concerning the concentration dynamics of two other herbicides (atrazine and mecoprop). The event was divided into three main intervals (Figure 8.5-184); the first rainfall was short and heavy (interval I) followed by two intervals of moderate rainfall (intervals II and III). During interval I, the discharge increased rapidly (URB$_{north}$ and URB$_{south}$), as a result of run-off from hard surfaces. Furthermore, high concentrations of urban wastewater tracers such as caffeine were observed (up to 6 µg/L) and the concentrations of the purely agricultural herbicide atrazine were generally low (up to 0.2 µg/L), which indicates that diffuse agricultural inputs were less significant. Additionally, the overflow in sub-catchment URB$_{south}$ was mainly active during interval I. These observations led to the conclusion that during interval I the discharge was mainly composed of water from urban areas. In intervals II and III, atrazine concentrations increased which indicates that the input from agricultural areas gained in importance.

Glyphosate concentrations at the outlets of the sub-catchments

Based on the source and the transport behavior of a compound its input dynamics may be predicted. Compounds applied in urban areas often show high concentrations during first flush and a subsequent fast concentration decrease as seen for mecoprop. Agricultural use leads to concentrations correlating with the discharge (except during first flush) comparable to the behavior of atrazine. High glyphosate concentrations were measured at every site during the selected event (Figure 8.5-184); only in catchment URB$_{south}$ the concentrations were significantly lower (Figure 8.5-184d). For all sub-catchments, the maximum glyphosate concentration was detected during interval I with the highest value of 4.2 µg/L in URB$_{north}$ (Figure 8.5-184b). During the recession part of the hydrograph in interval II, the concentrations decreased to base flow levels and thus followed the discharge pattern. In interval III, the concentrations increased again; however to lower values than during the discharge peak in interval I. In spite of no known agricultural application in sub-catchment AGR, glyphosate concentrations at the outlet were high (Figure 8.5-184c). In interval I, the concentration of glyphosate increased rapidly and earlier than the concentration of mecoprop and atrazine. Mecoprop concentration pattern showed a small increase at peak discharge but not as pronounced as glyphosate. Probably, fast runoff from roads was an important input pathway of glyphosate. In summary, the concentration dynamics of glyphosate at the outlet of the sub-catchments was dominated by first flush peaks from sealed areas followed by lower concentration peaks from diffuse sources.

Glyphosate concentrations in the urban sewer system

The concentrations in the urban drainage system were in the same range as those found in the surface water samples. The concentrations in the WWTP rose with the first discharge peak and slightly decreased after the second with concentrations ranging from 0.06 to 0.51 µg/L (Figure 8.5-184e). The CSO was only active during short time periods in intervals I and III with main contributions in interval I and concentrations ranging from 0.43 to 3.4 µg/L (Figure 8.5-184f). The peak concentrations of $\mathrm{URB_{south}}$ can be explained by this overflow activity. The concentrations in the StS were higher during interval III than during interval I (Figure 8.5-184g). Due to the high concentrations in the surface water during interval I and in the urban drainage system, we concluded that during this particular event urban sources were important for the occurrence in surface water.

AMPA concentrations in the surface water and urban sewer system

The main transformation product of glyphosate in soil and in water is aminomethylphosphonic acid (AMPA). However, since AMPA is also a transformation product of phosphonates, it is not a specific metabolite of glyphosate. Phosphonates are used as chelating agents in various industrial applications. Furthermore, they are ingredients of domestic laundry and cleaning products. In an urban sewer system, the main input of AMPA may result of the degradation of phosphonates used as detergents. At the outlet of the total catchment the concentrations of AMPA were between 0.12 and 0.55 µg/L and varied less than those of glyphosate. During the May/June event the concentrations in the sub-catchments were between 0.04 and 1.11 µg/L and showed concentration dynamics similar to glyphosate (Figure 8.5-185a) with the exception of sub-catchment $\mathrm{URB_{north}}$, where the AMPA concentration rose again during intervals II and III. This was probably due to a continuous input from the WWTP (Figure 8.5-185b).

Event loads

In order to confirm the importance of urban inputs for glyphosate, we calculated the load of the different parts of the urban drainage system (WWTP, CSO, and StS) by extrapolating the measured data. These loads were compared to the load in surface water. We only considered the three sub-catchments $\mathrm{URB_{north}}$, AGR, and $\mathrm{URB_{south}}$. DRAI was not included, since the load from this sub-catchment could only be determined indirectly by subtracting the load of $\mathrm{URB_{north}}$, AGR, and $\mathrm{URB_{south}}$ from the load found at the outlet of the catchment. The loads of the StS and the CSO were extrapolated according to the catchment area of the separate and combined sewer system. In total, 120 ha of the urban area (without buildings) were drained by the combined and 46 ha by the separate sewer system (Figure 8.5-182c). The calculated loads amounted to 29 g for the WWTP, 54 g for the CSO and 42 g for the StS. Compared to the sum of the load found in surface water at the outlets of the sub-catchments (209 g), the contributions of the three urban input ways were all in the same range (WWTP 14%, combined 26% and separate system 20%) and correspond in total to three fifths of the load in surface water.

Wastewater treatment plant – WWTP

The concentrations in the WWTP effluent (up to 0.51 µg/L) were somewhat lower compared to values of 2 µg/L measured in the US or 1.5–1.9 µg/L in Austria. In WWTPs, glyphosate partially dissipates due to sorption and degradation; however, until now only few studies have investigated the removal of glyphosate in WWTPs. In a pilot plant a removal rate of 90–95% was found for concentrations of 500 mg/L. Nowack *et al.* (2002) investigated phosphonates in WWTPs and found removal rates in the same range (85–93%). As glyphosate contains a phosphonate group, similar behavior in WWTP was assumed. Using an average removal rate of 90%, the resulting amount in the WWTP inflow during the May/June event would be approximately 300 g, which equals to 2% of the estimated total yearly amount (18 kg) used in the urban areas of the catchment.

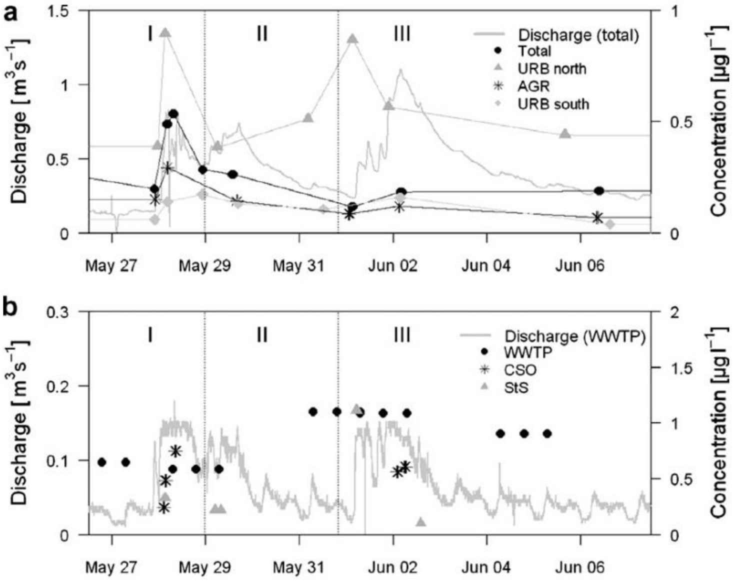
Combined sewer system – CSO

Although the investigated overflow of the combined sewer system was only active during short periods of time (mostly at the beginning of a rain event), the input was significant. During the first interval of the May/June event, the load from $\text{URB}_{\text{south}}$ was composed only of the load of the overflow. The activity of the CSO was thus crucial for the load dynamics of glyphosate.

Separate sewer system – StS

In contrast to the CSO where most of the input through over-flows of the combined system was covered by our sampling site and to the WWTP where the entire input was considered, the input through the separate sewer system was not optimally represented. Since there were several additional storm sewers present in the study catchment, the uncertainty of the extrapolation was high. Furthermore, the use data in the catchment area of the considered storm sewer was based on a comparatively small sample size. However, the main conclusion that urban sources had a wide influence was not affected by the uncertainty concerning the input from the separate sewer system.

Figure 8.5-185: **Concentration dynamics of AMPA during the May/June event in surface water (a) and in the urban drainage system (b)**



Event loads based on agricultural loss rates

To validate the loads, the input from agriculture was assessed by agricultural loss rates and the applied amount. The residual load was then assigned to urban inputs. The agricultural loss rate to surface waters was defined as the total amount reaching the surface waters divided by the amount applied on the fields in the catchment during one year. Although only one rain event was considered, we used overall loss rates, conscious that the input from agriculture was therefore overestimated. We assumed a loss rate of 0.1% to represent diffuse losses and a rate of 1.0% to consider improper handling or disposal. The loads based on these loss rates accounted for 3.9–39% of the overall load from the three sub-catchments, which means that less than two fifth of the overall load can be explained by agriculture. These approaches thus indicate that the application of glyphosate in urban areas has considerable effects on the total load of glyphosate in surface water.

Conclusion

Monitoring (over a period of 9 months) was conducted in four sub-catchments with differing land use; agricultural and urban use was surveyed allowing for a detailed interpretation of the monitoring results. The peak discharge concentrations of glyphosate during storm events were 4.15 µg/L. Fast runoff from hard surfaces led to a fast increase in glyphosate concentrations, which did not coincide with the concentration peak normally observed from agricultural fields. The load from the wastewater treatment plant, the combined sewer system, and the separate sewer system were all in the same range. It was clear that the majority of the total glyphosate load originated from urban areas. To evaluate the representativeness of the loss rate found for the study season (2.2%) at the investigated study site (25 km^2) the loss rate for the river Rhine was estimated using national use data and measured loads from the Rhine monitoring station at Basel. River Rhine is the most important Swiss stream and drains two third of the country (28 000 km^2). The calculated loss of approximately 2% for the river Rhine is in the same range as for the study site located in the North-East of Switzerland and thus confirms that the findings seem to be representative also for a larger scale.

Assessment and conclusion by applicant:
The article describes a monitoring experiment in Switzerland covering a catchment with urban and agricultural land use. Glyphosate and its metabolite AMPA were analyzed. A comparison between the contribution of agricultural use and urban use to the overall load was conducted. Due to a specific definition of sub-catchment areas and their evaluation, a specific conclusion for the agricultural area can be given. It was clear that the majority of the total glyphosate load originated from urban areas. Analytical approaches were sufficiently described.
The article is considered reliable.

Assessment and conclusion by RMS:

The article describes a monitoring experiment in Switzerland covering a catchment with urban and agricultural land use.

The study catchment covers 25 km^2, of which 75% is used for agriculture, whereas 470 ha of the agricultural area are used for arable farming. There are two villages with 10 000 and 2000 inhabitants respectively. The urban sewer system is a mixture of a combined and a separate system. In the combined sewer system, wastewater from households and the urban storm water are collected in the same sewer and discharged to the WWTP.

Conclusions from the article is that "The peak discharge concentrations of glyphosate during storm events were 4.15 µg/L. Fast runoff from hard surfaces led to a fast increase in glyphosate concentrations, which did not coincide with the concentration peak normally observed from agricultural fields. The load from the wastewater treatment plant, the combined sewer system, and the separate sewer system were all in the same range. "

The article is considered reliable, although it is acknowledged that inputs from agricultural and urban sources are difficult to distinguish.

Data point:	CA 7.5/070
Report author	Botta, F. *et al.*
Report year	2009
Report title	Transfer of glyphosate and its degradate AMPA to surface waters through urban sewerage systems
Document No	Chemosphere (2009), doi:10.1016/j.chemosphere.2009.05.008
Guidelines followed in study	None
Deviations from current test guideline	Not applicable

GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

A study of glyphosate and aminomethyl phosphonic acid (AMPA) transfer in the Orge watershed (France) was carried out during 2007 and 2008. Water samples were collected in surface water, wastewater sewer, storm sewer and wastewater treatment plant (WWTP). These two molecules appeared to be the most frequently detected ones in the rivers and usually exceeded the European quality standard concentrations of 0.1 µg/L for drinking water. The annual glyphosate estimated load was 1.9 kg/year upstream (agricultural zone) and 179.5 kg/year at the catchment outlet (urban zone). This result suggests that the contamination of this basin by glyphosate is essentially from urban origin (road and railway applications). Glyphosate reached surface water prevalently through storm sewers during rainfall events. Maximum concentrations were detected in storm sewers just after a rainfall event (75–90 µg/L). High concentrations of glyphosate in surface water during rainfall events reflected urban runoff impact. AMPA was always detected in the sewerage system. This molecule reached surface water mainly via WWTP effluent and also through storm sewers. Variations in concentrations of AMPA during hydrological episodes were minor compared to glyphosate variations. Our study highlights that AMPA and glyphosate origins in urban areas are different. During dry periods, detergent degradation seemed to be the major AMPA source in wastewater.

Methods

Study area

The research sites are situated in the Orge River catchment (956 km^2) in the North of France. The catchment is situated 30 km in the southern part of Paris metropolitan area and the Orge River is a tributary of the Seine River. This catchment shows an urbanization gradient from prevalently agricultural areas and partially forested upstream to more densely urbanized areas nearer the connection with the Seine River resulting in two zones of pesticides contribution. Glyphosate was one of the main molecules applied on roadsides and railways.

Sample campaigns were organized to gather data according four different levels: the first one at the basin scale to calculate the budget of glyphosate load in the Orge River, the second one at the urban area scale to verify the impact of the sewage network on the river contamination, the third part at the network scale to study the transfer of glyphosate and its degradate by runoff in urban areas and the last part at the waste water treatment plant scale to verify the potential impact of urban wastes on surface waters.

Basin area:
From January 2007 until December 2007, a bi-weekly sampling and analysis of glyphosate and AMPA were conducted in three locations in the Orge basin. Epinay-sur-Orge is situated downstream of the Yvette River, whereas Sermaise and Athis-Mons are situated, respectively, upstream and downstream of the Orge River. The Yvette River is the most important tributary of the Orge River (about 30% of the total surface) and represents a highly urbanized part of the watershed.

Urban area:
Sampling was carried out in three different seasons of the year (autumn, winter and spring) in order to determine if urban applications are responsible for surface water contamination by glyphosate. Three points were sampled one in the Orge river and the other two in a small urban tributary, the Boële river (upstream and downstream). To evaluate the sewer contribution to the surface water contamination, samples were collected in the outfalls of two storm sewers discharging directly to the Boële River, between the up- and downstream points in different weather conditions.

Urban sewerage system:
This urban catchment has two big sewers that are running parallel. One is the main wastewater sewer and the other one is a storm sewer called Ru de Fleury drains a surface of 4.4 km^2. The area is located

downstream of the Orge River in a residential zone. Sampling was carried out according to glyphosate application by public services. Samples were collected continuously with automated samplers during the sample campaigns.

Wastewater treatment plant effluent:
In order to know the wastewater treatment plant effluent contribution to surface water contamination, a small stream catchment was studied. The Predecelle River is a small tributary of the Orge River located in the centre of the Orge basin. Five sites were sampled on the Predecelle River and one in the WWTP effluent on September 25, 2007 during dry weather conditions.

Analytical conditions

Glyphosate and AMPA were analysed by HPLC with a fluorescence detector following use of a derivatization agent. The quantification limit for glyphosate and AMPA in water was 0.1 µg/L.

Results

Basin area:
In the Orge River, annual glyphosate fluxes increased from upstream to downstream. For glyphosate the estimated annual flux was 1.9 kg year^{-1} in the upstream point while the same compound had an annual flux of 179.0 kg year^{-1} in the downstream point of Orge catchment. AMPA had an annual flux of 156.8 kg year^{-1} in the Orge downstream point and 1.7 kg year^{-1} in the upstream point. For glyphosate, the downstream point loads were 100 times bigger compared to the loads in the Orge upstream. This difference is also detectable for AMPA. In the downstream point of the Orge River, the glyphosate load is more than 20 kg year^{-1} higher than the AMPA load. For the Yvette River outlet, the estimated annual flux was 92.3 kg year^{-1} for the glyphosate and 52.8 kg year^{-1} for the AMPA. Yvette fluxes represented 50% of glyphosate and 30% of AMPA of total fluxes of the Orge river.

The results of this study and the pesticide use inquiries indicate that urban applications of pesticides are responsible for Orge catchment contamination, particularly glyphosate. In the urban parts of the Orge watershed (downstream Orge and Yvette), glyphosate load was higher than AMPA. This is not the case in the agricultural area, where treatments are applied to soil.

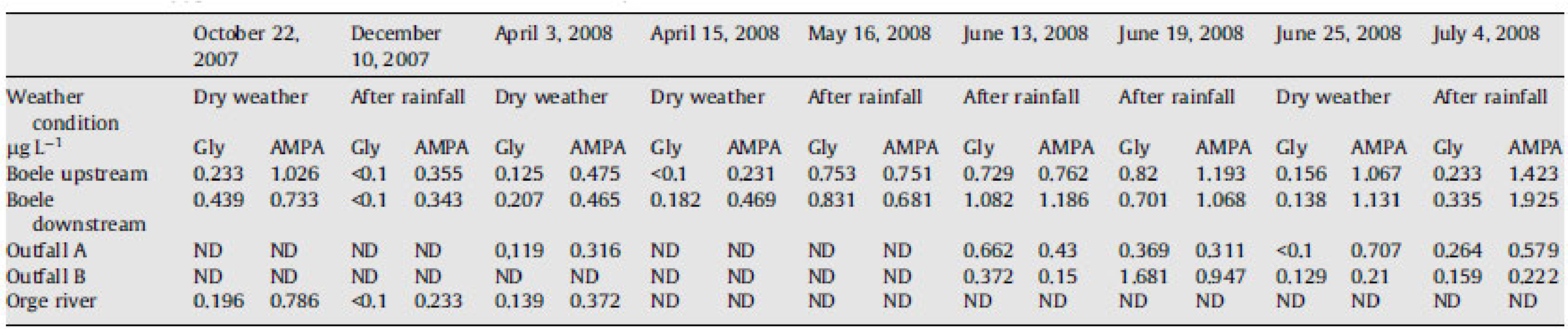
Urban area:
In order to assess the contribution of the urban applications, analyses were performed upstream and downstream of an Orge tributary in an urbanized sector (Boële River). Except for the sampling on December 10, 2007, glyphosate was always detected in the Boële River, as shown in the table below. Concentrations in the downstream point of the tributary were usually higher than in the one upstream and the concentrations registered in the Orge point were always lower. As the Orge River receives less urban rainfall via sewers than the Boële River, the increase in glyphosate concentration can be explained by the urban applications of glyphosate.

The concentrations of AMPA in the Boële River tributary points were always higher than concentrations registered in the Orge River. Values ranged from 0.3 to 1.0 µg/L in the tributary, whereas they ranged from 0.2 to 0.8 µg/L in the Orge River. Comparison of the observed concentrations upstream and downstream of the Boële River indicated that glyphosate and AMPA were essentially of urban origin. The impact of urban application was related to direct runoff from impervious surfaces towards the stream. AMPA occurrence during dry weather conditions in urban areas indicated that it might originate from detergent degradation especially out of the pesticide application period. A general increase in AMPA concentration after the beginning of treatment (campaigns of May, June and July) can be explained due to phosphonate and glyphosate degradation.

Evidence was given for a glyphosate concentration increase in the Boële River water flowing through an urbanized zone. Storm sewer outfalls were identified as a potential pinpoint pollution source. On the whole, glyphosate and its metabolite concentrations during the four samplings between June and July varied according to weather conditions. Glyphosate was always detected after rainfall events, ranging from 0.3 to

1.7 µg/L. After dry weather periods, glyphosate concentrations were detected in three out of four occasions at concentrations lower than 0.25 µg/L. AMPA was always detected in the outfalls during this period at up to 0.9 µg/L.

Table 8.5-222: Concentrations of glyphosate and AMPA in the Boële River, in the Orge River and in two outfalls



	October 22, 2007		December 10, 2007		April 3, 2008		April 15, 2008		May 16, 2008		June 13, 2008		June 19, 2008		June 25, 2008		July 4, 2008	
Weather condition	Dry weather		After rainfall		Dry weather		Dry weather		After rainfall		After rainfall		After rainfall		Dry weather		After rainfall	
$\mu g\ L^{-1}$	Gly	AMPA	Gly	AMPA	Gly	AMPA	Gly	AMPA	Gly	AMPA	Gly	AMPA	Gly	AMPA	Gly	AMPA	Gly	AMPA
Boele upstream	0.233	1.026	<0.1	0.355	0.125	0.475	<0.1	0.231	0.753	0.751	0.729	0.762	0.82	1.193	0.156	1.067	0.233	1.423
Boele downstream	0.439	0.733	<0.1	0.343	0.207	0.465	0.182	0.469	0.831	0.681	1.082	1.186	0.701	1.068	0.138	1.131	0.335	1.925
Outfall A	ND	ND	ND	ND	0,119	0.316	ND	ND	ND	ND	0.662	0.43	0.369	0.311	<0.1	0.707	0.264	0.579
Outfall B	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.372	0.15	1.681	0.947	0.129	0.21	0.159	0.222
Orge river	0.196	0.786	<0.1	0.233	0.139	0.372	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Urban sewerage system:
AMPA was found in the storm sewer during dry weather conditions outside of the glyphosate application period and resulted from detergent use. The glyphosate found in storm water (up to 90 µg/L) was linked to glyphosate application by the local authorities 2 days beforehand. Glyphosate was found also in the wastewater sewer after the beginning of rainfall due to water transfer from the storm sewer to the wastewater sewer.

Wastewater treatment plant effluent:
Samples taken from points in the Predecelle River indicate that the main input of glyphosate is from urban applications and WWTP effluent resulting in concentrations of 1.5 and 1.62 µg/L, respectively, which decrease downstream where no input of glyphosate occurred. For AMPA, concentrations of 0.51 and 3.54 µg/L were found at the urban and WWTP effluent sampling points, respectively. Under dry weather conditions, detergent degradation seemed to be the source of AMPA in surface water receiving treated wastewater.

Conclusion
Investigation in the Orge Basin showed that non-agricultural application of glyphosate has a significant contribution to the glyphosate annual load. Urban runoff is responsible for glyphosate peaks in the Orge River in accordance with literature and glyphosate is more sensitive to rainfall compared to AMPA.

Glyphosate was not found in the storm sewer under dry weather conditions and outside of application periods. However, it was detected during application periods and rainfall events in storm sewers and in wastewater sewers. This means that in a separate sewerage system, during rainfall events, glyphosate may be transferred to surface waters directly via storm sewers and also indirectly *via* WWTP discharge.

AMPA was always detected in all samples (waste, storm and surface waters). Highest concentrations were measured in wastewater samples. It was also found in storm sewers during dry weather conditions and outside of glyphosate application periods. The results show the domestic origin of AMPA in sewer systems. This AMPA can be a metabolite formed from some detergents.

The result of this study confirms AMPA inputs through WWTP discharge and underlines that glyphosate used in urban areas reaches streams mainly by storm sewers.

Assessment and conclusion by applicant:
The article investigates urban sources of glyphosate and AMPA in surface water in the Orge River catchment in the North of France over two years. The methods and results are sufficiently described. In surface water, glyphosate was found up to 1.7 µg/L and AMPA up to 1.93 µg/L.
The article is considered reliable with restrictions.

<u>Assessment and conclusion by RMS</u>:

The article is considered reliable with restrictions.

Sample campaigns were organized to gather data according four different levels: 1) at the basin scale to calculate the budget of glyphosate load in the Orge River, 2) at the urban area scale to verify the impact of sewage network on the river contamination, 3) at the network scale to study the transfer of glyphosate and its degradate by runoff in urban areas and 4) at the waste water treatment plant scale to verify the potential impact of urban wastes on surface waters.

It is noticeable that getting an overview of the sampling strategy and the results is not easy. Some maximum concentrations are given in Table 8.5-222 but the text gives addionnal maximum concentration that comes from another small catchment not reported in table results.

The following information from the study can be retained:
From January 2007 until December 2007, a bi-weekly sampling and analysis of glyphosate and AMPA was conducted in three locations in the Orge basin.

Five points were sampled in the basin: one in the Orge river and the other two in a small urban tributary, the Boële river (upstream and downstream, in order to assess the contribution of the urban applications) Also the urban catchment has two big sewers that are running parallel, that were also sampled (point A and B in the figure below). One is a storm sewer called Ru de Fleury, the other one is a wastewater sewer. Results from these are reported in Table 8.5-222.

The following figure from the full text study is reported to clarify the sampling points.

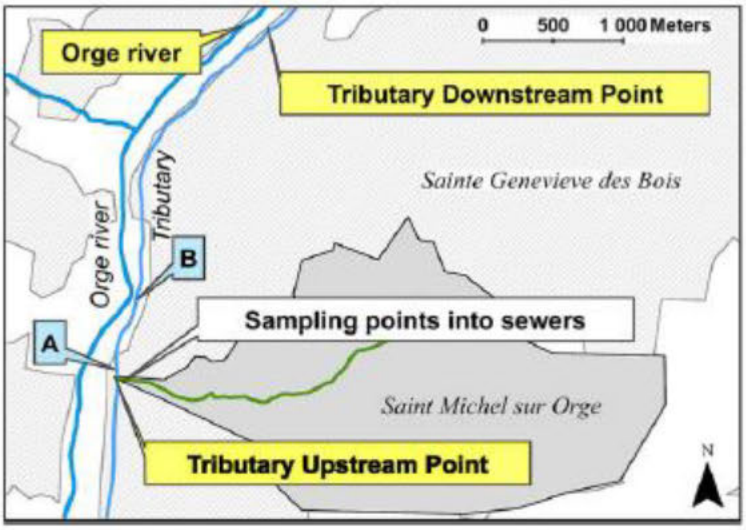


Fig. 1. Surface water sampling points: tributary Boële upstream, tributary Boële downstream and Orge river; storm sewer outfalls (point A and point B); the "Ru de Fleury" sewerage systems (grey area) with the storm sewer and the wastewater sewer running parallel (green line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Maximum concentration in surface water read from Table 8.5-222 are 1.7 µg/L for glyphosate and 1.93 µg/L for AMPA.

Data point:	CA 7.5/071
Report author	Ghanem, A. *et al.*
Report year	2007
Report title	Concentrations and specific loads of glyphosate, diuron, atrazine, nonylphenol and metabolites thereof in French urban sewage sludge
Document No	Chemosphere (2007), doi:10.1016/j.chemosphere.2007.05.022
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Not relevant (concentration in sewage sludges)

Indirect soil pollution by heavy metals and organics may occur when sewage sludge is used as fertilizer. The nature and amounts of pollutants contained in sewage sludge need to be defined in order to assess the environmental risk. Results were obtained for the surfactant nonylphenol and herbicides; glyphosate, diuron and atrazine and their major degradates in sewage sludge sampled from three wastewater treatment plants and one composting unit in the vicinity of Versailles, France for one year. The presence of glyphosate and aminomethylphosphonic acid was demonstrated at the mg kg^{-1} (dry matter) level in all samples.

Methods

Sewage sludge was sampled monthly from July 2004 to June 2005 in three urban wastewater treatment plants and one composting unit in the vicinity of Versailles (France). In all cases, the treatment process included screening, grit removal, primary sedimentation with use of chemical coagulants (except the plant of Saint-Cyr), phosphorus and nitrogen elimination and conventional activated sludge treatment.

The plants of Plaisir and Elancourt were each connected to a separate sewer system and an urban catchment area with moderate industrial activity. The plant of Saint-Cyr has a similar catchment area, but it is connected to a combined sewer system. The WWTP of Plaisir provided dried (pelleted) sludge, whereas sludge treatment was obtained by liming in Elancourt and Saint-Cyr. In the unit of Gazeran, sludge was composted with wood chips as a bulking material. Sludge also originated from several WWTPs, located in a rural area with a mixture of agricultural (cattle breeding) and industrial activities. Wastewaters were collected by several sewer systems, mainly of the combined type.

Centrifuged samples were used for all analyses, as these contained the highest extraction yields. Other samples were then collected after drying, composting or liming to show an effect of sludge treatment on chemical content. Unfortunately, some technical problems in the composting plant of Gazeran prevented a complete campaign of sampling. Sludge samples (1 kg wet weight) were collected, frozen within 1 h after sampling and stored at -20 °C until analysis.

The concentrations of glyphosate and AMPA in sludge samples were determined in alkaline extractions purified on a strong anion-exchanger resin before FMOC-Cl derivatization on the same solid support. Samples were concentrated by reversed-phase SPE before analysis by LC-ESI-MS/MS in the MRM (Multiple Reaction Monitoring) mode.

The method for glyphosate and AMPA analysis showed mean recoveries of 70% (RSD < 9%) for glyphosate and 63% (RSD < 5%) for AMPA, using centrifuged sludge samples collected before liming, composting or drying. Limits of quantifications (LOQs, S/N of 5) were 35 and 50 µg kg^{-1} d.m. (dry matter) for glyphosate and AMPA, respectively.

Results and discussion

Glyphosate and AMPA were quantified in all the samples. The highest mean values for glyphosate were detected in the samples from Plaisir and Elancourt (1.1 and 1.4 mg kg^{-1} d.m.), whereas sludge from Saint-Cyr was less contaminated (0.4 mg mg kg^{-1} d.m.). Accordingly, mean values of 20.3 (Plaisir), 11.5 (Elancourt) and 2.8 (Saint-Cyr) mg kg^{-1} d.m. were calculated in the sludge for AMPA. The concentrations of AMPA should be attributed to glyphosate degradation. Nevertheless, aminophosphonates (EDTMP and DTPMP) contained in household cleaning products can be converted to AMPA in wastewaters and WWTPs. This urban source could explain the high amounts of AMPA measured. Samples from Saint-Cyr were the most contaminated (46.6 µg kg^{-1} d.m.) as compared to those of Plaisir and Elancourt (11.2 and 20.0 µg kg^{-1} d.m.).

Despite incomplete sampling, the data for Gazeran revealed a contamination level similar to that observed for Plaisir and Elancourt for glyphosate and AMPA. Although these compounds are widely used in urban areas as herbicides, it was difficult to define a clear relationship between sludge contamination and periods of weed treatment.

Conclusion

Substantial amounts of herbicides (glyphosate and its metabolite AMPA) were detected in sewage sludge originating from urban areas in France. It can be concluded that an important part of the herbicides detected comes from domestic households.

Assessment and conclusion by applicant:
The article investigates indirect soil pollution by heavy metals and organics when sewage sludge is used as a fertilizer from three urban wastewater treatment plants and one composting unit in the vicinity of Versailles (France) over one year. The authors concluded that an important part of the glyphosate and AMPA detected came from domestic households.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:
The article is considered not relevant for surface water compartment. The study gives results of concentration of glyphosate and AMPA in sewage sludge originating from urban areas in France.

