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REPORT

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Diffuse trace contaminants with relevance for drinking water production in rural and semi-rural areas

Project acronym: AQUISAFE 1

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Preparation of this report was financed in part through funds provided by

VEOLIA WATER

Indianapolis, USA & Berlin, Germany

2009

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Title

Diffuse trace contaminants with relevance for drinking water production in rural and semi-rural environments

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Deliverable number

Aquisafe 1 D 1.1

Abstract

The Aquisafe project aims at mitigation of diffuse pollution from agricultural sources to protect surface water resources. The first project phase (2007-2009) focused on the review of available information and preliminary tests regarding

(i) most relevant contaminants,

(ii) system-analytical tools to assess sources and pathways of diffuse agricultural pollution,

(iii) the potential of mitigation zones, such as wetlands or riparian buffers, to reduce diffuse agricultural pollution of surface waters and

(iv) experimental setups to simulate mitigation zones under controlled conditions.

The present report deals with (i), providing information on trace substances, which enter surface water predominantly via diffuse sources in rural or semi-rural environments. In particular, it provides a priority list of relevant substances to aid planning of monitoring programs at waterworks, which abstract surface water from rural watersheds, for which information on substance use is sparse. As this ranking is limited to substances for which broad data sets are available from literature, it is compared to actual screening programs in predominantly rural catchments in Brittany (France) and Indiana (USA).

The literature review identified pesticides as the dominant known diffuse contaminant group in rural and semi-rural settings (section 2.1). This is confirmed for the agriculturally dominated Ic Catchment in France and Upper White River Watershed in the USA, where pesticides were found to dominate the diffuse source compounds (section 3). Seven agricultural pesticides were detected in the Ic Catchment with AMPA and atrazine being the most common compounds, detected in 54 % and 41 % of all the samples, respectively. In the White River Basin 26 of the 38 detected compounds were pesticides making them the largest group of chemicals detected.

Based on literature values on pesticide detection in surface waters in Germany, France and the USA, a priority list was established in section 2.2 of this report (see Table on page vi). Only seven substances were among the 20 most relevant pesticides, both in the USA and in Europe. Accordingly, US and European substances are distinguished in the priority list. Most frequently detected substances were atrazine, metolachlor and simazine for the USA, AMPA (metabolite of glyphosate), diuron and atrazine for France and diuron, atrazine and isoproturon for Germany. The importance of atrazine in Europe is interesting, since it was already banned at the time of the monitoring, indicating the high persistency of atrazine in groundwater. In some cases in Germany, concentrations in surface waters were found to follow typical seasonal application patterns, indicating illegal use (pers. Comm.. M. Bach).

Although the list of substances in the USA and in Europe differ, there is an agreement to the fact that many of the pesticides applied in agriculture find their way into surface waters. The concentrations found are often beyond 0.1 µg/L. For the EU this level already corresponds to the drinking water limit. Thus, if surface water is used for drinking water production pesticides seem to be of high relevance. In finished drinking water, frequently-used Isoproturon and Bentazon were most frequently detected in Germany and France. The importance for drinking water production is emphasized by frequent detections above 0.1 µg/L in finished drinking water in nine waterworks in the US. Regarding drinking water regulation, the thresholds in the USA are substance-specific and generally more than one magnitude higher than 0.1 µg/L. As a result threshold exceedance was mainly found for Atrazine. In terms of treatability in water works, the priority list includes the efficiency of classical treatment (flocculation, filtration, ozonation) and of powdered activated

carbon (PAC), which is often added in emergency situations. Particularly problematic are triazines (such as atrazine), phenoxy-type substances (such as 2,4-D and Mecoprop) and Anilides/Anilines (such as Metolachlor and Acetochlor).

The pesticides found in the screenings are in good agreement with the priority list of most problematic pesticides for the US and Europe. AMPA and atrazine, the substances detected most frequently in the Ic catchment, as well as 2,4-D and dichlorprop, which were found in high concentrations > 0.1 µg/L in one sample are all included in the Europe top 20 of the priority list. Other substances on the list may not have been found because they were not measured, because of relatively high analytical detection limits of the screening or simply because they are not used in the basin, dominated by corn and wheat cultures. In the White River Basin, atrazine, acetochlor and simazine were detected at concentrations exceeding early warning levels utilized by several states in the United States, indicating their high relevance concerning drinking water production. They are also included in the US top 20 of the priority list.

The priority list is a reliable basis for potentially problematic pesticides. It can thus be used as a starting point for monitoring programs in rural catchments, where no specific information on pesticide use are available. If looking for pesticides in surface water, it is important to take times of application of regarded pesticides into consideration, as shown by strong fluctuations in atrazine concentrations in the source water of a waterworks in Indiana (Figure 12 of this report).

The screening results indicate that also other contaminants than pesticides may play a role in rural catchments. In the screening in the semi-rural catchments in Indiana, twelve of the detected 38 substances were not pesticides, but belonged to other groups, such as domestic use products, manufacturing additives or gasoline hydrocarbons. Of these twelve substances, seven were only found in one of the two catchments, showing a strong catchment-specific relationship. The findings indicate that other substances than pesticides may be of local importance, though in the case study all 12 substances were at least 50-fold below human health benchmarks (if defined). We conclude that the pesticide priority list given below is a good starting point for diffuse pollution screening even though it may possibly not be sufficient if major local influences, such as factories, large roads with stormwater discharges, CSO or specific local pesticide uses are present.

Pesticide priority list, Comparison of 20 most relevant pesticides in USA (study by Gilliom et al. 2006) and EU (studies by IFEN 2009; TZW 2007), as well as treatability in drinking water treatment

Substance	legal application		Removability in drinking water treatment		Ranking based on occurence			
	in EU	in USA	floculation, filtration, ozonation	Powdered Activated Carbon	in Germany	in France	in USA	
DCMU (Diuron)	yes	yes	≥ 90%	≥ 50%	1	2	15	Pesticides in US and EU top 20
Atrazine	no	yes	< 50%	≥ 50%	*2*	*4*	1	
Simazine	no	yes	?	?	*4*		4	
Deethylatrazine	(no)	(yes)	?	< 50%	7	3	3	
Bentazon	yes	yes	≥ 90%	≥ 50%	9	11	11	
Metolachlor	restricted	yes	≥ 50%	≥ 50%	11	12	2	
2,4-D	yes	yes	< 50%	≥ 50%	16		13	
Cyanazine	no	yes	?	?			5	Pesticides only in US top 20
Prometon	-	yes	?	?			5	
Alachlor	no	yes	≥ 50%	≥ 50%			7	
Acetochlor	yes	yes	≥ 50%	≥ 50%			8	
Tebuthiuron	no	yes	?	?			9	
Metribuzin	yes	yes	?	?			10	
EPTC	yes	yes	?	?			12	
Dacthal	yes	yes	?	?			15	
Diazinon	no	*restricted*	*?*	*?*			*15*	
Trifluralin	no	yes	≥ 90%	≥ 50%			15	
Chlorpyrifos	yes	*restricted*	*?*	*?*			*18*	
Molinate	yes	yes	?	?			19	
Carbofuran	no	yes	?	?			20	
Isoproturon	yes		≥ 90%	≥ 50%	3	6		Pesticides only in EU top 20
MCPA	yes		≥ 50%	≥ 50%	5	14		
Terbutylazine	yes		?	?	6			
Mecoprop (MCPP)	yes		< 50%	< 50%	7	13		
Glyphosate	yes		≥ 90%	< 50%	9	5		
AMPA	(yes)		≥ 90%	< 50%	11	1		
Metazachlor	yes		?	?	11			
Flufenacet	yes		?	?	14			
Terbutryn	no		≥ 90%	?	*14*			
Dichlorprop (2,4-DP)	yes		?	?	16			
2,6-Dichlorbenzamid	(no)		?	?	*18*			
Bromoxynil	yes		?	?	18			
Desethylterbutylazin	(yes)		?	?	18			
1-(3,4-dichlorophényl)-3-méthyl-urée	(yes)		?	?		7		
Aminotriazole	yes		≥ 90%	< 50%		9		
Diflufenican	yes		?	?	40	10		
Oxadiazon	yes		?	?		15		

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Chapter 1
Introduction

Rivers and lakes across the world are subject to pollution from anthropogenic sources. Thanks to improved wastewater treatment in industrialized countries over the past decades, point-source pollution has decreased significantly and therefore diffuse pollution has gained in importance (e.g., EU 2004a). For instance, based on a detailed analysis of Swiss watersheds, diffuse pollution has become the major source of phosphates in all but one watershed, whereas it remained dominant for nitrates (Zobrist and Reichert 2006). As a result phosphate concentrations in Swiss surface water have generally decreased, whereas nitrate levels remained practically stable. Apart from nutrients, a large array of trace substances can enter surface waters from diffuse and point source pollution.

Surface water in turn is a key element for public water supply, e.g., contributing 40 % of EU (EEA 2003) and 63 % of US (Hutson et al. 2004) drinking water. However there is a strong geographical component. For instance, surface water is clearly the dominant source for public water supply in Belgium, Spain, United Kingdom, Norway and the US states Colorado, Virginia and Oklahoma, whereas groundwater is almost exclusively used in Austria, Italy, Portugal and the US states Florida, Mississippi and New Mexico. Differences are also evident on a smaller geographical scale. For instance in France, surface water is predominantly used for geological reasons in Western France and Southern France (Figure 1; French Ministry of Health 2005). When surface water is used for drinking water generation, point and diffuse pollution is leading to increased purification costs or even prevents water abstraction.

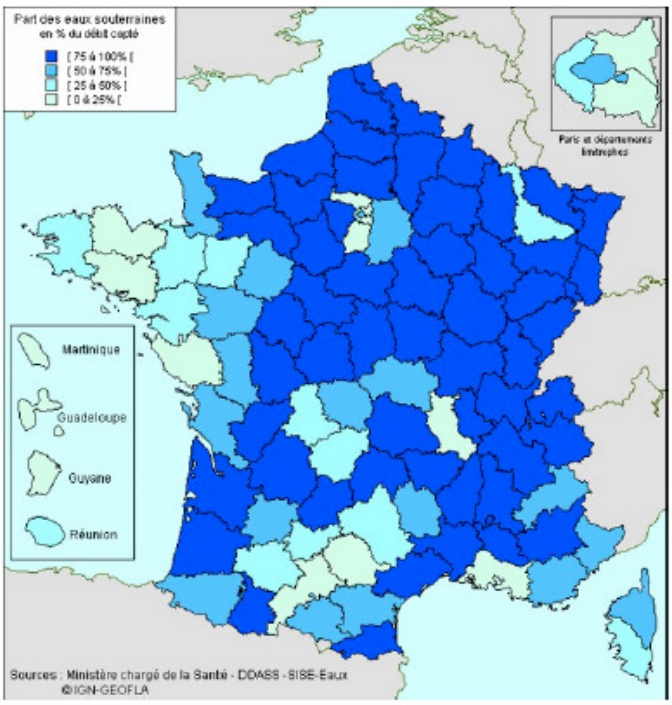

Figure 1: Origin of water used for drinking water supply in France in 2004 per state (French Ministry of Health 2005). Dark colours indicate high percentage from groundwater, light colors indicate dominance from surface water.

This can be the case for nutrients. Elevated nitrate concentrations can cause methaemoglobinaemia in infants (WHO 2007). As a result nitrate was regulated in the EU by the Surface Water Directive (EU 1975), which had set a maximum permissible concentration of 50 mg-NO_3/L for surface water intended for drinking water production. Since most of the requirements of this directive have been integrated into the 1980 Drinking Water Directive (EU 1980), the Surface Water Directive was repealed by the EU Water Framework Directive (EU 2000) in December 2007. Nitrate can also have a negative impact on ecosystems, particularly regarding eutrophication of coastal waters. For instance, nitrate export from midwestern US catchments was found to be the main cause of hypoxia in the Gulf of Mexico, leading to increased focus on nitrate reduction strategies for surface water in the area (Alexander et al. 2008). High phosphorus concentration is the dominant reason for eutrophication in freshwater systems across the world (Guildford and Hecky 2000). Eutrophication-related blooms of toxic cyanobacteria in drinking water reservoirs can in turn be a threat to human health (Chorus and Bartram 1999).

The situation is less clear for trace contaminants. In fact, most of the trace substances, which could potentially be found in source water, are substances for which knowledge is limited (so called contaminants of emerging concern). As a result the relevance of these substances for drinking water production is difficult to assess. Most of the substances are not at all or only implicitly regulated. The latter is the case in the EU, where a general drinking water threshold of 0.1 µg/L was set for single pesticides and 0.5 µg/L for the sum of all pesticides (EU 1998). It is interesting to note that at the time when the directive came into effect, the pesticide threshold was in the same order of magnitude as the limit of detection for most pesticides. In the US, several pesticides are regulated and have Maximum Contaminant Levels (MCLs) and a larger number have human based screening levels (HBSLs). HBSLs are not regulatory in nature and there is no monitoring requirement for regulated facilities such as drinking water production facilities. However, HBSLs are being used to assess potential risk of unregulated contaminants and can be used in screening studies to identify compounds that are occurring at levels that warrant inclusion in low-concentration trend monitoring programs and may be useful for selection of contaminants for research in Aquisafe 2.

The present report aims at providing information on trace substances, which enter surface water predominantly via diffuse sources in rural or semi-rural environments. A ranking is done for diffuse trace substances with representative information on occurrence in surface waters to aid planning of monitoring programs at waterworks in rural areas. As this ranking is limited to substances for which broad data sets are available, the “theoretical” list is compared to actual screening programs in predominantly rural catchments in Brittany (France) and Indiana (USA). In particular the latter screening involved a large number of pesticides, wastewater compounds, pharmaceuticals, and personal care and domestic use products that are commonly included in the category of contaminants of emerging concern of both diffuse and point-source origin.

The report is structured as follows. The first part (chapter 2) is based on published information and gives an overview of diffuse pollution sources and connected substance groups. In chapter 2.1 a pre-selection of substance group(s) is made for the relevance ranking, taking into account both, overall importance among diffuse pollution and data availability. Chapter 2.2 presents the ranking of relevant diffuse trace substances, based on available literature, both for Germany and the US. In the second part of the report (chapter 3) an extensive screening performed in the Upper White River basin (USA) in 2008 is presented and compared with an earlier pesticide screening from the Ic basin (France). The report concludes (chapter 4) with (i) a comparison of chapters 2 and 3, (ii) a final list of relevant diffuse substances and (iii) a recommendation on how the list can be applied.

