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Addressing Blind Spots in the Assessment of Pesticides in Surface Waters:

A Complete Screening using Trace-Level Mass Spectrometry Techniques and Complementary Sampling Strategies

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SUMMARY

Pesticides applied to agricultural fields and urban areas are detected in surface waters all over the world and can pose a risk to aquatic organisms. Pesticides comprise of plant protection products (PPPs) for the protection of plants, and biocides for the protection of other materials from weeds, diseases and pests. In addition, there are many transformation products (TPs) that can be formed in soil or water. Pesticides can enter surface waters by diverse pathways (e.g., rain driven surface runoff, spray drift, waste water treatment plant effluents), and are usually very dynamic. Comprehensive assessment of pesticide exposure is very important, but this sets high demands on analytics and on sampling. Major challenges are i) the need for broad analytical methods due to a highly diverse substance spectrum (roughly 400 registered synthetic organic pesticides with broad physico-chemical properties), ii) the need for detection limits in trace-levels (ng/L range) or even ultratrace-levels (pg/L range) due to low ecotoxicologically based thresholds (e.g. neonicotinoid insecticides, pyrethroid insecticides), and iii) practicable sampling strategies that depict the real environmental situation. Current monitoring activities and scientific studies usually investigate only 10 - 40 selected pesticides, mainly herbicides and legacy insecticides. Modern insecticides, fungicides and TPs are, however, often not included. For some very toxic pesticides (e.g. pyrethroids), detection limits achieved with current analytical methods are above the environmental quality standards (EQS). These factors can lead to error-prone interpretations in current pesticide monitoring activities.

Therefore, the first goal of this thesis was to develop and evaluate analytical methods and sampling strategies for comprehensively assessing the exposure of pesticides in surface waters. The second goal was to apply these tools in a large, representative field study in order to assess the actual pesticide exposure and associated risk, and to identify blind spots in conventional monitoring strategies.

To address the first goal, a combined target and suspect screening approach based on liquid-chromatography high-resolution tandem mass spectrometry (LC-HR-MS/MS) for the detection of nearly all polar and semi-polar synthetic-organic pesticides was developed. Thereby, an existing analytical method using solid phase extraction (SPE) was extended. Pesticides that were categorized as *surface water relevant* by theoretical considerations (roughly 90 substances) were measured by a classical target method using reference standards and isotope-labeled internal standards. The remaining substances were checked by a semi-automated suspect screening approach for which no reference standard was necessary a priori. Only the exact mass was used as initial information for picking peaks from the chromatogram. Different filtering steps including blank subtraction, intensity threshold, peak shape threshold, and isotopic pattern were optimized in order to reduce the incorrectly picked background peaks (e.g. coming from the environmental matrix). The validation found a success rate of 70%, and missed peaks were mainly those with low intensities. Hence, the detection limits only increased slightly with the fast, automated approach compared to the labor-intensive manual target method. The developed

approach was applied to the remaining pesticides from which 25 parent compounds and five TPs were detected and later confirmed by a reference standard. Two TPs were detected for the first time in the environment. This method therefore opens the door for the screening of, for example, TPs for which no reference standard is easily available. With the developed method, 86% of all polar and semi-polar organic pesticides sold in Switzerland can be covered with low detection limits and with one single method. With further improvements of commercial software packages and affordable high-resolution instruments in the future, this approach might also be of value in routine pesticide monitoring.

In the second part, passive sampling of polar to semi-polar micropollutants using Chemcatchers® (styrenedivinylbenzene polymer: SDB) was tested as an alternative to biweekly composite water samples. In a field study, 44 samples were taken in five rivers over five months with both sampling strategies, i.e. two-week passive samples and biweekly composite water samples, at the same locations during the same time windows. All samples were analyzed by LC-HR-MS/MS for 300 substances from the classes of pesticides, pharmaceuticals and industrial chemicals. With both sample types, roughly 200 substances could be detected in at least one sample and detection limits were similar. This shows that passive sampling by SDB passive samplers is perfectly suitable as a qualitative screening tool. By comparing water sample concentrations with the sampled mass on the SDB disk in the 44 samples, field sampling rates could be established for nearly 100 substances. Sampling rates are needed for the translation of passive sampler concentrations into water concentrations. However, substances with strongly fluctuating water concentrations (e.g. pesticides from surface runoff) could only be quantified with larger uncertainties compared to substances with moderately fluctuating concentrations (e.g. pharmaceuticals from wastewater effluents). Passive sampling for polar to semi-polar pesticides is therefore mainly useful in remote areas where it is not possible to install automated water samplers due to logistic restrictions.