Data point:	CA 7.5/072
Report author	Peschka, M. *et al.*
Report year	2006
Report title	Trends in pesticide transport into the River Rhine
Document No	Hdb Env Chem Vol. 5, Part L (2006): 155–175 DOI 10.1007/698_5_016
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The occurrence of relevant pesticides in the River Rhine and two of its tributaries is presented over a period of ten years. Trace determinations of 66 target pesticides and their metabolites in water from the River Main and the River Nidda were performed on continuously sampled wastewater and surface water utilizing different solid phase extraction protocols and detection by gas chromatography mass spectrometry, directly or after derivatization. The transport rates of pesticides in municipal wastewater treatment plant (WWTP) effluents and surface waters were determined from data obtained in 1994, and these show that WWTPs contribute significantly to the pesticide pollution in the surface water. A trial education program providing improved methodology, spraying equipment and support to farmers living close to a single WWTP lead to a drastic reduction (more than 90%) in the total pesticide transport caused by this WWTP.

During two extensive sampling campaigns in 1999 and 2000, mixed samples from a total of 106 (for 1999) and 35 (for 2000) WWTPs in agricultural used areas from Hesse (Germany) were investigated for selected priority pesticides and metabolites. In this case, the mitigation measures mentioned above were found to be unsuccessful overall, which is most likely attributable to less interaction with the pesticide users as compared to projects in small villages with high public attention.

Methods

A total of 62 pesticides were selected including glyphosate and its metabolite AMPA.

Sampling:
Receiving streams (the Main and the Nidda) and WWTP located in agricultural areas were chosen for study in Hesse, Germany. Mainly grain and maize, but also rape and sugar beet are grown over the catchment area of the River Nidda. No companies discharging industrial waste containing pesticides were located on the river. At Frankfurt-Nied, the Nidda joins with the River Main, which subsequently joins with the River Rhine close to Bischofsheim. The Main receives discharges from many chemical industries, including those producing pesticides. The period from April to May was selected for sampling, as this time frame reflects the peak period for pesticide application.

River samples were taken twice a week from the Rhine during a period of ten years (1993–2003). In the period from 6th April to 17th May 17 1999, a total of 106 WWTP effluent samples were collected twice as three-week mixed samples. The sites found to be most polluted in 1999 were then sampled again over the same period in 2000. During the same time period, mixed samples from the WWTP at Woelfersheim, Hesse, Germany were also taken daily from 1994 to 1998. Mixed weekly surface water samples were collected automatically from the Main during pesticide application time (April to June), and collected as two-week mixed samples for the rest of the year.

Analysis:
Rhine samples were filtered if necessary and then enriched over C-18 cartridges. Main, Nidda and WWTP samples were passed through glass fiber filters, prewashed with methanol and Milli-Q water before solid phase extraction (SPE) was performed. Analysis was by GC/MS.

Results and discussion
Glyphosate was present in the river Main from April to September at a concentration of up to 0.1 µg L^{-1}. In the Nidda it was present over the whole year at a maximum concentration of 0.4 µg L^{-1}, which is due to the higher amount of waste water in the Nidda. The concentration of the metabolite AMPA exceeded the glyphosate concentration by several times.

The results from bank filtration experiments showed that glyphosate was removed after a distance of about 200 m, whereas AMPA needed about 300 to 500 m to be completely eliminated. The experiments were carried out at the waterside of the Main.

Glyphosate and AMPA were not detectable in groundwater, even though they had been applied in massive amounts around rail tracks since 1991.

Water treatment at the WWTP included several steps, namely floc filtration, gravel filtration, and activated carbon filtration. In order to evaluate the efficiencies of those steps, samples were taken before and after each step so that the glyphosate and AMPA could be quantified. The first step, flocculation with activated silicic acid and addition of potassium permanganate and aluminum salts, gave an elimination rate of 39 ± 14% for glyphosate and 22 ± 15% for AMPA. Gravel filtration reduced both by less than 10%. Activated carbon filtration also reduced glyphosate by < 10%, and AMPA by 21 ± 9%.

These results showed that glyphosate and its metabolite were not completely removed in a raw water treatment facility.

Conclusion

Sampling from sewage drains leading to WWTPs showed that farms connected to sewage drains are the most important source of pollution. Analysis of puddles on roads and paths also showed pesticide contamination, which will also be a source of pesticide entry into sewage drains through rainfall wash-off. It can be assumed, however, that the main sources of pollution are the cleaning of spraying tools in farmyards and the pesticide lost from spraying machines traveling by road.

The diffuse pollution problem is a difficult one to tackle. Mitigation measures to circumvent diffuse pollution, even those resulting from many small point pollutions (such as those that were partially successful in this study) depend strongly on the motivation of the pesticide users and the level of interaction with them achieved, since a measurable result will only be obtained through the responsible application and use of pesticides by the farmers.

The removal rates for glyphosate and AMPA for some low-chemical processes were reported: flocculation with activated silicic acid and addition of potassium permanganate and aluminium salts, removal rate of 39±14% for glyphosate and 22±15% for AMPA; for gravel filtration removal rate of <10% for both compounds; and for activated carbon removal rates of <10% for glyphosate and 21±9% for AMPA.

Assessment and conclusion by applicant:

The article investigates urban sources of glyphosate in surface water in the Main and Nidda Rivers in Germany. The methods and results are briefly described. The removal rates for glyphosate and AMPA for some low-chemical processes were reported: flocculation with activated silicic acid and addition of potassium permanganate and aluminium salts, removal rate of 39±14% for glyphosate and 22±15% for AMPA; for gravel filtration removal rate of <10% for both compounds; and for activated carbon removal rates of <10% for glyphosate and 21±9% for AMPA.
Glyphosate was found in surface water at a concentration of up to 0.4 µg/L.
The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

This article is considered reliable with restrictions. The analytical method is not described for glyphosate, there is no indication of the pressure of use of glyphosate within the catchment.

In addition data from this study dates from 1993 to 2003 and may not be representative of current use of glyphosate.

Data point:	CA 7.5/073
Report author	Augustin, B.
Report year	2003
Report title	Urban areas - source of pesticide-contamination of surface water?
Document No	Mitt. Biol. Bundesanst. Land- Forstwirtsch. 394, 2003;
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

In Rhineland Palatinate in Germany, numerous (14-day-mix) samples of surface water (Mosel, Nahe, Selz) were repeatedly monitored for pesticide pollution between 1997 and 1999. Investigations focused on 35 different active ingredients including glyphosate. Glyphosate results were presented for the Selz river in 1997 and indicated detections in water sources in periods during the year. An additional investigation of a sewage disposal plant ("Hahnheim"), which drains into the Selz river, clearly showed that waste water contained glyphosate at a concentration about ten times as high as in the river water.

Up to the present there are no indications for the presence of glyphosate in drain water from agricultural areas. The author speculated that as glyphosate was detectable during the entire year, it is unlikely that it derived from application of farmland, vineyards or orchards. The fact that larger quantities are used on urban areas indicated that there might also be runoff from sealed areas.

Methods

14-day-mix samples from the Selz river at lngelheim in the period 3 March to 8 December 1997 and a wastewater treatment plant at Hahnheim (which drains into the Selz river) in the period 17 March to 9 July 1997 were analysed for glyphosate. Glyphosate was also analysed in runoff water from a concrete surface.

Results

In 14-day-mix samples from the Selz river at lngelheim, concentrations of glyphosate up to approximately 1.8 µg/L were measured with maximum concentrations occurring in April to June 1997. In 14-day-mix samples from a wastewater treatment plant at Hahnheim, concentrations of glyphosate up to approximately 9 µg/L were measured in the period April to July 1997.

Glyphosate analysed in runoff water from a concrete surface was found at much higher concentrations of up to 17.9 mg/L after 2 mm rain over 1 hour. The concentration decreased in runoff after longer periods.

Conclusion

Glyphosate was detected in the Selz river in periods during the year. An additional investigation of a sewage disposal plant ("Hahnheim"), which drains into the Selz river, clearly showed that waste water contained glyphosate at a concentration about ten times as high as in the river water. Glyphosate was found in runoff water from a concrete surface at much higher concentrations than in waste water and the river.

Up to the publication date (2003) there were no indications for the presence of glyphosate in drain water from agricultural areas. The author speculated that since glyphosate was detectable during the entire year, it was unlikely that it derived from application of farmland, vineyards or orchards. The fact that larger quantities were being used on urban areas indicated that there might be runoff from sealed areas.

Assessment and conclusion by applicant:

The article investigates urban sources of glyphosate in surface water in the Selz River in Germany over one year. The methods and results are only briefly described. The author speculated that as glyphosate was detectable throughout the year it was unlikely that it derived from application to farmland, vineyards or orchards; that larger quantities were used in urban areas (due to increased residential building) and probably originated from runoff from hard surfaces.

A maximum concentration of glyphosate up to 1.8 µg/L was reported in surface water.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

Agrees with applicant's conclusions. The article is considered reliable with restrictions.

Moreover, data from this study dates from 1997 and may not be representative of current use of glyphosate.

B.8.5.5. Monitoring data in transitional/tidal water

New studies/assessments

Data point:	CA 7.5/001
Report author	[redacted]
Report year	2020
Report title	Collection of public monitoring data for European countries for the compartments soil, water, sediment and air for Glyphosate, AMPA and HMPA
Document No	110057-1
Guidelines followed in study	Methodology is based on the Groundwater Monitoring guideline document (Gimsing *et al*., 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations') Minimum quality criteria of monitoring data described by the FOCUS Ground Water Work Group chapter 9.5 (European Commission, 2014)
Deviations from current test guideline	None
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Supportive

The report provides information about the outcome of a search for readily accessible and available monitoring data in European countries at a regional/national level for the time period 1995-2019. The main focus was on the time period 2012-2019 while earlier years are already covered by existing data. The search included raw data, requested from regional/national authorities or downloadable from their websites, as well as aggregated data extracted from reports compiled by authorities.

Data from 14 European countries were considered: Austria, Belgium, Denmark, France, Germany, Hungary, Ireland, Italy, The Netherlands, Poland, Romania, Spain, Sweden and the United Kingdom. The countries represent the major markets of products containing glyphosate sold in the EU. The data compilation included the active substance glyphosate and its metabolites AMPA and HMPA, in the soil, groundwater, surface water, tidal water, drinking water, sediment and air environmental compartments.

As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities and other bodies of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were not actually included in any of the monitoring programs.

Tidal Water Compartment Conclusion
Raw datasets for transitional water bodies were only provided by Germany and England. No aggregated datasets were identified or provided by any countries.

I. MATERIALS AND METHODS

The general methodology of data collection of public monitoring data and minimum quality criteria is based on existing guideline documents for groundwater monitoring programs.

RMS indicates this methodology have been described in the study summary under section Groundwater and surface water, it is not repeated here.

II. RESULTS AND DISCUSSION

The final data collection of raw data and aggregated data is summarised for each compartment and each country in Table 8.5-223.

Tidal Water

- Germany (DE)
    - The regional authority in Mecklenburg-Vorpommern provided raw data on tidal waters.
    - No aggregated data were provided.
- Poland (PL)
    - The responsible authorities for monitoring data in Poland are the Polish Geological Institute and the Chief Inspectorate Of Environmental Protection. The latter authority confirmed by e-mail that in Poland there is currently no public monitoring of glyphosate or its metabolites in surface water.
- Romania (RO)
    - The responsible authority for monitoring data is the Ministry of Water and Forests. The Water Resources Management Directorate confirmed on behalf of the Ministry of Water and Forests that no public monitoring of glyphosate or its metabolites is carried out in any water compartment in Romania.
- United Kingdom (UK)
    - For tidal waters, raw data were available for England from the EA webpage.
    - No other country in the UK provided raw data for tidal waters,
    - No aggregated monitoring data from reports were provided and included in this report.

Table 8.5-223: Overview of public monitoring data availability of raw data (R) and aggregated data (A)

Country	Soil	Water				Sediment	Air
		Ground	Surface	Tidal	Drinking		
Austria	-	R, A	R, A	-	A	-	-
Belgium	-	R	R	-	A (Flanders)	-	-
Denmark	-	R, A	A	-	A	-	-
France	-	R	R	-	A	R	-
Germany	R (Brandenburg)	R, A	R, A	R	R (Schleswig-Holstein), A	-	-
Hungary	-	A (one research article)	A (one research article)	-	-	-	-
Ireland	-	R, A	R, A	-	R, A	-	-
Italy	-	R (Lombardia), A	R, A	-	-	-	-
The Netherlands	-	R, A	R, A	-	R	-	-
Poland	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Romania	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Spain	-	R, A	R, A	-	A	-	-
Sweden	-	R, A	R	-	R, A	R	-

Table 8.5-223: Overview of public monitoring data availability of raw data (R) and aggregated data (A)

Country	Soil	Water				Sediment	Air
		Ground	Surface	Tidal	Drinking		
UK England	-	R	R	R	A	-	-
UK Northern Ireland	-	R	-	-	-	-	-
UK Scotland	-	-	R	-	-	-	-
UK Wales	-	-	R	-	A	-	-

R raw data available; A aggregated data from reports available; - no raw or aggregated data available

III. CONCLUSIONS

The present collection of public monitoring data for glyphosate, AMPA and HMPA in soil, groundwater, surface water, drinking water, tide water, sediment and air resulted in a comprehensive database of ‘raw monitoring data from national authorities’ and ‘aggregated monitoring data from reports published by national authorities’. As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were actually not included in any of the monitoring programs.

Raw datasets for transitional water bodies were only provided by Germany and England. No aggregated datasets were identified or provided by any countries.

Assessment and conclusion by applicant:

The study describes the collection process of public monitoring data for European countries for the compartment soil, water, sediment and air for Glyphosate, AMPA and HMPA

The study is considered valid.

Assessment and conclusion by RMS:

This report describes the methodology employed for collection of monitoring data for Glyphosate, AMPA and HMPA. The data collection refers to third party organization data regarding all environmental compartments (Soil, GW, SW, TD, DW, SD, AIR)

Two different data types were collected, *i.e.* raw data from national authorities and aggregated data from publicly available reports (from environmental agencies or research institute).

The general search strategy was similar for each compartment, country and substance. All details of data acquisition are given in the report, and all data sources are carefully listed and described.
Although the process can clearly not be reproduced, and cannot be checked in details for exhaustiveness, the search strategy is clearly exposed and considered acceptable.

For tidal water compartment, raw datasets for transitional water bodies were only provided by Germany and England. No aggregated datasets were identified or provided by any countries.

Findings from this data collection and corresponding analysis are given in a separate report; see [redacted] [redacted] 2020 below.

These data are considered as supportive since tidal water is not part of the assessment framework for active substance approval.

Data point:	CA 7.5/002
Report author	[redacted]
Report year	2020
Report title	Glyphosate (GLY) and the primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA): Public monitoring data assessment and interpretation
Report No	EnSa-20-0322
Document No	-
Guidelines followed in study	Groundwater monitoring guideline document (Gimsing *et al*., 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations'); Article 5 of Directive 2009/90/EC - Technical specifications for chemical analysis and monitoring of water status.
Deviations from current test guideline	Not relevant
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Supportive

Executive Summary

The report provides information about the outcome of an analysis of public monitoring data comprising environmental concentrations of glyphosate (GLY) and its primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA) collated from readily available public monitoring databases held by national/regional environment agencies. This data collection and analysis was designed to expand previous reviews to include other compartments and supplement them for surface water, groundwater and drinking water.

Transitional Waters

A small number (~800 samples from 22 sites) of GLY and AMPA analyses from brackish transitional/tidal environments were analysed. These were from two MS, namely DE and UK, from an individual region in each MS, Mecklenburg-Vorpommern and England, respectively. The data were assessed against the surface water RAC of 400 µg/L for GLY and 1200 µg/L for AMPA, given these are brackish waters. Additional ecosystem impact assessments were conducted using SW EQS-MAC and EQS-AA where these were defined for these MS. No information on HMPA was available.

Compliance was 100% with no exceedances of the RAC, EQS-MAC or EQS-AA indicated by the data for both GLY and AMPA. The maximum measured concentrations of 0.18 µg/L (DE) and 1.2 µg/L (UK) for GLY, as well as 0.9 µg/L (DE) for AMPA, were well below the RAC and EQS thresholds.

Transitional Waters Compartment Conclusion

While limited in number, spatial and temporal scope the available transitional water data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in this environmental compartment.

I. MATERIAL AND METHODS

The dataset analysed comprised individual groundwater analysis records as well as existing aggregated analyses extracted from reports sourced from regional/national environment agencies (see [redacted], 2020, CA 7.5/001). The approach taken for the data processing was precautionary in that it preserved samples in the analysis where there was any doubt regarding their reliability. No records were excluded from the analysis. Similarly, no attempt to remove outliers was undertaken. Analysis and assessment of the data against thresholds was undertaken in statistical software R (R Core Team, 2019) and graphs produced in Excel. The same endpoints as that used for surface water (SW) bodies were utilised. This is consistent with these being predominantly brackish waters rather than marine waters. The UK endpoints for such waters are reported as being the same as for SW:

- Ecotoxicological endpoint: Regulatory acceptable concentration (RAC) of 400 µg/L for GLY and 1200 µg/L for AMPA.
- Ecosystem endpoint: Environmental quality standards (EQS) where these were proposed/available (see Table 8.5-224) at a Member State level, comprising annual average EQS (EQS-AA) and maximum allowable concentration (EQS-MAC); No values for these endpoints are available at a European level.

Table 8.5-224: Summary of Environmental Quality Standards (EQS), average annual (AA) and Maximum allowable concentration (MAC) utilised for the different Member States

Member State	GLY		AMPA	
	EQS-AA	EQS-MAC	EQS-AA	EQS-MAC
	µg/L			
DE - Germany	28	NA	96	NA
UK – United Kingdom	196[1]	398[1]	NA	NA
EU Combined Dataset	NA	NA	NA	NA

NA – Not available as not defined

[1] - These are 90th percentiles, applied as maximum values in the first instance in a precautionary approach

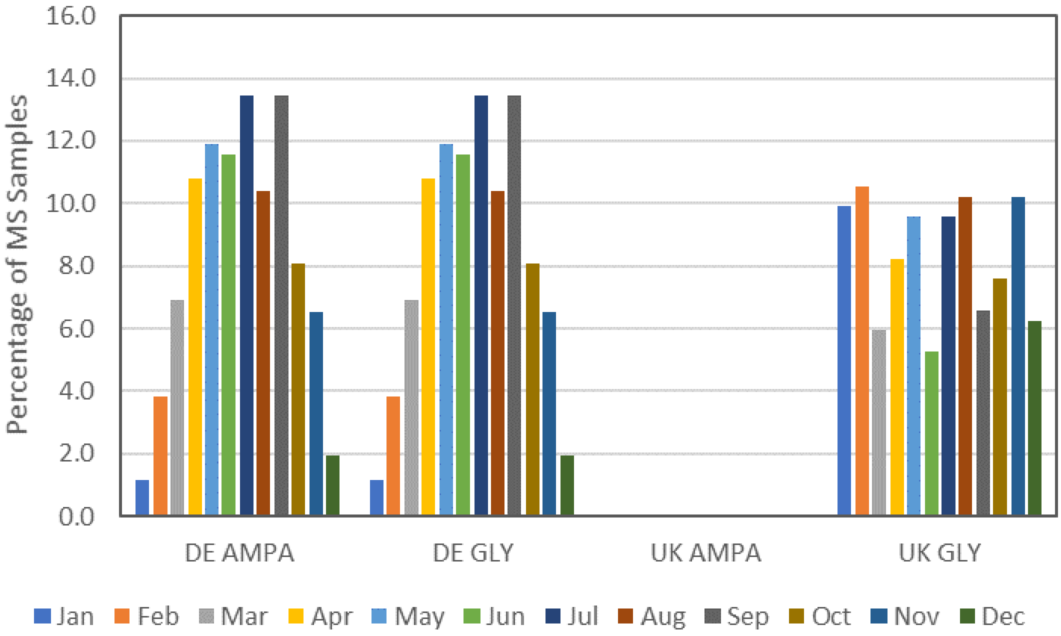
II. RESULTS AND DISCUSSION

The amount of data supplied and analysed for this study is very limited (~800 samples from 22 sites) and as such is biased both spatially and temporally. These include a variety of tidal water bodies including estuaries, lagoons and near shore brackish areas.

The bulk of the data (~46% for GLY and 100% for AMPA) came from the DE dataset which comprises 15 sites located along the Baltic Sea coastline of Germany in the Bundesland of Mecklenburg-Vorpommern. This dataset covered 9 years spanning the period 2009 – 2018 (see Table 8.5-225). Monthly sampling effort for both GLY and AMPA appeared to be unimodal with lower sampling intensities in the winter (see Figure 8.5-186).

The dataset from the UK comprised 8 sites distributed unevenly along the east coast of England. It covered 9 years spanning the period 2000 to 2009. Monthly sampling effort appeared to be variable throughout the year. There was insufficient data to create a combined European dataset and as such only individual MS data were presented.

Figure 8.5-186: Bar chart of tidal water monthly glyphosate (GLY) and AMPA sampling effort within each Member State



Analysis of the GLY tidal water dataset indicated that GLY was quantified in 6.9% (DE) to 8.9% (UK) of samples (see Table 8.5-225), albeit the number of samples was quite limited (260 in DE; 303 in UK).

Compliance was 100% given no analyses exceeded the RAC of 100 µg/L or came close to doing so with the maximum measured concentrations being 0.18 µg/L (DE) and 1.2 µg/L (UK). As such, compliance with the UK EQS-MAC was 100% given none of the UK samples exceed the national EQS-MAC of 398 µg/L. There was insufficient data in the DE dataset to calculate average annual concentrations, however, three sites in the UK do have sufficient data to do so (see Table 8.5-226). At these three sites 100% compliance with the UK EQS-AA of 196 µg/L was demonstrated as no exceedance of the EQS-AA was indicated. Intuitively, given the median and maximum concentrations (see Table 8.5-225) exceedance of the EQS-AA for either MS seems extremely unlikely at any sites.

All of the AMPA data came from the DE dataset and comprises 260 samples taken at 15 sites. Compliance of 100% with the RAC of 1200 µg/L was indicated given there were no exceedances of the RAC. The maximum measured concentration was low, being 0.9 µg/L. While no EQS-MAC was set for DE, the data available does not suggest such an EQS would be exceeded where it is available. There was insufficient data in the DE dataset to calculate average annual concentrations, however, given the median and maximum concentrations (see Table 8.5-225) exceedance of the EQS-AA of 96 µg/L seems extremely unlikely.

III. CONCLUSIONS

Compliance with transitional water regulatory endpoints and thresholds was 100% with no exceedances of the RAC, EQS-MAC or EQS-AA indicated by the data for both GLY and AMPA. The maximum measured concentrations of 0.18 µg/L (DE) and 1.2 µg/L (UK) for GLY, as well as 0.9 µg/L (DE) for AMPA, were well below the RAC and EQS thresholds. While limited in number, spatial and temporal scope the available transitional water data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in this environmental compartment.

Table 8.5-225: Summary results of glyphosate (GLY) and AMPA analyses in tidal water bodies

MS	Substance	Number of Sites	Number of Samples	Years	LOQ (µg/L)	Samples with LOQ≤0.1 µg/L		Detected >LOQ		Detected >RAC$			Detected > EQS-MAC			Measured Concentration (µg/L)
					Mean (min - max)	Sites	Samples	Samples	%	Sites	Samples	% Samples	Sites	Samples	% Samples	Median[1] (min - max)
DE	AMPA	15	260	2009 - 2018	0.03 (0.02 - 0.03)	15	260	86	33.1	0.0	0	0.0	ND	ND	ND	0.03 (0.014 - 0.9)
	GLY	15	260	2009 - 2018	0.02 (0.01 - 0.03)	15	260	18	6.9	0.0	0	0.0	ND	ND	ND	0.02 (0.010 - 0.18)
UK	AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	8	303	2000 - 2008	0.10 (0.10 - 0.10)	8	303	27	8.9	0.0	0	0.0	0	0	0.0	0.10 (0.100 - 1.2)

ND – not determined as data not available or EQS-MAC not defined

[1] Values <LOQ and <LOD are treated as equal to LOQ and LOD as a precautionary estimate of the median

Table 8.5-226: Summary of Annual Average (AA) Environmental Quality Standard (EQS) statistics for those Member States (MS) where such a threshold is available

MS	Substance	Number of Sites	Number of Years	Number of Sites with 12 Samples per Year	Number of Years with 12 Samples per Year	Number of Sites > AA-EQS	Percent of Sites > AA-EQS	Number of Years > AA-EQS	Percent of Years > AA-EQS
DE	AMPA	15	47	0[1]	0[1]	ND	ND	ND	ND
	GLY	15	47	0[1]	0[1]	ND	ND	ND	ND
UK	AMPA	NA	NA	NA	NA	NA	NA	NA	NA
	GLY	8	43	3	27	0	0.0	0	0.0

[1] Insufficient data available with <12 samples per year being taken at each site; ND – not determined as insufficient data; NA – no data available

Assessment and conclusion by applicant:
The report describes the analysis of public monitoring data for key European countries for the compartment transitional/tidal waters for glyphosate and AMPA. Monitoring data for two countries were available. The maximum measured concentrations in transitional waters of 0.18 µg/L (DE) and 1.2 µg/L (UK) for GLY, as well as 0.9 µg/L (DE) for AMPA, were well below the RAC and EQS thresholds. The available data do not indicate any risk to biota or ecosystems from measured GLY and AMPA concentrations in the transitional water compartment.
The study is considered valid.

Assessment and conclusion by RMS:
Data from monitoring in tidal water are reported for a limited number of sites (~800 samples from 22 sites) from DE and UK. These include a variety of tidal water bodies including estuaries, lagoons and near shore brackish areas.

There was insufficient data to create a combined European dataset and thus only individual MS data were presented. Main information from these data are reported below:

The bulk of the data (~46% for GLY and 100% for AMPA) came from the DE dataset which comprises 15 sites located along the Baltic Sea coastline of Germany in the Bundesland of Mecklenburg-Vorpommern. This dataset covered 9 years spanning the period 2009 – 2018.
Within the 260 samples, GLY was quantified in 6.9% of samples, and AMPA was quantified in 33.1%. The maximum measured concentrations were 0.18 µg/L for GLY, and 0.9 µg/L for AMPA, which are below the RAC and EQS thresholds.

The dataset from the UK comprised 8 sites distributed unevenly along the east coast of England. It covered 9 years spanning the period 2000 to 2009. Within the 303 samples, GLY was quantified in 8.9% of samples. The maximum measured concentrations was 1.2 µg/L for GLY which is below the RAC and EQS thresholds.

These data are considered as supportive since tidal water is not part of the assessment framework for active substance approval.

Existing studies/assessments

There was no monitoring data covering transitional waters considered reliable in RAR (2015).

Relevant literature articles

Data point:	
Report author	Skeff, W., *et al.*
Report year	2015
Report title	Pesticides in water supply wells in Zealand, Denmark: A statistical analysis
Document No	Marine Pollution Bulletin 100 (2015) 577–585
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Water samples from ten German Baltic estuaries were collected in 2012 in order to study the presence of the herbicide glyphosate, its primarymetabolite AMPA and their potential transport to the marine environment. For the analyses an LC–MS/MS based analytical method after derivatization with FMOC-Cl was optimized and validated for marine water samples. All investigated estuarine stationswere contaminated with AMPA and nine of themalso with glyphosate. Concentration ranges observed were 28 to 1690 ng/L and 45 to 4156 ng/L for glyphosate and AMPA, respectively with strong spatial and temporal fluctuations. Both contaminants were found at inbound sampling sites in the stream Muehlenfliess and concentrations decreased along the salinity gradient to the estuaries of the Baltic Sea. The data obtained in this study clearly depict the transport of glyphosate and AMPA to the Baltic Sea. Hence, detailed fate and risk assessment for both contaminants in marine environments are required.

The Baltic Sea is a semi-closed sea located in northern Europe. It is considered to be a small sea (412,000 km2) with an average depth of 52 m (Schiewer and Schernewski, 2004) and a catchment area of approximately 1,720,000 km2 (HELCOM, 2004). It is one of the largest isolated bodies of brackish water in the world. Salinity varies from 2 to 4 in the north up to 20 to 30 in the southwest caused by water exchange with the North Sea, freshwater inflow from the watershed and atmospheric interactions (Walday and Kroglund, 2002). Four German federal states share the catchment area with the Baltic Sea that is Mecklenburg-West Pomerania (16,720 km2), Brandenburg (5940 km2), Schleswig-Holstein (5250 km2) and Lower Saxony (880 km2) (BUND Mecklenburg-Vorpommern, 2012). The German Baltic drainage basin with riverine inflow from Oder, Peene and Uecker is characterized by a high degree of human activity. Agricultural use accounts for 72% of the German Baltic catchment area and therefore, Germany bears the highest agricultural activity of all Baltic countries (BUND Mecklenburg-Vorpommern, 2012; HELCOM, 2004).

The onset of industrialization in the late 19th century brought about extensive use of hazardous compoundswhich consequently entered the Baltic Sea, e.g. through riverine transport (Rheinheimer, 1998). Due to the long lasting and intensive exposure to those substances the Baltic Sea is considered to be one of the most polluted seas in the world (HELCOM, 2010). Therefore, a number of research and monitoring programs have been established that focus on persistent organic pollutants (POPs) that endure in the sediments even after their use was legally banned in the past. Among others, pesticides such as DDT and its metabolites or HCH (Lindane) and aldrin are considered to be one of themain problemswithmajor impact on biological diversity and belong to one of the substance groups regularly monitored. However, even though there is at least partially a declining trend since the 1970s of those compounds in the water, sediments and biota, their impacts on biological diversity remain (HELCOM, 2010).

Germany is the second largest consumer of pesticides in Europe after France (Zhang et al., 2011). In 2012 a total amount of 45,527 t of pesticides were used 44% of which were herbicides. German herbicide sales increased by 23% from 2003 to 2012 with glyphosate as the dominating compound on the German herbicide market. Glyphosate sales in 2012 ranged from 2500 t to 10,000 t (BVL, 2013; Steinmann et al., 2012). Glyphosate is the active ingredient in commercial products such as Roundup® or Touchdown® marketed through Monsanto Co. and Syngenta Co., respectively, in which the herbicidal activity is even enhanced through additives such as the surfactant tallow amine (Leaper and Holloway, 2000). Glyphosate has become one of the most used pesticides in the world (Duke and Powles, 2008). Predominant application modes of glyphosate in farming practice are pre-sowing, pre-harvest and stubble application (Steinmann et al., 2012). However, use of glyphosate is not limited to agricultural applications. It is also frequently applied in non-agricultural areas such as parks, gardens, railway tracks and industrial areas (Woodburn, 2000).