Chapter 2
Ranking of relevant substances

2.1 Pre-selection of substance group

A number of lists with emerging contaminants are available from various institutions:

- USA (USEPA priority pollutants, USEPA drinking water regulation, USGS emerging contaminants)
- Europe (EU WFD priority substances, IFEN (French Environmental Institute) pesticide list, EU Norman project, EU Microrisk project)
- International (UNEP Stockholm Convention on POP's, WHO, HELCOM, OSPAR Convention)

For a first overview of potentially relevant trace substances the above lists were assembled, resulting in list including more than 700 compounds. This number includes substances from point and diffuse sources. Moreover, since they are "emerging contaminants", information on many of the substances is sparse.

The goal of the following chapter is to narrow down the list to groups of substances:

- which stem pre-dominantly from diffuse sources,
- which are expected to be an issue in rural and semi-rural areas and
- for which enough monitoring data is available to do a ranking of occurrence in surface waters in chapter 2.2.

2.1.1 Sources of diffuse pollution

Figure 2 shows an overview of pathways, which lead to nitrogen loads to surface waters. It includes the main pathways of diffuse pollution (i) agriculture, (ii) runoff from impervious surfaces, (iii) atmospheric deposition and (iv) diffuse sewage effluents.

(i) Agriculture:

Diffuse pollution from agricultural sources is mainly the result of substances applied to fields. Substances, which are applied, can enter surface waters via atmospheric deposition (see point iii below), surface runoff, drainage pipes and channels as well as groundwater infiltration. A second pathway is loss at the farm during substance handling and cleansing of equipment (Reichenberger et al. 2007).

Involved trace substances are primarily pesticides. A pesticide consists of one or more active ingredients and some coformulants. The active ingredient is the substance that is specifically aimed at pests. Pesticides can be classified according to their target or according to their chemical composition. According to the different targets, the most frequently used pesticides are:

- Herbicides: effective against weeds and other plants that grow where they are not wanted. They represent 50% of the global sales of pesticides (UIPP 2006).

- Fungicides: effective against fungi (including blights, mildews, molds, and rusts).
- Insecticides: effective against insects and other arthropods.

The global sales of pesticides have accounted for 31.2 billion dollars in 2005, 7.1 billion of which were sold in Europe. In 2006 the global sales lowered to 30.4 billion dollars (UIPP 2006). These numbers also include important amounts used in urban areas, such as golf courses, nurseries, lawns and sidewalks (Gilliom et al. 2006) and as additives in building materials (Burkhardt et al. 2007).

Apart from pesticides, veterinary pharmaceuticals can enter surface waters via manure application (Stoob et al. 2007). However they seem to be well retained during percolation and can mainly enter streams if rain events occur shortly after application.

Finally, in many countries sludge from waste water treatment is applied to agricultural land. In the EU, sewage sludge may not be used if it exceeds level of certain contaminants, such as heavy metals (EU 1986). Other areas, such as Switzerland or the German state Bavaria, ban the use of sewage sludge on fields completely, as a precautionary measure. Main concerns concern soil contamination. The transfer to surface waters is less likely, since substances which are contained in sewage sludge are typically badly soluble in water and adsorb to agricultural soils. For instance, residues of human pharmaceuticals, which are mostly well soluble, are only found in sewage sludge in very small concentrations, if at all (Joss et al. 2005).

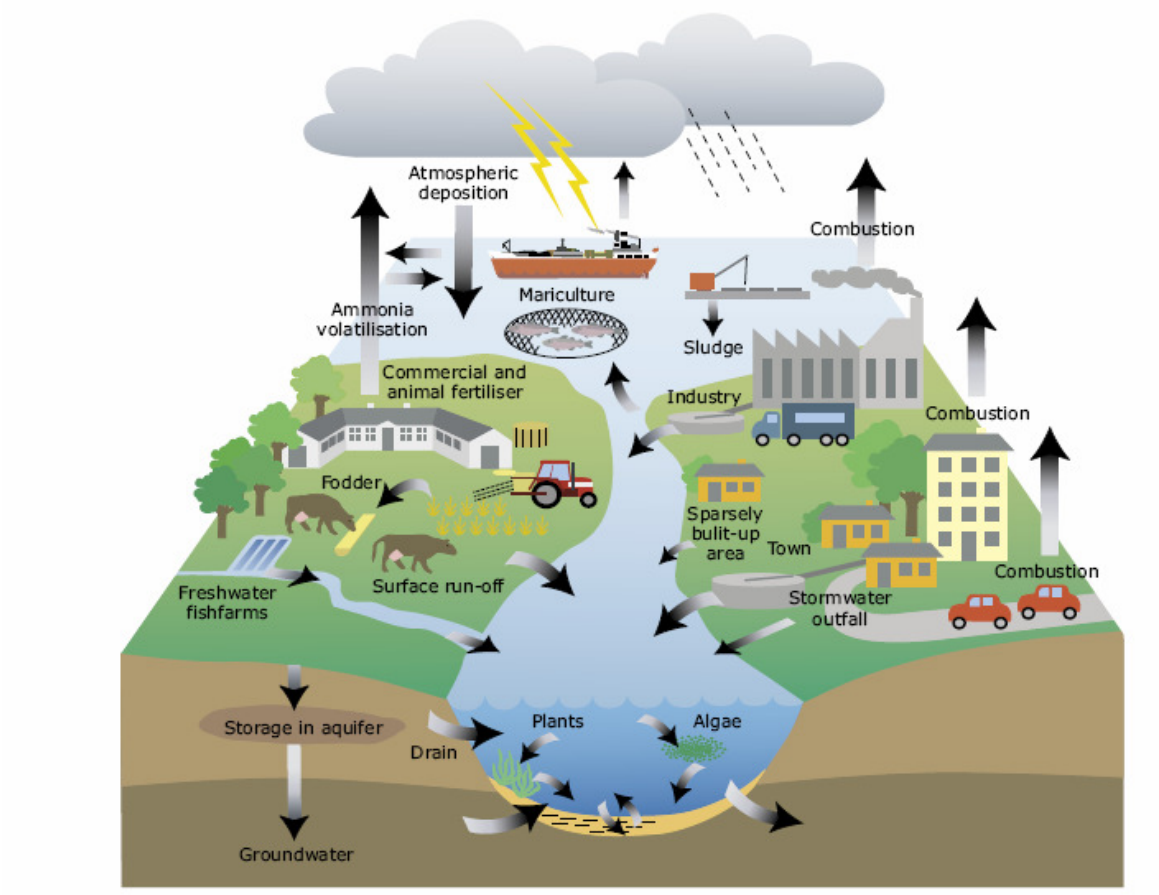

Figure 2: Overview of diffuse and point sources for nitrogen (from EEA WISE project)

(ii) Runoff from impervious surfaces:

Relevant contributions from impervious surfaces stem mainly from transportation networks and buildings.

Abrasion from car and railway traffic leads to significant amounts of heavy metals, which can enter surface waters via drains during rainstorms (Hillenbrand et al. 2005). Other substances, such as mineral oil or anti-corrosion agents may get on transport pathways via dripping loss from vehicles (Reemtsma et al. 2006). Finally combustion by-products, in particular PAH may be an issue via dry or wet deposition (Welker 2004).

Abrasion from building surfaces are mainly an issue for heavy metals from roofs and drain pipes (Hillenbrand et al. 2005) and biocides from paint and building materials (Burkhardt et al. 2007). In addition a great number of manufacturing additives can be released from synthetics.

Finally, urban stormwater runoff is an increasingly important additional source of veterinary pharmaceuticals via transport of companion pet feces.

(iii) Atmospheric deposition:

Atmospheric substance transport can occur via wet or dry deposition (Möller 2003). Main sources of atmospheric deposition are agriculture and combustion processes (Campbell et al. 2004).

For agriculture mainly the atmospheric transport of nutrient containing gases and dust to surface waters is well documented (Kalff 2003). Important atmospheric inputs via particle dislocation are also documented for other contaminants, such as the insecticide DDT (Kalff 2003). It can be expected that currently used pesticides can be transported in a similar way. Important substances from combustion processes are again PAH's (see (ii) above).

In general it can be expected that atmospheric deposition decreases with distance to source. For instance an exponential decrease in PAH contamination was found with increasing distance from roads (Benfenati et al. 1992).

(iv) Diffuse sewage effluents

In industrialized countries, sewage can enter surface waters diffusively (a) via combined sewer overflows (CSO) and faulty connections in areas with a sewer network and (b) via leakages from septic tanks or connections without treatment (Campbell et al. 2004). Septic tanks are often used in sparsely populated areas and can lead to minor concentrations of typical point source substances. However, in most areas point source substances in streams are dominated by effluents from waste water treatment plants (WWTP); e.g., even in strongly CSO-affected Berlin only 0.4 % of total raw sewage enter surface waters via CSO while the remainder is treated in WWTP (Plume et al. 2008). A potential issue of diffusive sewage effluents exists mainly for substances, which are well retained in WWTP (Plume et al. 2008) and for substances, which can have an acute impact on aquatic organisms during an overflow event, such as organic matter or ammonia (Matzinger et al. 2008).

2.1.2 Most relevant substance groups from diffuse pollution in rural areas

Of the above four sources, both (ii) runoff from impervious substances and (iv) diffuse sewage effluents can occur in rural and urban areas; nevertheless their influence can be expected to increase in general with population density. The substances, which can stem from (iv) are typically dominated by WWTP effluents and are not pre-dominantly from diffuse sources. In contrast (ii) is clearly an important diffuse pathway including a large number of emerging contaminants. Eriksson et al. (2005) assembled a list of 16 relevant stormwater based substances, focusing on their potential toxicity to aquatic organisms. Nevertheless, in the following report runoff from impervious substances is excluded as its impact occurs mainly in urban areas.

Atmospheric deposition (iii) can certainly be an important pathway, as it allows transport of substances from urban (ii) or agricultural (i) sources to areas, which are further apart. While this transport can lead to anthropogenic impacts in remote surface water bodies (e.g., Daly and Wania 2005), the contamination levels are typically small in comparison with watersheds, which are directly influenced by significant urban or agricultural sources. Moreover many trace substances which are subject to atmospheric transport (except gaseous or well soluble ones, such as nitrate) are deposited pre-dominantly in the vicinity of their sources (Benfenati et al. 1992).

Clearly the most important diffuse source for nutrients, sediments and trace contaminants is agriculture, both in the EU (EEA 2005) and the USA (EPA 2002). For watersheds with an important rural share this importance is further emphasized. The most important agricultural trace contaminants are pesticides and veterinary pharmaceutical residues (see chapter 2.1.1). Pesticides are covered in many monitoring programs worldwide, as they are used in large quantities and have been an environmental issue for decades. Moreover drinking water thresholds are defined both in the EU and the USA, giving a basis for the judging of occurring concentration in source water. For veterinary pharmaceuticals less information is available. They are applied in similar quantities as human pharmaceutics, but detected in lower concentrations in surface waters, since a large share of the substances are retained in the soil (Stamm et al. 2008; Stoob et al. 2007). The most relevant group of veterinary pharmaceutics are antibiotics (LANUV 2007). In particular sulfonamide antibiotics are occasionally detected in streams, however distinction from similar human products is often difficult (LANUV 2007). There is no indication for human health concerns from pharmaceutical residues in drinking water and definition of thresholds is very difficult (Dieter and Mückter 2007). Given the lack of regulations, pharmaceutical residues are currently dealt with in Germany in more detail if they exceed pesticide thresholds. However, exceedance of 0.1 µg/L is rarely found for veterinary pharmaceuticals (LANUV 2007).

Based on the above review of diffuse pollution sources and related substances we focus on pesticides in the following ranking, since they stem predominantly from diffuse pollution, are expected in large amounts in rural areas and are monitored for a representative number of surface water bodies in most countries. Moreover there are available drinking water thresholds for pesticides, which allow an evaluation of their relevance for drinking water production. The preliminary list of pesticides, relevant to drinking water production from surface waters, will be extended with other diffuse substances, such as veterinary pharmaceuticals or stormwater-based contaminants, if found in our screening in large concentrations (chapter 3). In the US HBSL's are also defined for other contaminant groups.

2.2 Pesticide priority list

In the following a ranking of pesticides is done, mainly based on occurrence and detected concentrations in a wide range of surface waters. The work aims at supporting precautionary monitoring activities by supplying a list of commonly found pesticides, which are most likely to exceed drinking water thresholds in rural catchments. Nevertheless, substances which are not included may play an important role in some watersheds, e.g., because of the dominance of a specific, but uncommon type of land use. By assembling a list for Germany and France as EU examples, as well as the USA we try to cover also geographical differences. Still, there may be specific substances used in other countries, which are not covered by the list provided.

2.2.1 Pesticide ranking based on occurrence in German and French surface waters

The ranking is mainly based on a recent report by the German Technical and Scientific Association for Gas and Water (DVGW-study) on pesticide occurrence detected by German waterworks in groundwater and surface waters (TZW 2007), as well as a list by the French Environmental Institute (IFEN-study) of most frequently detected pesticides in French surface water bodies in 2006 by IFEN (2009). In addition two other studies, one on the Rhine River (Rhine-study) and one by German Ministry for Environment (UBA-study) were used (also cited in TZW 2007).

Survey of German surface waters

The collected database for the DVGW-study is the result of a questionnaire, which was answered by 477 German waterworks. Although the measurements are not limited to raw water which is actually used for drinking water generation, most of the data can be expected to be from water bodies with relevance to raw water quality. Thus the results of the DVGW-study are an excellent basis for a ranking of pesticides in surface water with potential relevance for drinking water production.

As suggested by the authors, ranking was performed by using the number of reported surface water bodies with concentrations of a specific pesticide above detection limit. Moreover maximum concentrations were reported for each site, which allows additional evaluation. Table 1 shows the most frequently reported top 20 pesticides, as well as the median and 75 % quantile of reported maximum concentrations. Because of the large numbers of institutions, analytics are bound to be different. For instance, detection limits may vary significantly among laboratories. More importantly, most laboratories measure a standard set of pesticides, while some compounds are only measured by few laboratories. As a result substances, which are measured less frequently may not make it to the top 20, although being of high relevance. To make sure that no pesticide with major occurrence is missed out an alternative ranking was performed based on detection frequency of pesticides in the Rhine-study, which is based on regular monitoring with more than 100 samples, each analysed for a large number of pesticides between 2001 and 2005. Moreover the Rhine River can be assumed to be representative given its large, transboundary catchment. Finally the two rankings are double checked with the number of concentrations > 0.1 µg/L in German surface waters between 2002 and 2004 reported by the UBA (UBA-study). The results of both studies are also listed in TZW (2007).