For non-polar pesticides (i.e. pyrethroid and organophosphate insecticides) which could not be covered by the LC-HR-MS/MS method, passive sampling on silicone rubber (SR) followed by analysis with gas chromatography tandem mass spectrometry (GC-MS/MS) was shown – for the first time - to be very efficient and sensitive. Because SR has very high sampling rates between 10-100 L/d for non-polar substances, much lower detection limits could be achieved compared to water samples for which normally 1-10 L of water is extracted. The developed analytical method was based on i) efficient and fast extraction with accelerated solvent extraction (ASE), ii) optimized clean-up by a combined silica gel/C18 column and iii) sensitive and selective detection by GC-MS/MS. It allowed for the detection of all 12 investigated compounds in the pg/L range. Because substance specific sampling rates could not be determined for the investigated substances, the quantification is associated with large uncertainties. Thus, it is important that the passive sampling method for the detection of highly-toxic non-polar insecticides is further developed and uncertainties for quantification are minimized.

To address the second goal a field study was carried out between March and July 2012 where the developed comprehensive tools were applied. Five medium-sized Swiss rivers containing large areas of diverse crops and urban settlements within the respective catchments were investigated. The selected rivers were representative for agriculturally and urban influenced rivers of the Swiss Plateau. The results showed that the pesticide exposure is higher than previously identified: i) more than 100 parent compounds and 40 TPs were detected in total, ii) between 30–50 parent compounds were detected in each two-week composite sample, iii) the sum of pesticide concentrations was above 1 µg/L in nearly 80% of samples. As expected, herbicides had highest detection frequencies and concentrations, followed by fungicides and insecticides. During the entire study period, a risk for aquatic organisms could not be excluded because: i) the chronic EQS was exceeded for 19 polar to semi-polar pesticides (mainly herbicides and insecticides) and four non-polar insecticides in at least one sample, ii) 70% of the samples showed at least one exceedance of an EQS for a single substance and iii) using a mixture toxicity approach, exceedances occurred in nearly all samples (up to a factor of 25). Scenario calculations for which only 30–40 frequently measured pesticides were included, were applied to the same samples. It was shown that the number of detected substances and the mixture toxicity would be underestimated on average by a factor of two. In extreme cases, mixture toxicity would even be underestimated by a factor of ten, because one or several relevant substances (insecticides, in particular) were not incorporated into the analysis. Thus, more substances, especially insecticides (e.g. neonicotinoids) need to be incorporated into routine monitoring strategies.

As the results clearly demonstrated that pesticides are posing a risk to aquatic organisms, measures to reduce pesticide loads into surface waters should be discussed with all stakeholders and actions need to be taken on the political level.

ZUSAMMENFASSUNG

Pestizide werden in der Landwirtschaft und in Siedlungsgebieten angewendet und können von dort über verschiedene Wege in die Oberflächengewässer gelangen. Die wichtigsten Eintragspfade sind oberflächliche Abschwemmungen von Landwirtschaftsflächen, Abdrift während der Applikation und Einträge über die Kläranlagen. Pestizide werden unterteilt in Pflanzenschutzmittel (PSM), welche zum Schutz der Pflanzen vor Schädlingen, Krankheiten und Unkräutern angewendet werden, und Biozide, welche andere Materialien wie z.B. Gebäudefassaden vor dem Befall von verschiedenen Organismen schützen sollen. Pestizidrückstände, zusammen mit deren Transformationsprodukten (TPs), welche im Boden oder im Wasser gebildet werden, wurden bereits häufig in Fliessgewässern nachgewiesen. Es hat sich gezeigt, dass das Auftreten von Pestiziden im Gewässer ein Risiko für aquatische Lebensgemeinschaften darstellen kann. Eine umfassende Bewertung der Pestizidexposition in Fliessgewässern ist daher extrem wichtig, stellt aber hohe Anforderungen an die Analytik und an die Probenahme: i) es braucht eine analytische Methode, die möglichst das gesamte Pestizidspektrum abdeckt - ca. 400 organisch-synthetische Substanzen mit sehr unterschiedlichen physikalisch-chemischen Eigenschaften sind zurzeit in der Schweiz zugelassen, ii) aufgrund der z.T. sehr tiefen ökotoxikologisch basierten Grenzwerte (z.B. Neonicotinoid-Insektizide, Pyrethroid-Insektizide) müssen die analytischen Methoden empfindlich genug sein, um Pestizidrückstände in Spurenkonzentrationen (ng/L- oder sogar pg/L-Bereich) messen zu können, iii) Probenahmestrategien, welche die tatsächliche Belastung eines Gewässers repräsentieren, die aber auch in der Praxis anwendbar sind, müssen vorhanden sein. Derzeitige Gewässer-Monitoring Programme oder wissenschaftliche Studien untersuchen oft nur zwischen 10 und 40 verschiedene Pestizide (häufig Herbizide oder ehemals wichtige Insektizide). Moderne Insektizide, aber auch Fungizide und TPs sind häufig nicht in der Substanzauswahl. Hinzu kommt, dass für einige sehr toxische Substanzen (z.B. Pyrethroide) die heutigen Nachweisgrenzen weit über den definierten Umweltqualitätskriterien (EQS, aus Englisch: *environmental quality standards*) liegen. Diese Faktoren können daher zu einer fehlerhaften Interpretation der Ergebnisse führen.