In this study we provide data on the presence of glyphosate andAMPA in Baltic Sea estuaries. Furthermore, we are aiming to elicit possible routes of transport for both compounds from their place of application to the Baltic Sea. A key aspect of this work is the adaption and optimization of current glyphosate and AMPA methodology to Baltic Sea estuaries samples containing both compounds presumably in the low concentration levels. A sensitive and straightforward method in hand might allow monitoring programs to be expanded by glyphosate and AMPA measurements.

Water samples were collected in 2012 during the application period of pesticides between May and September from ten different estuarine stations distributed along the Baltic Sea coastline of Mecklenburg-

West Pomerania, Germany (Fig. 2A, Table 1) at different time intervals. Positional data have been obtained with a GPS Oregon 400t (Co. Garmin, Garching). For sampling, 1 L polypropylene bottles were rinsed with sampling water prior to sampling and subsequently filled. For each sample, data for salinity and temperature were obtained using the WTW conductivity meter ProfiLine Cond 1970i. The samples were transported to the laboratory and stored at 4 °C in the dark.

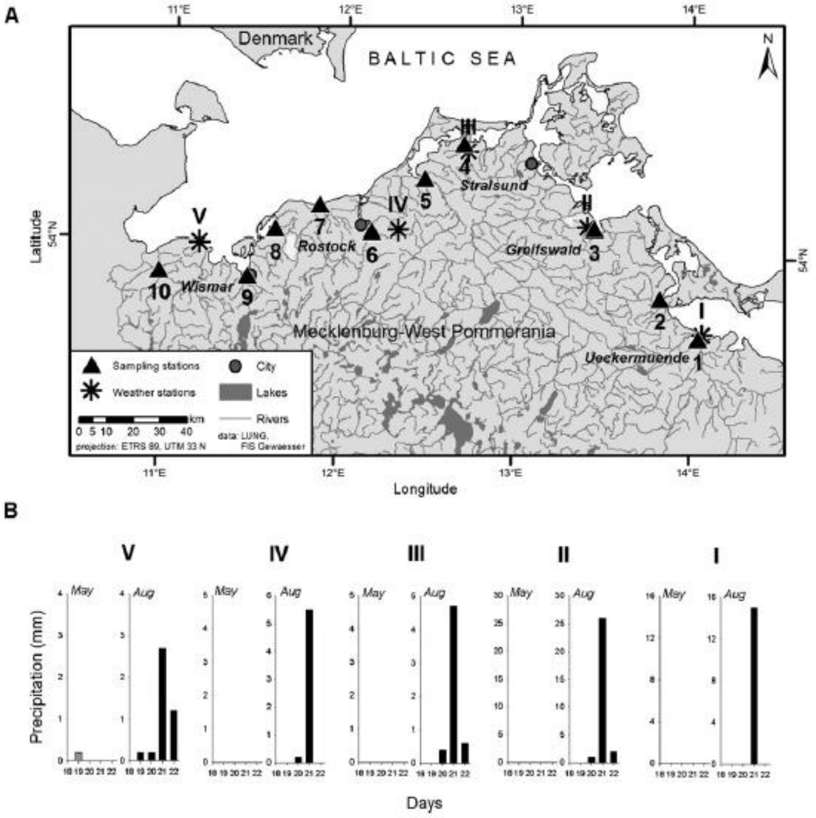


Fig. 2. A. The Baltic Sea estuary sampling sites 1 to 10 (closed triangles, 1: *Uecker*, 2: *Peene*, 3: *Ryck*, 4: *Barthe*, 5: *Recknitz*, 6: *Warnow*, 7: *Muehlenfliess*, 8: *Hellbach*, 9: *Wallensteigraben* and 10: *Stepenitz*) are distributed along the coast of *Mecklenburg-West Pomerania*. The numbers I to V present stations of the German Weather Service (DWD, Deutscher Wetterdienst) monitoring precipitations (open circles, I: *Ueckermuende*, II: *Greifswald*, III: *Barth*, IV: *Gross Luesewitz* and V: *Boltenhagen*). B. Presented are the precipitations at each DWD monitoring station for the sampling days in 22 May and 22 August in 2012 as well to three days before (Deutscher wetterdienst: ftp://ftp-cdc.dwd.de/pub/CDC/).

Table 1
The Baltic Sea estuary sampling sites are presented from east to west along the coast of the Baltic Sea in *Mecklenburg-West Pomerania*. The positional data are presented together with the data ranges obtained for salinity and temperature.

Station no.	Station name	Latitude	Longitude	Salinity	Temperature °C	Sampling dates in 2012
1	*Uecker*	53° 43′ 55.54″ N	14° 02′ 52.31″ E	0.1–0.5	12.3–20.9	05/22, 06/21, 08/22, 09/25
2	*Peene*	53° 51′ 56.91″ N	13° 49′ 40.11″ E	0.9–1.3	12.8–22.6	05/22, 06/21, 08/22, 09/25
3	*Ryck*	54° 05′ 36.54″ N	13° 26′ 54.90″ E	1.3–6.1	13.7–21.4	05/22, 06/21, 08/22, 09/25
4	*Barthe*	54° 21′ 58.78″ N	12° 41′ 14.97″ E	1.2–4.1	13.0–21.0	05/22, 06/21, 08/22, 09/25
5	*Recknitz*	54° 14′ 50.68″ N	12° 28′ 01.82″ E	0.3–2.6	11.8–20.9	05/22, 06/21, 08/22, 09/25
6	*Warnow*	54° 03′ 50.96″ N	12° 10′ 16.72″ E	0.1–0.3	12.9–20.6	05/22, 06/21, 08/22, 09/25
7	*Muehlenfliess*	54° 08′ 50.20″ N	11° 52′ 08.70″ E	0.1–0.8	11.7–20.2	05/23, 06/19, 06/22, 06/26, 07/10, 07/17, 08/07, 08/23, 09/26
8	*Hellbach*	54° 03′ 39.03″ N	11° 37′ 15.18″ E	0.1–0.4	11.2–17.1	05/23, 06/22, 08/23, 09/26
9	*Wallensteingraben*	53° 54′ 05.84″ N	11° 28′ 18.84″ E	0.0–0.3	13.2–21.5	05/23, 06/22, 08/23, 09/26
10	*Stepenitz*	53° 54′ 25.24″ N	10° 58′ 01.10″ E	0.9–3.1	12.0–20.0	05/23, 06/22, 08/23, 09/26

Glyphosate and AMPA analysis was conducted within the following three days. Samples obtained for glyphosate and AMPA measurement were derivatized with 9-Fluorenylmethyl chloroformate (FMOC-Cl) as described elsewhere (Bernal et al., 2012). For the derivatization of glyphosate and AMPA 800 µL of each water sample was placed in a 2 mL reaction tube (Eppendorf, Germany). To the sample 100 µL of 0.07 M borate buffer (sodium tetraborate decahydrate, Sigma-Aldrich, Tauffkirchen, Germany) at pH 9 and 100 µL of a 1 mMFMOC-Cl solution (purity 99.0%, Sigma-Aldrich, Germany) in acetonitrile were added and vigorously shaken. The samples were incubated at room temperature for 4 h for complete derivatization. Subsequently, the derivatized samples were filtered by passing through a 0.45 µm Phenex-RC 15 mm syringe filter (Phenomenex, Germany) and directed to LC–MS/MS analysis. Glyphosate and AMPA analysis was conducted on an LC triplequadrupole system (LC–MS/MS) from Thermo Fisher Scientific (Dreieich, Germany). The LC system consisted of an Accela autosampler (Series: 750477), Accela pump (Series: 700862) and Maylab Mistra Switch model 886 (Series: 100027). The mass analyzer was the TSQ vantage triple-quadrupole mass analyzer (Series-Nr.: TQU 02725) equipped with a heated electrospray ionization source interface (HESI). Instrument operation, data processing and evaluationweremanaged with XCalibur® 2.1 (Thermo Fisher).

Samples were directed to reverse phase chromatographic separation on a Gemini-NX C18 column (150 × 2.0 mm, 3 µm) coupled to a 4 × 2.0 mm Gemini-NX Security Guard cartridge (Phenomenex®, Germany). The column temperature was set at 20 °C and the injection volume was 50 µL. Themobile phase Awas a 2mMammonium hydrogen carbonate buffer and ammonia solution (32% (v/v)) with a pH of 9 (Sigma-Aldrich Germany) and the mobile phase B was acetonitrile (Walter-CMP GmbH, Kiel, Germany). Samples were eluted gradually from the column with a flow rate of 100 µL/min with an initial composition of 99% A down to 35% at 15 min and to 5% at 19 min until 27 min. There was a post column run until 30 min back to 99% A. Glyphosate and AMPA compounds were ionized through the HESI interface using optimized MS parameters and detected in the Selected Reaction Monitoring (SRM) mode (Fig. 3). However, for the initial method setup the MS/MS system was calibrated and tuned using the polytyrosine 1, 3, 6 standard solution (Thermo Fisher Scientific, Germany). The optimal HESI-MS/MS conditions were set as follows: capillary temperature 300 °C, vaporizer temperature 200 °C, spray voltage −3500 V, sheath gas pressure 20 psi, auxiliary gas flow rate 10 arbitrary units; S-lens offset 62 V and 43 V for glyphosate and AMPA, respectively. The used collision gas was argon and the collision energy was 21 and 20 eV for glyphosate and AMPA, respectively.

Two mass transitions were utilized to verify the presence of the compounds in a sample togetherwith the retention time in comparison to standard samples (glyphosate: $m/z = 390 \rightarrow 168$ and $m/z = 390 \rightarrow 150$, AMPA: $m/z=332 \rightarrow 136$ and $m/z=332 \rightarrow 110$). However, for quantification the higher abundant mass fragments have been utilized that is the fragment $m/z = 168$ for glyphosate and $m/z = 110$ for AMPA, respectively (Fig. 3). Glyphosate and AMPA calibrations were conducted using standards (Dr. Ehrenstorfer GmbH, Augsburg, Germany) in different concentration ranges covering the range from 25 ng/L to 3000 ng/L with correlation coefficients $R2 \geq 0.9990$. For method validation nine concentrations of glyphosate and AMPA were analyzed in triplicates. Precision and accuracy are expressed as relative standard deviation (RSD%, Eq. (1)) and relative error (RE%, Eq. (2)), respectively.

$$\mathrm{RSD\%} = \frac{s}{\overline{y}} \times 100 \tag{1}$$

$$\mathrm{RE\%} = \frac{\overline{x} - x_t}{x_t} \times 100 \tag{2}$$

s	standard deviation of the signal values of a sample set
$\overline{y}$	mean of the signal values of a sample set
$\overline{x}$	mean of the calculated concentrations of a sample set
x_t	true value of the spiked concentration

For the quantification of glyphosate and AMPA concentrations in natural samples the standard addition method has been utilized to avoid any matrix associated disturbances in the quantification process. Thus, each sample was divided into four subsamples. Three of them were spiked with increasing concentrations of glyphosate and AMPA leaving one subsample without any further additions. The subsamples were analyzed for glyphosate and AMPA and peak areas were plotted versus standard concentrations. The concentration value in the sample was obtained through linear regression of the data points of the subsamples and the intercept with the x-axis. To assure quality of the analysis and to control system stability throughout the measurements each sample sequence included one blank sample without addition of glyphosate and AMPA and several individual standard samples.

For the current study of glyphosate and AMPA in the Baltic Sea estuaries, analyses were conducted without any pre-concentration steps. The derivatization was processed in Milli-Q water (VWR International, Hannover,Germany) or samplematrix, respectively. Therefore, chromatographic and detector specific parameters were optimized to yield the best resolution of the compounds as well as the highest detector sensitivity possible. LC conditions were tested with respect to eluent compositions, different buffer concentrations in the eluent A and B, various variants gradient elution and different mobile phase flow rates. However, buffer concentrations showed an effect on peak shapes and noise level and the gradient elution on the chromatographic resolution and retention time for both glyphosate and AMPA (data not shown). The eluent composition primarily influenced the peak shape for glyphosate and AMPA and the chromatogram noise level while themobile phase flow rates influenced detection sensitivity and the retention time.Mass detector parameters such as spray voltage (Fig. 5B), auxiliary gas flow rates, sheath gas pressure, vaporizer temperature and capillary temperature have been varied for the HESI as ionization efficiency directly influences detector sensitivity.

Stability of glyphosate and AMPA derivatives in water were tested at 5 °C and 21 °C for a period of 300 h. However, only low concentration variations and no additional peaks in the chromatograms due to degradative processes could be observed. These data indicate that glyphosate and AMPA derivatized samples can be held for at least 12 days for their analysis with a satisfactory stability. The performance of the analytical method was evaluated according to the linearity of the regression analysis together with precision and accuracy of the method. A high degree of linearity was obtained for glyphosate and AMPA calibrations (R2 glyphosate = 0.9993, R2 AMPA =0.9994).

The optimized method allowed the measurement of glyphosate and AMPA until concentration limits (LODs) of 27 ng/L and 31 ng/L, respectively. Precision was expressed as the relative standard deviation RSD (%) and accuracy as the relative error RE (%) determined from nine standard concentrations in the low,middle and high concentration ranges that were analyzed in triplicates. The validation data are summarized in Table 2. The RSD ranged from 0.2% to 11.6% and from 1.0% to 10.9% for glyphosate and AMPA, respectively and RE was always below 16% (glyphosate: 0.5 to 14.5%, AMPA: 0.1 to 15.8%).

In order to assess potential contamination of the Baltic estuaries by glyphosate and AMPA, water samples were collected from ten German Baltic estuaries in 2012 between May and September and analyzed for the presence and concentrations of glyphosate and AMPA (Fig. 2A, Table 1). The presence of AMPA could be verified for all stations investigated; glyphosate was identified in nine of them. The concentrations of glyphosate and AMPA found ranged from 28 to 1690 ng/L and from 45 to 4156 ng/L, respectively (Table 3). The highest glyphosate concentrations were found at sampling sites seven and eight; for AMPA at sampling site seven. Moreover, these concentrations exceeded by far the highest glyphosate and AMPA concentrations observed at other sampling sites.

Table 3
Glyphosate and AMPA concentration ranges obtained from the Baltic Sea estuaries.

		Glyphosate			AMPA		
Station no.	Station name	Min (ng/L)	Mean ± SD (ng/L)	Max (ng/L)	Min (ng/L)	Mean ± SD (ng/L)	Max (ng/L)
1	*Uecker*	62	82 ± 21	101	273	650 ± 269	870
2	*Peene*	<LOD	<LOD	<LOD	50	65 ± 21	79
3	*Ryck*	<LOD	92 ± 139	252	<LOD	17 ± 35	69
4	*Barthe*	<LOD	82 ± 55	120	45	66 ± 31	101
5	*Recknitz*	<LOD	7 ± 14	28	45	93 ± 68	171
6	*Warnow*	<LOD	10 ± 17	29	99	127 ± 21	150
7	*Muehlenfliess*	160	665 ± 471	1690	497	1445 ± 1167	4156
8	*Hellbach*	150	561 ± 736	1664	296	476 ± 294	912
9	*Wallensteingraben*	<LOD	29 ± 37	70	55	145 ± 64	195
10	*Stepenitz*	45	55 ± 10	69	243	360 ± 94	467

To gain more information on the temporal variations of glyphosate and AMPA further sampling in shorter time intervals was conducted at sampling station seven (Muehlenfliess) as high glyphosate and AMPA concentrations had beenmeasured there. For both contaminants lowest concentrations were obtained in the May samples with a base increase to October 2012 (Fig. 7). However, glyphosate and AMPA concentrations varied by one order of magnitude within the sampling time period. Thus, the lowest concentration observed for glyphosate was 160 ng/L (May 23rd) and the peak concentration was 1690 ng/L (July 10th), while for AMPA lowest concentration observed was 497 ng/L (May 23rd) and highest was 4156 ng/L (August 23rd). However, a clear temporal trend is evident neither for glyphosate nor for AMPA and peak concentrations for both compounds do not correlate.

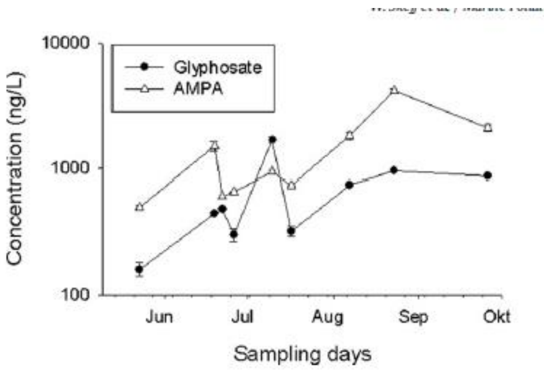


Fig. 7. Glyphosate and AMPA have been measured in samples collected at sampling site *Muehlenfliess* from May to September 2012. Peak concentrations were found on July 10th and on August 23rd for glyphosate and AMPA, respectively.

The stream Muehlenfliess was observed to be the sampling site most contaminated with glyphosate and AMPA compared to other stations investigated. To estimate the riverine transport of glyphosate and AMPA to the Baltic Sea estuaries the water samples from inbound sampling stations along Muehlenfliess were collected and analyzed (Fig. 8A). The measured glyphosate and AMPA concentrations are presented in Fig. 8B. The highest glyphosate and AMPA concentrations were found at sampling site Muehlenfliess (sampling site 1 at Fig. 8, 2768 ng/L and 5190 ng/L, respectively) followed by both inbound Muehlenfliess estuarine stations. The lowest concentrations were found at Bollhaeger Fliess (100 ng/L and 110 ng/L for glyphosate and AMPA, respectively) which flows into the Muehlenfliess. Glyphosate or AMPA could not be detected in the Baltic Sea coast (station 5, Fig. 8), i.e., concentrations were below 27 and 31 ng/L, respectively.

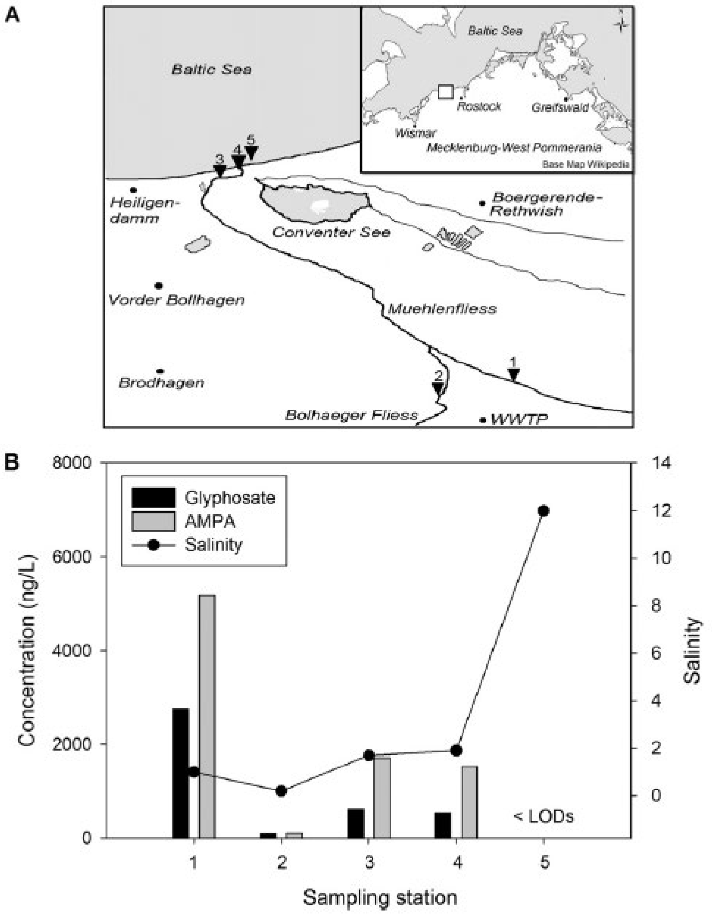
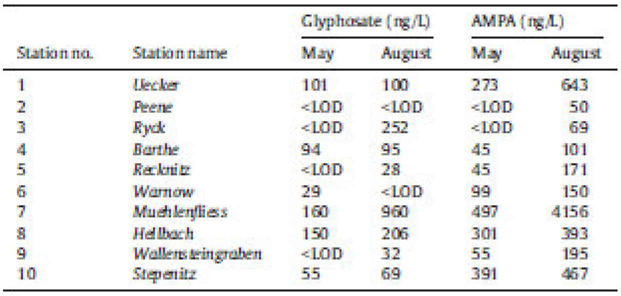


Fig. 8. A. Water samples from inbound sampling sites along *Muehlenfliess* were B. analyzed for glyphosate and AMPA. Station numbers 1 to 5 refer to 1: *Muehlenfliess*, 2: *Bollhaeger Fliess*, 3, 4: *Muehlenfliess estuary* and 5: *Baltic Sea coast*.

Transport of contaminants may arise through run off after rainfall events. To study the influence of this means of transport glyphosate and AMPA concentrations in the samples collected in May 2012 during dry weather conditions were compared to those sampled in August 2012 after a rainfall event (Fig. 2B, Table 5). In contrast to the samples collected in May 2012 AMPA was detectable at every station in August 2012. Moreover, if AMPA was found both times, AMPA concentrations were always higher in August than in the May 2012 samples. However, with respect to glyphosate the concentrations measured in May 2012 compared to those from August 2012 did not allow clear discrimination between sampling dates and thus, weather conditions.

Table 5
Glyphosate and AMPA concentrations were measured in the collected water samples in May and August in 2012 (see Table 1).



		Glyphosate (ng/L)		AMPA (ng/L)	
Station no.	Station name	May	August	May	August
1	*Uecker*	101	100	273	643
2	*Peene*	<LOD	<LOD	<LOD	50
3	*Ryck*	<LOD	252	<LOD	69
4	*Barthe*	94	95	45	101
5	*Recknitz*	<LOD	28	45	171
6	*Warnow*	29	<LOD	99	150
7	*Muehlenfliess*	160	960	497	4156
8	*Hellbach*	150	206	301	393
9	*Wallensteingraben*	<LOD	32	55	195
10	*Stepenitz*	55	69	391	467

In this study glyphosate and AMPA methodology was optimized and validated for their measurements in Baltic Sea estuaries water samples. The LC and MS–MS parameters were found to have a clear effect on the chromatographic performance and detector sensitivity for both glyphosate and AMPA and consequently the optimization of these parameters allows the detection and quantification of both compounds at concentrations below the European drinking water threshold of 100 ng/L (LODglyphosate: 27 ng/L, LODAMPA: 31 ng/L) and this without any further fortification steps. Performance analysis of the analytical method in terms of linearity, precision and accuracy lead to a high degree of linearity and RSD% and RE% were below 16% for both glyphosate and AMPA, thus, giving rise to a precise and accurate method for glyphosate and AMPA analyses even in the very low concentration ranges expected for the Baltic Sea estuaries.

Glyphosate was considered to be non-mobile due to its strong adsorbing properties to soil particles (Giesy et al., 2000). However, glyphosate along with its metabolite AMPA could be found in several aquatic environments (Battaglin et al., 2005; Coupe et al., 2012; Popp et al., 2008). In the federal state of Mecklenburg-West Pomerania fresh surface and groundwater bodies contained glyphosate above the European drinking water threshold of 100 ng/L (Bachor et al., 2008).

However, to our knowledge there is only one reported finding for marine environments with a glyphosate peak concentration of 1.2 µg/L at the French Atlantic coast (Burgeot et al., 2007). This is very close to the highest glyphosate concentration observed within this current study in which glyphosate and AMPA were detected at most sampling sites in the Baltic Sea estuaries of Mecklenburg-West Pomerania. Besides this, our data obtained from inbound sampling sites along Muehlenfliess strongly indicate riverine transport for both compounds from their place of application to the Baltic Sea. Hence, the data obtained here together with those fromother studies strongly suggest to rethink glyphosate as immobile compound which is exactly what has also been suggested elsewhere (Battaglin et al., 2005).
AMPA concentrations often exceeded those for glyphosate which was also shown for other sampling sites (Grunewald et al., 2001; Popp et al., 2008). Moreover, no correlation between concentration peaks for glyphosate and AMPA have been obtained at sampling site Muehlenfliess.

This might be attributable to higher biological stability for AMPA than for glyphosate (Grunewald et al., 2001). However, AMPA is also the key metabolite formed during degradation of a number of industrial phosphonates as ATMP (aminotrimethylene phosphonic acid), EDTMP ((ethylenediaminetetra (methylene-phosphonic acid)) and DTPMP (diethylene triamine pentamethylene-phosphonic acid) used in laundry agents, detergents and the textile industry (Jaworska et al., 2002; Nowack, 2003). Therefore, AMPA detected at the Baltic Sea estuaries may not be solely attributable to glyphosate metabolization, but also to degradation of other phosphonates of urban sources entering the estuaries.

Besides local variations, more detailed information on temporal variations of glyphosate and AMPA concentrations could be obtained from the sampling site Muehlenfliess. Despite a base increase, concentrations of both compounds fluctuated strongly. Similar results from time course field studies have been reported previously, e.g. (Battaglin et al., 2005; Coupe et al., 2012). The factors causing those temporal and local variations in glyphosate and AMPA concentrations are very diverse and probably arise from irregular dilution with seawater on the one hand, but also from their agricultural use. Therefore, different herbicide application methods and dosages in the agricultural fields, soil characteristics, microbial activity and geological aswell asweather conditions collectively may cause the observed variations of glyphosate and AMPA concentrations. Glyphosate is known for its non-agricultural applications in parks, gardens and rail way tracks. AMPA is a metabolite of glyphosate and also phosphonates used in industry.

Therefore, besides agricultural origins, urban sources, too, have to be considered as an important factor influencing glyphosate and AMPA concentrations in aqueous environments. Several studies have reported waste water treatment plants as significant sources of glyphosate and AMPA as they can be released from suspended particles during waste water processing (Botta et al., 2009; Popp et al., 2008). Salinity observed for the Muehlenfliess at sampling site 1 (Fig. 8A) and Bollhaeger Fliess differed strongly (Muehlenfliess: 1.0 and Bollhaeger Fliess: 0.2) and for the Muehlenfliess it was higher than expected for a freshwater stream. Increased salinization may arrive from natural accumulation of salts, but it was also shown, that anthropogenic influences such as mining activities, industrial discharges or waste water treatment plant effluents may give rise to increased salinization which is referred to as secondary salinization (Canedo-Arguelles et al., 2013). Salinization was elevated for only one of the two adjacent streams. This may indicate an urban point source near the Muehlenfliess which might explain the high concentrations observed for glyphosate and AMPA.

Glyphosate and AMPA concentrations obtained during dry weather conditions and after rainfall events were compared. In 7 out of the 10 sampling sites glyphosate concentrations were higher after rainfall as compared to those obtained during dry weather conditions. However, at every sampling site AMPA concentrations during dry weather conditions were below those after rainfall. This suggests higher mobility for AMPA than for glyphosate which is in agreement with previous studies (Botta et al., 2009; Coupe et al., 2012). Nevertheless, our data indicate that rainfall events also support glyphosate mobility.

In a microcosms experiment, glyphosate was found causing a change in riverine algal communities exposed to about 10 μg/L of glyphosate alone (Pesce et al., 2009). Glyphosate concentrations observed in Muehlenfliess was 2763 ng/L, therefore glyphosate may even reach this threshold concentration of 10 μg/L in rivers or streams of Mecklenburg- West Pomerania near to its application areas at which toxic effects to microorganisms might arise. In the marine environment, glyphosate was shown to exert toxic effects on some microorganisms such as diatoms as Nitzschia sp. or S. costatum or to cyanobacteria as A. flos-aquae when it was applied inmg/L concentration level. These concentrations are much higher than those found in the Baltic estuaries (Peterson et al., 1994; Tsui and Chu, 2003). In fact, glyphosate does not exist alone in the environment. Perhaps, it can exist with surfactants which usually enhance the herbicidal activity or application characteristic. Different classes of surfactants can reach estuaries and the marine environment via sewage sludge on land, industrial discharges and effluent from wastewater treatment plants (Alsalahi et al., 2014; Scott and Jones, 2000). Stachowski-Haberkorn et al. (2008) showed that Roundup® (i.e. glyphosate and surfactants) can cause a disturbance to the marine microbial community exposed to Roundup® even in a concentration of 1 μg/L of the ingredient glyphosate. In our study the peaks of glyphosate concentrations found in the estuaries of Muehlenfliess and Hellbach exceed 1.5 μg/L. Therefore, glyphosate can cause negative effects on the microbial communities of these two Baltic stations if there are enough concentrations of the additive surfactants to the Roundup® formulations. Moreover, in this study glyphosate and AMPA were found very frequently in the Baltic Sea estuaries and nothing is known about the long-term effects of both contaminants in concentration levels observed in the Baltic estuaries. Thus, fate and risk assessment studies for glyphosate and AMPA in the marine environments are required.

In this work an analytical method was developed and validated for the measurement of glyphosate and AMPA concentrations in Baltic estuarine water samples using LC–HESI-MS/MS after their derivatization with FMOC-Cl. Satisfying quality control data including linearity, limits of detection and quantification as well as precision and accuracy together with analytes and system stability were obtained. The results obtained from analysis of the collected water samples underline the contamination of all investigated German Baltic estuaries with AMPA and most of them also with glyphosate. Furthermore, this study illustrates possible transport of glyphosate and AMPA under both dry and wet weather conditions via rivers and streams into the marine environment. Clear spatial and temporal fluctuationswere found during their transport into the Baltic Sea. No correlation between glyphosate and AMPA concentrations was observed. Urban origin could be an important source of marine water contamination with glyphosate and AMPA. The fate of both contaminants and their risk assessments in estuaries and in the marine environment are still open questions.

Assessment and conclusion by RMS:
This study reference came out in the literature search performed by applicant and summarized under point B.8.6 of volume 3CA_B-8. The study has been considered relevant after detailed full-text assessment, as supplementary information by applicant (cat B) and was not summarized and not included in its submission for monitoring data. After review of the full text, RMS eventually considered it provides reliable information (with restrictions) that should be presented in the present section B.8.5.

This study aimed at optimizing an analytical method, which was further validated on Baltic Sea estuaries water samples. The analytical method is therefore well described.
Samples from 10 locations along the Baltic Sea coastline of Mecklenburg-West Pomerania, Germany were collected in 2012 and analysed in order to study the presence of the herbicide glyphosate, AMPA and their potential transport to the marine environment. Samples were collected during the application period of pesticides between May and September (see Table 1).

Concentration results are given in table 3 and 5, and in the text. Concentration ranges observed are reported to be between 28 to 1690 ng/L and 45 to 4156 ng/L for glyphosate and AMPA respectively, in the text and in table 3 and 5. However, it is also indicated in the conclusions that glyphosate concentrations observed in one of the site (Muehlenfliess) was 2763 ng/L, while this maximum concentration cannot be found in the table results or graphs. The study is therefore considered reliable with restrictions.