Survey of French surface waters

The IFEN-study is a vast overview of pesticide occurrence in French surface water bodies in 2006. For almost 2000 sampling points up to 476 substances were analysed. Based on the study results, 15 most detected pesticides are published by IFEN (2009). Since many laboratories are involved in the survey not all the 476 substances are analysed for each sample. To avoid underestimating the importance of substances, which are analysed by fewer laboratories, ranking in Table 1 is based on detection frequency among number of analyses.

Aggregation of surveys

In general the three rankings list similar substances among the most frequently detected. The top 20 DVGW-list was extended by seven substances, which were only among the top 20 in the Rhine River and by four substances which were only in the top 15 of the IFEN-study. As a result Table 1 lists 31 potentially relevant pesticides and their metabolites. Except banned Diazinon all the substances added from the Rhine data set had also been detected in at least one water body in the DVGW-study. Aminotriazole, Diflufenican and 1-(3,4-dichlorophenyl)-3-methyl-urea, a Diuron-metabolite were only measured in France. The relatively good agreement of the German survey, the River Rhine survey (as an international river) and the French survey indicates that while local phenomena exist, a similar set of substances can be expected in EU countries.

For 25 of 31 listed substances, at least 25 % of all maximal concentrations reported in the DVGW-study were beyond the threshold of 0.1 µg/L, thus indicating their high relevance for drinking water production. In France 41 % of the sampled water bodies exceeded this threshold for at least one substance. A concentration of 2 µg/L was exceeded in more than ten French surface waters for the five substances AMPA, Glyphosate, Isoproturon, DCMU and Metolachlor. The German UBA-study (Table 1) stresses this tendency. Moreover the UBA data confirm the choice of substances in Table 1, since all the pesticides, found above 0.1 µg/L in more than 10 % of samples in the UBA-study are also included in Table 1.

While the list of most relevant substances is similar for the four studies, the ranking differs significantly. This is reflected in the top five substances of the four studies (ordered by ranking):

- DCMU, Atrazine, Isoproturon, Simazine and MCPA in the DVGW-study,
- AMPA, DCMU, Desethylatrazine, Atrazine and Glyphosate in the IFEN-study,
- Isoproturon, DCMU, MCPA, Mecoprop and Dichlorprop in the UBA-study and
- AMPA, Glyphosate, Atrazine, Isoproturon and Desethylatrazine in the Rhine-study.

The differences can be partly explained by the approaches of the three studies. For instance, Glyphosate and its metabolite AMPA are not included in standard pesticide analytics. As a result it can be expected that many institutions reporting to the UBA and the DVGW studies simply did not measure Glyphosate, which may explain the lower number of detections. Atrazine and its metabolite Desethylatrazine, on the other hand, are banned in the EU and would therefore be expected mainly from groundwater influence and, in the case of the River Rhine, from upstream Switzerland, where its application is still legal.

Eight of the substances in Table 1 are banned for application or are a metabolite from illegal banned pesticide (Desethylatrazine and 2,6-Dichlorbenzamid), which leaves 23 substances which are currently applied. Although illegal use does certainly occur, the major pathway of banned substances into surface water is via groundwater infiltration from past pollution. The importance of storage of persistent banned pesticides in aquifers shows in the DVGW top 20 pesticides for

groundwater and wells (not shown here), which contains 12 banned substances versus five in the DVGW top 20 for surface water (TZW 2007).

The substances in Table 1 are predominantly herbicides, with the exception of the fungicides Penconazole and Tebuconazole and the insecticides Pirimicarb and Diazinon. The application range of the pesticides is broad. About half of the pesticides are applied at high amounts for crop production (indicated by stars in Table 1). Other uses are orchards (e.g., DCMU), vegetables (e.g., Metazachlor), footpaths (e.g., DCMU or Glyphosate) or lawns (e.g., MCPA).

Table 1: List of potentially relevant pesticides for German surface waters, based on data from TZW (2007) and IFEN (2007)

		German surface waters									French surface waters	
		DVGW survey in 2006				Rhine River, 2001-2005		UBA	IFEN data 2006			
Substance	Legal application in EU?	Surface waters with detections in DVGW survey	Median of max. concentrations	75% quantile	Ranking based on DVGW	detections	Ranking based on Rhine data	detections > 0,1 µg/L	detections		Ranking based on IFEN data	
	yes/no	[number]	[µg/L]	[µg/L]		[% of samples]			[% of samples]			
DCMU (Diuron)	yes	26	0,14	0,37	1	4,5	10	10-25 %	31	2		
Atrazine	*no*	*21*	*0,11*	*0,28*	*2*	*29,2*	*3*	*< 10 %*	28	4		
Isoproturon*	yes	18	0,16	0,32	3	20,6	4	> 25 %	21	6		
Simazine	*no*	*15*	*0,06*	*0,16*	*4*	*6,3*	*8*	*< 10 %*				
MCPA	yes	12	0,2	0,44	5	1,7	18	10-25 %	9	14		
Terbutylazine	yes	11	0,1	0,25	6	0,7	22	< 10 %				
Mecoprop (MCPP)*	yes	10	0,09	0,48	7	5	9	10-25 %	10	13		
Desethylatrazine	Metabolite of Atrazine (no)	10	0,13	0,2	7	15,2	5	n.r.	29	3		
Bentazone*	yes	8	0,19	0,52	9	4,2	11	< 10 %	11	11		
Glyphosate*	yes	8	0,1	0,16	9	42,8	2	n.r.	26	5		
Metazachlor	yes	7	0,14	0,75	11	0,7	22	< 10 %				
Metolachlor	yes	7	0,11	0,68	11	3,1	14	< 10 %	10	12		
AMPA	Metabolite of Glyphosate (yes)	7	0,27	0,63	11	92,6	1	n.r.	50	1		
Flufenacet*	yes	6	0,1	0,15	14	n.r.	n.r.	n.r.				
Terbutryn	*no*	*6*	*0,08*	*0,3*	*14*	*0,6*	*24*	*n.r.*				
2,4-D*	yes	5	0,16	0,45	16	2,2	15	< 10 %				
Dichlorprop (2,4-DP)	yes	5	0,1	0,29	16	0,9	20	10-25 %				
Bromoxynil*	yes	4	0,43	0,74	18	n.r.	n.r.	n.r.				
2,6-Dichlorbenzamid	Metabolite of Dichlobenil (no)	4	0,17	0,41	18	n.r.	n.r.	n.r.				
Desethylterbutylazin	Metabolite of Terbuthylazine (yes)	4	0,07	0,08	18	0,5	27	n.r.				
Penconazole	yes	2	2,59	3,55	25	10,2	6	n.r.				
Tebuconazole	yes	1	0,21		40	7,7	7	n.r.				
Ethofumesate	yes	2	0,08	0,08	25	4,1	12	n.r.				
Pirimicarb	yes	1	0,26		40	3,8	13	n.r.				
Chlortoluron	*no*	3	*0,15*	*0,25*	*21*	*2,2*	*15*	*< 10 %*	12	8		
Diazinon	*no*	*n.r.*			*n.r.*	*1,9*	17	*n.r.*				
Methabenzthiazuron	*no*	1	*1,1*		*40*	*1*	*19*	*< 10 %*				
1-(3,4-dichlorophényl)-3-méthyl-urée	Metabolite of DCMU (yes)	n.r.			n.r.	n.r.	n.r.	n.r.	13	7		
Aminotriazole	yes	n.r.			n.r.	n.r.	n.r.	n.r.	11	9		
Diflufenican	yes	1	0,45		40	n.r.	n.r.	n.r.	11	10		
Oxadiazon	yes	n.r.			n.r.	n.r.	n.r.	n.r.	9	15		

n.r. indicates that substance was not reported in respective study
substances in *italics* are banned in EU
* application in classical crop production (cereals, maize) > 100 g active substance per ha (TZW 2007)

2.2.2 Pesticide ranking based on occurrence in US surface waters

Ranking for pesticides in US streams is based on a recently published study by the USGS National Water-Quality Assessment (NAWQA) Program, including samples from 186 US streams in 51 major hydrologic systems taken between 1992 and 2001 (Gilliom et al. 2006). The study covers a wide range of river systems without focusing on their use as drinking water sources. However, the large number of samples from different streams and the nationally consistent sampling and analytical approach make the study highly representative. Most samples were analyzed for 75 pesticides and 8 pesticide degradates (metabolites).

Gilliom et al. (2006) have already made a selection of the 25 most frequently detected substances in all the catchments. The percentage of occurrence is reported separately by Gilliom et al. (2006), depending on type of catchment. The ranking of the top 20 substances in Table 2 is based here on occurrence in streams with agricultural catchments, since rural and semi-rural areas are the focus of this report. Moreover, all top 20 pesticides with the exceptions of Dacthal and Diazinon are applied in important amounts in US agriculture (Gilliom et al. 2006). As a result, most pesticides used in urban applications are also frequently detected in streams with agricultural catchments (Figure 3). Apart from the ranking based on total occurrence, an additional ranking was based on occurrence of concentrations ≥ 0.1 µg/L, corresponding to the EU drinking water limit.

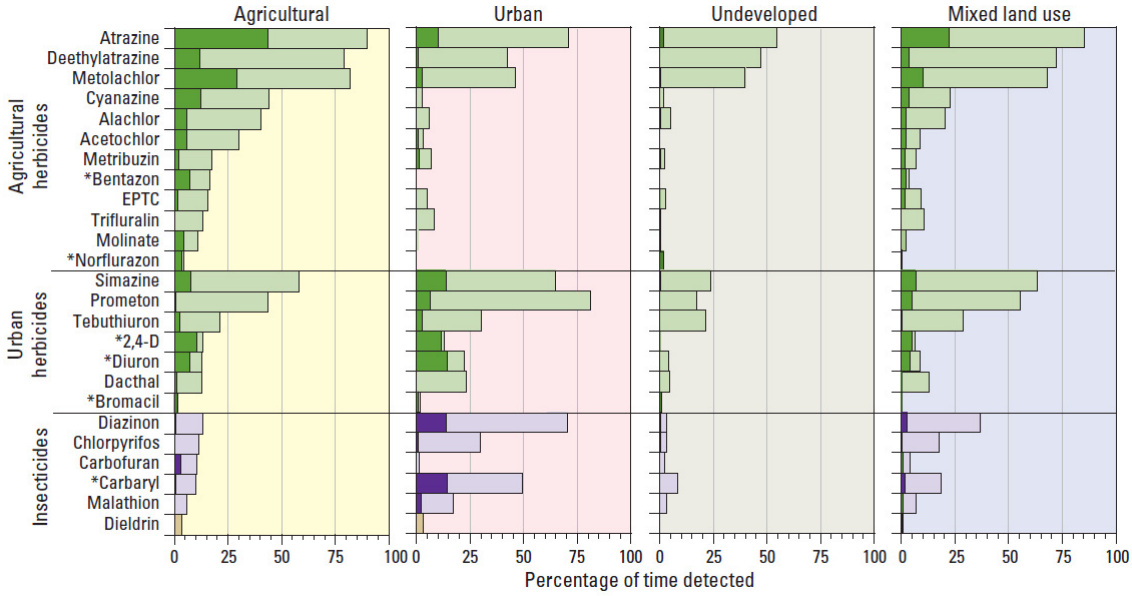

Figure 3: Percentage of pesticide detections for US streams by catchment type from Gilliom et al. (2006). Dark bars indicate detection frequency of concentrations > 0.1 µg/L. Asterisks indicate substances, which could not be measured at concentrations < 0.1 µg/L.

The main limitation of the USGS dataset is its lack in very recent data. On the one hand substance relevance in streams changes with actual application. Moreover, samples may not be analysed for more recently developed pesticides, because of a lack of analytical methods or simply because they were not an issue at the time of the study. To render the ranking more stable, it was compared to a second, more recent study by Kingsbury et al. (2008). Though the study by Kingsbury et al. (2008) includes only nine stream sites, it was used because (i) the data were collected between 2004 and 2005, including more substances (particularly a broader range

of metabolites) and (ii) all the samples were taken from source and finished water for drinking water production. Although more substances were measured in the study by Kingsbury et al. (2008), the herbicide Glyphosate and pyrethroid insecticides, which are judged as potentially relevant based on their current application (Gilliom et al. 2006) are not included in either of the two studies.

Only eight of the top 20 substances from Gilliom et al. (2006) made it to the top twenty in Kingsbury et al. (2008) (Table 2). As a result, the list by Gilliom et al. (2006) was extended with twelve substances found only by Kingsbury et al. (2008) to a list of 32 potentially relevant substances in Table 2. The main reason for the discrepancy is not the smaller occurrence of these twelve substances, although some herbicides such as Alachlor and Acetochlor are found in smaller quantities by Kingsbury et al. (2008). The main difference stems from the inclusion of a broader range of metabolites by Kingsbury et al. (2008). In fact, eleven of the twelve additionally considered substances are metabolites of Atrazine, Metolachlor, Alachlor, DCMU, Acetochlor and Fipronil.

The top five substances in the rankings are (order by ranking):

- Atrazine, Metolachlor, Deethylatrazine, Simazine and Cyanazine for total occurrence in streams by Gilliom et al. (2006),
- Atrazine, Metolachlor, Cyanazine, Deethylatrazine and 2,4 D for occurrences ≥ 0.1 µg/L in streams by Gilliom et al. (2006) and
- Atrazine, Simazine, Metolachlor oxanilic acid, Metolachlor ethane sulfonic acid and Alachlor ethane sulfonic acid at source water intakes in streams by Kingsbury et al. (2008).

If the metabolites, which were only measured by Kingsbury et al. (2008), are excluded, Metolachlor, Deethylatrazine and Prometon move up to the top five. Consequently, without the newly measured metabolites, only seven substances make up the three top five lists, indicating a very good agreement among the three approaches. The quantitative importance of metabolites, which is revealed by Kingsbury et al. (2008) indicates that even if pesticides are removed, their breakdown products may still be prevalent.