Das erste Ziel dieser Arbeit war deshalb die Entwicklung analytischer Methoden und Probenahmestrategien, die eine umfassende Beurteilung der Pestizidexposition in Fliessgewässern erlauben. Das zweite Ziel war, die entwickelten Tools in einer grossen, repräsentativen Feldstudie anzuwenden und damit die tatsächliche Pestizidbelastung und das damit verbundene Risiko für Gewässerorganismen zu identifizieren.

Um das erste Ziel zu erreichen, wurde in einem ersten Schritt eine analytische Methode basierend auf Festphasenextraktion und Detektion mittels Flüssigchromatographie – gekoppelt an die hochauflösende Massenspektrometrie (LC-HR-MS/MS, aus Englisch: *liquid chromatography high-resolution tandem mass spectrometry*) optimiert. Dabei wurde eine kombinierte *Target*- und *Suspect-Screening* Methode entwickelt und auf fast alle zugelassenen

polaren organischen Pestizide angewendet. Pestizide, welche aufgrund theoretischer Überlegungen als *für Oberflächengewässer relevant* eingestuft wurden (ca. 90 Substanzen), wurden mit einer klassischen *Target*-Methode mittels Referenzstandards und Isotopen-markierten internen Standards quantifiziert. Mit einem semi-automatischen *Suspect Screening* wurde geprüft, ob die weiteren Pestizide in den Gewässerproben auftreten. Nur durch die Information der exakten Masse jeder Substanz wurden mittels einer Software Peaks aus dem Chromatogramm gefiltert. Die nachträglichen Filter-Kriterien wie die Subtraktion des Blindwertes, die Begrenzung der Peakgrösse, die Bewertung der Peakform und des Isotopenmusters wurden optimiert, um fälschlicherweise detektierte Hintergrundpeaks (z.B. Umweltmatrix) zu entfernen. Die Validierung des optimierten Workflows zeigte, dass 70% aller Peaks mittels *Suspect Screenings* gefunden wurden. Die meisten der verpassten Peaks hatten jedoch nur sehr geringe Intensitäten. Durch die Anwendung des *Suspect Screenings* konnten zusätzlich 25 Pestizide und 5 TPs detektiert werden. Diese wurden später mittels hinzugekauften Referenzstandards bestätigt und quantifiziert. Zwei TPs wurden dabei zum ersten Mal in der Umwelt nachgewiesen. Das *Suspect Screening* hat somit den Vorteil, dass nur für Substanzen, die fast eindeutig bestätigt werden konnten, ein Referenzstandard beschafft werden muss. Das ist insbesondere für TPs, für welche oft kein Referenzstandard kommerziell zur Verfügung steht, von Bedeutung. Mit dieser Methode konnten 86% aller polaren organischen Pestizide, die in der Schweiz verkauft werden, mit tiefen Nachweisgrenzen detektiert werden. Durch weitere Verbesserungen kommerzieller Software und aufgrund erwarteter kostengünstigerer Analyseninstrumente könnte diese Methode in naher Zukunft auch in Routine-Monitorings von Bedeutung sein.

Im zweiten Schritt wurde getestet, inwiefern sich die passive Probenahmestrategie (im folgenden *Passive Sampling* genannt) mittels SDB *Passive Sampler* (Styrenedivinylbenzene-Polymer, Chemcatcher®) für die qualitative und quantitative Bewertung der Pestizidbelastung eignet. Dazu wurden in fünf Schweizer Fliessgewässern über fünf Monate 44 Wasserproben (Zweiwochenmischproben) genommen. An den gleichen Standorten und während denselben Zeitintervallen wurden SDB *Passive Sampler* installiert. Alle Proben wurden mittels LC-HR-MS/MS auf über 300 organische Mikroschadstoffe (Pestizide, Pharmazeutika, Industriechemikalien) analysiert. Mit beiden Probenahmestrategien konnten über 200 Substanzen mindestens einmal nachgewiesen werden und die Nachweisgrenzen waren im Durchschnitt vergleichbar. Dies zeigt das grosse Potential, das SDB *Passive Sampler* für ein qualitatives Screening haben. Für fast 100 Substanzen konnte mit diesem Versuchsaufbau eine Sammelrate bestimmt werden, welche für die Umrechnung der *Passive Sampler*-Konzentrationen auf die Wasserkonzentrationen nötig ist. Wenn die Konzentration in den Gewässern stark fluktuierte – was häufig bei Pestiziden der Fall ist – war die Quantifizierung durch die *Passive Sampler* jedoch mit grösseren Unsicherheiten verbunden. Dies bedeutet, dass *Passive Sampling* für polare und semi-polare Pestizide hauptsächlich in Gebieten von Vorteil ist, wo es aus logistischen Gründen nicht möglich ist, einen automatischen Probenehmer zu installieren.