Further evaluation of concentration towards salinity was performed and “concentrations decreased along the salinity gradient to the estuaries of the Baltic Sea.”

B.8.5.6. Monitoring data in drinking water

New studies/assessments

Data point:	CA 7.5/001
Report author	[redacted]
Report year	2020
Report title	Collection of public monitoring data for European countries for the compartments soil, water, sediment and air for Glyphosate, AMPA and HMPA
Document No	110057-1
Guidelines followed in study	Methodology is based on the Groundwater Monitoring guideline document (Gimsing *et al*., 2019) with respect to chapter 7 (‘Public monitoring data collected by third party organisations’) Minimum quality criteria of monitoring data described by the FOCUS Ground Water Work Group chapter 9.5 (European Commission, 2014)
Deviations from current test guideline	None
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

The report provides information about the outcome of a search for readily accessible and available public monitoring data in European countries at a regional/national level for the time period 1995-2019. The main focus was on the time period 2012-2019 while earlier years are already covered by existing data. The search included raw data, requested from regional/national authorities or downloadable from their websites, as well as aggregated data extracted from reports compiled by authorities.

Data from 14 European countries were considered: Austria, Belgium, Denmark, France, Germany, Hungary, Ireland, Italy, The Netherlands, Poland, Romania, Spain, Sweden and the United Kingdom. The countries represent the major markets of products containing glyphosate sold in the EU. The data compilation included the active substance glyphosate and its metabolites AMPA and HMPA, in the soil, groundwater, surface water, tidal water, drinking water, sediment and air environmental compartments.

As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities and other bodies of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were not actually included in any of the monitoring programs.

Drinking Water Compartment Conclusion
Public monitoring data for glyphosate or its metabolites in drinking water were available for 10 countries (AT, BE, DE, DK, ES, FR, IE, NL, SE and UK). In most cases information was only accessible as aggregated monitoring data. Raw data were rarely available for reasons of national security in the case of public wells or due to data protection in cases where data were owned by private companies. Raw data was provided by the German federal state Schleswig-Holstein, Ireland and Sweden.

I. MATERIALS AND METHODS

The general methodology of data collection of public monitoring data and minimum quality criteria is based on existing guideline documents for groundwater monitoring programs.

RMS indicates this methodology have been described in the study summary under section Groundwater and surface water, it is not repeated here.

II. RESULTS AND DISCUSSION

The final data collection of raw data and aggregated data is summarised for each compartment and each country in Table 8.5-227.

Drinking water

- Austria (AT)
    - No raw monitoring data from national authorities for drinking water in Austria were identified.
    - Aggregated monitoring data from annual reports on drinking water quality were downloaded from the Federal Ministry of Labour, Social Affairs, Health and Consumer Protection.
- Belgium (BE)
    - No raw monitoring data from national authorities for drinking water in Belgium were identified.
    - Aggregated monitoring data from reports published by national authorities in Belgium for drinking water were obtained from the Flemish EPA.
- Germany (DE)
    - Raw monitoring data from national authorities for drinking water were provided by the state of Schleswig-Holstein.
    - Aggregated monitoring data from reports published by national authorities for drinking water were downloaded from the German EPA.
- Denmark (DK)

  - No raw monitoring data from national authorities for drinking water in Denmark were identified.
  - Aggregated monitoring data from reports published by national authorities for drinking water were downloaded from the Danish EPA.
- Spain (ES)
  - No raw monitoring data from national authorities for drinking water in Spain were identified.
  - Aggregated monitoring data from reports published by national authorities for drinking water were obtained from the Ministry of Health, Consumption and Social Welfare in form of annual reports.
- Europe (EU)
  - No aggregated monitoring data from reports published by EU institutions or international organizations for drinking water at EU level were identified for glyphosate or its metabolites.
- France (FR)
  - No raw monitoring data from national authorities for drinking water in France were identified.
  - Aggregated monitoring data from reports published by national authorities for drinking water were obtained from the Ministry of Solidarity and Health.
- Hungary (HU)
  - The Ministry of Interior confirmed that no monitoring programs were in place that included glyphosate or metabolites.
- Ireland (IE)
  - Raw monitoring data from national authorities for drinking water were downloaded from the SAFER portal of the Irish EPA.
  - Aggregated monitoring data from reports published by national authorities for drinking water were downloaded from the Irish EPA and from the governmental page on the Water Framework Directive.
- Italy (IT)
  - No drinking water monitoring data for glyphosate or its metabolites were identified for Italy.
- The Netherlands (NL)
  - No raw monitoring data from national authorities for drinking water in the Netherlands were identified.
  - Aggregated monitoring data from reports published by national authorities for drinking water were downloaded from RIVM, the Inspection of Environment and Transport and the E-depot of Wageningen University & Research.
- Poland (PL)
  - The responsible authorities for monitoring data in Poland are the Polish Geological Institute and the Chief Inspectorate of Environmental Protection. The latter authority confirmed by e-mail that in Poland there is currently no public monitoring of glyphosate or its metabolites.
- Romania (RO)
  - The responsible authority for monitoring data is the Ministry of Water and Forests. The Water Resources Management Directorate confirmed on behalf of the Ministry of Water and Forests that no public monitoring of glyphosate or its metabolites is carried out in any water compartment in Romania.
- Sweden (SE)
  - The national monitoring data sent to us by SLU do not comprise drinking water. However, SLU also provided another in-official database containing raw data for drinking water issued from other sources than national monitoring.
  - Aggregated monitoring data from reports published by national authorities in tabular form for drinking water were downloaded from the SLU homepage.
- United Kingdom (UK)

- Aggregated monitoring data from reports published by national authorities for drinking water in England and Wales were downloaded from the Drinking Water Inspectorate.

Table 8.5-227: Overview of public monitoring data availability of raw data (R) and aggregated data (A)

Country	Soil	Water				Sediment	Air
		Ground	Surface	Tidal	Drinking		
Austria	-	R, A	R, A	-	A	-	-
Belgium	-	R	R	-	A (Flanders)	-	-
Denmark	-	R, A	A	-	A	-	-
France	-	R	R	-	A	R	-
Germany	R (Brandenburg)	R, A	R, A	R	R (Schleswig-Holstein), A	-	-
Hungary	-	A (one research article)	A (one research article)	-	-	-	-
Ireland	-	R, A	R, A	-	R, A	-	-
Italy	-	R (Lombardia), A	R, A	-	-	-	-
The Netherlands	-	R, A	R, A	-	A	-	-
Poland	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Romania	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Spain	-	R, A	R, A	-	A	-	-
Sweden	-	R, A	R	-	R, A	R	-
UK England	-	R	R	R	A	-	-
UK Northern Ireland	-	R	-	-	-	-	-
UK Scotland	-	-	R	-	-	-	-
UK Wales	-	-	R	-	A	-	-

R raw data available; A aggregated data from reports available; - no raw or aggregated data available

III. CONCLUSIONS

The present collection of public monitoring data for glyphosate, AMPA and HMPA in soil, groundwater, surface water, drinking water, tide water, sediment and air resulted in a comprehensive database of ‘raw monitoring data from national authorities’ and ‘aggregated monitoring data from reports published by national authorities’. As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were actually not included in any of the monitoring programs.

Public monitoring data for glyphosate or its metabolites in drinking water were available for 10 countries (AT, BE, DE, DK, ES, FR, IE, NL, SE and UK). In most cases information was only accessible as aggregated monitoring data. Raw data were rarely available for reasons of national security in the case of public wells or due to data protection in cases where data were owned by private companies. Raw data was provided by the German federal state Schleswig-Holstein, Ireland and Sweden.

Assessment and conclusion by applicant:

The report describes the collection process of public monitoring data for European countries for the compartment soil, water, sediment and air for Glyphosate, AMPA and HMPA

The report is considered valid.

Assessment and conclusion by RMS:

This report describes the methodology employed for collection of monitoring data for Glyphosate, AMPA and HMPA. The data collection refers to third party organization data regarding all environmental compartments (Soil, GW, SW, TD, DW, SD, AIR)

Two different data types were collected, i.e. raw data from national authorities and aggregated data from publicly available reports (from environmental agencies or research institute).

The general search strategy was similar for each compartment, country and substance. All details of data acquisition are given in the report, and all data sources are carefully listed and described.
Although the process can clearly not be reproduced, and cannot be checked in details for exhaustiveness, the search strategy is clearly exposed and considered acceptable.

For drinking water compartment, public monitoring data for glyphosate or its metabolites in drinking water were available for 10 countries (AT, BE, DE, DK, ES, FR, IE, NL, SE and UK). In most cases information was only accessible as aggregated monitoring data. Raw data were rarely available for reasons of national security in the case of public wells or due to data protection in cases where data were owned by private companies. Raw data was provided by the German federal state Schleswig-Holstein, Ireland and Sweden.

Also, there is no precise indication on the the origin of raw data for drinking water (i.e. ground water, surface water..) although this was part of the information to be collected in the described methodology; it seems that few information is publicly available on the sampling location and the origin of raw water cannot be further indicated when collecting raw data.

Findings from this data collection and corresponding analysis are given in a separate report; see [redacted] 2020 below.

The study (drinking water part) is considered acceptable.

Data point:	CA 7.5/002
Report author	[redacted]
Report year	2020
Report title	Glyphosate (GLY) and the primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA): Public monitoring data assessment and interpretation
Report No	EnSa-20-0322
Document No	-

Guidelines followed in study	Groundwater monitoring guideline document (Gimsing *et al.*, 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations'); Article 5 of Directive 2009/90/EC - Technical specifications for chemical analysis and monitoring of water status.
Deviations from current test guideline	Not relevant
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary

The report provides information about the outcome of an analysis of public monitoring data comprising environmental concentrations of glyphosate (GLY) and its primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA) collated from readily available public monitoring databases held by national/regional environment agencies. This data collection and analysis was designed to expand previous reviews to include other compartments and supplement them for surface water, groundwater and drinking water. Public monitoring data from the following Member States (MS) were assessed for the water, sediment and soil compartments: Austria (AT), Belgium (BE), Denmark (DK), France (FR), Germany (DE), Ireland (IE), Italy (IT), Netherlands (NL), Spain (ES), Sweden (SE) and the United Kingdom (UK). Three MS, namely Poland (PL), Hungary (HU), and Romania (RO) confirmed that they do not conduct analyses for GLY, AMPA and HMPA in any environmental compartment. No data for HMPA was identified for any MS or compartment. Note that at the time the study was started the UK was a Member State and is referred to as a Member State throughout the report.

Analyses of the large spatial and temporal dataset of measured concentrations occurring in several environmental compartments, namely surface water, groundwater, drinking water, tidal water, sediment and soil, were conducted to assess their state. This analysis not only sought to assess the state of the environmental compartment but also to consider the potential impacts this might have on biota, ecosystems and human health by using regulatory endpoints and thresholds from a range of European (EU) Directives. These included the Water Framework Directive (Directive 2000/60/EC) and associated Groundwater (2006/118/EC), Drinking Water (1998/83/EC) and Priority Substances (2008/105/EC28) Directives in addition to the Plant Protection Products Directive (1107/2009/EC).

<u>Drinking water</u>

Drinking water monitoring data were identified and evaluated for DE (German federal state Schleswig-Holstein), IE (GLY only) and SE. These data comprise analyses from both treated and untreated sources likely taken at the tap of the consumer. In addition, data analysis of SW data was undertaken assuming these were used as raw water for drinking water considering water treatment removal efficiencies when treating these waters. Case study investigations of raw drinking water sources in the Meuse river and around Berlin (DE) were conducted to investigate elevated frequencies of detection highlighted by regulators in NL and DE.

<u>Glyphosate</u>

The GLY public monitoring dataset was comparatively small (~8 000 samples collected from ~3 100 sampling sites). Compliance with the DrW threshold of 0.1 µg/L is very high (99.90% of samples) with detections ≥ 0.1 µg/L being rare (~0.10% of analyses). All 5 samples in SE that are ≥ 0.1 µg/L come from apparently untreated sources. All exceedances are old (≤2007) and significant strides have been made in SE since the introduction of the water protection regulations in 2004 through delineation of water protection zones. Where exceedances do occasionally occur the maximum concentration of 0.61 µg/L (recorded in DE) is well below the lifetime health-based ADI concentration of 1500 µg/L. These findings are consistent with aggregated report values of ~0.16% sample exceedance and maximum concentrations up to 0.92 µg/L (recorded in ES). Likewise, this maximum value is well below the lifetime health-based ADI concentration.

These values compare favourably with the ~0.09% of samples ≥ 0.1 µg/L in the previous data collection.

Case studies of GLY concentrations in SW, conducted for the river Meuse and the Spree/Havel river system in the Berlin area, conclude that the glyphosate sources from agriculture and urban and railway hard surface uses cannot clearly be distinguished. However, the data does suggest that baseline concentrations likely derive from agricultural uses and that urban and railway uses are key drivers of peak concentrations and in turn exceedance of the 0.1 µg/L water quality threshold of raw surface waters.

AMPA

The AMPA public monitoring dataset was similarly small (~7 000 samples collected from ~2 300 sampling sites). Compliance with the regulatory threshold of 10 µg/L is absolute at 100%. Compliance with the DrW threshold of 0.1 µg/L is very high (99.87% of samples) with exceedances being rare (~0.13% of analyses). All 7 samples in SE that are ≥ 0.1 µg/L come from apparently untreated sources. All exceedances are old (≤2007) and significant strides have been made in SE since the introduction of the water protection regulations in 2004 through delineation of water protection zones. Where exceedances do occasionally occur the maximum concentration of 0.85 µg/L is well below the lifetime health-based ADI concentration of 3960 µg/L. This is consistent with aggregated report values of ~0.05% exceedance and maximum concentrations of up to 3.0 µg/L (recorded in NL). Likewise, this maximum value is well below the lifetime health-based ADI concentration. These values compare favourably with the ~0.22% of samples ≥ 0.1 µg/L in the previous data collection. It should be borne in mind that AMPA may originate from sources other than GLY, for example detergents.

HMPA

No monitoring data were available for HMPA.

Surface Water as a Raw Drinking Water Source

For surface water destined to be drinking water, there are almost always water treatment processes applied to remove bacteria and viruses and other organic micro-pollutants. Undertaking a simplistic data analysis where raw SW concentrations are factored with the known optimal treatment removal efficiencies (95% for AMPA, and 99% for GLY) does not alter the conclusions of no risk to human health from the assessment of drinking water datasets, especially when considered within the broader context of abstraction (selective abstraction into bank side storage, bank abstraction) and source management (blending of sources) within the water supply chain.

Drinking Water Compartment Conclusion

No information on HMPA was available. The analysis of the dataset available for drinking water for GLY and AMPA indicates that compliance is very high given detections above 0.1 µg/L are very rare and when they do sporadically occur, they occur at low concentrations that are well below human health thresholds. The measured environmental concentrations available suggest neither GLY nor AMPA pose a risk to human health *via* drinking water.

I. MATERIAL AND METHODS

The dataset analysed comprised individual surface water analysis records as well as existing aggregated analyses extracted from reports sourced from regional/national environment agencies (see [redacted], 2020, CA 7.5/001). The approach taken for the data processing was precautionary in that it preserved samples in the analysis where there was any doubt regarding their reliability. As such no records were excluded from the analysis. Similarly, no attempt to remove outliers prior to the analysis or calculation of statistics was undertaken. Analysis and assessment of the data against thresholds was undertaken using the statistical software R. For drinking water the monitoring data was evaluated against the following thresholds and endpoints:

- Drinking water endpoint: Standard drinking water threshold of 0.1 µg/L for parent compounds (GLY) and relevant metabolites;
- Drinking water threshold: Regulatory drinking water threshold of 10 µg/L for non-relevant metabolites (AMPA);

- Regulatory toxicology endpoints: Drinking water concentrations (see Table 8.5-228) based on 10% of the lifetime Acceptable Daily Intake (ADI) values for a 60 kg person consuming 2 L of water per day (EFSA, 2010; WHO, 1993; 2011). This is more precautionary than the current WHO guidelines (2011) which use 20% of ADI:
    - GLY – 1500 µg/L based on an ADI of 0.5 mg/kg bw/day derived from the NOAEL using a safety factor of 100 (EFSA, 2012)
    - AMPA – 3960 µg/L based on 1.32 mg/kg bw/day for AMPA derived from the NOAEL using a safety factor of 200 (EFSA, 2012)

In addition, the raw SW datasets were analysed further against the threshold of 0.1 µg/L following implementation of the following treatment effectiveness factors to the dataset:

- GLY – 60 to 99% removal
- AMPA – 25 to 95% removal

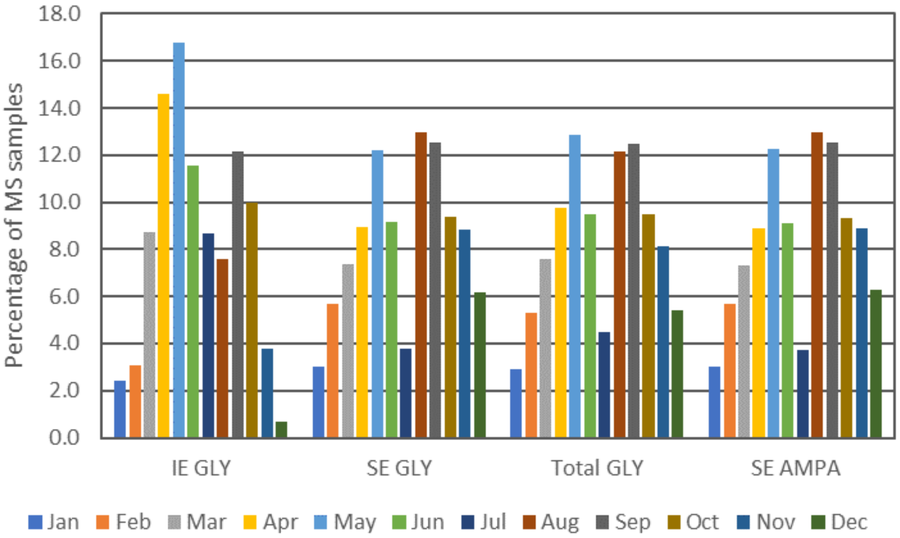
The combined European surface water dataset for GLY and AMPA was factored by the lower and upper removal efficiencies for each compound and then reanalysed using the same approach as was undertaken for surface water.

II. RESULTS AND DISCUSSION

Monitoring Data Assessment

Very little unaggregated drinking water data was available for analysis. This is largely because it is considered confidential by either the agency holding it or the organisation that supplied it to the agency, often on the grounds of consumer/national security. The data supplied and analysed was biased both spatially and temporally. The bulk of the data (~86% for GLY and 99% for AMPA) came from the SE dataset and while this dataset comprises >2 000 sites the coordinates for these sites were unavailable and as such the spatial distribution of these could not be assessed further. Similarly, none of the 767 sites in the IE dataset were supplied with coordinates. The small unrepresentative dataset from Germany is limited to the federal state of Schleswig-Holstein. The SE data comprises records from 1998 to 2014, the DE data covers 2012 to 2018 while that from IE are from 2017 only. Both the IE and SE datasets displayed a bimodal distribution of monthly sampling effort (see Figure 8.5-187), with peaks in the spring/summer (April/May/June) and autumn (August/September/October). There was insufficient data to create a combined European dataset and as such only individual MS data were presented. There was insufficient data to plot the DE data.

Figure 8.5-187: **Bar chart of drinking water monthly glyphosate (GLY) and AMPA sampling effort within each Member State.**



Glyphosate

Across all MS the GLY public monitoring dataset compiled comprised >8 300 samples collected from >3 100 sampling sites (see Table 8.5-229). Given the limited size of the dataset and the limited number of MS from which it was sourced, a combined European dataset was not created.

Compliance with the drinking water threshold of 0.1 µg/L was high (99.90%) given few exceedances (~0.10%). All 5 samples in SE that are ≥ 0.1 µg/L came from 5 apparently untreated sources (2 drilled wells, 2 dug wells, 1 unspecified GW source). Only 1 site had more than a single sample to assess if exceedance was systematic and for that dug well a further sample 7 weeks later was <LOD. All exceedances were old (≤2007) and significant strides have been made in SE since the introduction of the water protection regulations in 2004. Maximum concentrations were 0.61 µg/L in DE, 0.074 µg/L in IE and 0.17 µg/L in SE. These were well below the life-time ADI based concentration of 1500 µg/L (see Table 8.5-228). In addition, GLY exceedances extracted from aggregated data in official reports (see Table 8.5-230) ranged between 0.00% in AT and 0.29% in ES with an average of ~0.16% of samples ≥ 0.1 µg/L. Maximum concentrations were up to 0.92 µg/L in ES. This value was well below the life-time ADI based concentration. These values compared well with the previous data collection ([redacted] 2008, CA 7.5/075; [redacted], 2015, CA 7.5/074) where ~0.09% of samples analysed for GLY were found to equal or exceed 0.1 µg/L (see Table 8.5-231).

AMPA

Across all MS the AMPA public monitoring dataset compiled comprised >7 000 samples collected from >2 300 sampling sites (see Table 8.5-229). Compliance with the regulatory drinking water threshold of 10.0 µg/L for non-relevant metabolites was 100%. Compliance with the more precautionary threshold of 0.1 µg/L was high (99.87% of samples) given the small number of exceedances (0.13% of samples). Five of the SE samples that were ≥ 0.1 µg/L came from 5 apparently untreated sources (2 drilled wells, 3 dug wells) while 2 further samples came from “treated surface water from groundwater” from a single site. Only 1 site had more than a single analysis to assess the temporal nature of these exceedances and for this site the 4 samples of treated surface water from groundwater the concentrations suggested an exceedance event of <12 months in duration. In all 4 samples the GLY concentration was <LOD which suggests this AMPA was from SW from other sources than GLY. All exceedances were old (≤2007) and significant strides have been made in SE since the introduction of the water protection regulations in 2004. The maximum concentration was 0.85 µg/L (DE). This is well below the life-time based ADI concentration of 3960 µg/L (see Table 8.5-228). In addition, AMPA exceedance rates extracted from aggregated data in official reports (see Table 8.5-230) range between 0.00% in DK and 0.05% of samples in DE with an average of ~0.05%

for all MS combined. Maximum concentrations were up to 3.0 µg/L in NL. This value is well below the life-time based ADI concentration. These values compared well with the previous data collection ([redacted], 2008, CA 7.5/075; [redacted], 2015, CA 7.5/074) where ~0.22% of samples analysed for AMPA were found to equal or exceed 0.1 µg/L (see Table 8.5-231). It should be borne in mind that AMPA may originate from sources other than GLY, for example detergents.

Table 8.5-228: Summary of acceptable daily intake (ADI) concentrations used in the assessment (*after* EFSA, 2010; WHO, 1993; 2011)

Compound	**Intake in % of ADI**	**ADI derived from NOAEL and safety factor (mg/kg bw/day)**	**Maximum daily intake (mg/kg person/day)**	**Maximum daily intake 60 kg person consuming 2 L water /day (mg/day)**	**Acceptable intake based on 10% ADI (µg/L)**
GLY	10	0.5	0.05	3	1500
AMPA	10	1.32	0.132	7.92	3960

Raw Surface Water as a Source of Drinking Water

For completeness, an assessment of raw surface water bodies against the threshold of 0.1 µg/L was undertaken on the assumption that they might be used as raw water sources for drinking water production. The effects of factoring the raw surface water data to account for typical treatment on the exceedance rate were calculated (Table 8.5-232). For GLY the compliance rate improved with water treatment as the exceedance rate of 0.1 µg/L of ~23% in the baseline scenario was reduced to ~12% considering 60% reduction during water treatment and reduced even further to ~0.1% for treatment reduction rates near 99%. Similarly, for AMPA the compliance rate improved with water treatment as the exceedance rate of 0.1 µg/L of ~48% in the baseline scenario was reduced to ~42% considering 25% reduction during water treatment and reduced even further to ~5% for treatment reduction rates near 95%. If one considers a threshold of 10 µg/L for the non-relevant metabolite AMPA then the compliance was high (99.9%, 99.8% and 100% respectively) in the baseline, the 25% reduction and 95% reduction scenarios. Water treatment is geared to the quality of the raw waters, for better quality source waters lower water treatment removal rates would ensure compliance with the drinking water threshold. For source waters of lower quality the higher removal rates suggest compliance. These basic analyses suggest that the water treatment process would likely account for any environmental concentrations of GLY and AMPA in raw SW abstracted to produce potable water for human consumption, especially when compared against the life-time based ADI concentrations.

Limitations of the simplistic analysis were highlighted e.g. it was unable to take account of the fact that water companies would construct and optimise water treatment processes in order to achieve compliance. It should also be borne in mind that a significant portion of the AMPA in raw SW arises from other parent compounds like detergents. As such, this simplistic analysis indicates that raw SW abstracted and treated for human consumption would meet the required quality as the actual data on measured concentrations at the consumers tap demonstrates.

An evaluation of Member State specific thresholds is also outlined to illustrate the nuance specific in these systems and their drinking water supply with a view illustrating how these might be considered alongside public monitoring datasets. These are not summarised further here.

Table 8.5-229: Summary of the unaggregated drinking water (DrW) data for glyphosate (GLY) and AMPA sourced from Ireland and Sweden

Member State	**DE**					**IE**		**SE**				
Substance	**GLY**		**AMPA**			**GLY**		**GLY**		**AMPA**		
Threshold	**DrW: 0.1 µg/L**	**LTHAC: 1500 µg/L**	**Threshold: 0.1 µg/L**	**DrW: 10.0 µg/L**	**LTHAC: 3960 µg/L**	**DrW: 0.1 µg/L**	**LTHAC: 1500 µg/L**	**DrW: 0.1 µg/L**	**LTHAC: 1500 µg/L**	**Threshold: 0.1 µg/L**	**DrW: 10.0 µg/L**	**LTHAC: 3960 µg/L**
Number of sites	16	16	14	14	14	767	767	2335*	2369*	2321	2356	2356
Number of samples	18	18	15	15	15	1211	1211	6917*	7135*	6848	7054	7058
Number of samples > threshold	3	0	1	0	0	0	0	5	0	7	0	0
% of samples > threshold	16.7	0.00	13.3	0.00	0.00	0.00	0.00	0.072	0.0	0.10	0.00	0.0
Number of sites > threshold	3	0	1	0	0	0	0	5	0	6	0	0
% of sites > threshold	18.8	0.0	14.3	0.0	0.0	0.00	0.0	0.21	0.0	0.26	0.00	0.0
Number of consecutive samples > threshold	0	0	0	0	0	0	0	0	0	2	0	0
% of samples that are consecutive samples > threshold	0.0	0.0	0.0	0.0	0.0	0.00	0.0	0.00	0.0	0.029	0.00	0.0
Max number of samples > threshold at a single site	1	0	1	0	0	0	0	1	0	5	0	0
Max number of consecutive samples > threshold at a single site	1	0	1	0	0	0	0	1	0	5	0	0

NA – No data available
LTHAC - lifetime health-based ADI concentration

*RMS indicates that the number of samples considered should be the same whatever the threshold considered. No justification is given in the study report. The corresct number of samples is assumed to be 7135. However, the correct number of samples and sites cannot be checked from the information available in the full report.

Table 8.5-230: Summary of drinking water (DrW) monitoring data aggregated in reports for glyphosate (GLY) and AMPA

MS	Substance	Number of reports identified	Reports with data relating to threshold						Maximum value (µg/L)
			Number of reports	Date range	Number of samples	Threshold (µg/L)	Samples above threshold	% samples above threshold	
AT	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	2	2	2011 - 2017	2020	0.1	0	0.00	NS
BE	AMPA	1	1	2016	1169	0.1	1	0.09	0.087
	GLY	1	1	2016	1157	0.1	2	0.2	0.051
DE	AMPA	3	3	2011-2016	9525	0.1	5	0.05	NS
	GLY	3	3	2011-2014	4531	0.1	9	0.20	NS
DK	AMPA	1	1	2014-2016	1336	0.1	0	0.00	NS
	GLY	1	1	2014-2016	1337	0.1	1	0.07	NS
ES	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	10	9	2008-2018	>5313	0.1	>10	0.22/0.29[1]	0.92
EU Trans	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
FR	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
IE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	1	0	NA	NA	NA	NA	NA	NS
IT	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
NL	AMPA	11	0	NA	NA	NA	NA	NA	3.0
	GLY	11	0	NA	NA	NA	NA	NA	0.3
SE	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	ND	ND	ND	ND	ND	ND	ND	ND
UK	AMPA	ND	ND	ND	ND	ND	ND	ND	ND
	GLY	9	0	NA	NA	NA	NA	NA	NS

[1] Report data includes sample counts and % values – The first value is the average using count data only while the second is the average of report averages

ND – No data identified; NS – Not specified; > as missing values to calculate total

Table 8.5-231: **Summary of glyphosate (GLY) and AMPA monitoring data in drinking water across Europe, 2008-2015 (*after* [redacted], 2015, CA 7.5/074)**

Country	Years	Monitoring number of sites or samples		Detection number		Concentration ≥ 0.1 µg/L	
		GLY	AMPA	GLY	AMPA	GLY	AMPA
Austria	2011-13	751	15	?	?	0	0
Belgium - Flanders	2013	17	17	0	2	0	0
Czechia	2014-15	64	67	2	3	0	0
Denmark	2011-13	882	-	?	?	0	0
France	2008-12	2624	589	10	13	10	13
Germany	2009-13	2484	2952	3	1	3	1
Ireland	2012-13	0	-	0	-	0	-
Portugal	2013-14	-	-	0	-	0	-
Spain	2009-13	2038	-	7	-	7	-
Sweden	2009-14	2848	2825	3	6	0	0
Switzerland	2014	2	-	0	-	0	-
Netherlands	2010-13	4	-	?	?	0	0
UK	2008-14	13487	-	4	-	4	-
Total	**2008-15**	**25201**	**6465**	**29**	**25**	**24**	**14**
%				**0.11**	**0.39**	**0.09**	**0.22**

Table 8.5-232: **Summary of the exceedance rate of the baseline and treatment mitigated scenarios for glyphosate (GLY) and AMPA**

Metric	GLY		AMPA		
	DrW: 0.1 µg/L	LTHAC: 1500 µg/L	Threshold: 0.1 µg/L	DrW: 10.0 µg/L	LTHAC: 3960 µg/L
	%	%	%	%	%
Baseline	23.0	0.0034	47.5	0.4	0.0011
Lower limit - 25%/60% Reduction	12.0	0.0024	42.3	0.2	0.0007
Upper limit - 95%/99% Reduction	0.1	0.00	4.8	0.0	0.0004

LTHAC - lifetime health-based ADI concentration

III. CONCLUSIONS

No information on HMPA was available. The analysis of the dataset available for drinking water for GLY and AMPA indicates that compliance is very high given detections above 0.1 µg/L are very rare and when they do sporadically occur, they occur at low concentrations that are well below human health thresholds. The measured environmental concentrations available suggest neither GLY nor AMPA pose a risk to human health *via* drinking water.