With one exception the most frequently detected substances by Gilliom et al. (2006) are also the most frequently detected above the concentration of 0.1 µg/L. Nevertheless, Gilliom et al. (2006) judge the relevance of pesticides for drinking water sources as minor, as US drinking water thresholds were only exceeded in a few streams with high agricultural influence. It has to be noted that only long term issues were assessed by comparing average annual concentrations to drinking water limits. However, pesticide concentrations show a marked seasonal pattern. For instance Atrazine, which was the main reason for drinking water concern regarding annual averages, shows seasonal variations over two orders of magnitude in agriculturally influenced White River (Figure 4). Moreover, the US drinking water limit (MCL) for annual averages of atrazine is comparably high with 3 µg/L. The results by Kingsbury et al. (2008) indicate that a large number of pesticides are found also in source and finished drinking water. Although concentrations in finished drinking water are generally lower, the rate of detection is similar as in source water. Maximal concentrations found in finished drinking water were beyond 0.1 µg/L for ten herbicides and eight herbicide metabolites. US human health benchmarks (for carcinogens) are only exceeded in finished drinking water by Atrazine. For most of the numerous metabolites no thresholds are defined.

The relevance of pesticides for aquatic organisms was assessed by Gilliom et al. (2006), comparing US EPA thresholds to single measurements. 57 % of agricultural and 83 % of urban

streams showed occasional concentrations of at least one pesticide above the thresholds, indicating a high significance of pesticides and pesticide residues to aquatic life. The most critical substances are mainly insecticides, such as Diazinon and Chlorpyrifos.

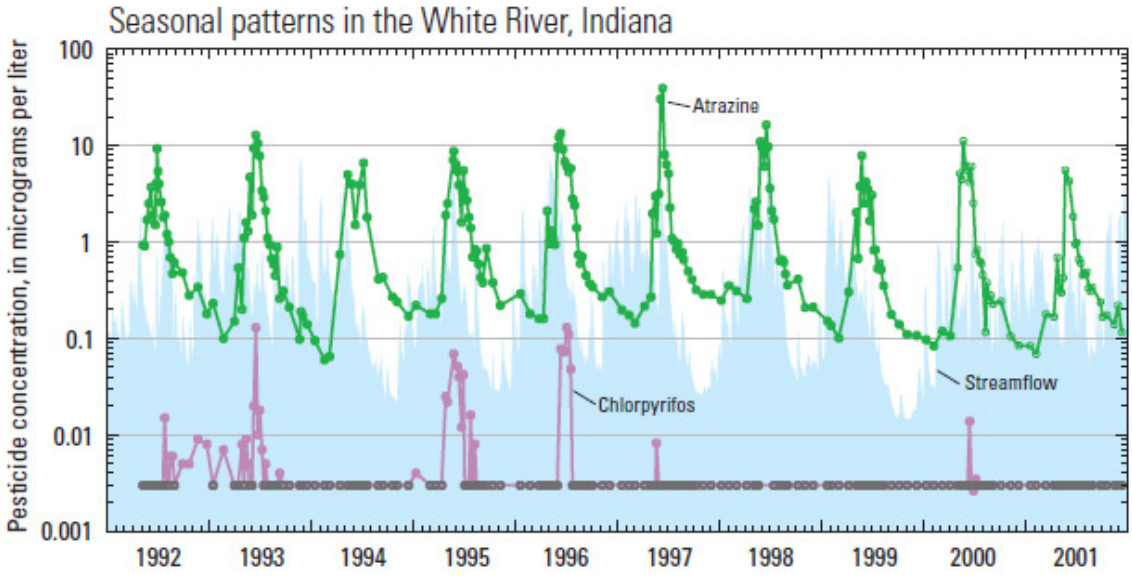

Figure 4: Seasonal patterns in Atrazine and Chlorpyrifos concentrations in the White River, Indiana from Gilliom et al. (2006)

These two insecticides are also the only pesticides in Table 2, which are restricted in the USA today. As this is only the case since 2001, the situation can be expected to have improved compared to Gilliom et al. (2006), who used data collected earlier. Current measurements will be presented in Chapter 3.

Regarding their application, 26 of the 32 substances in Table 2 are herbicides or herbicide metabolites, while the remaining six are insecticides and insecticide metabolites. The top 16 and 12 substances were exclusively herbicides, for the studies of Gilliom et al. (2006) and Kingsbury et al. (2008), respectively. Most insecticides were detected more frequently in urban watersheds (Gilliom et al. 2006).

Table 2: List of potentially relevant pesticides for US surface waters, based on data from Gilliom et al. (2006) and Kingsbury et al. (2008)

				USGS stream survey, 1992-2001 Gilliom et al. (2006)				USGS source water survey in 9 waterworks, 2004-2005, Kingsbury et al. 2008		
Substance	**Type of pesticide**	**Legal application in USA?**	**Main use**	**Surface waters with detections**	**Surface waters with detections > 0,1 µg/L**	**Ranking based on number of detections**	**Ranking based on number of detections > 0,1 µg/L**	**Percentage of time detected in source water**	**Percentage of time detected in finished water**	**Ranking of pesticides detected > 10 % of source water samples**
		yes/no	**agricultural/urban**	**[%]**	**[%]**			**[%]**	**[%]**	
Atrazine	Herbicide	yes	mainly agricultural	90,2	42,9	1	1	82	87	1
Metolachlor	Herbicide	yes	mainly agricultural	82,1	28,8	2	2	59	54	6
Deethylatrazine	Metabolite	Metabolite of Atrazine (yes)		79,3	12,0	3	4	58	68	7
Simazine	Herbicide	yes	both	58,2	7,6	4	6	82	89	1
Cyanazine	Herbicide	yes	mainly agricultural	43,5	12,5	5	3	-	-	
Prometon	Herbicide	yes	both	43,5	0,0	5	19	56	25	9
Alachlor	Herbicide	yes	mainly agricultural	40,2	5,4	7	9	13	10	26
Acetochlor	Herbicide	yes	mainly agricultural	29,9	5,4	8	9	16	11	24
Tebuthiuron	Herbicide	yes	both	21,2	2,2	9	14	6,7	5,7	
Metribuzin	Herbicide	yes	mainly agricultural	17,4	1,6	10	15	3,3	1,1	
Bentazon	Herbicide	yes	mainly agricultural	16,3	7,6	11	6	18	16	21
EPTC	Herbicide	yes	mainly agricultural	15,8	1,1	12	17	-	-	
2,4-D	Herbicide	yes	both	13,6	10,3	13	5	44	52	12
DCMU (Diuron)	Herbicide	yes	both	13,0	7,1	15	8	42	24	13
Dacthal	Herbicide	yes	mainly urban	13,0	1,1	15	17	5,6	6,9	
Diazinon	*Insecticide*	*yes, restricted since 2001*	*mainly urban*	*13,0*	*0,0*	*15*	*19*	*17*	*1,1*	*22*
Trifluralin	Herbicide	yes	mainly agricultural	13,0	0,0	15	19	6,7	2,3	
Chlorpyrifos	*Insecticide*	*yes, restricted since 2001*	*both, but ca. 70% agricultural*	*11,4*	*0,0*	*18*	*19*	*5,6*	*n.d.*	
Molinate	Herbicide	yes	mainly agricultural	10,9	4,3	19	11	-	-	
Carbofuran	Insecticide	yes	?	10,3	2,7	20	13	-	-	
Metolachlor oxanilic acid	Metabolite	Metabolite of Metolachlor (yes)						77	59	3
Metolachlor ethane sulfonic acid	Metabolite	Metabolite of Metolachlor (yes)						68	59	4
Alachlor ethane sulfonic acid	Metabolite	Metabolite of Alachlor (yes)						61	59	5
Deisopropylatrazine	Metabolite	Metabolite of Atrazine (yes)						58	63	7
2-Hydroxyatrazine	Metabolite	Metabolite of Atrazine (yes)						52	51	10
3,4-Dichloroaniline	Metabolite	Metabolite of DCMU (yes)						47	2,4	11
Desulfinylfipronil	Metabolite	Metabolite of Fipronil (restricted)						42	24	13
Fipronil	*Insecticide*	*restricted*						*39*	*1,1*	*15*
Acetochlor oxanilic acid	Metabolite	Metabolite of Acetochlor (yes)						32	25	16
Acetochlor/metolachlor ethane sulfonic acid 2nd amide	Metabolite	Metabolite of Acetochlor (yes)						27	27	17
Acetochlor ethane sulfonic acid	Metabolite	Metabolite of Acetochlor (yes)						25	27	18
Fipronil sulfide	Metabolite	Metabolite of Fipronil (restricted)						20	12	20

substances in *italics* are restricted in USA

2.2.3 Comparison between relevant pesticides in the EU and the USA

Table 3 shows a comparison of the substance rankings in the EU (i.e. Germany and France) and the USA. Just seven substances appear in the top 20 of both rakings, indicating a significant difference in use. Only Atrazine, its metabolite Deethylatrazine and Simazine, three substances which are banned in the EU today, appear in the top five of both the EU and the USA. One reason for the difference lies certainly in non-uniform regulations of some pesticides. Atrazine is banned in the EU (EU 2004b), which has led to its replacement by other herbicides, e.g., Terbutylazine for treatment of corn. In turn, MCPA, which is frequently detected in EU surface waters, is only registered for restricted use in the US.

Apart from regulatory issues, the reason for the difference in substances can be an analytical one. Glyphosate and its metabolite AMPA, which are applied in large amounts in the USA, were not included in the monitoring program by Gilliom et al. (2006). In turn, Molinate, which appears in the US top 20, has not been analysed in the German samples, although it is a registered pesticide in the EU.

Finally the divergent results in the two countries can be explained economically. Typically, pesticides are primarily marketed where they are first developed. Isoproturone, one of the most important pesticides in Germany, was developed by a European company. In turn, US based Acetochlor, Prometon or EPTC are not even registered for use in the EU (EU Pesticide Registration 2008).

Although the list of substances from the two countries differ, there is an agreement to the fact that many of the pesticides find their way into surface waters. The concentrations found are often beyond 0.1 µg/L. For the EU this level already corresponds to the drinking water limit. Thus, if surface water is used for drinking water production pesticides seem to be of high relevance. In finished drinking water, frequently-used Isoproturon and Bentazon were most frequently detected in Germany (TZW 2007) and France (DGS 2007). The importance for drinking water production is emphasized by frequent detections above 0.1 µg/L in finished drinking water in nine waterworks in the US (Kingsbury et al. 2008). Regarding drinking water regulation, the thresholds in the USA are substance-specific and generally more than one magnitude higher than 0.1 µg/L. As a result threshold exceedance was mainly found for Atrazine.

In terms of treatability in water works, Table 3 judges the efficiency of classical treatment (flocculation, filtration, ozonation) and of powdered activated carbon (PAC), which is often added in emergency situations. Particularly problematic are triazines (such as atrazine), phenoxy-type substances (such as 2,4-D and Mecoprop) and Anilides/Anilines (such as Metolachlor and Acetochlor).

Metabolites are an important issue arising in both, the European and US monitoring schemes (Tables 1 and 2). The few metabolites that were included by Gilliom et al. (2006), TZW (2007) and IFEN (2009) are typically found with similar frequency as their parent substances. The study by Kingsbury et al. (2008), which includes a greater number of metabolites, ranks six metabolites among the top ten substances. The results indicate that metabolites of pesticides with wide application are typically detected if looked for. The question remains of how to deal with them. In the USA, no threshold is defined for most metabolites. In the EU “relevant metabolites” are to be treated as pesticides, but it is debated what the term relevant stands for. Metabolites are often assumed to be less biologically active and therefore less toxic than their parent substances. While this is true for many degradation products, some metabolites were shown to be similarly or even more toxic than their parent substances (e.g., Kross et al. 1992).

Table 3: Pesticide priority list, Comparison of 20 most relevant pesticides in USA (study by Gilliom et al. 2006) and EU (studies by IFEN 2009; TZW 2007), as well as treatability in drinking water treatment

Substance	legal application		Removability in drinking water treatment		Ranking based on occurence			
	in EU	in USA	floculation, filtration, ozonation	Powdered Activated Carbon	in Germany	in France	in USA	
DCMU (Diuron)	yes	yes	≥ 90%	≥ 50%	1	2	15	Pesticides in US and EU top 20
Atrazine	no	yes	< 50%	≥ 50%	*2*	*4*	1	
Simazine	no	yes	?	?	*4*		4	
Deethylatrazine	(no)	(yes)	?	< 50%	7	3	3	
Bentazon	yes	yes	≥ 90%	≥ 50%	9	11	11	
Metolachlor	restricted	yes	≥ 50%	≥ 50%	11	12	2	
2,4-D	yes	yes	< 50%	≥ 50%	16		13	
Cyanazine	no	yes	?	?			5	Pesticides only in US top 20
Prometon	-	yes	?	?			5	
Alachlor	no	yes	≥ 50%	≥ 50%			7	
Acetochlor	yes	yes	≥ 50%	≥ 50%			8	
Tebuthiuron	no	yes	?	?			9	
Metribuzin	yes	yes	?	?			10	
EPTC	yes	yes	?	?			12	
Dacthal	yes	yes	?	?			15	
Diazinon	no	*restricted*	*?*	*?*			*15*	
Trifluralin	no	yes	≥ 90%	≥ 50%			15	
Chlorpyrifos	yes	*restricted*	*?*	*?*			*18*	
Molinate	yes	yes	?	?			19	
Carbofuran	no	yes	?	?			20	
Isoproturon	yes		≥ 90%	≥ 50%	3	6		Pesticides only in EU top 20
MCPA	yes		≥ 50%	≥ 50%	5	14		
Terbutylazine	yes		?	?	6			
Mecoprop (MCPP)	yes		< 50%	< 50%	7	13		
Glyphosate	yes		≥ 90%	< 50%	9	5		
AMPA	(yes)		≥ 90%	< 50%	11	1		
Metazachlor	yes		?	?	11			
Flufenacet	yes		?	?	14			
Terbutryn	no		≥ 90%	?	*14*			
Dichlorprop (2,4-DP)	yes		?	?	16			
2,6-Dichlorbenzamid	(no)		?	?	*18*			
Bromoxynil	yes		?	?	18			
Desethylterbutylazin	(yes)		?	?	18			
1-(3,4-dichlorophényl)-3-méthyl-urée	(yes)		?	?		7		
Aminotriazole	yes		≥ 90%	< 50%		9		
Diflufenican	yes		?	?	40	10		
Oxadiazon	yes		?	?		15		

() Parentheses refer to application of parent substance

Chapter 3
Exemplary screenings from France and the USA

A series of chemical analyses have been done on both the Ic Catchment in Brittany, France and the Upper White River Watershed, central Indiana. The results of the two screenings are presented in the following as a local situation, in contrast to the global view of chapters one and two. Since the US screening was done in the framework of Aquisafe the presented data are more extensive.