Für extrem toxische, unpolare Insektizide (Pyrethroide, Organophosphate), welche mit der LC-HR-MS/MS Methode nicht gemessen werden konnten, hat sich *Passive Sampling* mittels Silikon-Polymer als äusserst empfindlich bewährt. Verschiedene Studien mit anderen unpolaren Substanzen haben gezeigt, dass Silikon-Polymer sehr hohe Sammelraten von 10-100 L/d aufweist. Dieser *Passive Sampler*-Typ wurde bisher nie für unpolare Pestizide verwendet. Deshalb wurde eine analytische Methode basiert auf einer effizienten und schnellen Extraktion mittels beschleunigter Lösemittelextraktion (ASE, aus Englisch: *accelerated solvent extraction*), einer optimierten Aufreinigung durch eine kombinierte Kieselgel/C18-Säule und einer sensitiven und selektiven Detektion mittels Gaschromatographie gekoppelt an die Massenspektrometrie (GC-MS/MS) entwickelt und validiert. Damit konnten die zwölf analysierten Insektizide mit Nachweisgrenzen im pg/L-Bereich nachgewiesen werden. Da keine substanzspezifischen Sammelraten bestimmt werden konnten, verbleibt die Quantifizierung jedoch mit grossen Unsicherheiten behaftet. Es ist folglich wichtig, mehr Forschung für die Bestimmung dieser Sammelraten zu betreiben und den gesamten Aufarbeitungsprozess weiter zu optimieren.

Um das zweite Ziel zu erreichen, wurden die entwickelten Tools in einer grossen Feldstudie angewendet. Dabei wurden zwischen März und Juli 2012 fünf mittelgrosse, repräsentative Schweizer Fliessgewässer mit unterschiedlicher landwirtschaftlicher und urbaner Nutzung in ihren Einzugsgebieten untersucht. Die Resultate zeigten, dass die Exposition der Fliessgewässer mit Pestiziden höher ist als bisher identifiziert: über 100 Pestizide und mehr als 40 TPs wurden mindestens einmal nachgewiesen, zwischen 30-50 Pestizide in jeder Probe mit Konzentrations-Summen von über 1 µg/L in 80% der Proben. Wie erwartet wiesen Herbizide die höchsten Konzentrationen auf, gefolgt von den Fungiziden und Insektiziden. Während der gesamten Untersuchungsdauer konnten negative Effekte auf Gewässerorganismen nicht ausgeschlossen werden, wie eine Risikoanalyse zeigte: der chronische EQS wurde für 19 polare Pestizide (hauptsächlich Herbizide und Insektizide) sowie für vier unpolare Insektizide mindestens einmal überschritten, 70% aller Proben wiesen mindestens eine Überschreitung auf und ein Mischungstoxizitäts-Ansatz hat Überschreitungen in fast jeder Probe angezeigt (Richtwert wurde bis zu 25 mal überschritten). Berechnungen für Szenarien, bei denen die gleichen Proben mit nur 30-40 häufig gemessenen Pestiziden ausgewertet wurden, zeigten, dass die Anzahl detektierter Substanzen sowie die Mischungstoxizität im Schnitt um einen Faktor zwei tiefer lagen als die Auswertungen mit dem fast vollständigen Pestizid-Screening ergaben. Im Extremfall wäre die Mischungstoxizität sogar um einen Faktor zehn unterschätzt worden, da eine oder mehrere relevante Pestizide (hauptsächlich Insektizide) in diesen Szenarien nicht mit inbegriffen waren. Für zukünftige Monitoring-Strategien ist es also wichtig, dass zusätzliche Substanzen, speziell Insektizide (z.B. Neonicotinoide) in die Standardanalytik aufgenommen werden.

Da die Resultate klar zeigten, dass die Pestizide im Fliessgewässer ein Risiko für aquatische Organismen darstellen, müssen Möglichkeiten zur Reduktion des Pestizideinsatzes und des Pestizideintrags in die Gewässer mit allen Beteiligten diskutiert werden und Massnahmen auf politischer Ebene getroffen werden.