Assessment and conclusion by applicant:

The report describes the analysis of public monitoring data for key European countries for the compartments soil, water and sediment for Glyphosate and AMPA.

The available data do not indicate any risk to human health from measured GLY and AMPA concentrations in the drinking water compartment.

The report was seen to be valid.

Assessment and conclusion by RMS:

The report describes a review of glyphosate and AMPA monitoring results for drinking water across Europe. Data from this collection may overlaps those from previous review of [redacted], 2012 and [redacted], 2015. This is not perfectly clear to RMS, since identifying the origin of the data reported in the different reports (and themselves coming from reports from public authorities) is quite hard. The different sets of data are anyway quite consistent.

Also, as indicated in the comments on [redacted], 2020 which provides the methodology for data collection, there is no precise indication on the the origin of raw data for drinking water (i.e. ground water, surface water..) although this was part of the information to be collected in the described methodology; RMS aknowledges that few information is usually publicly available on the sampling location and the origin of raw water cannot be further indicated when collecting raw data.

Also, it is not always clear whether the data reported refers to raw or treated water.

Therefore the data presented here should be considered with caution, and further information might be requested at MS level for product registration.

Very little unaggregated drinking water data was available for analysis (~8000 samples for GLY, ~7000 for AMPA). Bulk of the data (~86% for GLY and 99% for AMPA) came from the SE dataset. Only data for GLY were available in IE (14% of the data), and none of the 767 sites in the IE dataset were supplied with coordinates.

The small unrepresentative dataset from Germany is limited to the federal state of Schleswig-Holstein. The SE data comprises records from 1998 to 2014, the DE data covers 2012 to 2018 while that from IE are from 2017 only.

For DE, results from the raw data are consistent with those reported in [redacted] 2105, indicating 3 exceedances of 0.1 µg/L for GLY and 1 for AMPA, likely being isolated cases although the overall number of analysis is very limited (limited to the federal state of Schleswig-Holstein). Aggregated data provides information on a wider set of data. Exceedances were very marginal representing less than 0.2% of samples.

For SE, raw data collected indicated 5 sampling >0.1 µg/L for GLY and 6 for AMPA, with maximum concentration of 0.17 µg/L for GLY. All exceedances are indicated to be old (≤2007) and significant strides have been made in SE since the introduction of the water protection regulations in 2004 through delineation of water protection zones. This is consistent with data from [redacted], 2015 that does not further report any detection above 0.1 µg/L for the period 2008-2015.

For FR, no raw data neither aggregated data were collected. Data were collected in [redacted] 2015 (see below).

In BE, detection above >0.1 µg/L are reported from aggregated data for year 2016 (2 for GLY, 1 for AMPA) representing less than 0.2 % of total samples.

In DK, single detection above >0.1 µg/L for GLY is reported from aggregated data for period 2014-2016, representing 0.07% of total samples.

For NL, a maximum concentration up to 3.0 µg/L from aggregated report is reported, but no further details are given (number of samples, time of sampling).

Raw surface water as a source of Drinking water

Calculation of hypothetical compliance with the drinking water trigger accounting for typical treatment rates of raw surface water was provided by study authors. Taking as a baseline the results from surface water raw monitoring data (indicating 23% samples > 0.1 µg/L for GLY and 47.5% for AMPA throughout EU), the exceedance would be reduced to 12% and 42.3% respectively for GLY and AMPA considering a lower limit of 60% and 25% reduction (for GLY and AMPA respectively). The exceedance

could be reduced to 0.1 % and 4.8% for GLY and AMPA if considering the upper limit of 99% and 95% reduction factor (for GLY and AMPA respectively).
Those reduction factors are taken from the analysis of water exposed to chemical water treatment processes (disinfection), after Jönsson et al., 2013 (CA 7.5/084). See section B.8.4.2 on drinking water treatment.
However, this evaluation is purely theoretical.

Data point:	CA 7.5/074
Report author	[redacted]
Report year	2015
Report title	Survey of glyphosate and AMPA in drinking water supplies in Europe - 2015 update report
Report No	-
Document No	-
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary

The report represents a review of glyphosate and AMPA monitoring results for drinking water across Europe. This review is based on an earlier review carried out in 2008, which has been updated to include the latest available information with respect to glyphosate and AMPA in drinking water. For this update, information was sought for all 28 Member States of the European Union plus Norway and Switzerland. For 19 countries, no monitoring data was available. Where available, drinking water quality reports issued by the national or regional responsible authorities were assessed. For Sweden a pesticide database, which included drinking water monitoring results, was available. Other information was obtained from web and literature searches, the EU synthesis report and from professional contacts.

Glyphosate and AMPA were present in water intakes in Belgium, Czech Republic, France, Germany, Spain, Sweden and in England & Wales. With the exception of France (23 samples in the period of 2008-2012), Germany (4 samples in the period of 2009-2013), Spain (7 samples in the period of 2009-2013) and England & Wales (4 samples in the period of 2008-2014) the measurements did not exceed the individual pesticide standard for drinking water of 0.1 µg/L. Glyphosate has not been found at concentrations at or above 0.1 µg/L in Austria, Belgium, the Czech Republic, Denmark, Sweden, Switzerland and the Netherlands.

All exceedances were isolated cases (different years and locations) not indicating any consistent contamination. Whilst there is much more monitoring data available than in 2008, there is clearly no evidence of an increasing number of glyphosate detections over the period of 2008-2015.

In France, the exceedances mainly occur in small supplies, which are much more vulnerable to contaminations, as they are often wells situated in farms where pesticides are handled. Where separate information is available, it is clear that the highest proportion of detections or exceedances is found in small supplies. There were no reported exceedances for AMPA in most countries, with exceptions in France (13 samples) and Germany (one sample).

I. MATERIAL AND METHODS

The report represents a review of glyphosate and AMPA monitoring results for drinking water across Europe. This review is based on an earlier review carried out in 2008, which has been updated to include the latest available information with respect to glyphosate and AMPA in drinking water. For this update, information was sought from Austria, Belgium, Czech Republic, Denmark, France, Germany, Ireland, Italy, Norway, Poland, Portugal, Slovak Republic, Spain, Sweden, Switzerland, the Netherlands and the UK. Information was obtained from web and literature searches, the EU synthesis report and from professional contacts. Where available, drinking water quality reports issued by the national or regional responsible authorities were assessed. For Sweden, data was extracted from a national pesticides database, which includes drinking water monitoring results. No relevant information was available for Bulgaria, Croatia, Cyprus, Estonia, Finland, Greece, Hungary, Latvia, Lithuania, Luxembourg, Malta, Romania and Slovenia.

II. RESULTS AND DISCUSSION

Table 8.5-233: Summary of glyphosate and AMPA monitoring and detection in drinking water in 13 EU countries, 2008 – 2015

Country	**Year(s)**	**Monitoring**		**Detection (number)**		**Concentration ≥ 0.1 µg/L (number)**		**Reliability of results**
		Glyphosate	**AMPA**	**Glyphosate**	**AMPA**	**Glyphosate**	**AMPA**	
Austria	2011-13	751	15	?	?	0	0	good
Belgium-Flanders [1]	2013	17 [2]	17 [2]	0	2	0	0	good
Czech Republic [1]	2014-15	64	67	2	3	0	0	x
Denmark	2011-13	882	-	?	?	0	0	good
France [1]	2008-12	≥2624	589 2)	≥10	≥13	10	13	x
Germany	2009-13	2484	2952	≥3	≥1	3	1	x
Ireland	2012-13	?	-	0	-	0	-	+
Portugal	2013-14	-	-	0	-	0	-	+
Spain [1]	2009-13	>2038	-	≥7	-	7	-	x
Sweden [1]	2009-14	2848	2825	3 [3]	6 [3]	0	0	x
Switzerland	2014	2 [2]	-	0	-	0	-	x
The Netherlands	2010-13	>4	-	?	?	0	0	x
UK								
-England & Wales	2008-14	13487	-	≥4	-	4	-	good
-Northern Ireland	2012-13	?	-	?	-	0	-	+
-Scotland [1]	2012-13	?	-	?	-	0	-	+
Total	***2008-15***	***≥25 201***	***≥6 465***	***≥29***	***≥25***	***24***	***14***	
%				***0.11***	***0.39***	***0.09***	***0.22***	

- not relevant
? no information
x insufficient information to judge reliability of results
+ based on risk assessment
[1] may include small supplies
[2] sites or water supply zones (WSZ)
[3] no Glyphosate detection after 2009, no AMPA detection after 2012

Glyphosate has not been found at concentrations at or above 0.1 µg/L in Austria, Belgium, the Czech Republic, Denmark, Sweden, Switzerland and the Netherlands. A small number of sporadic results >0.1 µg/L has been reported from France (23 samples in the period of 2008-2012), Germany (4 samples in the period of 2009-2013), Spain (7 samples in the period of 2009-2013) and England & Wales (4 samples in the period of 2008-2014). All exceedances were isolated cases (different years and locations) not indicating any consistent contamination. Whilst there is much more monitoring data available than in 2008, there is clearly no evidence of an increasing number of glyphosate detections over the period of 2008-2015.

III. CONCLUSION

A considerable amount of glyphosate monitoring has been carried out in drinking water in recent years in several European countries. There are only a small number of isolated detections or exceedances of the drinking water standard. It is clear that glyphosate detections are more frequent in small supplies (e.g. private wells on farms where pesticides are handled). These isolated glyphosate detections cannot be considered significant in terms of a risk of non-compliance with the drinking water standard. Despite its widespread usage, there is no evidence of any increase in glyphosate detections in drinking water over the period 2000-2015.

Assessment and conclusion by applicant:

The study provides an overview on monitoring data for drinking water from 13 European countries. No specific guideline is applicable to this data point.

The study was considered valid.

Assessment and conclusion by RMS:

The report presents a review of glyphosate and AMPA monitoring results for drinking water across Europe. This report is an update of the previous review performed in [redacted], 2008 that was included in the RAR 2015. For this update, information was sought from Austria, Belgium, Czech Republic, Denmark, France, Germany, Ireland, Italy, Norway, Poland, Portugal, Slovak Republic, Spain, Sweden, Switzerland, the Netherlands and the UK. It includes data from the period 2008-2015.

It should be noted that the data collated in this report seem very limited and outdated for many countries. It is also worth noting that the process of determining the reliability of the data is not clearly described. Furthermore the definition of drinking water taken into account in this report is not always clear. Results from different water supplies (groundwater, surface water and "other sources") are gathered for each country and it is not known whether the data reported refers to raw or treated water.

On this additional period of 2008-2015, glyphosate concentration > 0.1 µg/L have been reported for France, Germany, Spain and the UK.

In France, data comes from different sources with variable degree of detail. There is very few details on the samples exceeding the trigger. As in previous review of [redacted], 2008, the report indicates that further investigations failed to establish any coherent relationships between these detections and factors, such as seasonal occurrence, raw water quality, type of aquifer, analysis and water treatment. In fact, several of the samples with glyphosate were found in chlorinated waters; although it has been shown that chlorine effectively remove glyphosate. Overall, the evidence points to isolated detections, most likely due to contamination at the sampling stage or problems with analyses, rather than any indication of a persistent presence in drinking water.

In Germany, the findings of glyphosate > 0.1 µg/L were reported to be isolated exceedances (one sample in 2013 and two samples in 2013 from 2 different Water Supply Zone), no further action, such as remedial measures, were deemed necessary.

In Spain, the sampling which exceeded 0.1 µg/L seem to be isolated cases (2 in 2013, 1 in 2012, 4 in 2011) However, the report indicates that there is no detail on the samplings such as actual concentrations found, whether they occurred at one or more sampling points. Data indicates that glyphosate was monitored in a relatively small proportion of water supply zones; the number of sites and sampling frequency is not known, as only the total number of analyses per year has been reported.

In the UK, there is no further details on the sampling found above 0.1 µg/L. They are isolated cases, representing 0.030 % of the analyses performed during the 2008-014 period.

In Austria, results are from the latest available drinking water quality report at the time of review (BMG, 2015) and covers the years 2011-2013. It is indicated that although the report covers large and small supplies, the glyphosate and AMPA analyses relate to large supplies only. All results were in compliance, none at or above 0.1 µg/L.

The report indicates that glyphosate has not been found at concentrations at or above 0.1 µg/L in Austria, Belgium, the Czech Republic, Denmark, Sweden, Switzerland and the Netherlands. This shall be further qualified for Sweden and the Netherlands:
For Sweden, exceedance are reported before 2009 and consistent with those reported in [redacted], (2020) They are however indicated as being isolated incidents, as they never occurred more than once a year in the same region, and all detections were in three of a total of 21 regions. No glyphosate detections were reported after 2009 and no AMPA detections after 2012.

For the Netherlands, it is explained in the full text report that no exceedance are reported in the annual drinking water quality reports for the years 2010 to 2013 (Versteegh and Dijk, 2014 and 2011; Ministry of Infrastructure and Environment, 2014 and 2012) although both were reported to exceed 0.1 µg/L in some raw water intakes (surface water only) in 2010 and 2012 (water intake data is not included in the 2013 report).

Data from NL is in any case outdated and it is indicated here that annual reports up to 2019 are made available by RIWA for both the Rhine (Annual Reports Archieven - Riwa (riwa-rijn.org)) and the Meuse catchment (Publicaties – RIWA-Maas (riwa-maas.org)). These report are not available in English, the following results are given, indicating that the drinking water threshold is occasionally exceeded at surface water location where drinking water is abstracted:

- In the Meuse catchment there are some locations intended for the abstraction of drinking water persistently exceeding the threshold. Exceedance in recent years (2015-2019) show maximum value for GLY of 0.46 µg/L, and for AMPA of 7.9 µg/L.

For all others countries, no exceedance are indeed reported, but the data sets are often very limited and sometimes outdated. More recent data may be available at MS level.

The study (drinking water part) is considered acceptable.

Existing studies/assessments

Data point:	CA 7.5/075
Report author	[redacted]
Report year	2008
Report title	Review of glyphosate and AMPA in drinking water in selected European countries
Report No	UCC7729.04
Document No	BVL No. 2310278
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
Previous evaluation	Yes, accepted in RAR (2015)
GLP/Officially recognised testing facilities	No (no experimental work performed)
Acceptability/Reliability:	Acceptable

Executive Summary

Drinking water quality reports issued by the responsible national authorities in Belgium, Denmark, France, Germany, Ireland, The Netherlands and the UK, together with some additional information, were assessed with respect to glyphosate and AMPA in drinking water for public supplies (private supplies also for Denmark and Northern Ireland), and in some cases for raw water intakes (Germany and The Netherlands). For Sweden a pesticides database which included drinking water results was available.

Glyphosate and AMPA were present in water intakes in Belgium, Germany and The Netherlands, but did not exceed the individual pesticide standard for drinking water of 0.1 µg/L. A small number of sporadic results > 0.1 µg/L in finished water have been reported from France (25 samples in the period 2001-03), The Netherlands (two each in 2005 and 2006) and the UK (four in England & Wales in 2004, three in Northern Ireland in 2004 and one in 2005). All were isolated detections and none were considered significant, i.e. no reports of improvement measures being needed because of the presence of glyphosate in drinking water. Three of the four exceedances in England & Wales were attributed to probable problems with the analysis, due to the generally spurious occurrences; similar explanations may well apply to exceedances reported from elsewhere. There were no reported exceedances for glyphosate (or AMPA) in large public supplies in Denmark, there were however some detections and exceedances in small private supplies. Special investigations revealed that all wells affected were abstracting shallow groundwater (probably supplied untreated) in conditions where there was rapid infiltration of surface water from nearby fields or run-off from treated court yards in the vicinity. A similar situation may be the case in Sweden, where a small number of glyphosate and AMPA detections and exceedances were found in drinking water; these seemed to be mainly derived from groundwater, but no further sample details were available.

I. MATERIAL AND METHODS

Reporting by EU Member States to the Commission under the Drinking Water Directive 98/83/EC (1998) will be incorporated into WISE (Water Information System for Europe) in the near future. However, at present, there are no clear indications of the details of reporting, and data are available in various forms for some Member States.

Available information was sought for Belgium, Denmark, France, Germany, Ireland, Spain, Sweden, The Netherlands, Czech Republic, Greece, Italy and the UK. Information was obtained from web searches and professional contacts.

Drinking water quality reports issued by the responsible national authorities were reviewed for Belgium, Denmark, France, Germany, Ireland, Spain, The Netherlands and the UK. For Sweden data were accessed from a database.

No relevant information was obtained from Greece and Italy. The Czech Republic confirmed that glyphosate was not among the substances monitored.

II. RESULTS AND DISCUSSION

The results are summarized in the table below.

Table 8.5-234: Summary of glyphosate and AMPA monitoring and detection in drinking water in eight EU countries

Country	Year(s)	Monitoring		Detection (number)		Concentration ≥ 0.1 µg/L (number)	
		Glyphosate	AMPA	Glyphosate	AMPA	Glyphosate	AMPA
Belgium	2002-04	not known	not known	?	?	0	0
Denmark	2002-04 [1]	probably	probably	?	?	0	0
	2001-05 [2]	yes	yes	54 [3]		21 [3]	
France	1993-98	not known	not known	?	?	0	0
	2001-03	yes	yes	26	22	18	15
	2004-06	probably	probably	?	?	0	0
Germany	2002-04	probably	probably	?	?	0	0
	2005	yes	yes	0	0	0	0
Ireland	2005-06	not known	not known	?	?	0	0
Sweden	2000-07	yes	yes	7	14	4	≥ 4
Spain	2002-04	nm	nm	nr	nr	nr	nr
The Netherlands	2000-06	yes	probably	14	?	2	?
UK							
- England	2000-06	yes	not known	?	?	4	?
- Northern Ireland	2002-06	yes	not known	?	?	6 [4]	?
- Scotland	2005	not known	not known	?	?	≤ 2 [5]	?

[1] large public supplies
[2] small/private wells of shallow groundwater, probably untreated
[3] glyphosate and AMPA presented as combined amounts
[4] 2 of these in private supplies
[5] only 2 exceedances of the pesticide standard but substance(s) not specified
nm = not monitored, nr = not relevant, ? = no information

III. CONCLUSION

No glyphosate exceedances of the individual pesticide standard for drinking water of 0.1 µg/L were reported from Belgium, Germany and Ireland. A small number of sporadic results > 0.1 µg/L have been reported from France (25 samples in the period 2001-03), The Netherlands (two each in 2005 and 2006) and the UK (four in England & Wales in 2004, three in Northern Ireland in 2004 and one in 2005). All were isolated detections and none were considered significant, i.e. no reports of improvement measures being needed because of the presence of glyphosate in drinking water.

Assessment and conclusion by applicant:
The study compiles drinking water quality data for glyphosate and AMPA from national authorities in Europe. The methods and results are sufficiently described.
Therefore, the study was considered valid.

Assessment and conclusion by RMS:
The report presents a review of glyphosate and AMPA monitoring results for drinking water across Europe, for different periods, but all before 2006. The study of [redacted], 2015 above reviews more recent data (2008-2015).
The present study has already been evaluated in the RAR 2015. RMS (DE) evaluation from RAR 2015 is reported below:

No glyphosate exceedances of the individual pesticide standard for drinking water of 0.1 µg/L were reported from Belgium, Germany and Ireland, whereas concentrations > 0.1 µg/L have been reported from France, the Netherlands, Sweden and the UK.

For AMPA, concentrations > 0.1 µg/L were reported from France and Sweden.

Three of the four glyphosate exceedances in England and Wales were attributed to probable problems with the analysis, due to the occasional occurrences. Whilst there were no reported exceedances for glyphosate or AMPA in large public supplies in Denmark, there were some detections and exceedances in small private supplies. Special investigations revealed that all wells affected were abstracting shallow groundwater (probably supplied untreated) in conditions where there was rapid infiltration of surface water from nearby fields or run-off from treated court yards in the vicinity. A similar situation may be the case in Sweden, where glyphosate and AMPA exceedances were found in drinking water; these seemed to be mainly derived from groundwater, but no further sample details were available. Since the findings of glyphosate > 0.1 µg/L in the Netherlands were isolated exceedances (one sample only in each case), no further action, such as remedial measures, were deemed necessary. One of the glyphosate detections in France turned out to be for raw water rather than finished drinking water. Strangely, the majority of glyphosate detections in France were at sites where groundwater is used. Further investigations failed to establish any coherent relationships between these detections and factors, such as seasonal occurrence, raw water quality, type of aquifer, analysis and water treatment. In fact, several of the samples with glyphosate were found in chlorinated waters; although it has been shown that chlorine effectively remove glyphosate. Overall, the evidence points to isolated detections, most likely due to contamination at the sampling stage or problems with analyses, rather than any indication of a persistent presence in drinking water.

The study is considered acceptable.

Data point:	CA 7.5/076
Report author	[redacted]
Report year	1997
Report title	Glyphosate in drinking water/ letter from [redacted] (PSD York)
Report No	-
Document No	-
Guidelines followed in study	None
GLP	No
Previous evaluation	Not accepted in RAR (2015)
Short description of study design and observations:	*Summary was compiled from information available in the glyphosate Monograph (2000).* In the United Kingdom the Drinking Water Inspectorate of the Department of Environment collates information and publishes reports on the quality of drinking water. Data for 1991-1994 are taken from the report "Nitrate, Pesticides and Lead 1991 to 1994". Data for 1995 and 1996 are from the individual years reports "Drinking Water 1995" and "Drinking Water 1996". Data from “Drinking Water” for the years 1995 and 1996 are given for each individual company. In this period the number of water companies in existence was 31 in 1995 and 29 in 1996. However, only three companies monitored glyphosate.
Short description of results:	Glyphosate monitoring data from "Nitrate, Pesticides and Lead 1991 to 1994”:

	1991	**1992**	**1993**	**1994**
Total number of determinations	61	138	1217	1347
Number of determinations >0.1 µg/L	0	0	3	3
Max. concentration in drinking water (µg/L)	-	-	0.35	0.37

Glyphosate monitoring data from "Drinking Water 1995” and "Drinking Water 1996”:

Water company	**Dwr Cymru Cyfyngedig**	**Mid Southern Water plc**	**South East Water Ltd.**
Determinations in 1995			
Total	904	84	386
Number exceeding 0.1 µg/L	1	2	0
% exceeding 0.1 µg/L	0.1	2.4	0
Determinations in 1996			
Total	829	66	274
Number exceeding 0.1 µg/L	1	0	0
% exceeding 0.1 µg/L	0.1	0	0

Reasons for why the study is not considered relevant/reliable or not considered as key study:	Monitoring data from 1991 to 1996 are considered not representative for current use conditions of glyphosate. Data are superseded by new monitoring data collection.
Reasons why the study report is not available for submission	The notifier has not access to this study report. The study was recovered from former RMS of the active substance glyphosate by AGG.

Assessment and conclusion by RMS:
The mentioned document is not a report but a short letter, with no detailed data. It cannot be relied on.

Relevant literature articles

Data point	**Study (Author, year)**	**Study type**	**Substance(s)**	Status
CA 7.5/077	Malaguerra, F. *et al*., 2012	Pesticides in water supply wells in Zealand, Denmark	Glyphosate AMPA	Reliable with restrictions
CA 7.5/027	Bruchet, A. *et al*., 2011	Monitoring experiment in France	Glyphosate AMPA	Reliable

Data point:	CA 7.5/077
Report author	Malaguerra, F., *et al.*
Report year	2012
Report title	Pesticides in water supply wells in Zealand, Denmark: A statistical analysis
Document No	Science of the Total Environment 414 (2012) 433–444
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

Data from the Danish National Borehole Database are used to predict drinking water well vulnerability to contamination by pesticides, and to identify the dominant mechanisms leading to well pollution in Zealand, Denmark. The frequency of detection and concentrations of 4 herbicides and 3 herbicide metabolites are related to factors accounting for geology (thicknesses of sand, clay and chalk layers), geographical location (distance to surface water and distance to contaminated sites), redox conditions and well depth using logistic regression, the binomial test and Spearman correlation techniques. Results show that drinking water wells located in urban areas are more vulnerable to BAM and phenoxy acids contamination, while non-urban area wells are more subject to bentazone contamination. Parameters accounting for the hydraulic connection between the well and the surface (well depth and thickness of the clay confining layer) are often strongly related to well vulnerability. Results also show that wells close to surface water are more vulnerable to contamination, and that sandy layers provide better protection against the leaching of oxidizable pesticides than clay aquitards, because they are more likely to be aerobic. 4-CPP is observed more often at greater well depth, perhaps because of anaerobic dechlorination of dichlorprop. The field data are used to create a set of probabilistic models to predict well vulnerability to contamination by pesticides.

Materials & Methods

Study area

The island of Zealand, Denmark, includes the city of Copenhagen and was selected as a study area for this study. Geologically, the island is mainly composed of a succession of clayey and sandy tills deposited during the Last Glaciation over a chalk bedrock. This geological setting is characteristic of high latitudes and can be found in many parts of the world, like Canada and the northern United States. Zealand is a good case for statistical analysis of drinking water well data because it is highly populated but still contains large agricultural areas, wells contaminated by pesticides or other compounds are common, and rigorous water well sampling data is available over a long period. Moreover, Zealand has a relatively uniform geology, and so the processes relevant to pesticide transport can be assumed to be similar for the whole island. In order to examine the importance of the geological setting, a statistical analysis was also performed on data from wells placed in the west part of Denmark's Jutland peninsula. The area lies west of the limit of the last glacier front and is mainly composed of thick sandy layers originating from glacial erosion of tertiary or glaciofluvial deposits. The region is less populated than Zealand but includes a larger number of drinking water wells.

Pesticides considered

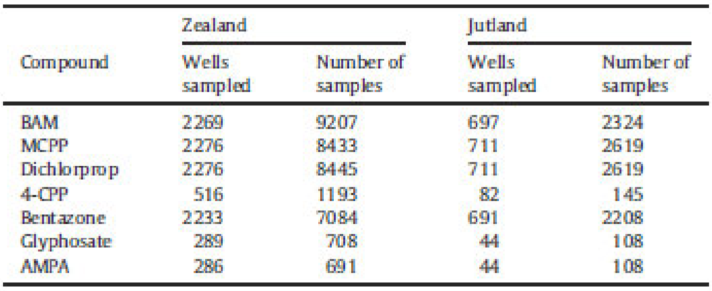
Seven compounds were considered in the study: 2,6-dichlorobenzamide (BAM), MCPP (mecoprop), dichlorprop, 4-chlorophenoxypropanoic acid (4-CPP), bentazone, glyphosate and aminomethylphosphonic acid (AMPA). These compounds are among the most frequent pesticides and pesticide by-products observed in Danish drinking water wells. BAM is the degradation metabolite of dichlobenil, an herbicide mostly used in urban areas such as paths, roads, courtyards and sports grounds, and which has been banned in Denmark since 1997. Unlike its mother compound, dichlobenil, which is strongly sorbed in topsoils, BAM is leachable. Thus, the stock of dichlobenil sorbed onto soil organic matter is slowly degrading and BAM is being continuously released into groundwater. Even though BAM degradation has been observed, it is widely believed to be very persistent in aquifers. In 2009, BAM was detected in 17.1% of the groundwater wells investigated in the Danish groundwater monitoring program and the MAC was exceeded in 5.2% of the wells. BAM findings are the most important cause of drinking water well closure in Denmark.

MCPP and dichlorprop are phenoxy acids employed as selective, hormone-type herbicides and are widely used for agricultural, horticultural and domestic purposes. In Denmark these pesticides were partially banned in 1997 and are now used only for limited purposes. MCPP and dichlorprop do not sorb significantly onto aquifer sediments and are only weakly degraded under anaerobic conditions. 4-CPP is often found in con- junction with MCPP and dichlorprop since it is an impurity of the production process, but some studies suggests that 4-CPP may originate from the anaerobic dechlorination of dichlorprop. In 2009, these three phenoxy acids have been found in 8% of active water supply wells, and the MAC was exceeded in 1% of the cases: after BAM, they were the most frequently found compounds. Bentazone is a selective herbicide mainly used in cultivated areas. It is very mobile and leachable. Bentazone can be quickly degraded in the upper soil layer, but there is evidence of its persistence in aquifers. It has been found in 3.9% of Danish monitoring wells and herbicide concentrations were higher than the MAC in 0.9% of sampled wells. Glyphosate is a broad-spectrum non-selective herbicide, and is mostly commercialized under the trade name of Roundup and is the most sold chemical for weed control in agricultural, silvicultural and urban environments (both worldwide and in Denmark). Microbial degradation of glyphosate produces AMPA as a primary degradation product. Glyphosate and AMPA sorb strongly onto aquifer sediments, especially to clay minerals, and they are degradable under both aerobic and anaerobic conditions. Little monitoring data are available for glyphosate and AMPA, because their sampling is not recommended by Danish regulations and because they are difficult to analyse. However, glyphosate and AMPA have been recently found in 4.4% and 3.8% of the GRUMO monitoring wells respectively, and the MAC was exceeded in 1.4% (glyphosate) and 1.1% (AMPA) of the wells. The frequency of detection of glyphosate and AMPA in Danish wells has been increasing in recent years. MCPP, bentazone, glyphosate and AMPA are all included in the list of substances being considered for addition to the list of priority substances in the European Union (European Union directive 2008/105/EC).

Data

In Denmark, water is provided by a large number of clustered drinking water wells where water quality is regularly monitored. Over the last few decades, a unique comprehensive well database has been assembled recording the specifications of each well, and the results of regular chemical analyses. The full database for the Zealand Island was obtained from the Geological Survey of Denmark and Greenland (GEUS). Active drinking water wells were selected from the full database; both wells belonging to waterworks and private wells were included in the analysis. The number of wells sampled and the number of analyses for the compounds considered in this study are presented in Table 8.5-235. Well depths (*D*) were extracted from the database and defined to be the distance from the surface to the bottom of the well. The data- base describing borehole geology used a classification scheme containing 205 different categories. This categorization is too detailed for the purpose of this study, and so the geological information was grouped into 3 main geology types: sand, clay and chalk. For each well, the sum of the layer thicknesses of every group was calculated and provided the parameters *Ds* (total sand layer thickness), *Dcl* (total clay layer thickness) and *Dch* (total chalk thickness). It has to be noted that information on layer discontinuity was lost in this procedure. The data on pesticide concentrations are very heterogeneous because the wells were monitored at different times with different frequencies. The value *C* was chosen to be the maximum value of pesticide concentration recorded at a given well. The distance between the drinking water wells and the closest stream (*dSW*), and the minimum distance between the drinking water wells and contaminated sites (*dCS*) were calculated using a Geographical Information System; stream coordinates were provided by the Danish National Environmental Research Institute, and the locations of contaminated sites were provided by the Danish Environmental Protection Agency. The CORINE 2006 database was used to determine whether wells were located in urban areas or not: the binary variable *LU* had a value of 1 if the well was included in the category "artificial surface" and 0 otherwise. The selection criterion was based on the well location and not on the well catchment. The predominant redox conditions were determined at each well from records of oxygen, nitrate, ferrous iron and sulfate concentrations. If several measurements were available at the well, the classification was made using the mean value of the selected compound.