3.1 Ic Catchment, Brittany, France

Data from the Ic Catchment was collected by Goël'eaux (Syndicat Mixte de la Cote du Goëlo, Pordic France). Samples were collected at nine stations between July, 1997 and June, 2007 (Figure 5). A total of 2489 analyses were done on 87 pesticides. An overview of the analytes is presented in Table A.1 in appendix A. There were a total of 92 samples with measurements above detection limit (3.7% of the samples) representing seven chemical compounds. The detected compounds were AMPA, Atrazine, Desethylatrazine, 2,4-D, Carbaryl, Carbofuran, and Dichlorprop. The detected compounds, their concentrations, sample collection date, and location are presented in Table B.1 in appendix B.

Sample results reveal several key points. Three compounds account for ~96% of all detections. AMPA accounted for 50 of the 92 detections (54%) and atrazine and Desethylatrazine together account for 38 of the 92 detections (41%). These three compounds are agricultural herbicides or their degradates. The remaining four compounds each have one detection. Additionally, sample site IC6, the most downstream sampling site, appears to be a site of concern with 76 of the 92 detections occurring at that site. All seven compounds were detected at site IC6. Only 14 of the 92 detections were at sites other than IC6. These include 1 detection at IC2, 2 detections at IC4, 6 at IC8, 3 at IC10, 1 at IC11, and 1 at IC12. The only compound detected at these stations was AMPA. Thus AMPA is the most widely occurring compound and site IC6 is the site with the highest number of contaminants and highest diversity of contaminants found.

When AMPA was detected, the concentrations ranged from 0.09 – 3.0 µg/L with a mean of 0.59 µg/L for the samples above the detection limit of the analyses. When atrazine was detected, concentrations ranged from 0.04-0.265 µg/L with a mean of 0.118 µg/l for the samples above detection limit. When Desethylatrazine was detected, concentrations ranged from 0.35-0.155 µg/L with a mean of 0.079 µg/l for the samples above detection limit (Table 4).

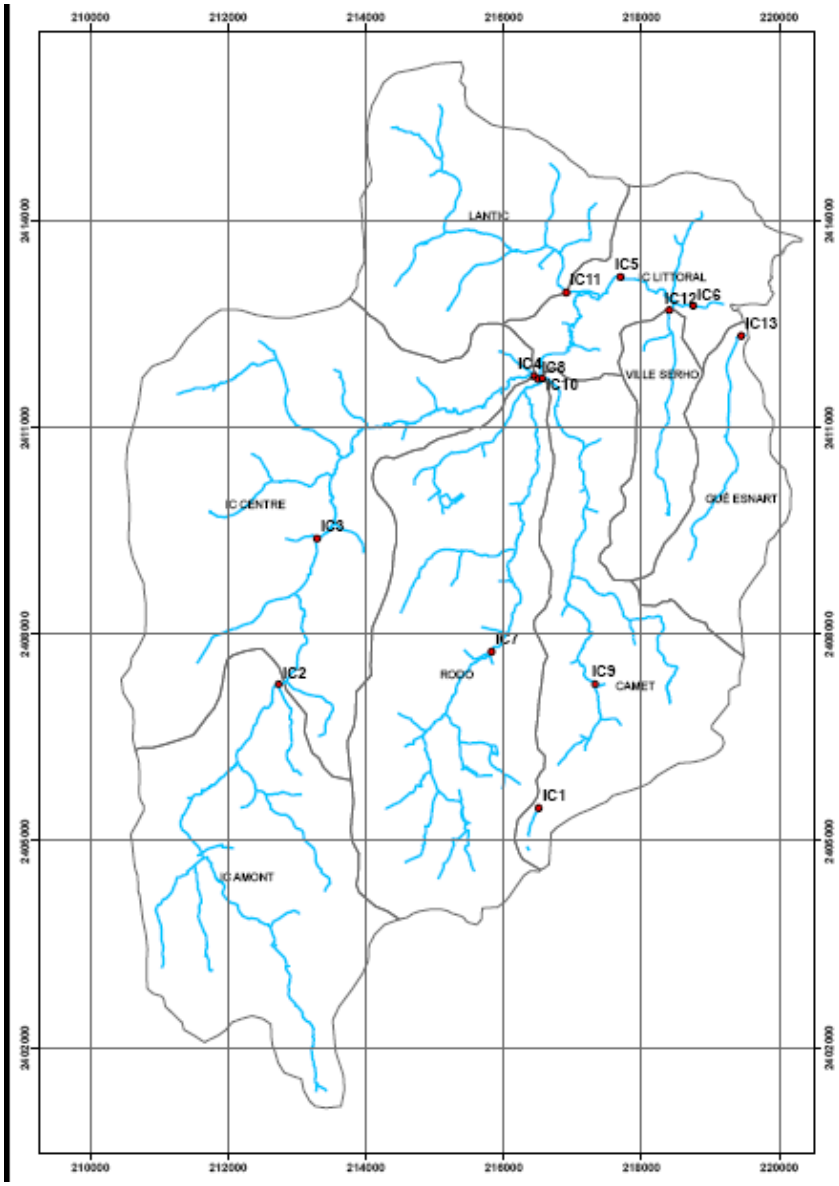

Figure 5: Sample Location Map of Ic Catchment Chemical Analyses

The detection of AMPA, Atrazine and Desethylatrazine as the dominant compounds beyond the EU pesticide threshold of 0.1 µg/L indicates that glyphosate and atrazine remain a threat to surface water supplies though diffuse source pollution. The detection of a total of seven compounds in the Ic Catchment by this data set is difficult to interpret. There was no information provided about the flow conditions during sampling, but the high sampling frequency over several years and through all seasons suggests that a representative sampling was collected to have a complete understanding of compounds in surface waters in the Ic Catchment. It is difficult to determine if method detection limits for some compounds were too high to detect some chemicals or if they are generally not present. In either scenario, the concentration levels of the analysed chemicals in the Ic Catchment are generally low (<0.1 µg/L) with the exception of the seven chemicals shown above. However, several pesticides which were found to be important in Europe, such as Bentazone or MCPA were not measured.

Table 4: Summary statistics for Ic Catchment compounds with multiple detections. Range and mean are calculated only on samples above detection limit.

Compound	Range (µg/L)	Mean (µg/L)	N
AMPA	0.09 - 3.0	0.59	49
Atrazine	0.04 - 0.265	0.118	16
Desethylatrazine	0.035 - 0.155	0.079	22

3.2 Upper White River Watershed, Central Indiana, USA

A component of work package 1 includes a screening of surface waters in the Upper White River Watershed. Two sampling stations were established for sample collection. The sampling strategy was designed as a screening to detect the occurrence, range on concentrations, and seasonal distribution of a series of contaminants in two streams (Eagle Creek and White River) of importance to Veolia Water Indianapolis, LLC. as they are source waters for the drinking water supply for central Indiana.

3.2.1 Sampling Locations

The White River sampling site is situated 7.4 km upstream of the intake to the White River North drinking water treatment facility operated by Veolia Water Indianapolis, LLC. The catchment upstream of the sampling station encompasses 2,945 km^2 and drains predominantly agricultural land use (Figures 6 and 7). Agricultural land use at both the White River and Eagle Creek catchments is intense row crop agriculture that is rotational corn and soy bean crops.

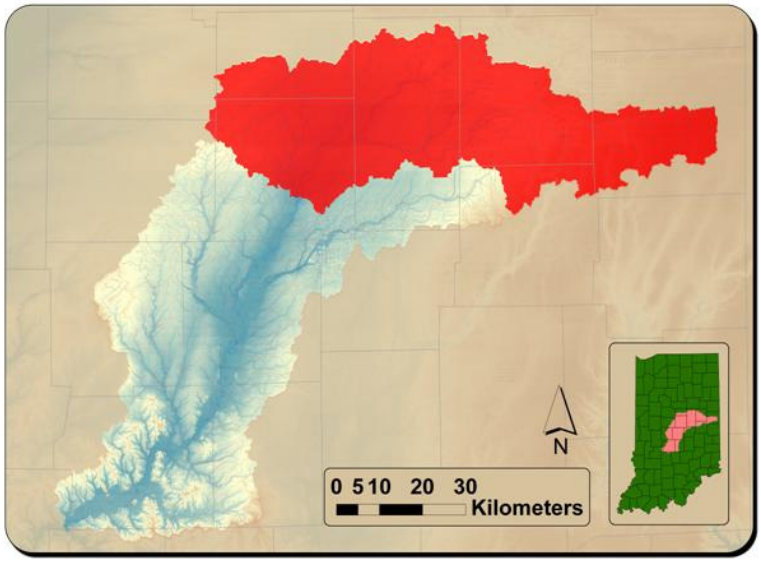

Figure 6: Watershed area upstream of White River sampling station encompasses 2,945 km^2.

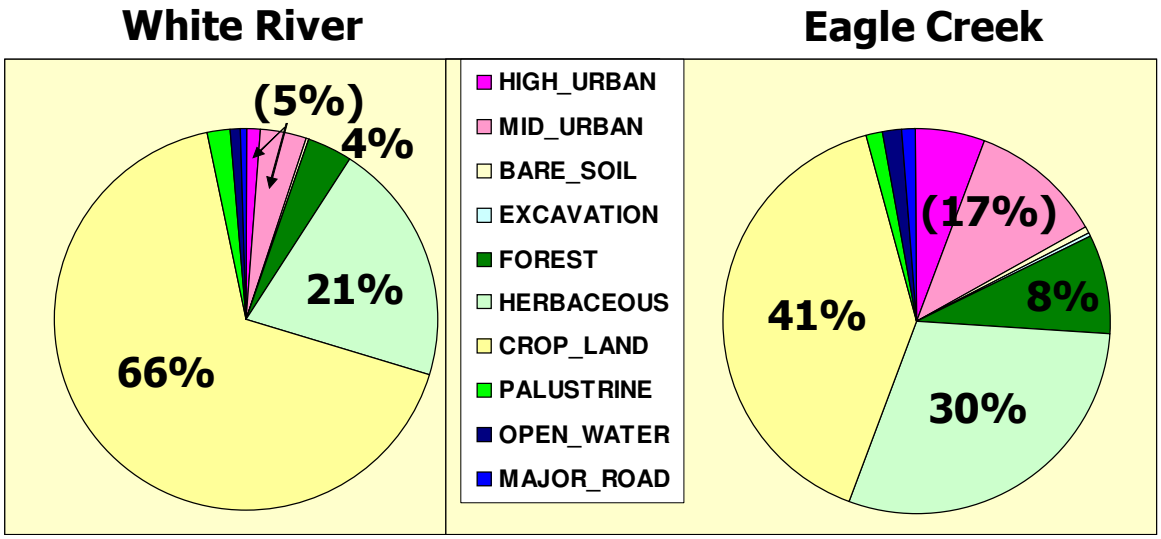

Figure 7: Land use and land cover charts for the catchment area draining to the White River and Eagle Creek sampling sites.

The Eagle Creek sampling station is situated on the main river draining into Eagle Creek Reservoir, 5.5 km upstream of the reservoir. There is a drinking water intake in the center of Eagle Creek Reservoir that feeds the T.W. Moses Treatment Facility, operated by Veolia Water Indianapolis, LLC. The catchment upstream of the sampling station encompasses 266 km^2 (Figure 8). Land use is also predominantly agricultural, but has a higher percentage of urban land use (17%). Herbaceous land cover in both catchments is a mixture of pasture (cattle and minor horses), haying operations, and suburban turf including parks, golf courses and private yards.

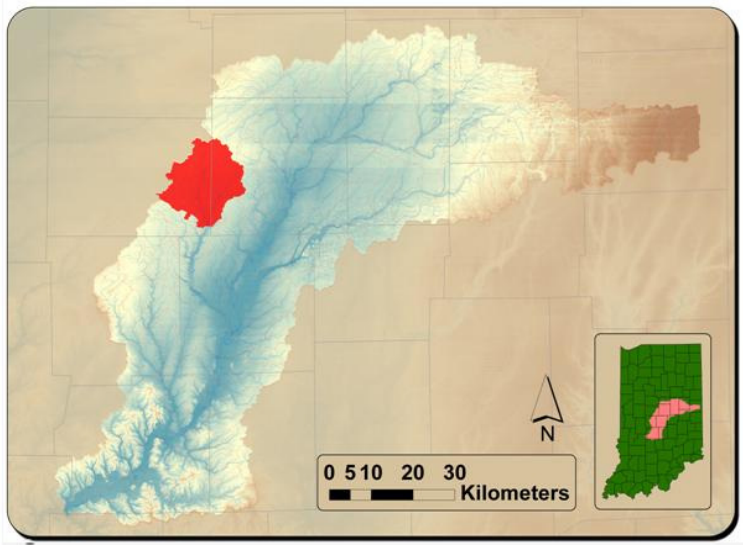

Figure 8: Watershed area upstream of Eagle Creek sampling station encompasses 266 km^2.

3.2.2 Methods and Laboratory Analyses

Samples were collected by research scientists and staff at IUPUI's Center for Earth and Environmental Science and were collected from bridges at stream crossings. Samples were collected and delivered to the United States Geological Survey, Indiana Water Science Center for filtration and shipped to the National Water Quality Laboratory in Denver, Colorado. Analyses were conducted under contract with the US Geological Survey in their National Water Quality Laboratory in Denver Colorado. Analyses from the USGS labs are conducted utilizing set lists of analytes. Analyses include 146 waste water compounds and pesticides (Schedule 1433 – Waste Water Compounds and Schedule 2033 – Pesticides) that include 89 herbicides, insecticides, fungicides and their degradates; 27 personal care and domestic use products; 21 hydrocarbons, solvents, refrigerants, manufacturing additives, and combustion-derived compounds; and 9 plant and animal biochemicals, organic synthesis, and disinfection-by-product compounds. A complete list of analytes measured, the CAS number for the compound and the reporting limit is presented in Appendix C (Tables C.1 and C.2). In addition, to analyses being done by the USGS, samples were also shipped to a commercial laboratory and analyzed for glyphosate and AMPA. The method detection limit for glyphosate was very high at 6 µg/L making comparison of results difficult.