1. INTRODUCTION

1.1. CHALLENGES IN THE ASSESSMENT OF PESTICIDES IN SURFACE WATERS

Pesticides are applied to agricultural fields and in urban areas to protect plants and materials from weed, pests and diseases. A part of the applied pesticides enter surface waters by either diffuse pathways (e.g. surface runoff, preferential flow via sub-surface drains, spray drift, or accidental spills, Carter 2000, Leu et al. 2004) or via point sources (e.g. waste water treatment plants (WWTPs) or sewage overflows, Gerecke et al. 2002, Neumann et al. 2002, Wittmer et al. 2010). Residues of a large number of pesticides and their transformation products (TPs) have been found in surface waters all over the world (e.g. Bonansea et al. 2013, Dabrowski et al. 2002, Gilliom et al. 1999, Heeb et al. 2012, Herrero-Hernández et al. 2013, Hladik et al. 2008, Kreuger 1998, Leu et al. 2004, Oliver et al. 2012, Reemtsma et al. 2013a, Reilly et al. 2012, Schäfer et al. 2011, Tanabe et al. 2001). Pesticides are designed to act on target organisms (e.g. weeds, fungi, pests), but they also pose a risk to aquatic non-target organisms once the substances have entered the environment (e.g., Beketov et al. 2013, Gilliom et al. 1999, Köhler and Triebskorn 2013, Liess and Von Der Ohe 2005, Malaj et al. 2014, Schulz 2004, Wan 2013). Although synthetic-organic pesticides usually occur in surface waters at low concentrations (ng/L to µg/ range), for some of these micropollutants, direct effects on aquatic organisms are already seen at concentrations below 10 ng/L (e.g. pyrethroids, Weston and Lydy 2010).

The comprehensive assessment of the occurrence of pesticides in surface waters is therefore very crucial and is the basis for evaluating the risks that result from the exposure. In many countries (e.g. Switzerland), local environmental authorities are required to monitor the water quality for pesticides. In other countries such as the USA, monitoring studies are also carried out national-wide (e.g. Gilliom et al. 1999). In the EU, countries are required to monitor the 45 priority pollutants, of which 17 are pesticides (EC 2013). In addition to this, river-basin specific pesticides have to be monitored.

Assessing the full exposure of pesticides in surface waters is a very challenging task. The main reasons for this challenge are i) a highly diverse substance spectrum, ii) the need for low detection limits due to low environmental quality standards (EQS) and iii) the high spatial and temporal dynamics of the pesticide exposure. These three aspects are discussed in detail in the following sections.

A) Highly Diverse Substance Spectrum

Because several hundred synthetic-organic pesticides are allowed for use in each country (see **Box 1**), the number of substances that are potentially present in surface waters is very large. In addition, transitioning authorization, market conditions and pest pressure lead to a continuous shift in the substance spectrum.

The structural diversity of the synthetic-organic pesticides is huge. Most important PPP classes worldwide (based on sold amounts) are phenoxy alkanoic acids, amides, bipyridyls, triazines, urea derivatives, organophosphates, carbamates, pyrethroids, dithiocarbamates, and triazoles (Fenner et al. 2013). Molecular weights range from 150 g/mol to 500 g/mol, $\log K_{ow}$ values (octanol-water partitioning coefficient) range from -3 to 7, and the substances have different speciation at ambient pH values (neutral, anionic, cationic and zwitterionic, University of Hertfordshire 2013) (see **Figure 1.1** for exemplary substances). Nearly all synthetic-organic pesticides registered in Switzerland have functional groups containing oxygen (85%, usually in the form of ether, ester, carboxylic acids, or carbamates), nitrogen (80%, usually in the form of amines, amides, or nitro groups), and/or sulfur (30%, usually in the form of sulfonic acids or thioester). Nearly half of the substances are chlorinated and roughly 15% are fluorinated (University of Hertfordshire 2013). The stability in the soil and in the water phase is very different, from quickly degrading substances with half-lives (DT_{50}) < 1 d to very persistent substances with DT_{50} > 300 d (University of Hertfordshire 2013).

In addition to the above mentioned pesticide diversity, an even greater range of TPs can be expected in the water because each of the parent compounds can be degraded to different TPs either in the soil or in the water. Main degradation routes are photolytical (direct or indirect phototransformation), hydrolysis, and microbial degradation (Fenner et al. 2013). The TPs are usually more polar than the parent compounds and can be very stable in the environment so that the exposure in surface waters can be very significant (Battaglin et al. 2003, Reemtsma et al. 2013a, Scribner et al. 2000). TPs are often also detected in groundwater (e.g. Kern et al. 2011b, Kolpin et al. 2001), thus, there is a risk that they subsequently also enter drinking water.

This huge diversity in pesticides and TPs sets a lot of demands on the development of appropriate analytical methods. It may be possible to prioritize the surface water relevance of the substances by sold amounts (if available), physico-chemical properties, and fate; and to optimize the analytical methods for the selected substances. However, there is always the chance that some important substances are missed because exact application numbers in the investigated catchments are very difficult to gather. Methods that cover the complete pesticide spectrum are not available yet and are very challenging due to the high structural diversity of the compounds.