Table 8.5-235: Number of samples analyzed for pesticides and number of sampled wells in Zealand and Jutland



	Zealand		Jutland	
Compound	Wells sampled	Number of samples	Wells sampled	Number of samples
BAM	2269	9207	697	2324
MCPP	2276	8433	711	2619
Dichlorprop	2276	8445	711	2619
4-CPP	516	1193	82	145
Bentazone	2233	7084	691	2208
Glyphosate	289	708	44	108
AMPA	286	691	44	108

Results

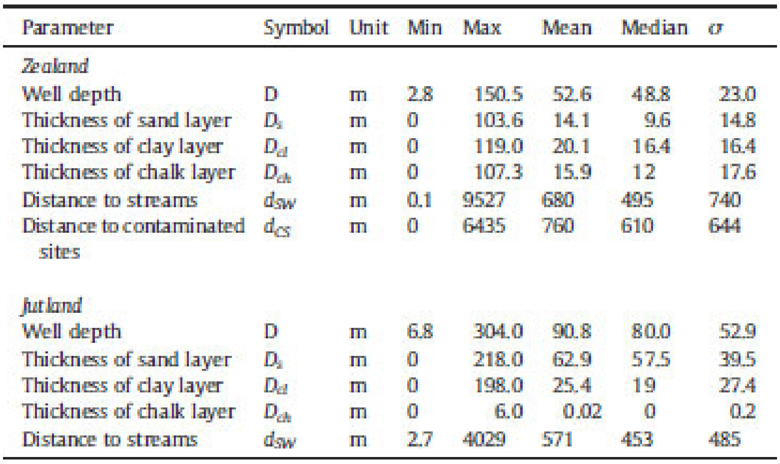
Well characteristics

General statistics for the well characteristics were calculated for 2605 wells in Zealand and 2156 in western Jutland, and results are presented in Table 8.5-236. Jutland wells are generally deeper, are placed in thicker sand layers and are overlain by more variable clay layer thicknesses. Despite the depth of the wells in Jutland, almost none are as deep as the chalk bedrock. As expected, the depth of the well and the thickness of the clay and sand layers influenced the redox conditions, due to their effect on the water travel time. The thickness of the clay layer was the most significant parameter: almost no wells were found to pump oxic water when clay layers were thicker than 30 m, while about 20% of the wells overlain by a clay layer thinner than 8.5 m had an oxic redox chemistry. In Zealand, well redox conditions were insensitive to the distance from streams, while in Jutland, less reduced conditions were observed as the distance from surface water increased. More oxic wells were found in Jutland, where about 30% of the shallow wells (less than 35 m deep) were oxic, compared to only 20% in Zealand.

Redox dependence

Glyphosate and AMPA were analyzed in a limited number of wells, and mainly low concentrations were detected. Nevertheless, results show that the occurrence of glyphosate was slightly higher in anoxic water. The percentage of wells contaminated with AMPA was not dependent on the redox conditions, but higher concentrations were found in oxic and anoxic waters.

Table 8.5-236: Characteristics of Danish drinking water wells



Parameter	Symbol	Unit	Min	Max	Mean	Median	σ
Zealand							
Well depth	D	m	2.8	150.5	52.6	48.8	23.0
Thickness of sand layer	D_s	m	0	103.6	14.1	9.6	14.8
Thickness of clay layer	D_{cl}	m	0	119.0	20.1	16.4	16.4
Thickness of chalk layer	D_{ch}	m	0	107.3	15.9	12	17.6
Distance to streams	d_{SW}	m	0.1	9527	680	495	740
Distance to contaminated sites	d_{CS}	m	0	6435	760	610	644
Jutland							
Well depth	D	m	6.8	304.0	90.8	80.0	52.9
Thickness of sand layer	D_s	m	0	218.0	62.9	57.5	39.5
Thickness of clay layer	D_{cl}	m	0	198.0	25.4	19	27.4
Thickness of chalk layer	D_{ch}	m	0	6.0	0.02	0	0.2
Distance to streams	d_{SW}	m	2.7	4029	571	453	485

Logistic regression

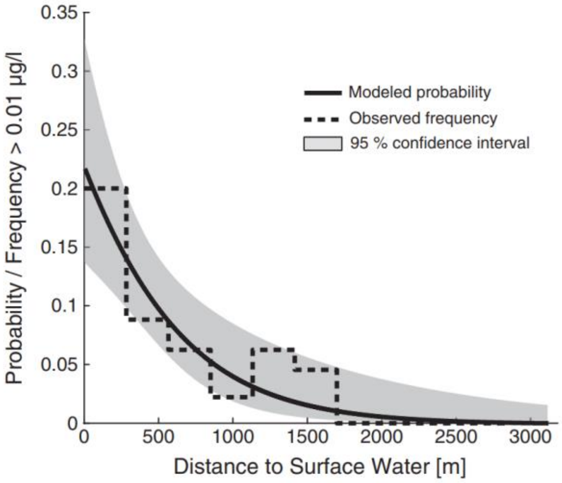
Pesticide occurrences above two concentration thresholds were used to perform logistic regression: 0.01 µg/L, which is the usual detection limit and 0.1 µg/L, which is the maximum allowable concentration according to the EU Groundwater Directive. For dichlorprop, 4-CPP, bentazone, glyphosate and AMPA, the logistic regression did not produce any significant results for occurrences above 0.1 µg/L.

Ordinary logistic regression coefficients were used to predict the probability of pesticide occurrence, while standardized coefficients provided information on the relative importance of each parameter. The thickness of the clay layer and the distance between pumping wells and streams were significant for most of the compounds, and suggested that thicker clay layers and a greater distance to surface water will lead to a smaller probability of well contamination. The occurrence of phenoxy acids and bentazone were negatively correlated to the thickness of the clay layer. Logistic regression confirmed the dependence of BAM, MCPP and bentazone occurrence on land use. In fact, the coefficients linked to land use were well determined for all three compounds, and the sign of the regression coefficients was positive for BAM and MCPP and negative for bentazone. The occurrence of glyphosate and AMPA could only be linked to the distance to streams.

Standardized logistic regression coefficients indicated that the thickness of the clay layer was the most important parameter influencing the occurrence of BAM, dichlorprop and low MCPP concentrations, while the thickness of the sand layer controlled findings of bentazone, 4-CPP and high MCPP concentrations.

Results from the logistic regression were used to build logistic models for predictions of well contamination. Figure 8.5-188 shows the predicted probability of well contamination by glyphosate (>0.01 µg/L), depending on the distance between the well and the closest stream. Predicted probabilities, 95% confidence intervals for predictions and the observed frequency of detection are plotted in the same graph. The model fits the observed frequencies well and observations are always included in the 95% confidence intervals. It should be noted that these probabilities should not be interpreted as a probable frequency of detection, but rather the probability of finding the compound at least once.

Figure 8.5-188: Observed frequency of detection of glyphosate and the associated logistic model



Less data on drinking water well contamination were available for west Jutland drinking water wells, both because fewer wells have been sampled (Table 8.5-235), and because only a few wells have recorded pesticide concentrations above the detection limit. Thus, the p-values of the results were often above 0.05, and significant results were obtained only for BAM.

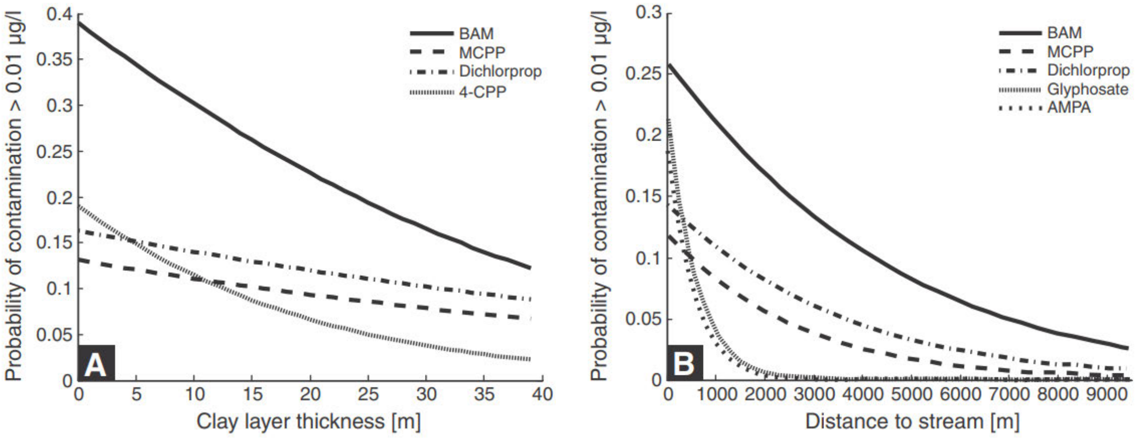
As in Zealand, BAM was found more frequently in urban area wells. The frequency of BAM findings above 0.1 and 0.01 µg/L were inversely related to the thicknesses of the clay and sand layers, and were positively correlated to the distance to streams.

Discussion

Glyphosate and AMPA

The low number of glyphosate and AMPA samples increases uncertainty in the determination of correlation coefficients and logistic regression parameters, and data interpretation becomes difficult. Nevertheless, the concentration and the occurrence of these compounds seem to decrease with the distance from streams. Moreover, logistic regression shows that the dependence between distance to streams and pesticide occurrence is much stronger for glyphosate and AMPA than for the other pesticides (Figure 8.5-189B). Previous studies show that glyphosate transport to surface water in agricultural areas is mainly due to surface runoff and that glyphosate is usually not transported in subsurface drainflow. A run- off transport mechanism is suggested by the fact that glyphosate and its metabolite AMPA are the most common compounds found in Danish streams at concentrations over 0.1 µg/L, with 26.7% and 38.2% respectively of samples in Danish streams recording such high concentrations. The greater occurrence of these compounds close to streams may be due to the infiltration of runoff water containing high glyphosate concentrations in riparian zones or because of slower degradation rates due to the prevalence of anaerobic conditions close to surface water.

Figure 8.5-189: Influence of the thickness of the clay layer (A) and the distance to streams (B) on well contamination. The plots show the modeled probabilities of well contamination by selected pesticides, and were obtained considering a hypothetical well 53 m-deep with a 14 m-thick sand layer. In (A) the distance to the stream was kept fixed at 680 m, in (B) the thickness of the clay layer was assumed to be 20 m.



Conclusion

This study has shown that in Denmark, the land use affects the contamination of drinking water wells by pesticides: wells in urban areas are more contaminated by BAM and phenoxy acids, while wells in non-urban areas are more contaminated by bentazone. Logistic regression and correlation analysis suggests that the thickness of the clay layer overlying the wells is the most important parameter affecting contamination by persistent pesticides and that thicker sand layers are promoting degradation of aerobically degradable contaminants. In Zealand, well contamination was higher in the wells close to streams, suggesting that groundwater–surface water processes can play a major role in drinking water contamination by pesticides, even when pumping from confined aquifers. This study also suggest that 4-CPP in aquifers may originate from the dechlorination of dichlorprop in anaerobic environments, and that contaminated sites can be a major source of dichlorprop. Comparison of well pollution between Zealand and Jutland suggested that sandy layers can provide a better protection against the leaching of aerobically degradable pesticides than clay aquitards, since they are more likely to host aerobic conditions and therefore promote pollutant oxidation. Finally, we provided probability estimates of drinking water well pollution by BAM, MCPP, dichlorprop, 4-CPP, glyphosate and AMPA, which can be used for risk assessment purposes.

Assessment and conclusion by applicant:

The article describes the statistical correlation of the occurrence of some pesticides, incl. glyphosate in groundwater wells with different characteristics of the wells (e.g. geology, geographic information, depth etc.). No measured values are reported.

Glyphosate and its metabolite AMPA are the most common compounds found in Danish streams at concentrations over 0.1 µg/L, with 26.7% and 38.2% respectively of samples in Danish streams recording such high concentrations (despite the lower number of samples for these two substances). Infiltration of surface runoff proposed.

The article is considered reliable with restrictions.

Assessment and conclusion by RMS:

This article describes the use of data from the Danish National Borehole Database to predict drinking water well vulnerability to contamination by pesticides, and to identify the dominant mechanisms leading to well pollution in Zealand, Denmark.
No measured value are indeed reported, but several information on glyphosate and AMPA can be picked up from this article:

Monitoring data
In DK little monitoring data are available for glyphosate and AMPA, because their sampling is not recommended by Danish regulations and because they are difficult to analyse. However, glyphosate and AMPA have been recently found in 4.4% and 3.8% of the GRUMO monitoring wells respectively, and the MAC was exceeded in 1.4% (glyphosate) and 1.1% (AMPA) of the wells. The frequency of detection of glyphosate and AMPA in Danish wells has been increasing in recent years.

Redox dependence
Glyphosate and AMPA were analyzed in a limited number of wells, and mainly low concentrations were detected. Nevertheless, results show that the occurrence of glyphosate was slightly higher in anoxic water. The percentage of wells contaminated with AMPA was not dependent on the redox conditions, but higher concentrations were found in oxic and anoxic waters.

Predicted probability of well contamination by glyphosate – correlation between distance from stream and concentration
The low number of glyphosate and AMPA samples increases uncertainty in the determination of correlation coefficients and logistic regression parameters, and data interpretation becomes difficult. Nevertheless, the concentration and the occurrence of these compounds seem to decrease with the distance from streams. Moreover, logistic regression shows that the dependence between distance to streams and pesticide occurrence is much stronger for glyphosate and AMPA than for the other pesticides (Figure 8.5-189B).

Previous studies show that glyphosate transport to surface water in agricultural areas is mainly due to surface runoff and that glyphosate is usually not transported in subsurface drainflow. A run- off transport mechanism is suggested by the fact that glyphosate and its metabolite AMPA are the most common compounds found in Danish streams at concentrations over 0.1 µg/L, with 26.7% and 38.2% respectively of samples in Danish streams recording such high concentrations. They postulated that infiltration from SW sources or slower degradation in riparian areas were possible reasons for this observation.

The article is considered reliable with restrictions.

Data point:	CA 7.5/027
Report author	Bruchet, A. *et al.*
Report year	2011
Report title	Natural attenuation of priority and emerging contaminants during river bank filtration and artificial recharge
Document No	European Journal of Water Quality 42 (2011) 123-133
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at an officially recognised testing facility
Acceptability/Reliability:	Reliable

The article was found relevant for multiple subchapters. The summary is provided in the groundwater monitoring subchapter of this document.

Assessment and conclusion by RMS:

This study describes monitoring experiment in the area of Paris, FR. The sampling points examined comprised Seine river water downstream of the Paris area, water from a primary well after bank filtration, water from a secondary well influenced by an artificial recharge process and water from the mixture of secondary wells after drinking water treatment.

In the river, glyphosate was found at <0.1 – 0.12 µg/L, and AMPA at 0.25 – 0.65 µg/L: but, in both the primary well and the secondary well, and in the drinking water samples (treated water at the outlet of the drinking water plant), concentrations of both substances were <0.1 µg/L.

The article is considered reliable with restrictions.

B.8.5.7. Monitoring data in sediment

New studies/assessments

Data point:	CA 7.5/001
Report author	[redacted]
Report year	2020
Report title	Collection of public monitoring data for European countries for the compartments soil, water, sediment and air for Glyphosate, AMPA and HMPA
Document No	110057-1
Guidelines followed in study	Methodology is based on the Groundwater Monitoring guideline document (Gimsing *et al*., 2019) with respect to chapter 7 (‘Public monitoring data collected by third party organisations’) Minimum quality criteria of monitoring data described by the FOCUS Ground Water Work Group chapter 9.5 (European Commission, 2014)
Deviations from current test guideline	None
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary

The report provides information about the outcome of a search for readily accessible and available monitoring data in European countries at a regional/national level for the time period 1995-2019. The main focus was on the time period 2012-2019 while earlier years are already covered by existing data. The search included raw data, requested from regional/national authorities or downloadable from their websites, as well as aggregated data extracted from reports compiled by authorities.

Data from 14 European countries were considered: Austria, Belgium, Denmark, France, Germany, Hungary, Ireland, Italy, The Netherlands, Poland, Romania, Spain, Sweden and the United Kingdom. The countries represent the major markets of products containing glyphosate sold in the EU. The data compilation included the active substance glyphosate and its metabolites AMPA and HMPA, in the soil, groundwater, surface water, tidal water, drinking water, sediment and air environmental compartments.

As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities and other bodies of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were actually not included in any of the monitoring programs.

Sediment Compartment Conclusion

There were hardly any official programs in place targeting monitoring of glyphosate or its metabolites residues in sediment. Raw data for glyphosate and AMPA were available for France and Sweden.

I. MATERIAL AND METHODS

The general methodology of data collection of public monitoring data and minimum quality criteria is based on existing guideline documents for groundwater monitoring programs. The underlying principles have been applied to all environmental compartments, especially where no specific guidance is at hand. Data search, acquisition and processing approaches are described below. The same approach was applied for each country, compartment and substance. Country specific adaptations to the general procedure were made in order to generate a harmonized database. The data collected for this report refers to third party organization data regarding all environmental compartments (SOIL, GW, SW, TD, DW, SD, AIR) and was further differentiated into the two different data types, i.e. raw data and aggregated data. Aggregated data refers to information provided in publicly available reports, e.g. from environmental agencies or research institutes. Such reports might hold only summary information on substance findings over space and time and may intersect with the raw data. Raw data refers to mid to long term time series of data that are provided on request by e-mail or by database from governmental authorities and are therefore recognized as official monitoring data. These datasets hold the information of sampling values, quality information (sampling, treatment, limit of detection - LOD, limit of quantification - LOQ) as well as information of location and time of sampling.

The following data source types were taken into account in order to collect monitoring data:

- E-mail requests: a general e-mail was sent to the national responsible authorities with regard to the required information.
- Governmental webpages: the official webpages of the national responsible authorities were searched for information regarding available reports and datasets.
- Public online databases: available data from online databases were downloaded as provided by the webpages of governmental authorities and other institutions.
- Professional contacts: information indicated by experts in frequent professional contact to governmental authorities and other institutions were considered in order to complement data sources and datasets.

The data search resulted in a very heterogeneous collection of tabular data and reports in different formats and structure. Data were processed into a harmonized tabular format by selecting relevant information and adapting data organisation. In general, the complete datasets were included in the final harmonized database as provided by the authorities, but obvious duplicates were deleted. In general, all entries for the digital database were checked for consistency and plausibility. For the raw data it was assumed that information was already subjected to critical scrutiny by the respective organization. For the aggregated data the same assumption was made with quality assurance of the data (mostly summaries) being the responsibility of the authors of the respective reports.

II. RESULTS AND DISCUSSION

The final data collection of raw data and aggregated data is summarised for each compartment and each country in Table 8.5-237.

Sediment

- France (FR)
  - Raw monitoring data for sediment were downloaded from NAIADES.
- Sweden (SE)
  - Raw monitoring data from national authorities for sediment were provided by SLU per e-mail. Furthermore, raw monitoring data for sediment for Sweden was directly downloaded from the SLU homepage.

Table 8.5-237: Overview of public monitoring data availability of raw data (R) and aggregated data (A)

Country	Soil	Water				Sediment	Air
		Ground	Surface	Tidal	Drinking		
Austria	-	R, A	R, A	-	A	-	-
Belgium	-	R	R	-	A (Flanders)	-	-
Denmark	-	R, A	A	-	A	-	-
France	-	R	R	-	A	R	-
Germany	R (Brandenburg)	R, A	R, A	R	R (Schleswig-Holstein), A	-	-

Hungary	-	A (one research article)	A (one research article)	-	-	-	-
Ireland	-	R, A	R, A	-	R, A	-	-
Italy	-	R (Lombardia), A	R, A	-	-	-	-
The Netherlands	-	R, A	R, A	-	R	-	-
Poland	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Romania	confirmation by corresponding authorities that no monitoring programs were in place that included glyphosate or metabolites						
Spain	-	R, A	R, A	-	A	-	-
Sweden	-	R, A	R	-	R, A	R	-
UK England	-	R	R	R	A	-	-
UK Northern Ireland	-	R	-	-	-	-	-
UK Scotland	-	-	R	-	-	-	-
UK Wales	-	-	R	-	A	-	-

R raw data available; A aggregated data from reports available; - no raw or aggregated data available

III. CONCLUSIONS

The collection of public monitoring data for glyphosate, AMPA and HMPA in soil, groundwater, surface water, drinking water, tide water, sediment and air resulted in a comprehensive database of ‘raw monitoring data from national authorities’ and ‘aggregated monitoring data from reports published by national authorities’. As a result of the search, the corresponding authorities of the three countries Hungary, Poland and Romania confirmed that neither glyphosate nor its metabolites were included as analytical targets in official monitoring programs. Authorities of all other countries provided raw data or aggregated data for at least one compartment and compound. Moreover, the metabolite HMPA and the compartment air were actually not included in any of the monitoring programs.

There were hardly any official programs in place targeting monitoring of glyphosate or its metabolites residues in sediment. Raw data for glyphosate and AMPA were available for France and Sweden.

Assessment and conclusion by applicant:
The report describes the collection process of public monitoring data for European countries for the compartment soil, water, sediment and air for Glyphosate, AMPA and HMPA.
The report is considered valid.

Assessment and conclusion by RMS:
This report describes the methodology employed for collection of monitoring data for Glyphosate, AMPA and HMPA. The data collection refers to third party organization data regarding all environmental compartments (Soil, GW, SW, TD, DW, SD, AIR).

Two different data types were collected, *i.e.* raw data from national authorities and aggregated data from publicly available reports (from environmental agencies or research institute).

The general search strategy was similar for each compartment, country and substance. All details of data acquisition are given in the report, and all data sources are carefully listed and described.
Although the process can clearly not be reproduced, and cannot be checked in details for exhaustiveness, the search strategy is clearly exposed and considered acceptable.

For sediment compartment, there were hardly any official programs in place targeting monitoring of glyphosate or its metabolites residues in sediment. Raw data for glyphosate and AMPA were available for France and Sweden.

Findings from this data collection and corresponding analysis are given in a separate report; see [redacted] [redacted] 2020 below.

The study (sediment part) is acceptable.

Data point:	CA 7.5/002
Report author	[redacted]
Report year	2020
Report title	Glyphosate (GLY) and the primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA): Public monitoring data assessment and interpretation
Report No	EnSa-20-0322
Document No	-
Guidelines followed in study	Groundwater monitoring guideline document (Gimsing *et al.*, 2019) with respect to chapter 7 ('Public monitoring data collected by third party organisations'); Article 5 of Directive 2009/90/EC - Technical specifications for chemical analysis and monitoring of water status.
Deviations from current test guideline	Not relevant
Previous evaluation	No, not previously submitted
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Acceptable

Executive Summary
The report provides information about the outcome of an analysis of public monitoring data comprising environmental concentrations of glyphosate (GLY) and its primary metabolites amino methyl phosphonic acid (AMPA) and hydroxy methyl phosphonic acid (HMPA) collated from readily available public monitoring databases held by national/regional environment agencies. This data collection and analysis was designed to expand previous reviews to include other compartments and supplement them for surface water, groundwater and drinking water. Public monitoring data from the following Member States (MS) were assessed for the water, sediment and soil compartments: Austria (AT), Belgium (BE), Denmark (DK), France (FR), Germany (DE), Ireland (IE), Italy (IT), Netherlands (NL), Spain (ES), Sweden (SE) and the

United Kingdom (UK). Three MS, namely Poland (PL), Hungary (HU), and Romania (RO) confirmed that they do not conduct analyses for GLY, AMPA and HMPA in any environmental compartment. No data for HMPA was identified for any MS or compartment. Note that at the time the study was started the UK was a Member State and is referred to as a Member State throughout the report.

Analyses of the large spatial and temporal dataset of measured concentrations occurring in several environmental compartments, namely surface water, groundwater, drinking water, tidal water, sediment and soil, were conducted to assess their state. This analysis not only sought to assess the state of the environmental compartment but also to consider the potential impacts this might have on biota, ecosystems and human health by using regulatory endpoints and thresholds from a range of European (EU) Directives. These included the Water Framework Directive (Directive 2000/60/EC) and associated Groundwater (2006/118/EC), Drinking Water (1998/83/EC) and Priority Substances (2008/105/EC28) Directives in addition to the Plant Protection Products Directive (1107/2009/EC).

Sediment

A small number (~2 700 analyses from ~550 sampling sites) of GLY and AMPA analyses from riverine sediment were collected and analysed. These were from two MS, FR and SE. No Information on HMPA was available. No GLY or AMPA RACs were available for the sediment compartment as such studies are not triggered because of low toxicity.

The maximum measured concentrations were 2.84 mg/kg (FR) and 0.05 mg/kg (SE) for GLY, 9.56 mg/kg (FR) and 0.15 mg/kg (SE) for AMPA.

Sediment compartment conclusions

Limited sediment monitoring data, in number, spatial and temporal scope, are available.

I. MATERIAL AND METHODS

The dataset analysed comprised individual sediment analysis records as well as existing aggregated analyses extracted from reports sourced from regional/national environment agencies (see [redacted] 2020, CA 7.5/001). The approach taken for the data processing encompassed a precautionary approach that preserved samples in the analysis where there was any doubt regarding their reliability. As such the number of records excluded from the analysis were small, especially relative to the total number of samples prior to removal. Similarly, no attempt to remove outliers was undertaken. Analysis and assessment of the data against thresholds was undertaken in Excel. The monitoring data was not evaluated against thresholds or endpoints as these are not available:

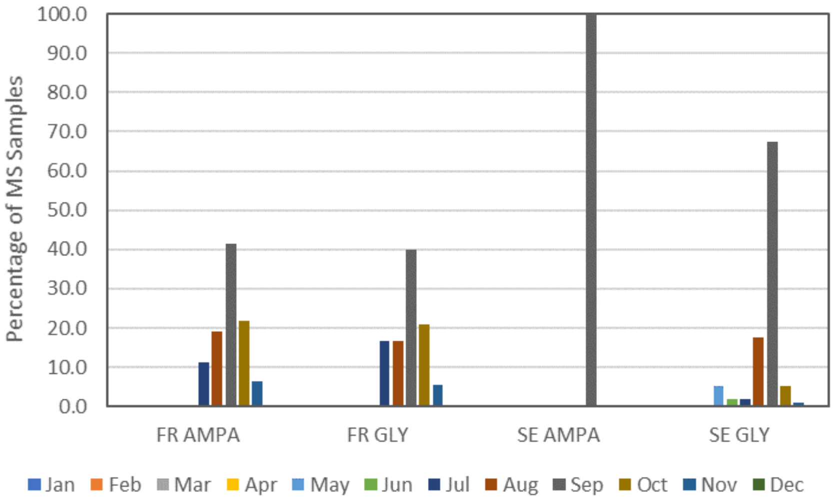
- Ecotoxicological endpoint: No ecotoxicological endpoints in this compartment are available for GLY and AMPA because sediment studies are not triggered.
- Ecosystem endpoint: Environmental quality standards (EQS) are not available at a Member State or at a European level.

II. RESULTS AND DISCUSSION

The data is limited (~2 700 analyses from ~550 sampling sites) and as such is biased both spatially and temporally. While it is not stated which kinds of waterbody were sampled, visual assessment of monitoring locations in GIS suggests that the samples are predominantly riverine. The bulk of the data (~91% for GLY and ~99% for AMPA) comes from the FR dataset which comprises ~541 sites, primarily in the north of France from a subset of departments. This dataset covers 13 years spanning the period 2005 – 2017. Monthly sampling effort for both GLY and AMPA is limited to the months of May through December and appears to be unimodal with lower sampling intensities in the early/latter months (see Figure 8.5-190).

The dataset from SE comprises ~12 sites distributed around the country targeting research catchments and locations. The GLY dataset covers 10 years spanning the period 2003 to 2012 while the AMPA data is restricted to 2006. Monthly sampling effort appears to be inconsistent and targets predominantly September. There was insufficient data to create a combined European dataset and as such only individual MS data were presented.

Figure 8.5-190: **Bar chart of sediment monthly glyphosate (GLY) and AMPA sampling effort within each Member State**



Analysis of the GLY sediment dataset indicates that GLY is quantified in ~5.6% (FR) to ~48.2% (SE) of samples (see Table 8.5-238), albeit the number of samples is quite limited (66 samples in µg/L and 1051 in mg/kg for FR; 114 in mg/kg for SE). The maximum measured concentrations were 2.84 mg/kg (FR), <4.0 µg/L (FR) and 0.05 mg/kg (SE).

Analysis of the AMPA sediment dataset indicates that AMPA is quantified in ~20.0% (SE) to ~48.2% (FR) of samples (see Table 8.5-238), albeit the number of samples is quite limited (66 samples in µg/L and 1088 in mg/kg for FR; 114 in mg/kg for SE). The maximum measured concentrations were 9.56 mg/kg, <4.0 µg/L (FR) and 0.15 mg/kg (SE).

III. CONCLUSIONS

There are limited sediment data available. The maximum measured concentrations were 2.84 mg/kg (FR) and 0.05 mg/kg (SE) for GLY, 9.56 mg/kg (FR) and 0.15 mg/kg (SE) for AMPA.

Table 8.5-238: Summary results of glyphosate (GLY) and AMPA analyses in sediment

Member State	Substance	Number of Sites	Number of Samples	Years	LOQ	Detected >LOQ		Detected >RAC			Measured Concentration
					Mean (min - max)	**Samples**	**%**	**Sites**	**Samples**	**% Samples**	**Median[1] (min - max)**
FR	GLY	503	1051	2007 - 2017	0.1 mg/kg (0.01 - 1.0)	59	5.6	NA	NA	NA	0.1 mg/kg (0.01 - 2.84)
	GLY	48	66	2005 - 2017	0.2 µg/L (0.02 – 4.0)	17	25.8	NA	NA	NA	0.2 µg/L (0.02 – <4.0)
	AMPA	505	1088	2007 - 2017	0.1 mg/kg (0.01 - 1.0)	281	25.8	NA	NA	NA	0.1 mg/kg (0.0014 - 9.56)
	AMPA	48	66	2005 - 2017	0.1 µg/L (0.01 - 4.0)	31	47.0	NA	NA	NA	0.2 µg/L (0.02 – <4.0)
SE	GLY	12	114	2003 - 2012	0.04 mg/kg (0.004 - 0.1)	55	48.2	NA	NA	NA	0.06 mg/kg (0.0 - 0.9)
	AMPA	10	10	2006	0.2 mg/kg (0.2 - 0.2)	2	20.0	NA	NA	NA	0.0 mg/kg (0.0 - 0.15)

[1] Values <LOQ and <LOD are treated as equal to LOQ and LOD as a precautionary estimate of the median NA – Not applicable

<u>Assessment and conclusion by applicant</u>:
The report describes the analysis of public monitoring data for key European countries for the compartments soil, water and sediment for Glyphosate and AMPA. The maximum measured sediment concentrations were 2.84 mg/kg (FR)/<4.0 µg/L (FR) for GLY and 9.56 mg/kg (FR)/<4.0 µg/L (FR) for AMPA.
The report is considered valid.