The sampling strategy called for seasonal sampling during both high flow (typically >80th percentile flow) and during base flow (<20th percentile flow) in both Eagle Creek and the White River at stations that are upstream of drinking water intakes. White River was sampled six times in 2008 during both event and base flow, while Eagle Creek was sampled four times, mostly during low flow periods.

Figure 9 is a hydrograph of the White River at a station just downstream of the sampling location showing the timing of sample collection relative to discharge. Two samples were collected during a high flow event in February, 2008. Sample collection corresponded to peak discharge and the falling limb of the hydrograph. During spring, 2008 an additional 2 samples were collected at the White River sampling station. One sample was taken during base flow and a second during the rising limb of a spring storm. Two more samples were collected during base flow conditions in summer and fall. Analyses of the hydrograph shows that there were no high flow events during this time period so that sampling was limited to low flow (Table 5).

Figure 10 is a hydrograph of Eagle Creek at a station just downstream of the sampling location showing the timing of sample collection relative to discharge. Two samples were collected during the spring. One sample was at base flow and the second during the rising limb of a spring storm. Two additional samples were collected during summer and fall base flow conditions. Analyses of the hydrograph shows that there were no high flow events during this time period so that sampling was limited to low flow (Table 5). Spring sampling in both the White River and Eagle Creek occurred during the first storm following major agriculture activity in the watersheds.

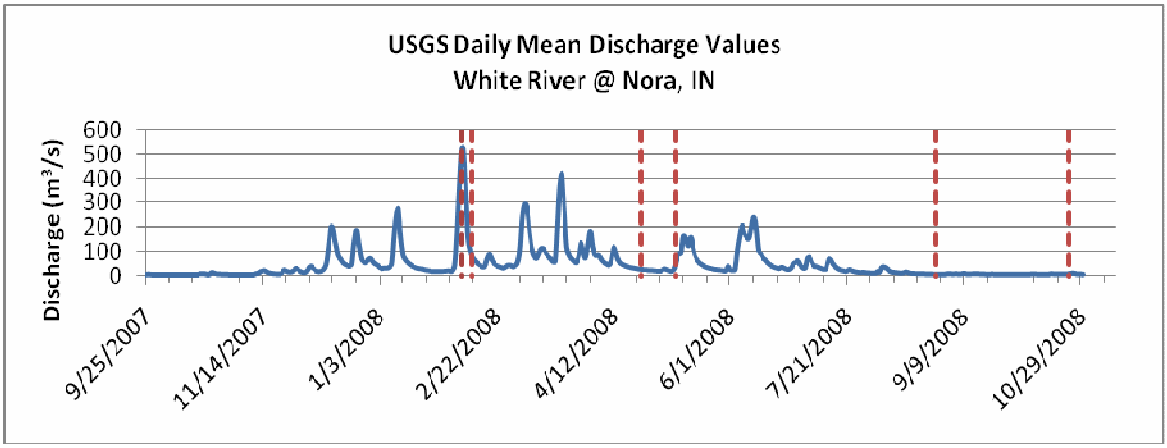

Figure 9: White River Hydrograph showing Aquisafe sampling (red dashed lines) relative to discharge. The White River was sampled six times.

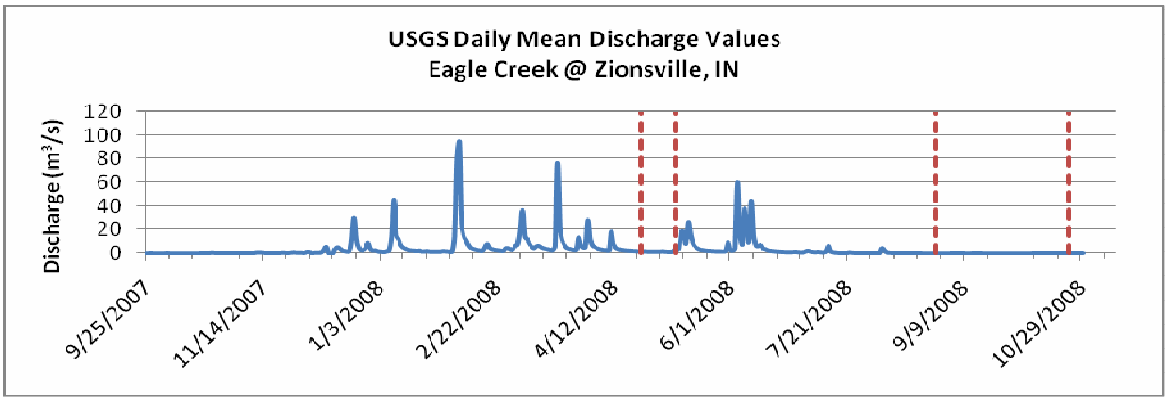

Figure 10: Eagle Creek Hydrograph showing Aquisafe sampling (red dashed lines) relative to discharge. Eagle Creek was sampled four times.

Table 5: Sampling Dates and River Discharge for White River and Eagle Creek.

White River		Eagle Creek	
Date	**Discharge (m^3/s)**	**Date**	**Discharge (m^3/s)**
2/7/2008	523.86		
2/12/2008	73.62		
4/24/2008	26.56	4/24/2008	1.61
5/9/2008	21.95	5/9/2008	5.80
8/28/2008	7.05	8/28/2008	0.13
10/24/2008	9.63	10/24/2008	0.28

3.2.3 Results

Screening of the Upper White River catchment indicates that pesticides (herbicides and insecticides) are the dominant contaminant measured. Of the 32 herbicides and degradates analyzed, 17 were found and of the 45 insecticides and degradates analyzed, 8 were found. In addition, 1 of 8 fungicides were also detected (Figure 11). In addition, personal care and domestic use products (4 of 25 compounds) and manufacturing additives (3 of 7 compounds) were also detected frequently, documenting both the influence of waste water effluent in area streams as well as the industrial land use influence in the urban portions of the watershed.

In all, a total of 38 compounds were detected during the screening. Table 6 shows the detected compounds, the maximum concentration detected, and the location and frequency of detection for the detected compounds. There were some differences in the compounds detected as well as the frequency of detection between the two sites, Eagle Creek and White River. The White River screening had detections for gasoline hydrocarbons and a solvent, while Eagle Creek did not. In contrast, manufacturing additives had more detections and more frequent detections in Eagle Creek than White River (Table 6). Personal care and domestic use products were detected more often in White River. Among the pesticides, there were also differences in which compounds were detected in which watershed but overall the same number of pesticides was detected in each (Table 6).

Among the pesticides that were detected in the watersheds, there are differences in the frequency of detection among the 26 compounds detected with 9 being detected during most of the sampling events. These include the fungicide, metalaxyl; the herbicides acetochlor, atrazine (and its degradate 2-chloro-4-isopropylamino-6-amino-s-triazine ciat), 3,4-dichloroaniline, metolachlor, prometon, simazine, and terbuthylazine (Table 6).

In addition to differences in the frequency of detection by compound, there were also differences related to both the season of sampling and whether the sample was collected at low or higher flows. As can be expected, spring and summer sampling events had the highest number of detections in both Eagle Creek (17, 17, respectively) and White River (15, 12, respectively) at both event and base flow. Spring sampling was conducted following the initiation of farming activities when agricultural water discharge (both overland flow and via tile drainage) could be expected to transport chemicals into surface water bodies. This transfer of chemicals during event flows was evident in both watersheds as well with White River having three times as many detections (15 vs. 5) and Eagle Creek having more than twice as many detections (17 vs. 7) during high flow spring sampling than low flow spring sampling. Diffuse pollution was still an important component of contamination in surface waters during the winter as evidenced by the White River event high flow sampling when 13 and 14 compounds were detected. During the low flow periods in summer and fall when there was very little runoff (Figures 9 and 10), sample analyses still showed numerous detections (White River 12, 7; Eagle Creek 17, 12) of chemicals dominated by agricultural chemicals. It is difficult to determine the source of these chemicals as tile drainage had stopped discharging by the end of June in both watersheds.

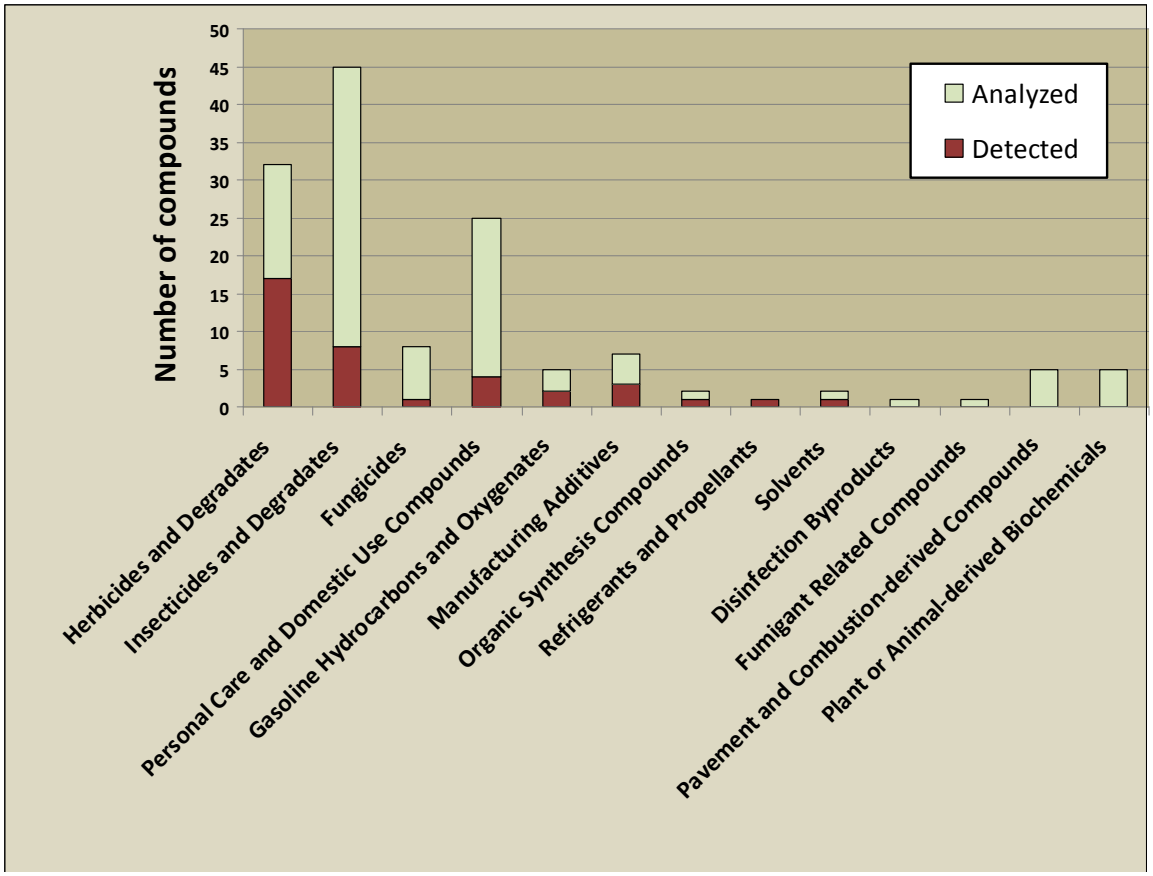

Figure 11: Chart showing the number of compounds in each class that were analyzed along with the number of compounds that were detected. Herbicides, Insecticides and their degradates were the most common substances detected in the agriculturally dominated watersheds in central Indiana.

Several of the detected pesticides have human health benchmarks associated with them allowing for an analysis of the concentration levels that were detected. The human health benchmarks may be regulatory in nature in the United States as is the case for those benchmarks that are established for drinking water maximum contaminant levels (acetochlor, atrazine, and simazine). Other human health benchmarks are non-regulatory in nature but the result of risk assessments (Kingsbury et al. 2008). The US EPA calculates a value called the Benchmark Quotient (BQ). This quotient is used as an early warning by some states to identify compounds whose environmental occurrence levels are approaching levels of concern. Two different benchmark quotients can be calculated based on data availability; the Benchmark Quotient is calculated as the annual average concentration/human health benchmark concentration or the BQmax can be calculated from the maximum concentration/human health benchmark. In this study, BQmax values were calculated due to the limited number of samples available (Tables 8 and 9).

Table 6. Summary of Pesticides Detected in Eagle Creek and White River Samples*.

Chemical Compound	Type of pesticide	Eagle Creek (µg/L max)	White River (µg/L max)	Human Health Benchmark (µg/L)	BQmax
metalaxyl	fungicide	0.01	0.0117	600	0.00002
2-chloro-4-isopropylamino-6-amino-s-triazine ciat	herbicide	0.068	0.142		
3,4-dichloroaniline	herbicide	0.144	0.0081		
4-chloro-2-methylphenol	herbicide	0.0057			
acetochlor	herbicide	0.239	0.283	1	0.28300
alachlor	herbicide	0.0083	0.0078	**2**	0.00415
atrazine	herbicide	0.588	2.39	**3**	0.79667
benfluralin	herbicide		0.005		
dacthal	herbicide		0.004	70	0.00006
eptc	herbicide	0.0045			
metolachlor	herbicide	0.242	1.16	700	0.00166
metribuzin	herbicide	0.0472	0.068	90	0.00076
molinate	herbicide	0.0049			
prometon	herbicide	0.0501	0.0165	400	0.00013
prometryn	herbicide		0.006	300	0.00002
simazine	herbicide	0.152	0.397	**4**	0.09925
terbuthylazine	herbicide	0.0334	0.0129	2	0.01670
tribufos	herbicide	0.1			
azinphos-methyl-oxon	insecticide	0.06	0.06	10	0.006
carbaryl	insecticide	0.0749		40	0.00187
chlorpyrifos	insecticide		0.0061	2	0.00305
diazinon	insecticide		0.0059	1	0.00590
fipronil	insecticide	0.0264			
phosmet	insecticide		0.008		
phosmet_oxon	insecticide	0.06	0.06		
tefluthrin	insecticide	0.005	0.005		

* Maximum concentrations detected (µg/L), the human health benchmark, and maximum benchmark quotient are also shown. USEPA and states in the United States use a BQmax value of 0.1 as an early warning that environmental concentrations are reaching levels of concern. Atrazine, acetochlor, and simazine were detected at concentrations that exceeded this early warning approach in 2008. Bold Human Health Benchmark Values are MCL's.