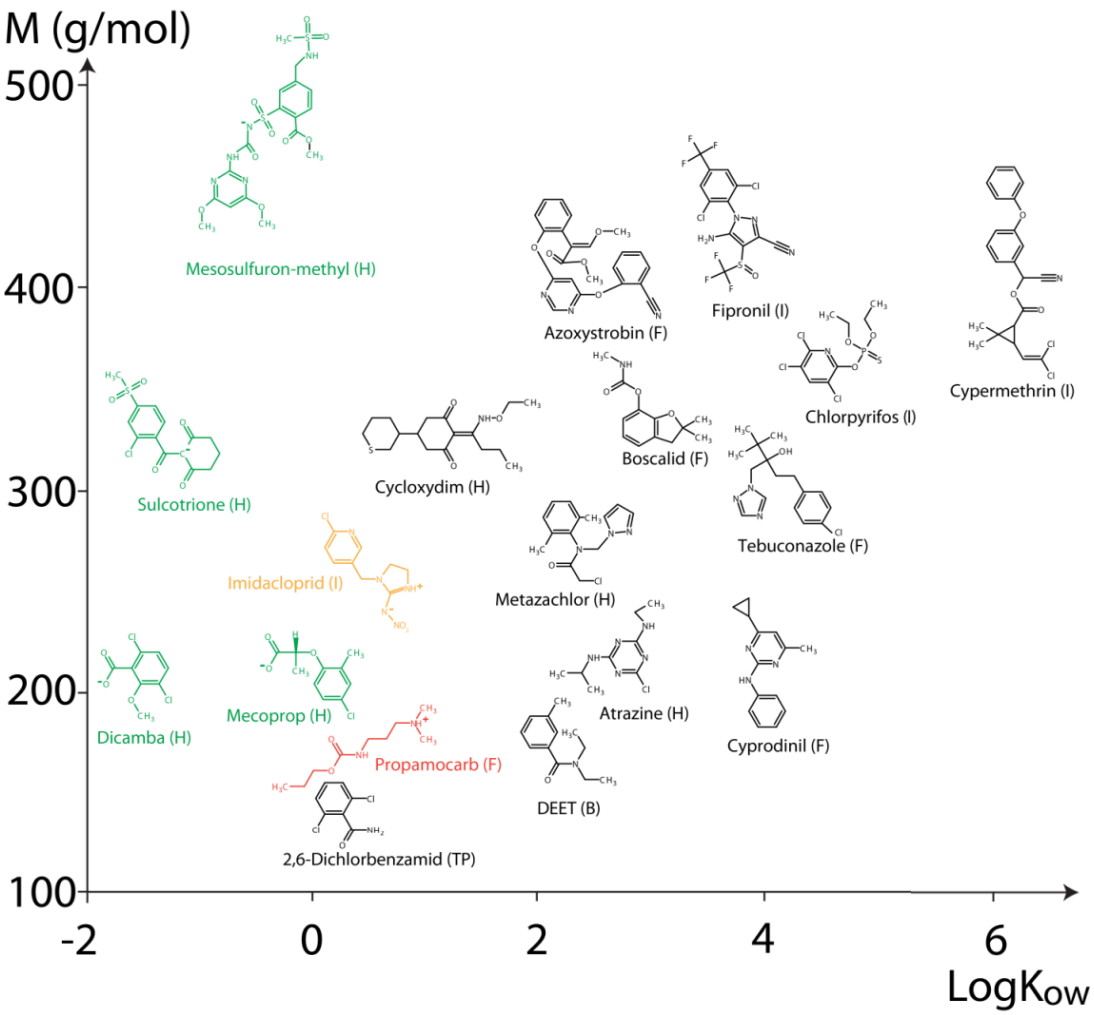

Figure 1.1. Huge diversity in physico-chemical properties of pesticides indicated by 18 exemplary substances. Structures (drawn by ACD/ChemSketch software from smiles codes (from University of Hertfordshire 2013) are plotted approximately at the position of their logK_{ow} and molecular weight (M). H: herbicide, F: fungicide, I: insecticide, B: biocide, TP: transformation product. Main speciation at pH=8 (average pH in Swiss rivers) is indicated by colors: green: anionic, red: cationic, orange: zwitterionic.

B) Low Detection Limits Needed Due to Low Effect Concentrations for Some Substances

In order to evaluate measured pesticide concentrations and to assess the risk that pesticides pose, ecotoxicologically based thresholds, so called EQS, are derived by the EU (see Box 2). **Figure 1.2** shows that many pesticides, mainly insecticides, have AA-EQS (chronic EQS, AA: annual average) values in the low ng/L range (e.g. diazinon, imidacloprid, diuron, irgarol). The AA-EQS of the pyrethroid insecticide cypermethrin is even in the pg/L range (Swiss Center for Applied Ecotoxicology Eawag/EPFL 2013).