<u>Assessment and conclusion by RMS</u>:
A small number (~2 700 analyses from ~550 sampling sites) of GLY and AMPA analyses from riverine sediment were collected and analysed. These were from two MS, FR and SE. No information on HMPA was available.

The bulk of the data (~91% for GLY and ~99% for AMPA) comes from the FR dataset which comprises ~541 sites, primarily in the north of France from a subset of departments. This dataset covers 13 years spanning the period 2005 – 2017. Monthly sampling effort for both GLY and AMPA is limited to the months of May through December and appears to be unimodal with lower sampling intensities in the early/latter months

The dataset from SE comprises ~12 sites distributed around the country targeting research catchments and locations. The GLY dataset covers 10 years spanning the period 2003 to 2012 while the AMPA data is restricted to 2006. Monthly sampling effort appears to be inconsistent and targets predominantly September.

No GLY or AMPA RACs were available for the sediment compartment. Applicant indicated that "such studies are not triggered because of low toxicity." This should however be confirmed, considering the deviations pointed out on the chironomous study evaluated in the ecotox section.

RMS indicates that same limitations as underlined in the surface water monitoring section of this study applies for sediment monitoring data.

The maximum measured concentrations were 2.84 mg/kg (FR) and 0.9 mg/kg (SE) for GLY, 9.56 mg/kg (FR) and 0.15 mg/kg (SE) for AMPA.

The study (sediment part) is acceptable.

Existing studies/assessments

Data point:	CA 7.5/035
Report author	[redacted]
Report year	1972
Report title	Run-off of MON-0573 from Inclined Soil Beds
Report No	AgRR 275
Document No	
Guidelines followed in study	US EPA Guidelines for Registering Pesticides, 2nd draft, 5172, part XI
GLP	No
Previous evaluation	Not accepted in RAR (2015)
Acceptability/Reliability:	Not acceptable

Assessment and conclusion by RMS:

The summary is provided in the surface water monitoring subchapter of this document. The study is considered invalid due to the following deficiencies

- Study type is not relevant to the data requirement

No substance-specific analysis performed

Experimental conditions cannot be transferred to field scale and are therefore not relevant for risk assessment

Uncontrolled leaching out of the test vessels

Relevant literature articles

Data point:	CA 7.5/041
Report author	Lerch, R.N. *et al.*
Report year	2017
Report title	Vegetative Buffer Strips for Reducing Herbicide Transport in Runoff: Effects of Buffer Width, Vegetation, and Season
Document No	Journal of the American Water Resources Association (JAWRA) 53(3):667-683.
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The article was found relevant for multiple subchapters. The summary is provided in the surface water monitoring subchapter of this document.

Assessment and conclusion by RMS:
The article describes a runoff experiment to evaluate the effectiveness of vegetative buffer strips in USA.

This article is considered reliable with restrictions. It does not give any measured concentration of glyphosate, but the resulting effect of VBS are expressed as "input normalised loads %".

Data point:	CA 7.5/005
Report author	Napoli, M. *et al.*
Report year	2016
Report title	Transport of Glyphosate and Aminomethylphosphonic Acid under Two Soil Management Practices in an Italian Vineyard
Document No	Journal of Environmental Quality 45:1713-1721 (2016)
Guidelines followed in study	None
Deviations from current test guideline	N Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

The article was found relevant for multiple subchapters. The summary is provided in the soil monitoring subchapter of this document.

Assessment and conclusion by RMS:
This study reports a runoff experiment in a vineyard in Italy. The runoff was measured for glyphosate and AMPA residues. This is however in the context of the vineyard with great slope (16%), indicating important losses through run-off, while the results also indicate that transport of glyphosate and AMPA on a hillslope varies over time and according to the soil management practices (harrowed plot vs grass covered plot).

The following glyphosate uses on the plots are reported: Application of glyphosate every year in March. Equivalent dose of 34.8 g per plot of 283 m². (Equivalent to 1225 g/ha)

Concentration in runoff water and sediment were monitored for 4 years from March 2007 to February 2011. Runoff and associated sediment from each plot were intercepted by a Gerlach trough placed along the lower side of the plot. A downstream automated runoff gauge was used for measuring the runoff volume (RV) for separate rainfall events. The runoff gauges collected runoff aliquots of about 0.2 L every 300 L of RV.

Maximum concentrations of glyphosate and AMPA associated with runoff sediment were 680 µg/kg and 710 µg/kg respectively.

The study is considered reliable.

Data point:	CA 7.5/051
Report author	Maillard, E., Imfeld, G.
Report year	2014
Report title	Pesticide Mass Budget in a Stormwater Wetland
Document No	Environmental Science & Technology 2014, 48, 8603−8611
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The article was found relevant for multiple subchapters. The summary is provided in the surface water monitoring subchapter of this document.

<u>Assessment and conclusion by RMS</u>:

The article reports the pesticide loss and input in a stormwater wetland in an agricultural region in France. Several pesticides were analyzed, among them glyphosate and AMPA.

RMS highlights that information from laboratory water sediment studies (B.8.2.2) conducted on glyphosate or AMPA also indicate a potential accumulation of AMPA in sediment.

It is worth noting that the results are expressed as loads (mg) in wetland compartments (inlet and outlet) for the three phases of the investigation period, and not in concentration.

Data point:	CA 7.5/078
Report author	Sabatier, P. *et al.*
Report year	2014
Report title	Long-term relationships among pesticide applications, mobility, and soil erosion in a vineyard watershed
Document No	PNAS vol. 111 no. 44
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities (CARSO-Laboratoire Santé Environement laboratory, Lyon, France)
Acceptability/Reliability:	Reliable

In this article, a retro-observation approach is presented, based on lake sediment records to monitor micropollutants and to evaluate the long-term succession and diffuse transfer of herbicides, fungicides, and insecticide treatments in a vineyard catchment in France. The sediment allows for a reliable reconstruction of past pesticide use through time, validated by the historical introduction, use, and banning of these organic and inorganic pesticides in local vineyards. The results also revealed how changes in these practices affect storage conditions and, consequently, the pesticides' transfer dynamics. For example, the use of post-emergence herbicides (glyphosate), which induce an increase in soil erosion, led to a release of a banned remnant pesticide (dichlorodiphenyltrichloroethane, DDT), which had been previously stored in vineyard soil, back into the environment. Management strategies of ecotoxicological risk would be well served by recognition of the diversity of compounds stored in various environmental sinks, such as agriculture soil, and their capability to become sources when environmental conditions change.

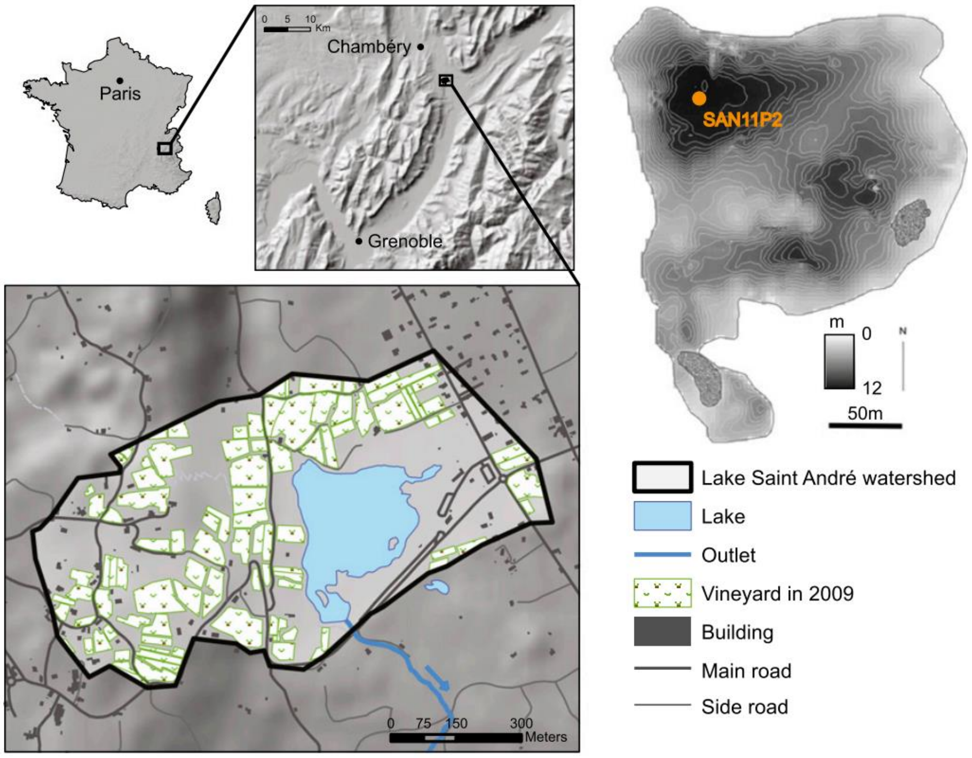
Materials and Methods

The study focused on Lake Saint André, which is located in eastern France at an elevation of 295 m above sea level. Vineyards make up 36% of the watershed and drain only this landslide deposit.

Logging

Three 1-m-long cores [registered in the International Geo Sample Number (IGSN)/System for Earth Sample Registration Database (www.geosamples.org) as SAN11P1 (IGSN: EDYSAN004), SAN11P2 (IGSN: EDYSAN001), and SAN11P3 (IGSN: EDYSAN007)] were collected from Lake Saint André in December 2011 (Figure 8.5-191), using an Uwitec gravity corer (Environnement, Dynamique et Territoires de Montagne). In the laboratory, the cores were split, photographed, and logged in detail, noting all physical sedimentary structures and the vertical succession of facies. The sediment colors were determined, with a spatial resolution of 5 mm, using a Minolta CM 2600d. The grain size distributions of core SAN11P2 were determined using a Malvern Mastersizer S (Environnement, Dynamique et Territoires de Montagne) at a continuous interval of 1 cm. After inserting the bulk sediment into the fluid module of the granulometer, ultrasound was applied to minimize particle flocculation. Core SAN11P2 was also sampled at 1-cm steps and dried at 60°C over the course of 4 d to obtain its dry bulk density, and then the loss on ignition (LOI) of each 1-cm interval was measured using the protocol of Heiri (40). The LOI at 550°C and 950°C corresponds to the organic and carbonate components of the sediment, respectively. The XRF analysis was performed on the surfaces of the split sediment SAN11P3 core at 2-mm intervals, using a non-destructive Avaatech core-scanner (Environnement, Dynamique et Territoires de Montagne, at the Université de Savoie) on the upper 50 cm. The split core surface was first covered with 4-µm-thick Ultralene to avoid contamination of the XRF measurement unit and desiccation of the sediment. The geochemical data were obtained at various tube settings: 10 kV at 1.5 mA for Al, Si, S, K, Ca, Ti, Mn, and Fe; 30 kV at 1 mA for Cu, Zn, Br, Sr, Rb, Zr, and Pb; and 50 kV at 2 mA for Ba. Each individual power spectrum was converted through a deconvolution process into relative components (intensities), expressed in counts per second. The PCA was performed using “R” software.

Figure 8.5-191: **The Lake Saint André watershed and the vineyards in 2009 (interpreted from aerial photographs), as well as the bathymetric map with the location of core SAN11P2 retrieved from the deeper part of the lake.**



Dating

The ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{234}Th, ^{241}Am, ^{137}Cs, ^{7}Be, and ^{40}K activities of the samples were analyzed using well-type, germanium detectors placed at the Laboratoire Souterrain de Modane, which is located under 1,700 m of rock. The detector sensitivity allows for the reduction of the sample mass required for a measurement. These improvements allowed for the measurement of both very low radioactivity levels (with background levels of less than 0.6 cpm in the 30-3,000 keV energy range) and small sample weights (1 g). In general, counting times of 24-48 h were required to reach a statistical error of less than 10 % for excess ^{210}Pb in the deepest samples and for the 1963 ^{137}Cs peaks.

Pesticide Analysis

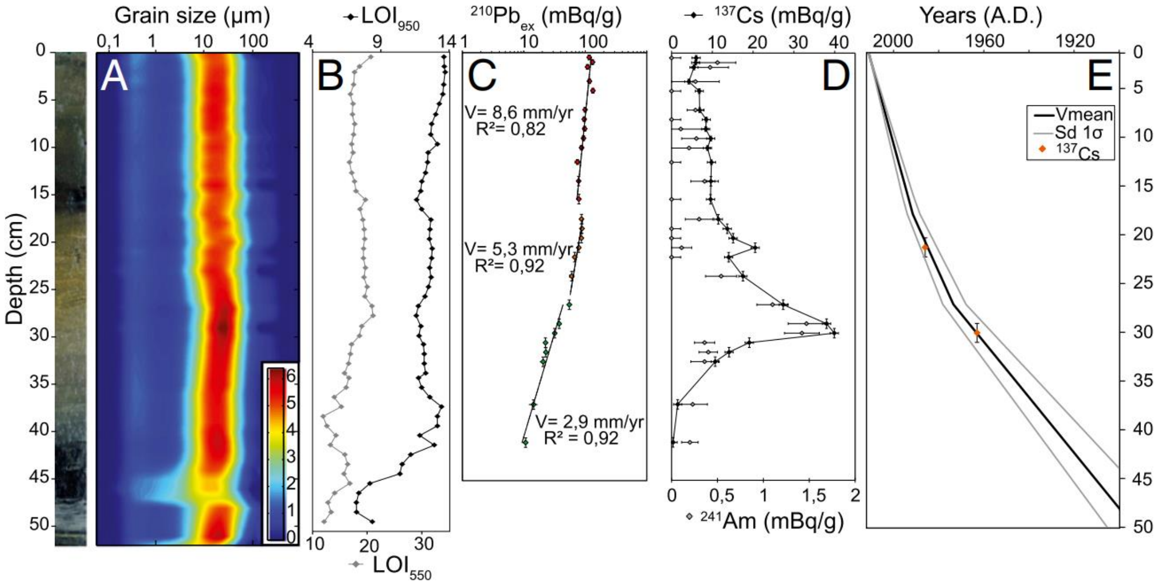
Pesticides were analysed on cores SAN11P1 and SAN11P2 by the CARSO-Laboratoire Santé Environement laboratory, Lyon, France (www.groupecarso.com), which is COFRAC (Comité français d'accréditation)-accredited (1-1531). Two hundred eighty-two compounds were searched, using three runs: solid dried and sieved sample was extracted with dichloromethane by an accelerated solvent extractor (ASE) system and then concentrated and analyzed by GC/MS in accordance with AFNOR standard XP ×33-012 (205 pesticides searched); solid dried and sieved sample was extracted with dichloromethane by an ASE system and analyzed by high performance liquid chromatography (HPLC) with diode-array detection in accordance with a certified inner standard method (75 pesticides search); and solid dried and sieved sample was extracted with water and evaporated and analyzed by HPLC, using post derivatization in accordance with a certified inner standard method for glyphosate and AMPA.

Results and discussion

Lake Sediment

The lake-bottom sediment cores were characterized in terms of their color, grain size, LOI, and sedimentary structure. The upper 41 cm consists of olive-gray silty clay with constant fractions of carbonate (30 %) and organic content (7.5 %) (Figure 8.5-192B). The grain size distribution of this upper sequence is homogeneous and exhibits two main populations centered at 0.3 µm (carbonate fraction) and 14 µm (Figure 8.5-192A). The levels of major and trace elements were measured using an X-ray fluorescence (XRF) core scanner and were subjected to principal component analysis to constrain sediment end-members. This PCA of the bulk sediment resulted in the identification of four geochemical endmembers: (i) Al, Si, K, Fe, Ti, Rb, Ba, and Zr, which are related to terrigenous input from the watershed (aluminosilicates and heavy minerals present in marls); (ii) Ca and Sr, which are linked to the carbonate productivity in the lake; (iii) S and Mn, which are related to the lake's oxidation state; and (iv) a Cu source that may be correlated with periods of significant vineyard-related activities in the watershed, during which a blend of copper sulfate and calcium hydroxide (Bordeaux mixture) was sprayed as a fungicide. A chronological framework was established via measurements of short-lived radionuclides. A logarithmic plot of ($^{210}Pb_{ex}$) activity (Figure 8.5-192C) shows a general decrease with three distinct linear trends. According to the "constant flux, constant sedimentation rate" (CFCS) model, as applied to each part of the profile, the levels of ^{210}Pb indicate mean accumulation rates of 2.9 ± 0.2 mm/y between depths of 41 and 26.5 cm, 5.2 ± 0.6 mm/y between 26.5 and 17 cm, and 8.7 ± 1.3 mm/y in the upper 17 cm of the core (Figure 8.5-192C). The plot of ^{137}Cs data (Figure 8.5-192D) displays a peak at a depth of 29.5 ± 1 cm, which apparently correlates with the maximum atmospheric production of ^{137}Cs in 1963. This temporal correlation is supported by the ^{241}Am peak at the same depth, which was a result of the decay of ^{241}Pu in fallout from atmospheric nuclear weapons tests. In the upper part of this core, at a depth of 20.5 ± 0.5 cm, a second ^{137}Cs peak corresponds to the time of the Chernobyl accident in 1986 (Figure 8.5-192D). The good agreement between the ages derived from the $^{210}Pb_{ex}$-CFCS model, and the artificial radionuclide peaks provide a well-constrained, continuous age-depth relationship (Figure 8.5-192E) within the sediment sequence, with two primary sedimentation rate changes in ∼1973 ± 5 y and 1994 ± 2.5 y.

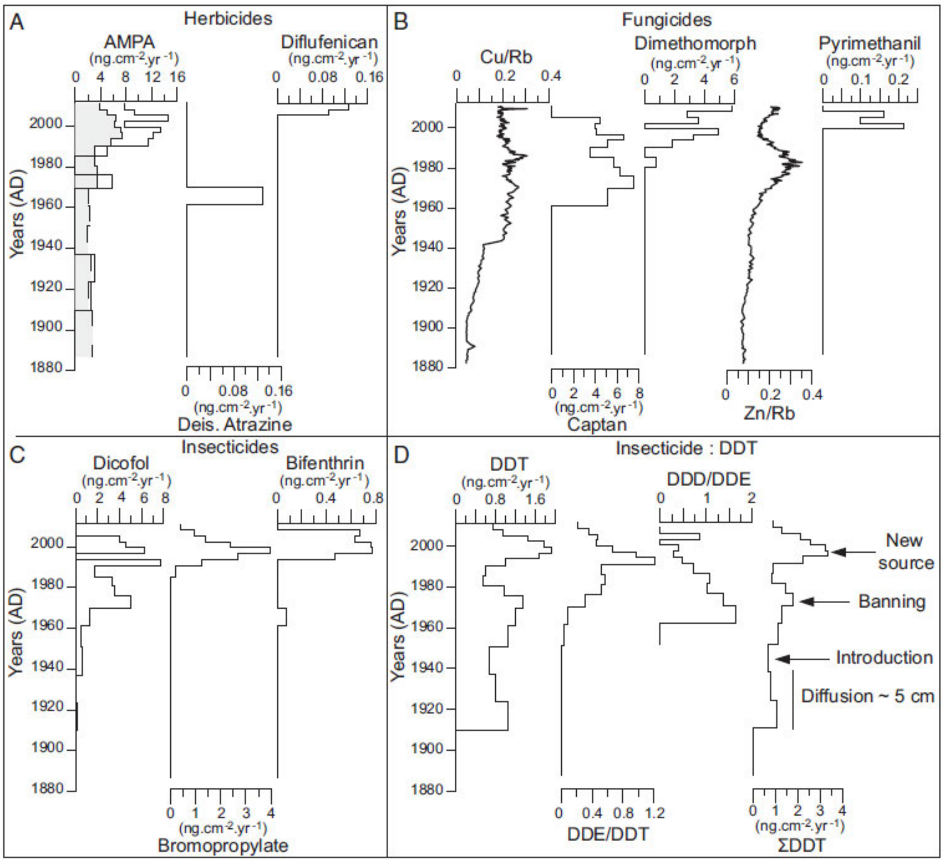
Figure 8.5-192: **Data from core SANP2. From left to right: (A) photograph and grain size contour plot with two primary populations centered at 0.3 and 14 µm, (B) LOI at 550°C (organic matter) and 950°C (carbonates), (C) $^{210}Pb_{ex}$ activity, (D) ^{137}Cs activity, and (E) the age model.**



Sediment Chronology of Pesticides Use

No significant variations in the grain size distribution or the organic content were observed during the last century. Thus, these two parameters could not have affected the absorption/degradation of pesticides in this sediment sequence. Three herbicides (or their metabolites) were identified in the Lake Saint André sediment (Figure 8.5-193A): AMPA [a metabolite of glyphosate]; deisopropyl atrazine (a metabolite of triazine herbicides); and diflufenican [a main ingredient in Buffalo (Bayer)], which is used as a preemergence herbicide. High levels of AMPA were found in the core representing deposition during the previous 20 y, with a primary increase since 1990. AMPA is also present in low but significant concentrations before this period, most likely because of contamination of the deeper part of the core by downward smearing of the very high concentrations found in the upper layers. The metabolite of atrazine, which was used at the end of the 1950s and was banned in 2003, was observed in a sample that dates to the period between 1960 and 1970. Diflufenican, which was introduced at the end of 1990s and is still allowed, was identified in the sediments deposited beginning in 2005.

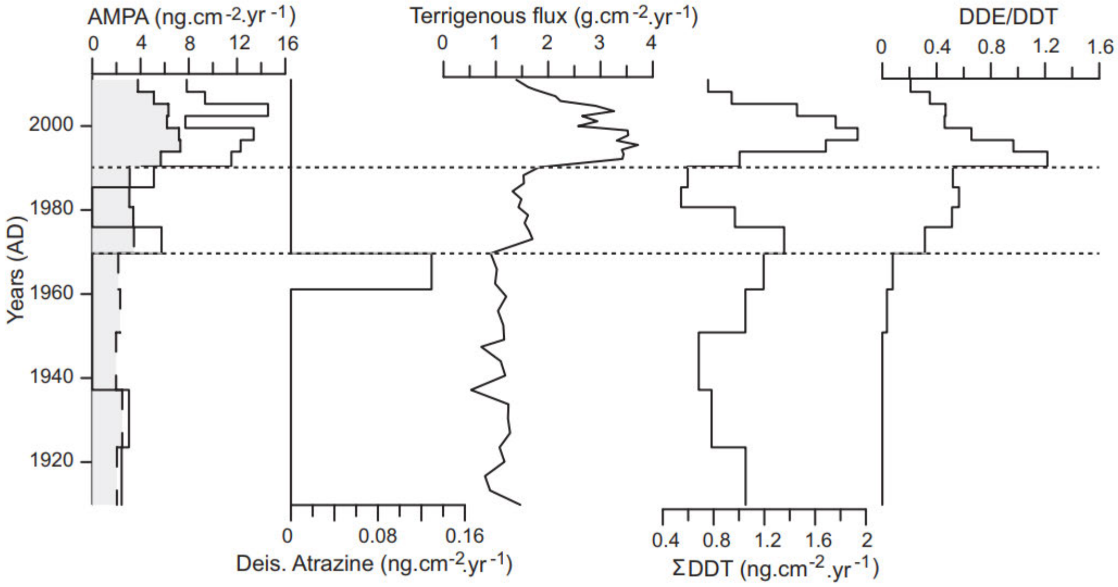
Figure 8.5-193: **Chronological variations in pesticide fluxes. (A) Herbicides: AMPA, deisopropyl atrazine, and diflufenican; (B) fungicides: Bordeaux mixture (Cu/Rb), captan, dimethomorph, mancozeb (Zn/Rb), and pyrimethanil; (C) insecticides: dicofol, bromopropylate, and bifenthrin; (D) DDT and metabolites: DDT, DDE/DDT, DDD/DDE, and ΣDDT. The gray area in the AMPA profile denotes the lower detection limit for this compound.**



Herbicides and Soil Erosion

We observed three changes in the sedimentation rate (Figure 8.5-192) in this sediment sequence, which display a general increase in the terrigenous flux into the lake going from ~0.9 g cm^{-2}/y (1900–1972) to 1.7 g cm^{-2}/y (1973-1993), and then to as much as 3.4 g cm^{-2}/y (1994-2005). A drastic decrease was then observed during the following years. These variations in the terrigenous sediment supply from the watershed may be directly attributed to soil erosion via vineyard practices. In the early 1970s, the local use of heavy farm machinery, which is known to contribute to soil erosion and is associated with the first application of preemergence herbicides (Atrazine metabolite) to combat grass between the rows of vines, may have induced the first increase of terrigenous flux into the lake (Figure 8.5-194). In 1990, we observed synchronous increases in AMPA, ΣDDT (with a low DDD/DDE ratio), and terrigenous soil fluxes into the lake (Figure 8.5-194). In the early 1990s, applications of post-emergence herbicides increased widely, including the use of Roundup, as indicated by the high flux of AMPA dating from this period. It has been demonstrated that application of this chemical has a strong effect on soil erosion, as it acts on grass development and leads to permanently bare soil. Moreover, this high flux of sediment supply to the lake is synchronous with the reemergence of banned pesticides, such as DDT and its aerobic metabolites (DDE), which were most likely stored in the vineyard and other agricultural soils in the watershed and subsequently remobilized by the herbicide-triggered rise in soil erosion. In this study, it was demonstrated that the recent widespread use of herbicides (glyphosate) induced an important release and reemergence of contaminants into the environment 20 y after their use was banned. The soils underwent a change in storage conditions, converting from sinks to sources of pesticides. The decrease in pesticide concentrations during the most recent years (Figures 7.5-188 and 7.5-189) may be attributed to French and European regulations controlling the use of micropollutants in agriculture. In summary, our study demonstrates the possibility of reconstructing the use of various pesticides (herbicides, fungicides, insecticides) in an agricultural watershed over the last century, using sedimentary archives. The dates of first use and prohibition of products used to control pests in vineyards and the changes in the soil erosion flux are recorded in the lake sediments. This work demonstrates that this high-resolution analysis of lake sediment allowed the reconstruction of past agricultural practices in this watershed and to precisely determine the 100-y-long dynamics of chemicals (organic and inorganic) used in vineyards. In particular, this study highlights the effects of post-emergence herbicides (glyphosate) on soil erosion and the remobilization of banned remnant pesticides (DDT) stored in vineyard soil.

Figure 8.5-194: Chronological variation in levels of AMPA, deisopropyl atrazine, subaerial flux, and sum of DDT and DDE/DDT. The horizontal dotted lines denote the two primary changes in the sedimentation rate.



<u>Assessment and conclusion by applicant</u>:
The article evaluates the long-term relationship among pesticide applications, mobility and soil erosion in a French vineyard watershed. The sediment of an adjacent lake was investigated and compared with available information on historical usage of pesticides. It is postulated, from increasing levels of AMPA in the sediment core post-1990 that the increasing use of glyphosate from the early 1990s led to the remobilization of banned remnant pesticides (e.g. DDT) from vineyard soils.
The article is considered reliable.

Assessment and conclusion by RMS:
The study focused on Lake Saint André, which is located in eastern France at an elevation of 295 m above sea level. Vineyards make up 36% of the watershed and drain only this landslide deposit.

Pesticides were analysed on 2 sediment cores by the CARSO-Laboratoire Santé Environement laboratory, Lyon, France (www.groupecarso.com), which is COFRAC (Comité français d'accréditation) accredited (1-1531).

The results of AMPA concentration are given throughout the core profile in ng.cm^{-2}/y. The main observation from these results is that "High levels of AMPA were found in the core representing deposition during the previous 20 y, with a primary increase since 1990. AMPA is also present in low but significant concentrations before this period, most likely because of contamination of the deeper part of the core by downward smearing of the very high concentrations found in the upper layers."

The study is considered reliable.

Data point:	CA 7.5/055
Report author	Imfeld G. *et al.*
Report year	2013
Report title	Transport and attenuation of dissolved glyphosate and AMPA in a stormwater wetland
Document No	Chemosphere 90 (2013) 1333–1339
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted by officially recognised testing facilities (Pasteur Institute of Lille (France))
Acceptability/Reliability:	Reliable

The article was found relevant for multiple subchapters. The summary is provided in the surface water monitoring subchapter of this document.

Assessment and conclusion by RMS:
This article provides a detailed study on glyphosate and AMPA concentration measurements in an artificial wetland in a vineyards. The study is considered reliable. See summary and comments on this study under point B8.5.4.

Glyphosate and AMPA were analysed in the wetland sediment in 2009 and 2011, as described previously (Maillard *et al*., 2011).
Glyphosate and AMPA were extracted from sediment samples by ultrasonic and methanol extraction.
Both compounds had a quantification limit of 10 µg/kg in sediment samples.
Glyphosate and AMPA were not detected in the wetland sediment.
Study authors emphasises that sorption on the wetland vegetation, which increased over time, and biodegradation were prevailing attenuation processes.

Data point:	CA 7.5/060
Report author	Zgheib, S. *et al.*

Report year	2012
Report title	Priority pollutants in urban stormwater: Part 1 – Case of separate storm sewers
Document No	Water research 46 (2012) 6683-6692
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable with restrictions

The article was found relevant for multiple subchapters. The summary is provided in the surface water monitoring subchapter of this document.

Assessment and conclusion by RMS:

The aim of this research has been to assess the potential presence of 88 storm water priority substances in three watersheds located within the Paris metropolitan area. Therefore agricultural uses are not in the focus.

RMS notes that the analytical method is not described within this study, but in another one (Zgheib, 2011) that is not submitted within this review. Concentration are given in dissolved + particulate phases, and particular phase.

Storm water quality was monitored in 16 samples from three different catchments, all located in Paris and its suburbs. The sites differed in terms of land development and housing density. However, the concentration results of the pollutants are given as % occurrence, min & max concentrations, median of the 16 analysed samples. The results cannot be assigned to the respective sites

Maximum concentration of glyphosate and AMPA associated with particulate phase are reported to be 8.3 mg/kg and 4 mg/kg respectively.

The study is considered reliable with restrictions.