A review of the other chemical compounds detected during the screening shows that there were several other classes of chemicals found (Figure 11). Table 7 shows the maximum concentration detected in both Eagle Creek and White River and the BQmax value for compounds with human health benchmarks.

Table 7: Summary of Other Contaminants Screened in the White River Basin in 2008*.

Chemical Compound	Type of substance	Eagle Creek (µg/L max)	White River (µg/L max)	Human Health Benchmark (µg/L)	BQmax
2-methylnaphthalene	Gasoline hydrocarbon		0.0895	30	0.00298
naphthalene	Gasoline hydrocarbon		0.105	100	0.00105
5-methyl-1h-benzotriazole	Manufacturing additive	0.821			
tri(2-chloroethyl) phosphate	Manufacturing additive	0.2	0.234		
tri(dichloroisopropyl) phosphate	Manufacturing additive	0.19			
anthraquinone	Organic synthesis compound	0.22			
benzophenone	Personal care and domestic use product		0.132		
caffeine	Personal care and domestic use product		0.235		
hexahydrohexamethyl cyclopentabenzopyran (hhcb)	Personal care and domestic use product	0.57			
n,n-diethyl-meta-toluamide (deet)	Personal care and domestic use product	0.117	0.414		
isophorone	Refrigerant and propellant	0.18	0.119	100	0.00180
tetrachloroethylene	Solvent		0.11	**5**	0.02200

* Chemical classes include manufacturing additives, solvents, personal care and domestic use products, gasoline hydrocarbons, refrigerants and propellants, and organic synthesis compounds. Maximum concentrations detected (µg/L), the human health benchmark, and maximum benchmark quotient are also shown. Only the refrigerant and propellant, isophorone, and the solvent, tetrachloroethylene have human health benchmarks and the BQmax for both is well below levels of concern. Bold Human Health Benchmark Values are MCL's.

The Benchmark Quotient values are utilized by USEPA and states in the United States as an early warning that environmental concentrations are reaching levels of concern. A value of 0.1 is commonly used as the level indicating additional vigilance is warranted. In the White River screening, three herbicides, atrazine, acetochlor, and simazine, were detected at concentrations that exceeded this early warning benchmark in 2008. Additional information on the occurrence and concentration of atrazine is available from Veolia Water Indianapolis process sampling for the White River Treatment Plant located in close proximity to the sampling station established in this study on the White River. These datasets (Figure 12) indicate that concentrations of atrazine are typically found at levels significantly higher than was documented in this screening study. Similar data sets for other surface raw water systems in central Indiana and throughout the Midwestern United States show similar results making atrazine the agricultural diffuse source pollutant of most concern.

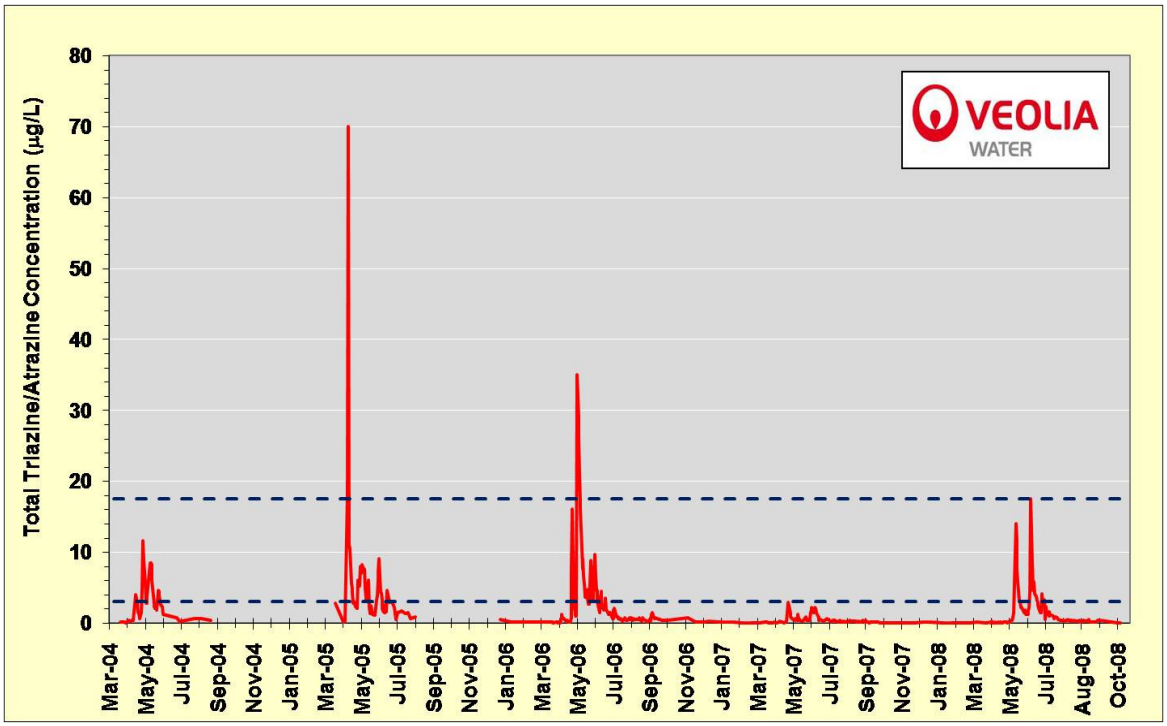

Figure 12: Atrazine concentrations (measured as total triazine by ELISA) measured in the White River frequently exceed the US drinking water maximum contaminant level of 3 µg/L (lower blue dashed line) and periodically exceed USEPA Chronic Aquatic Community Life Guidelines of 17.5 µg/L (upper blue line) as well as several other aquatic health benchmarks (not shown).

3.3 Implications of screening results

A series of chemical analyses have been done on both the Ic Catchment in Brittany, France and the Upper White River Watershed, central Indiana. The data indicate that there are numerous contaminants, especially pesticides, present relatively frequently in source waters. Some contaminants occur at concentrations that exceed drinking water maximum contaminant levels. These contaminants are from diffuse sources and are anticipated based on the current land use practices in each catchment. There were seven chemicals detected in the Ic Catchment screening, all of which are agricultural chemicals with three compounds (AMPA, atrazine, and Desethylatrazine) accounting for 96% of the detections. In the Upper White River Watershed, there were 38 compounds detected with pesticides being the dominant detected class with 26 compounds detected. Direct comparison between contaminant occurrence in the Ic Catchment and Upper White River Catchment are difficult due to the significant differences in method detection limits between the two studies. In some cases, method detection limits are similar, but in others they are widely different with several of the detections in the White River system occurring at concentrations that are below the detection limits used in the Ic Catchment. Thus, it is difficult to conclude whether the lack of occurrence in the Ic Catchment is related to less agricultural chemical usage or better agricultural water management or simply differences in the analytical methods. In the Ic Catchment, AMPA appears to be the chemical of concern for continued study based solely on this screening as atrazine is no longer applied in the catchment. However, given the treatability of AMPA in the drinking water treatment process, AMPA may not be deemed to warrant further study. In the Upper White River Basin, atrazine, acetochlor and simazine occur at concentrations that exceed early warning levels calculated from their maximum measured concentration relative to the human health benchmarks for the compounds. These three

agricultural chemicals are therefore identified as priority chemicals for study in Aqusiafe 2 based solely on the screening. Other characteristics (i.e. treatability in the drinking water process) may result in a preferential ranking of these chemicals (cf. chapter 2.2).

Chapter 4
Conclusions

The literature review identified pesticides as the dominant known diffuse contaminant group in rural and semi-rural settings (section 2.1). This is confirmed for the agriculturally dominated Upper White River Watershed in the USA, where pesticides were found to dominate the diffuse source compounds (section 3). In fact, 26 of the 38 detected compounds were pesticides making them the largest group of chemicals detected. In a pesticide screening in the Ic catchment in France seven agricultural pesticides were detected with AMPA and atrazine being the most common compounds, detected in 54 and 41 % of all the samples, respectively. In the White River Basin

Based on literature values on pesticide detection in surface waters in Germany, France and the USA, a priority list was established in section 2.2 of this report (see Table 3 for a summary). Only seven substances made to the top 20 substances in the USA and in Europe. Accordingly, US and European substances are distinguished in the priority list. Most frequently detected substances were atrazine, metolachlor and simazine for the USA, AMPA (metabolite of glyphosate), diuron and atrazine for France and diuron, atrazine and isoproturon for Germany. The importance of atrazine in Europe is interesting, since it was already banned at the time of the monitoring.

The pesticides found in the screenings are in good agreement with the priority list of most problematic pesticides for the US and Europe. AMPA and atrazine, the substances detected most frequently in the Ic catchment, as well as 2,4-D and dichlorprop, which were found in high concentrations > 0.1 µg/L in one sample are all included in the Europe top 20 of the priority list. Other substances on the list may not have been found because they were either not measured or because of relatively high analytical detection limits of the screening. In the White River Basin, atrazine, acetochlor and simazine were detected at concentrations exceeding early warning levels utilized by several states in the United States, indicating their high relevance concerning drinking water production. They are also included in the US top 20 of the priority list.

The priority list is a reliable basis for potentially problematic pesticides. It can thus be used as a starting point for monitoring programs by waterworks in rural catchments. If looking for pesticides in surface water, it is important to take times of application of regarded pesticides into consideration, as shown by strong fluctuations in atrazine concentrations in the source water of a waterworks in Indiana (Figure 12).

The screening results indicate that also other contaminants than pesticides may play a role in rural catchments. In the screening in the semi-rural catchments in Indiana, twelve of the detected 38 substances were not pesticides, but belonged to other groups, such as domestic use products, manufacturing additives or gasoline hydrocarbons. Most of the twelve substances are expected rather from point sources, with the exception of the solvent tetrachloroethylene, which is also expected from diffuse sources. Of these twelve substances, seven were only found in one of the two catchments, showing a strong catchment-specific relationship. The findings indicate that other substances than pesticides may be of local importance, though in the case study all 12 substances were at least 50-fold below human health benchmarks (if defined). Still, for future screenings in agricultural watersheds, a focus on rarely researched diffuse substances, such as veterinary pharmaceuticals, may be of interest.

We conclude that the pesticide priority list given in Table 3 is a good starting point for diffuse pollution screening in watersheds with a lack of information on pesticide use or dosage. If information is available, alternative systems can be used to estimate pesticide relevance in

surface waters (e.g., INERIS 2009) even though it may possibly not be sufficient if major local influences, such as factories, large roads with stormwater discharges or CSO are present.

Appendix A

List of Analytes: Screening on the Ic, Brittany, France

Table A.1: List of Analytes and Detection Limits for Analyses from the Ic Catchment

Analyte	Detection limit (µg/L)		Analyte	Detection limit (µg/L)
2,4,5-T	0.100		Métalaxyl	0.050
2,4-D	0.100		Métamitrone	0.050
2,4-DB	0.100		Métazachlore	0.050
2,4-MCPA	0.100		Méthabenzthiazuron	0.020
2,4-MCPB	0.100		Méthomyl	0.025
Acétochlore	0.020		Métobromuron	0.050
Alachlore	0.020		Métolachlore	0.025
Amétryne	0.025		Métoxuron	0.050
Aminotriazole	0.100		Métoxuron	0.050
AMPA	0.025		Métribuzine	0.050
Atrazine	0.025		Metsulfuron methyl	0.100
Atrazine déisopropyl	0.050		Monolinuron	0.050
Atrazine déséthyl	0.025		Monuron	0.050
Benalaxyl	0.020		Néburon	0.020
Bifénox	0.020		Nicosulfuron	0.050
Bromacil	0.020		Oxadiazon	0.025
Bromoxynil	0.100		Pencycuron	0.050
Buturon	0.050		Pendiméthaline	0.025
Carbaryl	0.025		Piclorame	0.100
Carbofuran	0.025		Pirimicarbe	0.020
Chlorsulfuron	0.020		Pretilachlore	0.050
Chlortoluron	0.050		Pretilachlore	0.025
Clopyralide	0.100		Prométone	0.050
Cyanazine	0.050		Prométryne	0.050
Desmétryne	0.025		Propachlore	0.050
Dicamba	0.100		Propazine	0.050
Dichlorprop	0.100		Propazine	0.025
Diflufenicanil	0.020		Propiconazole	0.100
Dimethenamide	0.020		Prosulfuron	0.020
Diuron	0.050		Secbuméton	0.050
EPTC	0.020		Simazine	0.050
Fenpropimorphe	0.025		Sulcotrione	0.100
Fénuron	0.050		Tébuconazole	0.050
Flazasulfuron	0.050		Tébutame	0.050
Fluométuron	0.050		Terbuméton	0.050
Fluroxypyr	0.100		Terbuthylazine	0.050
Glufosinate	0.100		Terbutryne	0.050
Glufosinate	0.100		Thiafluamide	0.025
Glyphosate	0.1,0.05,0.025		Thifensulfuron methyl	0.050
Hexazinone	0.050		Triasulfuron	0.050
Imazaméthabenz-méthyl	0.020		Triazines	0.050
Iodosulfuron	0.050		Triclopyr	0.100
Ioxynil	0.100			
Isoproturon	0.050			
Linuron	0.050			
Mécoprop	0.100			
Mésotrione	0.050			

Appendix B

Pesticide detections: Screening on the Ic, Brittany, France

Table B.1: Results of Chemical Analyses Showing Sample Date, Location, and Concentration for Samples with Concentrations Above Detection Limit