Box 1: Legislation and Application Spectrum of Pesticides

In the EU and Swiss legislation, there is a distinction between active ingredients in plant protection products (further referred as PPPs) and active ingredients in biocide products (further referred as biocides). PPPs are used to protect plants (e.g. cereals, corn, vegetables, orchards) in agricultural fields and in private gardens (regulated under the PPP regulations, EC 2009b, SR916.161 2010), whereas biocides are used to protect other materials (e.g. wood, building facades, roofs) in urban areas (regulated under the biocide regulations, EC 2012, SR813.12 2005). In Switzerland, for example, roughly 340 synthetic-organic pesticides are registered today. This consists of roughly 230 PPPs (SR916.161 2010) and roughly 160 biocides (SR813.12 2005). Around 50 of these substances have a dual registration as PPP and as biocide. Similar numbers of registered substances are found in other countries (see EPPO 2014 for a list of all PPPs registered in all European countries).

The detailed application of each PPP to the different agricultural crops depends on many factors: i) the authorization status, ii) the market conditions, iii) the pest pressure and iv) the behavior of farmers. The application is different in every country/region and can change from year to year. Within PPPs, herbicides, fungicides and insecticides are the three major substance classes. In general, in temperate climate zones such as central Europe, herbicides are mainly sprayed on large field crops (e.g., cereals, corn), fungicides are applied to large field crops and intensively to special crops (e.g., potatoes, orchards, vineyards), and insecticides are mainly sprayed on special crops (e.g., orchards, vegetables). In addition, seeds of large field crops are coated with insecticidal seed dressings (Moschet 2011). PPPs are applied between March and November with the main application period between May and July. In Switzerland, the amount sold of synthetic-organic PPPs is collected by the Federal Office for Agriculture. Herbicides account for the largest quantities (750 tons of synthetic organic substances in 2009), followed by fungicides (550 tons) and insecticides (60 tons) (BLW 2010).

Biocides also include herbicides, fungicides and insecticides depending on the pest that is controlled. In addition, there are algaecides and insect repellents that are important. Biocides are used as disinfectants, preservatives (for different materials), in-house pest control and as antifouling agents in very diverse applications (EC 2012). In contrast to PPPs, many biocides are applied all year round. Sales numbers of biocides are not collected systematically in Switzerland, nor any other European country, as they are for PPPs. Only few consumption estimations with large uncertainties exist (FRIEDLIPARTNER 2007, Lassen et al. 2001).

In order to properly assess the risk posed by pesticides, monitoring studies need to be able to measure the substances with detection limits below the EQS values. In the EU Directive 2009/90/EC, it is even required that the limits of quantification (LOQ) are 30% lower than the EQS (EC 2009a).

This means that highly sensitive analytical methods are needed to detect these substances in (ultra)trace-level concentrations. For many substances, this is not possible yet and improvements in the analytics are needed.

C) Temporal and Spatial Differences

The third challenge for the monitoring of pesticides are the high spatial and temporal differences in the input of pesticides into surface waters. Due to the different factors that influence the application pattern of pesticides in agriculture and urban areas (see **Box 1**), it is very difficult to find out which pesticides were actually applied on which crops in the investigated catchment. The land use in the catchment is thereby the main driver of what can finally be found in the water. In very small catchments, it might be possible to do farmer surveys so that the actually used substances can be traced. In larger catchments, this is not feasible and only an estimation is possible based on crop specific use statistics (e.g. Spycher et al. 2013) or expert interviews (e.g. Moschet 2011). The selection of study sites is therefore very important and depends on the research question. Results will be completely different if an intense agricultural catchment is investigated compared to a catchment that includes a large percentage of forests or meadows.