Data point:	CA 7.5/064
Report author	Maillard, E. *et al.*
Report year	2011
Report title	Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment
Document No	The Science of the total environment (2011), Vol. 409, No. 11, pp. 2317-24
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	Yes, conducted at officially recognised testing facilities (Pasteur Institute of Lille (France))
Acceptability/Reliability:	Reliable

The article was found relevant for multiple subchapters. The summary is provided in the surface water monitoring subchapter of this document.

<u>Assessment and conclusion by RMS</u>:
This article provides a detailed study on glyphosate and AMPA concentration measurements in an artificial wetland in a vineyards. The study is considered reliable. See summary and comments on this study under point B8.5.4.

10 sampling campaigns were performed every two weeks during quiescent period (i.e. in the period between two runoff events) on day 21 (21 April 2009), 35, 49, 63, 76, 91, 111, 128, 141 and, after harvesting grapevine, on day 182 (29 September 2009) to collect water and sediment samples within the wetland.
Glyphosate and AMPA were extracted from sediment samples by ultrasonic and methanol extraction. Both compounds had a quantification limit of 10 µg/kg in sediment samples.

It is not clear if glyphosate and AMPA were found in the sediment of the wetland. No clear concentration results are reported. It is written in the article text that “The results indicate no significant transfer of dissolved or particle-laden pesticides from the water column to the bed sediments, and thus no accumulation or persistence of pesticides in the wetland sediments.”

In table results, inlet particle bound concentration of glyphosate and AMPA are reported. Maximum concentration are 0.045 mg/kg for glyphosate and 0.021 mg/kg for AMPA.

B.8.5.8. Monitoring data in air

New studies/assessments

No data was identified by the applicant from requests to and from searches of online data of regional/national environment agencies for the compartment air.

However, RMS indicates there is existing monitoring data at FR national level from a national exploratory pesticide campaign[3] that was likely not published at the time the applicant conducted its review. This sampling campaign lasted 12 months, from June 2018 to June 2019 and focused on the monitoring of 74 substances and 1 metabolite (AMPA). It included 50 sites, but for glyphosate and AMPA, due to specific material needed to sample these substances, sampling was performed on 8 sites. There were 3 urban/peri-uban areas and 5 rural areas. Six sites had different agricultural profile (field crops, vineyards, orchards, market gardening and breeding). Two site were indicated without agricultural profile, due to the very low proportion of surfaces agricultural fields within a radius of 1 and 5 km.

Overall, Glyphosate was quantified in 56% of the analyses (LOQ 0.009 ng/m^3). AMPA was quantified in 1.3% of the analyses (LOQ 0.009 ng/m^3). In details within the different agricultural typology, the frequency of quantification was as follow: 65% of quantification for field crops areas, 75.5% for orchards, 76.9% in vineyards areas, 24.5% in breeding areas, 41.2% in market gardening areas and 54.1% for areas without agricultural profile.

Maximum concentration for glyphosate was 1.225 ng/m^3. The 25th percentile concentration is 0.004 ng/m^3 and 95th percentile concentration is 0.088 ng/m^3. Most of the concentrations (99.5th percentile) are below 0.25 ng/m^3 and mainly in vineyard sites. The maximum concentration of 1.25 ng/m^3 is observed on the orchard site of Cavaillon and is a unique high value.
RMS reminds that these results were obtained in a national exploratory campaign on a limited number of sites and duration. Although the frequency of quantification for glyphosate is quite high and unexpected when considering its intrinsic properties (vapour pressure, DT50 in air), further data would be necessary to confirm these observations.

Existing studies/assessments

There was no monitoring data in air considered reliable in RAR (2015)

Relevant literature articles

Data point:	CA 7.5/079
Report author	Ravier, S. *et al.*
Report year	2019
Report title	Monitoring of Glyphosate, Glufosinate-ammonium, and (Aminomethyl) phosphonic acid in ambient air of Provence-Alpes-Côte-d'Azur Region, France
Document No	Atmospheric Environment 204 (2019) 102-109
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Reliable

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[3] Résultats de la Campagne Nationale Exploratoire des résidus de Pesticides dans l'air ambiant (2018-2019) - DRC-20-172794-02007A – Ineris, Juin 2020

Glyphosate, AMPA, its main metabolite, and glufosinate-ammonium were monitored in ambient air samples collected for two years (2015-2016), at four sampling sites in Provence-Alpes-Côte-d'Azur Region (PACA, France) in areas of different types (i.e. non-agricultural like: city centre, zones of 'zero pesticide' policy, industrial areas and agricultural use like: orchards and vineyards). Neither glufosinate-ammonium nor AMPA were detected. The summary focuses on results published for glyphosate and AMPA.

Neither glufosinate-ammonium nor AMPA were detected. Glyphosate was detected at a global frequency of 7% with frequencies ranging from 0% (Nice) to 23% (Cavaillon), according to the sampling site.

Glyphosate concentration reached a maximum level of 1.04 ng/m^3 in the rural site of Cavaillon. This is despite the physicochemical characteristics of glyphosate, which are not favourable to its passage into the atmosphere. The absence of simultaneous detection of glyphosate and AMPA suggests that drift during spraying operation is the main atmospheric source of glyphosate and that resuspension from soil particles is minor.

Materials and methods

Chemicals and reagents

Glyphosate (99%), glufosinate-ammonium (95%), and (aminomethyl)phosphonic acid (AMPA, 99%) reference standards were purchased from Sigma-Aldrich. The main physicochemical properties, the agricultural uses and the legal situation of pesticides studies are summarized in Table 8.5-239.

9-Fluorenmethylcholoroformate (FMOC-Cl, ≥99%) and stable isotope labeled glyphosate (2-^{13}C, 99 atom% ^{13}C) from Sigma-Aldrich were used as derivatization reagent and internal standard (IS), respectively. HPLC-grade dichloromethane (Sigma-Aldrich), ethylenediaminetetraacetic acid (EDTA), sodium tetraborate decahydrate (Borax), ammonium formate, formic acid, ammonia solution (35%), LC/MS-grade acetonitrile, and LC/MS-grade methanol (Fisher Scientific) were used for extraction and chromatographic elution. Ultra-High Quality water (UHQ water, 18.2 MΩ/cm at 25°C) was obtained by tap water passed through a Milli-Q water purification system (Direct 8 MilliQ, Merck Millipore). Underivatized standards were dissolved in UHQ water and the stock solutions of each compound at 0.5 g/L for glyphosate and glufosinate-ammonium, and 0.9 g/L for AMPA were stored in a polypropylene bottle (PP) at 4°C.

Sampling and site characterization

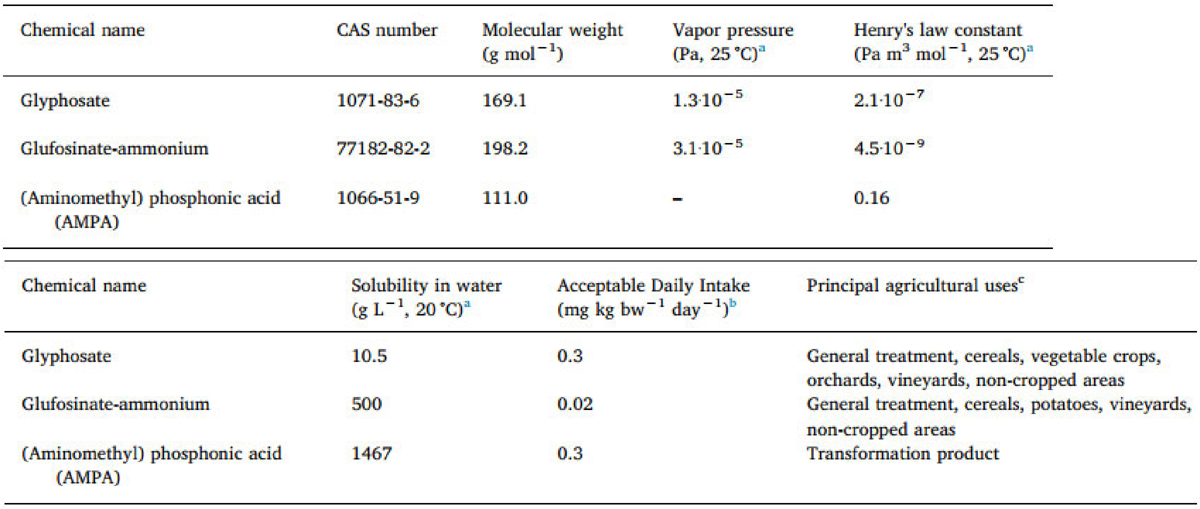
Sampling was undertaken at four sampling sites distributed throughout the Provence-Alpes-Côte-d'Azur (PACA) region, France, from January 2015 to December 2016. The description of sampling sites and sampling periods are summarized in Table 8.5-240. The three urban sampling sites (i.e., Avignon, Nice, and Port-de-Bouc) were located in the city centres, whereas the rural site of Cavaillon (hamlet of Les Vignères) was located in an intensive arboriculture area.

Glyphosate and glufosinate-ammonium are expected to exist solely in the particulate-phase. As a result, glyphosate, glufosinate-ammonium, and AMPA concentrations in the atmosphere are assumed to be equal to their particulate-phase concentrations.

Sampling was carried out using a high-volume sampler (Digitel Aerosol Sampler DHA-80) equipped with a PM-10 size selective inlet. Particulate samples (n = 142) were collected on 150 mm diameter ashless quartz microfiber filter (ALBET LabScience). The sampling flow was 30 m^3/h for 24 h. A total of 71 analyses were performed. Each analysis groups two filters, giving a total volume of filtered air around 1400 m^3.

Once collected, samples were stored and protected from light at -18°C until analysis. Moreover, in order to quantify the background contamination from sample handling and storage, field air blanks were done at each site. Typically, they consisted in a brief installation of a filter in the high-volume sampler without air pumping to simulate the sample handling. No contamination was detected, i.e., below the limit of detection.

Table 8.5-239: Physicochemical properties, agricultural uses, and legal situation

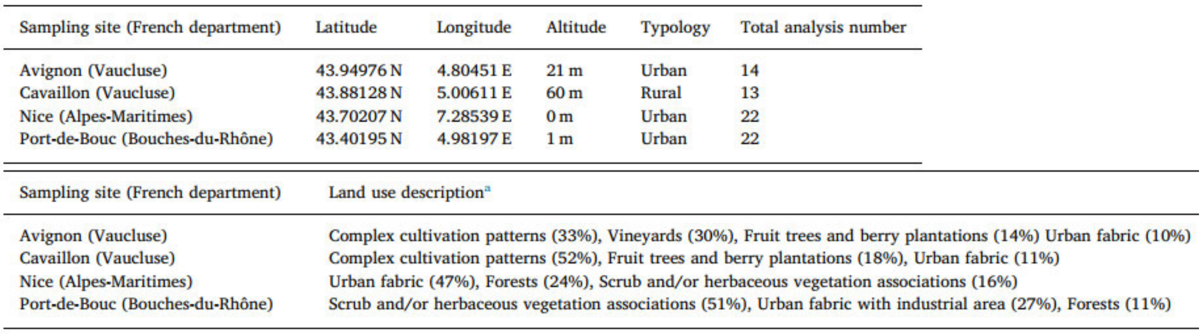


Chemical name	CAS number	Molecular weight ($g\ mol^{-1}$)	Vapor pressure (Pa, 25 °C)[a]	Henry's law constant ($Pa\ m^3\ mol^{-1}$, 25 °C)[a]
Glyphosate	1071-83-6	169.1	$1.3{\cdot}10^{-5}$	$2.1{\cdot}10^{-7}$
Glufosinate-ammonium	77182-82-2	198.2	$3.1{\cdot}10^{-5}$	$4.5{\cdot}10^{-9}$
(Aminomethyl) phosphonic acid (AMPA)	1066-51-9	111.0	-	0.16

Chemical name	Solubility in water ($g\ L^{-1}$, 20 °C)[a]	Acceptable Daily Intake ($mg\ kg\ bw^{-1}\ day^{-1}$)[b]	Principal agricultural uses[c]
Glyphosate	10.5	0.3	General treatment, cereals, vegetable crops, orchards, vineyards, non-cropped areas
Glufosinate-ammonium	500	0.02	General treatment, cereals, potatoes, vineyards, non-cropped areas
(Aminomethyl) phosphonic acid (AMPA)	1467	0.3	Transformation product

[a] PPDB: Pesticide Properties DataBase (Lewis *et al*., 2016).
[b] APVMA, 2017.

Table 8.5-240: Description of sampling sites



Sampling site (French department)	Latitude	Longitude	Altitude	Typology	Total analysis number
Avignon (Vaucluse)	43.94976 N	4.80451 E	21 m	Urban	14
Cavaillon (Vaucluse)	43.88128 N	5.00611 E	60 m	Rural	13
Nice (Alpes-Maritimes)	43.70207 N	7.28539 E	0 m	Urban	22
Port-de-Bouc (Bouches-du-Rhône)	43.40195 N	4.98197 E	1 m	Urban	22

Sampling site (French department)	Land use description[a]
Avignon (Vaucluse)	Complex cultivation patterns (33%), Vineyards (30%), Fruit trees and berry plantations (14%) Urban fabric (10%)
Cavaillon (Vaucluse)	Complex cultivation patterns (52%), Fruit trees and berry plantations (18%), Urban fabric (11%)
Nice (Alpes-Maritimes)	Urban fabric (47%), Forests (24%), Scrub and/or herbaceous vegetation associations (16%)
Port-de-Bouc (Bouches-du-Rhône)	Scrub and/or herbaceous vegetation associations (51%), Urban fabric with industrial area (27%), Forests (11%)

[a] Corine Land Cover nomenclature (zone of 10 km radius around the sampling site).

Sample extraction and derivatization

Extraction: Extractions of samples and blanks were carried out using PolyTetraFluoroEthylene (PTFE) or PolyPropylene (PP) vessels to avoid any loss of studied compounds by wall adsorption. In a 70 mL PTFE centrifugation tube, two filters (i.e., one sample) were spiked with 40 µL of IS solution (15.4 mg/L). The sample was then extracted with 20 mL of UHQ water added by 2 mL of Borax (0.05 M) and 0.8 mL of EDTA (0.1 M) solutions using first a mechanical shaker (30 s), then an ultrasonic bath (10 min). Sample was finally centrifuged at 12,000 rpm (12 min). A second extraction was performed with half volume of solutions according to the same procedure. The supernatants of the two successive extractions were collected and filtered together through a polyethersulfone (PES) membrane of 0.45 µm pore size under vacuum.

FMOC (FluorenylMethylOxyCarbonyl) derivatization: The filtrate was derivatized in 10 mL of acetonitrile with 2 mL of FMOC-Cl (50 g/L in acetonitrile). The mixture was stirred, cap closed, for 90 min in the dark at room temperature. After derivatization, acetonitrile was evaporated under nitrogen flow using a concentration workstation (TurboVap II, Biotage) with pressure 1.1 bar and a water bath at 40°C. To remove unwanted by-products and FMOC excess, 6 mL of dichloromethane were added at the residual aqueous solution then removed by settling.

Purification and concentration: Prior to purification and concentration on Solid Phase Extraction (SPE), the pH of the aqueous fraction was adjusted to pH 3 with formic acid 5% which corresponds to the optimum analyte retention. The extraction cartridge (OASIS HLB cartridge, 6 mL, 150 mg, Waters) was successively conditioned by 2 mL of methanol then 2 mL of formic acid 0.1%. Impurities were eliminated by a selective washing step constituted by 2 mL of formic acid 0.1% then 2 mL of UHQ water. Elution was achieved by 4 mL of [methanol/H_2O (70/30) (v/v) + NH_4OH 2%] solution. The extract was reduced to 1.5 mL by evaporating methanol using a concentration workstation and filtered through a PTFE membrane of 0.2 µm pore size before analysis.

UPLC-MS/MS analysis

Sample extracts were analyzed using an Ultra Performance Liquid Chromatographic (UPLC) system (Acquity, Waters) interfaced with a Quadrupole-Time-of-Flight Mass Spectrometer (Synapt G2 HDMS, Waters) equipped with an electrospray ion source (ESI). The mass spectrometer was used in its resolution mode, up to 18,000 FWHM (Full Width at Half Maximum) at 400 Th and allowed extracted chromatograms with 0.01 Th mass accuracy. The chromatographic separations were carried out on an Acquity UPLC column BEH C18, 1.7 µm particle size, 100 mm × 2.1 mm i.d. (Waters, Milford, MA, USA), at 40°C. The mobile phases consisted in (A) UHQ Water + 5 mM ammonium formate and (B) acetonitrile (Optima®, LC/MS grade, Fisher Scientific). The gradient elution was performed at a flow rate of 0.6 mL/min using 5%-95% of (B) within 7.5 min and held at 95% of (B) for 1.5 min. The injection volume was 10 µL. Analyses were carried out in negative ionization mode and optimum ESI conditions were found using a -0.85 kV capillary voltage, -15 V sampling cone voltage, 450°C desolvation temperature, 120°C source temperature, 20 L/h, and 1200 L/h cone gas and desolvation gas flow rate respectively. Dwell times of 0.25 s/scan were chosen. Data acquisition and mass spectra treatments were provided by the MassLynx software (v.4.1, Waters).

Analytical performance of the method

Method validation was carried out using spiked quartz filter as solid sorbent. The accuracy (including the recoveries) of the analytical method was integrated during calibration (i.e. each concentration levels were spiked on quartz filter and followed by the extraction, derivatization, and analytical protocol). Each concentration level (from 0.04 to 0.63 ng/m^3 for glyphosate, from 0.17 to 2.67 ng/m^3 for glufosinate-ammonium, and from 0.25 to 4.06 ng/m^3 for AMPA, n = 6) are triplicate. Calibration plots showed good linearity with correlation coefficients $R^2 \geq 0.98$ for glyphosate, $R^2 \geq 0.95$ for glufosinate-ammonium, and $R^2 \geq 0.99$ for AMPA. The detection limit (LOD) and quantification limit (LOQ) were determined using the calibration graph residuals for each compound (ICH, 2005). The LOD and LOQ obtained using spiked quartz filter, when air volumes of 1400 m^3 were collected, are equal to 0.05 and 0.14 ng/m^3 for glyphosate, 0.30 and 0.90 ng/m^3 for glufosinate-ammonium, and 0.28 and 0.84 ng/m^3 for AMPA, respectively.

Results

Detection frequency and atmospheric concentrations

Glyphosate was detected at a global frequency of 7% with frequencies ranging from 0% (Nice) to 23% (Cavaillon), according to the sampling site. AMPA, the main glyphosate degradation product, was never detected at any sampling sites. As AMPA is a bio-degradation product formed only in soils, its atmospheric concentrations could be only due to soils aeolian erosion. Since no simultaneous detection of glyphosate and AMPA was observed in the present work, it can be assumed that the aeolian erosion was a pesticide atmospheric source of minor importance and thus, the atmospheric glyphosate concentrations were mainly due to drift during spraying. Glyphosate concentration reached a maximum level of 1.04 ng/m^3 in Cavaillon (Table 8.5-241).

Spatial and temporal detections of glyphosate

According to sampling sites and years, spatial and temporal detection frequencies varied from 0% (e.g., Nice) to 66% (i.e., Cavaillon in 2015). With respect to the context of sources (e.g., rural vs. urban), it was not easy to correlate the detections and the environment of the sampling sites.

Spatial distribution

In Nice, sampling was performed in a wooded square in city center, near a cemetery (∼550 m South-West), urban parks (∼400 m East), and port (∼500 m South). Nice was the only site where glyphosate has never been detected (0/22 analysis). The explanation probably lies in the fact that, since 2009, Nice has adopted a 'zero pesticide' policy for the maintenance of green spaces, cemeteries, and roads.

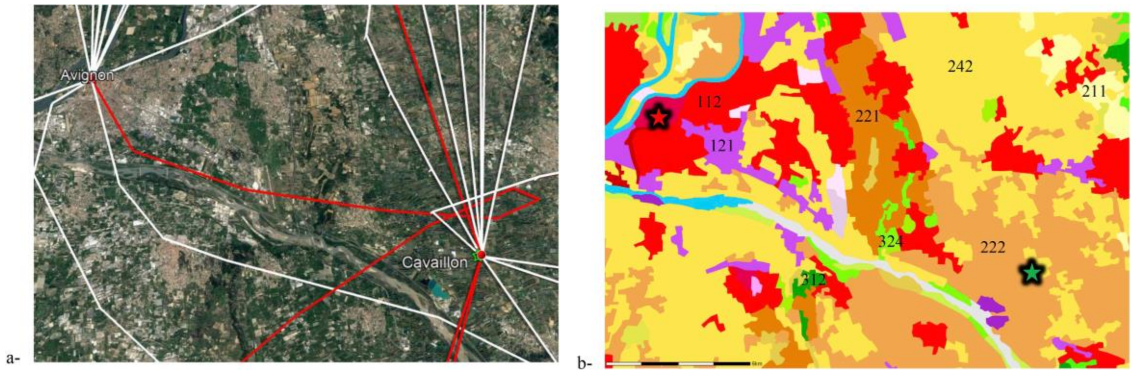
On the other hand, the Cavaillon sampling had a glyphosate detection frequency of 23% (3/13 analyses). In addition, the highest concentrations, until 1.04 ng/m^3 in April 2015 were measured on this site. Back-trajectories calculated using the NOAA HYSPLYT model (Figure 8.5-195) indicated two regional sources: from North (May 2015) and South-West (April 2015 and June 2016). Samples of Cavaillon were collected in a hamlet named "Les Vignères", a rural site located in an intensive arboriculture area (the nearest orchard is less than 200 m from the sampler). According to the French National Institute for Agricultural Research, mechanical weeding is not always possible in established orchards if it has not been thought upstream, which leads to use of herbicides and especially glyphosate.

The sampling site of Avignon is located in the city center, near a public garden (∼200 m North and North-West) and train station (∼900 m South). From an agricultural point of view, there is also arable lands (∼600 m North), orchards (∼2 km North-East), and vineyards (∼5 km North-West). Glyphosate was detected only once, in April 2015 (1/14 analysis, 7%). Back-trajectories (Figure 8.5-195) suggest a South-East source with an air mass passing especially over the orchards surrounding the sampling site of Cavaillon.

The sampling site of Port-de-Bouc is located at the harbor near the train station (∼600 m North) and less than 2 km from an industrial complex (refinery, petrochemical facilities). As in Avignon, glyphosate was detected only once in March 2016 (1/22 analysis, 5%). However, the origin of the air mass coming from the East does not indicate specific areas where glyphosate is intensively used.

These results highlight a higher detection frequency of glyphosate in rural areas than in urban areas, i.e., 87% (3/13 analysis) against 13% (2/58 analysis), respectively. If rural and urban sites correspond rather to agricultural and non-agricultural applications, respectively, this is consistent with French sales with non-agricultural applications estimated at 18.6% in 2015 and 16.1% in 2016.

Figure 8.5-195: Geographical environment of Avignon and Cavaillon: a- Calculated back-trajectories (NOAA HYSPLIT model - GDAS meteorological data) during sampling (red line: detection of Glyphosate, white line: <LOD). b- Corine Land Cover nomenclature: 112/121-Urban fabric, 211-Arable land, 221-Vineyards, 222-Fruit trees and berry plantations, 242-Heterogeneous agricultural areas, 312-Forests, 324-Scrub and/or herbaceous vegetation associations.



Temporal distribution
All detections were made between March and June which is consistent with the main phase of glyphosate applications in late winter and during spring and early summer periods (Table 8.5-241).

It should be noted that of the three sampling sites where glyphosate has been detected (i.e., Avignon, Cavaillon, and Port-de-Bouc), there is no reproducible detection pattern from 2015 to 2016.

Influence of meteorological conditions
The meteorological data collected at the four sampling sites allow the influence of precipitation, temperature, and wind speed on the glyphosate concentrations to be observed. However, it is necessary to be cautious because only 5 out of 71 samples contained glyphosate.

The 5 detections of glyphosate were registered when mean daily temperatures ranged between 9.7°C (Port-de-Bouc, March 2016) and 21.0°C (Cavaillon, June 2016), which is consistent with the temperatures commonly measured during the application period.

In France, it is forbidden to apply as soon as the wind speed reaches an intensity greater than about 19 km/h. During the days when glyphosate was detected, the wind speed exceeded this value 33% of the time (hourly measurement), reaching up to a maximum of more than 40 km/h in Port-de-Bouc. These wind speeds can lead to greater resuspension and then long-range transport by aerial drift which will cause injury to nontarget plants. The probability of drift injury occurring increased when winds are gusty or when wind speed will allow spray drift to occur.

Due to its high solubility in water, glyphosate is expected to be removed by rainfall. Only the sampling collected in Port-de-Bouc in March 2016 showed glyphosate detection during a rainy period (precipitation 18.6 mm), suggesting that the measured concentration (0.38 ng/m^3) was potentially higher before the rain event.

Table 8.5-241: Precipitation and atmospheric concentrations of glyphosate, glufosinate-ammonium, and AMPA in all sampling sites

Date		Avignon				Cavaillon			
		Precipitation (mm)	Concentration (ng m^{-3})			Precipitation (mm)	Concentration (ng m^{-3})		
			GLY	GLU	AMPA		GLY	GLU	AMPA
2015	01/21-23								
	02/18-20								
	03/10-12	0	–	–	–	0	–	–	–
	04/20-22	0.2	0.30	–	–	0.2	1.04	–	–
	05/18-20	0	–	–	–	0	0.62	–	–
	06/12-14	12.0	–	–	–				
	07/23-25								
	08/24-26								
	09/15-17								
	10/09-11								
	11/14-16								
	12/04-06								
2016	01/24-26								
	02/25-27	0.2	–	–	–	0.2	–	–	–
	03/15-17	25.3	–	–	–	25.3	–	–	–
	04/25-27	0	–	–	–	0	–	–	–
	05/27-29	0	–	–	–				
	06/14-16	0.4	–	–	–	0.4	0.18	–	–
	07/15-17	0	–	–	–	0	–	–	–
	08/02-04	0	–	–	–	0	–	–	–
	09/04-06	0	–	–	–	0	–	–	–
	10/25-27	2.0	–	–	–	2.0	–	–	–
	11/20-22					24.1	–	–	–
	12/20-22	3.8	–	–	–	3.8	–	–	–

Date		Nice				Port-de-Bouc			
		Precipitation (mm)	Concentration (ng m^{-3})			Precipitation (mm)	Concentration (ng m^{-3})		
			GLY	GLU	AMPA		GLY	GLU	AMPA
2015	01/21-23	20.2	–	–	–	28.8	–	–	–
	02/18-20	0	–	–	–	0	–	–	–
	03/10-12	0	–	–	–	0	–	–	–
	04/20-22	0	–	–	–	0.6	–	–	–
	05/18-20	0	–	–	–	0.2	–	–	–
	06/12-14	0.4	–	–	–	0	–	–	–
	07/23-25	0	–	–	–				
	08/24-26	11.0	–	–	–	5.6	–	–	–
	09/15-17	2.4	–	–	–	0	–	–	–
	10/09-11	0	–	–	–	0	–	–	–
	11/14-16					0	–	–	–
	12/04-06	20.6	–	–	–	2.8	–	–	–
2016	01/24-26	0	–	–	–	0	–	–	–
	02/25-27	0	–	–	–	0.8	–	–	–
	03/15-17	3.6	–	–	–	18.6	0.38	–	–
	04/25-27	0	–	–	–				
	05/27-29					0	–	–	–
	06/14-16	6.6	–	–	–	0	–	–	–
	07/15-17	0	–	–	–	0	–	–	–
	08/02-04	0	–	–	–	0	–	–	–
	09/04-06	0	–	–	–	0	–	–	–
	10/25-27	1.4	–	–	–	1.4	–	–	–
	11/20-22	28.3	–	–	–	20.9	–	–	–
	12/20-22	3.6	–	–	–	5.2	–	–	–

(−) means < Limit of Detection.

Conclusion
Neither glufosinate-ammonium nor AMPA were detected. However, at the same sampling sites, during the same period, detection frequency and maximum concentration of glyphosate were sometimes higher than those found for other pesticides, especially herbicides. This is despite the physicochemical characteristics of glyphosate which are not favorable to its passage into the atmosphere.

The absence of simultaneous detection of glyphosate and AMPA suggests that drift during spraying operation is the main atmospheric source of glyphosate, and that resuspension from soil particles is minor.

However, in the worst-case scenario (1.04 ng/m^3), the expected dose of glyphosate for an average consumer (70 kg body weight) respiring at a rate of 1.5 m^3/h during light exercise is 0.54 ng/(kg day). In these conditions, this value remains well below the chronic reference dose for glyphosate of 1.75 mg/(kg day).

Assessment and conclusion by applicant:
The article describes the results of monitoring glyphosate and AMPA in the air of 4 different sites in the southeast of France. Maximum concentration of glyphosate measured at 1.04 ng/m^3
The article is considered reliable.

Assessment and conclusion by RMS:
The following information can be retained from this study:

Glyphosate was detected at a global frequency of 7% with frequencies ranging from 0% (Nice) to 23% (Cavaillon), according to the sampling site.

These results highlight a higher detection frequency of glyphosate in rural areas than in urban areas, i.e., 3/13 analysis against 2/58 analysis, respectively.

Glyphosate concentration reached a maximum level of 1.04 ng/m3 in the rural site of Cavaillon. This is despite the physicochemical characteristics of glyphosate, which are not favourable to its passage into the atmosphere. The absence of simultaneous detection of glyphosate and AMPA suggests that drift during spraying operation is the main atmospheric source of glyphosate and that resuspension from soil particles is minor.

The article is considered reliable.

Data point:	CA 7.5/050
Report author	Gasperi, J., *et al.*
Report year	2014
Report title	Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric contributions for a wide range of contaminants in three French sites
Document No	Environmental Science and Pollution Research (2014) 21:5267-5281
Guidelines followed in study	None
Deviations from current test guideline	Not applicable

GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Not relevant for air compartment

The article was found relevant for multiple subchapters. The summary is provided in the surface water monitoring subchapter of this document including the findings for total atmospheric fallout.

Assessment and conclusion by RMS:
This article however does not give any relevant measured concentration of Glyphosate or AMPA in air, neither information on the contribution of atmospheric deposition of these susbtances to the stormwater concentration.

Data point:	CA 7.5/056
Report author	Vialle, C., *et al.*
Report year	2013
Report title	Pesticides in roof runoff: Study of a rural site and a suburban site
Document No	Journal of Environmental Management 120 (2013) 48 - 54
Guidelines followed in study	None
Deviations from current test guideline	Not applicable
GLP/Officially recognised testing facilities	No
Acceptability/Reliability:	Not relevant for air compartment

The article was found relevant for multiple subchapters. The summary is provided in the surface water monitoring subchapter of this document.

Assessment and conclusion by RMS:
This article does not give any relevant information on the concentrations in the air compartment.