Analyte	Sample Site	Date	Concentration (µg/l)	Detection limit
AMPA	IC02	2003-04-29	0.14	0.050
AMPA	IC04	2003-01-10	0.40	0.100
AMPA	IC04	2003-04-29	0.09	0.050
AMPA	IC06	1999-06-30	0.10	0.025
AMPA	IC06	2000-03-29	0.11	0.025
AMPA	IC06	2000-07-26	0.12	0.025
AMPA	IC06	2000-11-10	0.25	0.025
AMPA	IC06	2001-07-16	0.10	0.025
AMPA	IC06	2001-07-20	0.18	0.100
AMPA	IC06	2001-09-05	0.15	0.100
AMPA	IC06	2002-05-27	0.34	0.025
AMPA	IC06	2002-05-28	1.50	0.100
AMPA	IC06	2002-06-08	0.51	0.025
AMPA	IC06	2002-10-09	1.00	0.100
AMPA	IC06	2002-10-15	0.30	0.025
AMPA	IC06	2003-01-07	0.35	0.100
AMPA	IC06	2003-01-10	0.28	0.100
AMPA	IC06	2003-04-29	0.18	0.100
AMPA	IC06	2003-05-15	1.50	0.025
AMPA	IC06	2003-05-20	0.55	0.100
AMPA	IC06	2003-10-24	1.60	0.025
AMPA	IC06	2003-11-27	1.20	0.025
AMPA	IC06	2004-04-19	0.18	0.100
AMPA	IC06	2004-09-13	0.13	0.100
AMPA	IC06	2005-02-14	1.95	0.100
AMPA	IC06	2005-03-22	0.66	0.100
AMPA	IC06	2005-04-29	0.36	0.100
AMPA	IC06	2005-05-30	0.78	0.100
AMPA	IC06	2005-06-27	0.75	0.100
AMPA	IC06	2005-09-16	0.11	0.100
AMPA	IC06	2005-10-11	0.19	0.100
AMPA	IC06	2005-10-14	0.63	0.100
AMPA	IC06	2006-05-07	0.31	0.100
AMPA	IC06	2006-06-13	0.85	0.100
AMPA	IC06	2006-09-25	0.40	0.100
AMPA	IC06	2007-02-05	0.20	0.100
AMPA	IC06	2007-02-05	0.27	0.100
AMPA	IC06	2007-04-13	0.19	0.100
AMPA	IC06	2007-06-27	0.20	0.100
AMPA	IC08	2001-06-06	0.20	0.100
AMPA	IC08	2002-05-28	1.20	0.100
AMPA	IC08	2002-10-09	1.00	0.100
AMPA	IC08	2003-01-10	2.00	0.100
AMPA	IC08	2003-04-29	0.21	0.100

AMPA	IC08	2004-09-13	0.16	0.100
AMPA	IC10	2002-10-09	0.27	0.100
AMPA	IC10	2003-01-10	0.26	0.100
AMPA	IC10	2004-01-13	0.15	0.100
AMPA	IC11	2002-10-09	3.00	0.100
AMPA	IC12	2002-10-09	2.15	0.100
Atrazine	IC06	1998-03-06	0.265	0.025
Atrazine	IC06	1998-05-27	0.165	0.025
Atrazine	IC06	1998-10-09	0.095	0.025
Atrazine	IC06	1999-04-16	0.105	0.025
Atrazine	IC06	1999-06-30	0.24	0.025
Atrazine	IC06	2000-06-07	0.215	0.025
Atrazine	IC06	2000-11-10	0.105	0.025
Atrazine	IC06	2002-05-27	0.09	0.025
Atrazine	IC06	2002-06-08	0.06	0.025
Atrazine	IC06	2003-01-07	0.06	0.05
Atrazine	IC06	2003-05-15	0.07	0.025
Atrazine	IC06	2003-05-20	0.11	0.05
Atrazine	IC06	2003-10-24	0.16	0.025
Atrazine	IC06	2004-01-13	0.06	0.025
Atrazine	IC06	2004-04-19	0.055	0.025
Atrazine	IC06	2005-04-29	0.04	0.025
Atrazine déséthyl	IC06	1998-03-06	0.065	0.025
Atrazine déséthyl	IC06	1998-05-27	0.08	0.025
Atrazine déséthyl	IC06	1998-07-20	0.05	0.025
Atrazine déséthyl	IC06	1998-10-09	0.06	0.025
Atrazine déséthyl	IC06	1999-04-16	0.07	0.025
Atrazine déséthyl	IC06	1999-06-30	0.105	0.025
Atrazine déséthyl	IC06	2000-06-07	0.08	0.025
Atrazine déséthyl	IC06	2000-07-12	0.105	0.025
Atrazine déséthyl	IC06	2000-11-10	0.075	0.025
Atrazine déséthyl	IC06	2001-01-10	0.07	0.025
Atrazine déséthyl	IC06	2001-07-16	0.065	0.025
Atrazine déséthyl	IC06	2002-05-27	0.06	0.025
Atrazine déséthyl	IC06	2002-06-08	0.055	0.025
Atrazine déséthyl	IC06	2003-05-15	0.095	0.025
Atrazine déséthyl	IC06	2003-07-07	0.045	0.025
Atrazine déséthyl	IC06	2003-10-24	0.155	0.025
Atrazine déséthyl	IC06	2004-04-19	0.08	0.025
Atrazine déséthyl	IC06	2004-09-13	0.1	0.025
Atrazine déséthyl	IC06	2004-11-02	0.07	0.025
Atrazine déséthyl	IC06	2005-04-29	0.14	0.025
Atrazine déséthyl	IC06	2005-05-30	0.07	0.025
Atrazine déséthyl	IC06	2005-06-27	0.035	0.025
2,4-D	IC06	2005-06-27	0.24	0.100
Carbaryl	IC06	2005-04-29	0.05	0.025
Carbofuran	IC06	2006-06-13	0.065	0.025
Dichlorprop	IC06	2006-06-13	0.545	0.100

Appendix C

List of Analytes: Screening on the Upper White River Watershed, Central Indiana, USA

Table C.1: Schedule 1433 – Waste Water Compounds. USGS-National Water Quality Lab, Denver, CO

Analyte	CAS Number*	RL	Unit
Cotinine	486-56-6	0.4	ug/L
5-Methyl-1H-benzotriazole	136-85-6	1.8	ug/L
Anthraquinone	84-65-1	0.16	ug/L
Acetophenone	98-86-2	0.10	ug/L
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	21145-77-7	0.5	ug/L
Anthracene	120-12-7	0.08	ug/L
1,4-Dichlorobenzene	106-46-7	0.08	ug/L
Benzo[a]pyrene	50-32-8	0.12	ug/L
Benzophenone	119-61-9	0.18	ug/L
Bromacil	314-40-9	0.4	ug/L
Bromoform	75-25-2	0.08	ug/L
3-tert-Butyl-4-hydroxy anisole (BHA)	25013-16-5	0.6	ug/L
Caffeine	58-08-2	0.2	ug/L
Caffeine-C13			
Camphor	76-22-2	0.10	ug/L
Carbaryl	63-25-2	1.0	ug/L
Carbazole	86-74-8	0.08	ug/L
Chlorpyrifos	2921-88-2	0.20	ug/L
Cholesterol	57-88-5	1.4	ug/L
3-beta-Coprostanol	360-68-9	1.6	ug/L
Isopropylbenzene	98-82-8	0.10	ug/L
Fluoranthene-d10	93951-69-0		pct
Bisphenol A-d3			
Decafluorobiphenyl	434-90-2		pct
N,N-diethyl-meta-toluamide (DEET)	134-62-3	0.2	ug/L
Diazinon	333-41-5	0.16	ug/L
Bisphenol A	80-05-7	0.4	ug/L
Triethyl citrate (ethyl citrate)	77-93-0	0.4	ug/L
Tetrachloroethylene	127-18-4	0.18	ug/L
Fluoranthene	206-44-0	0.08	ug/L
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	1222-05-5	0.5	ug/L

Indole	120-72-9	0.14	ug/L
Isoborneol	124-76-5	0.06	ug/L
Isophorone	78-59-1	0.14	ug/L
Isoquinoline	119-65-3	0.4	ug/L
d-Limonene	5989-27-5	0.14	ug/L
Menthol	89-78-1	0.2	ug/L
Metalaxyl	57837-19-1	0.2	ug/L
Metolachlor	51218-45-2	0.16	ug/L
Naphthalene	91-20-3	0.10	ug/L
1-Methylnaphthalene	90-12-0	0.10	ug/L
2,6-Dimethylnaphthalene	581-42-0	0.2	ug/L
2-Methylnaphthalene	91-57-6	0.08	ug/L
4-Nonylphenol diethoxylates		5	ug/L
4-Octylphenol diethoxylates		1	ug/L
4-Octylphenol monoethoxylates		1	ug/L
p-Cresol	106-44-5	0.18	ug/L
4-Cumylphenol	599-64-4	0.14	ug/L
para-Nonylphenol (total)	84852-15-3	1.8	ug/L
4-n-Octylphenol	1806-26-4	0.16	ug/L
4-tert-Octylphenol	140-66-9	0.10	ug/L
Phenanthrene	85-01-8	0.08	ug/L
Phenol	108-95-2	0.4	ug/L
Pentachlorophenol	87-86-5	2	ug/L
Tributyl phosphate	126-73-8	0.2	ug/L
Triphenyl phosphate	115-86-6	0.16	ug/L
Tris(2-butoxyethyl)phosphate	78-51-3	0.5	ug/L
Tris(2-chloroethyl)phosphate	115-96-8	0.18	ug/L
Prometon	1610-18-0	0.4	ug/L
Pyrene	129-00-0	0.08	ug/L
Methyl salicylate	119-36-8	0.18	ug/L
Sample volume			mL
set number, schedule 1433			no.
3-Methyl-1(H)-indole (Skatole)	83-34-1	0.08	ug/L
beta-Sitosterol	83-46-5	2	ug/L
beta-Stigmastanol	19466-47-8	2	ug/L
Triclosan	3380-34-5	0.2	ug/L
Tris(dichlorisopropyl)phosphate	13674-87-8	0.18	ug/L

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Table C.2: Schedule 2033 – Pesticides. USGS-National Water Quality Lab, Denver, CO

Analyte	CAS Number*	RL	Unit
1-Naphthol	90-15-3	0.0882	ug/L
2-Chloro-2,6-diethylacetanilide	6967-29-9	0.0065	ug/L
2-Ethyl-6-methylaniline	24549-06-2	0.010	ug/L
3,4-Dichloroaniline	95-76-1	0.0045	ug/L
3,5-Dichloroaniline	626-43-7	0.012	ug/L
4-Chloro-2-methylphenol	1570-64-5	0.0050	ug/L
Acetochlor	34256-82-1	0.006	ug/L
Alachlor	15972-60-8	0.005	ug/L
2,6-Diethylaniline	579-66-8	0.006	ug/L
Atrazine	1912-24-9	0.007	ug/L
Azinphos-methyl	86-50-0	0.08	ug/L
Azinphos-methyl-oxon	961-22-8	0.042	ug/L
Benfluralin	1861-40-1	0.01	ug/L
Carbaryl	63-25-2	0.06	ug/L
Carbofuran	1563-66-2	0.02	ug/L
Chlorpyrifos	2921-88-2	0.005	ug/L
Chlorpyrifos, oxygen analog	5598-15-2	0.0562	ug/L
cis-Permethrin	54774-45-7	0.01	ug/L
cis-Propiconazole	60207-90-1	0.013	ug/L
Cyanazine	21725-46-2	0.018	ug/L
Cyfluthrin	68359-37-5	0.053	ug/L
Cypermethrin	52315-07-8	0.046	ug/L
Dacthal	1861-32-1	0.003	ug/L
2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT)	6190-65-4	0.014	ug/L
Diazinon	333-41-5	0.005	ug/L
Diazinon, oxygen analog	962-58-3	0.006	ug/L
Diazinon-d10	100155-47-3		pct
Dichlorvos	62-73-7	0.013	ug/L
Dicrotophos	141-66-2	0.0843	ug/L
Dieldrin	60-57-1	0.009	ug/L
Dimethoate	60-51-5	0.0061	ug/L
Disulfoton	298-04-4	0.02	ug/L
Disulfoton sulfone	2497-06-5	0.014	ug/L
alpha-Endosulfan	959-98-8	0.011	ug/L
Endosulfan sulfate	1031-07-8	0.022	ug/L
EPTC	759-94-4	0.002	ug/L
Ethion	563-12-2	0.016	ug/L

Ethion monoxon	17356-42-2	0.021	ug/L
Ethoprophos	13194-48-4	0.012	ug/L
Fenamiphos	22224-92-6	0.029	ug/L
Fenamiphos sulfone	31972-44-8	0.053	ug/L
Fenamiphos sulfoxide	31972-43-7	0.040	ug/L
Desulfinylfipronil amide		0.029	ug/L
Fipronil sulfide	120067-83-6	0.013	ug/L
Fipronil sulfone	120068-36-2	0.024	ug/L
Desulfinylfipronil		0.012	ug/L
Fipronil	120068-37-3	0.016	ug/L
Fonofos	944-22-9	0.006	ug/L
alpha-HCH-d6	86194-41-4		pct
Hexazinone	51235-04-2	0.026	ug/L
Iprodione	36734-19-7	0.026	ug/L
Isofenphos	25311-71-1	0.011	ug/L
lambda-Cyhalothrin	91465-08-6	0.014	ug/L
Malaoxon	1634-78-2	0.039	ug/L
Malathion	121-75-5	0.016	ug/L
Metalaxyl	57837-19-1	0.0069	ug/L
Methidathion	950-37-8	0.0087	ug/L
Parathion-methyl	298-00-0	0.008	ug/L
Metolachlor	51218-45-2	0.010	ug/L
Metribuzin	21087-64-9	0.012	ug/L
Molinate	2212-67-1	0.003	ug/L
Myclobutanil	88671-89-0	0.033	ug/L
Oxyfluorfen	42874-03-3	0.017	ug/L
Paraoxon-methyl	950-35-6	0.019	ug/L
Pendimethalin	40487-42-1	0.02	ug/L
Phorate	298-02-2	0.02	ug/L
Phorate oxygen analog	2600-69-3	0.027	ug/L
Phosmet	732-11-6	0.0079	ug/L
Phosmet oxon	3735-33-9	0.0511	ug/L
Prometon	1610-18-0	0.01	ug/L
Prometryn	7287-19-6	0.0059	ug/L
Propyzamide	23950-58-5	0.004	ug/L
Propanil	709-98-8	0.011	ug/L
Propargite	2312-35-8	0.02	ug/L
Sample volume			mL
Set number			no.

Simazine	122-34-9	0.006	ug/L
Tebuconazole	107534-96-3	0.0136	ug/L
Tebuthiuron	34014-18-1	0.016	ug/L
Tefluthrin	79538-32-2	0.0033	ug/L
Terbufos	13071-79-9	0.012	ug/L
Terbufos oxygen analog sulfone	56070-15-6	0.045	ug/L
Terbuthylazine	5915-41-3	0.0083	ug/L
Thiobencarb	28249-77-6	0.010	ug/L
trans-Propiconazole	60207-90-1	0.034	ug/L
Tribufos	78-48-8	0.035	ug/L
Trifluralin	1582-09-8	0.009	ug/L

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