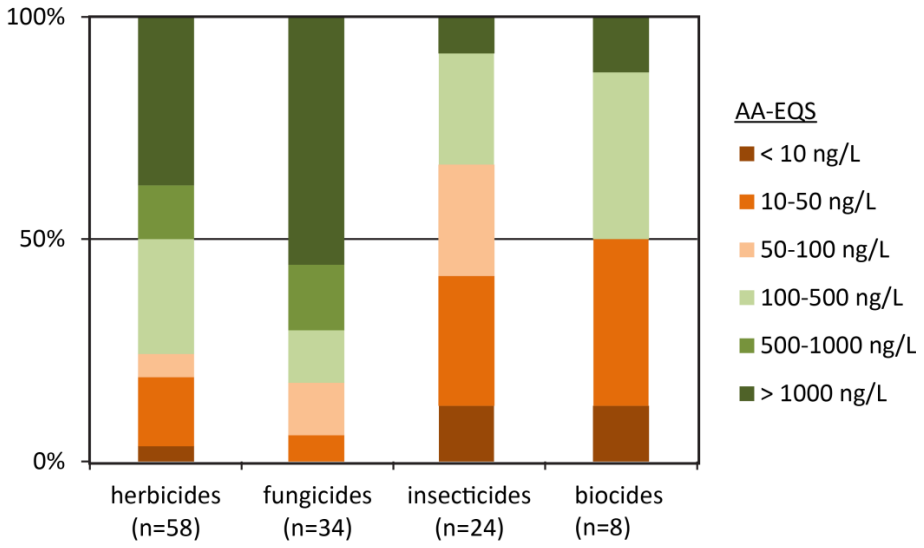

Figure 1.2. Distribution of annual average environmental quality standards (AA-EQS) of herbicides, fungicides, insecticides (registered as PPP or with dual registration as PPP and biocide) and pesticides only registered as biocide in Switzerland (see **Table D.2** for all values)

Box 2: Environmental Quality Standards and Mixture Toxicity

Depending on their mode of action, pesticides affect different aquatic organisms in different ways. A chemical's risk is usually investigated by classical ecotoxicological studies. Thereby, a single substance is tested in the laboratory on one model organism. There is the differentiation between acute tests (normally 24 h for determination of EC_{50}, the concentration at which 50% of the organism are affected) and chronic tests (normally 7-21 d for determination of NOEC, the highest concentration at which no effect is observed) (Van Leeuwen and Vermeire 2007, EC 2011a). In order to be representative of an ecosystem, it is important that for each trophic level (primary producer, primary consumer, secondary consumer) a representative species (e.g. algae, daphnia, fish) is tested. More comprehensive approaches include the derivation of species sensitivity distribution (SSD) curves or more involved microcosm studies.

In order to account for differences in sensitivities of all species in the environment, the values from the ecotoxicological tests are divided by so called *assessment factors* (AF). Guidelines for the selection of the AF were defined on EU level (EC 2011a). The AF range between 2 and 1000 depending on the set of data that is available. With this method, environmental quality standards (EQS) are defined, which can go into regulations for the water quality assessment. In the EU, for example, EQS have been introduced in the Water Framework Directive (WFD) (EC 2000). In Switzerland, EQS are not (yet) legally founded. There is the distinction between acute EQS (MAC-EQS: maximum allowable concentration) and chronic EQS (AA-EQS: annual average). Risk quotients (RQ) are calculated by dividing the measured substance concentration by its EQS. If the RQ is above one, a risk to the aquatic ecosystem cannot be excluded. If average concentrations over longer periods are measured, the AA-EQS is taken for comparison, whereas if short-term concentrations are measured, the MAC-EQS is taken (Wittmer et al. 2014a).

Due to the large number of possibly occurring substances at the same time, models to estimate the mixture toxicity have been established. The two most frequently used approaches are the *concentration addition* (CA) model and the *independent action* (IA) model (e.g. Altenburger et al. 1993, Rodney et al. 2013). Rodney (2013) conclude in their review that the CA approach is a practical and conservative first tier approach for the mixture toxicity assessment of pesticides.

The input of pesticides into surface waters is also temporally variable and is dependent on the season (e.g. application time of the pesticides) and on the weather conditions (e.g. rain events). For PPPs entering via surface runoff and sub-surface drains, concentration peaks generally occur during rain events up to 3 months after the application (e.g. Doppler et al. 2012, Garmouma et al. 1997, Leu et al. 2004, Petersen et al. 2012, Thurman et al. 1991). Spray drift and accidental spills on the farmyards lead to very distinct short concentration peaks that cannot be forecasted very well. A significant part of PPPs also enter the environment in WWTP effluents (e.g. Gerecke et al. 2002, Müller et al. 2002, Neumann et al. 2002). For biocides that are applied to facades, concentration peaks can be observed after rain events all year round (e.g. Jungnickel et al. 2008, Wittmer et al. 2010). Biocides that are used indoors have either a constant or an unpredictable input in WWTP effluents.

Due to the large spatial and temporal differences, it is crucial to choose an appropriate sampling strategy. This is dependent on the research question. If the interest is on acute concentration peaks, rain-event triggered samples are needed, if long-term concentrations are in focus, composite samples give meaningful results. The selection of the sampling strategy also depends on the size of the surface waters; in small streams, much higher dynamics are observed than in large streams (e.g. Müller et al. 2003, Wittmer et al. 2014a, see **Figure 1.3**).

1.2. STATE-OF-THE-ART SAMPLING STRATEGIES AND ANALYTICAL METHODS

Sampling Strategies Based on Ambient Water Sampling or Passive Sampling

Most frequently applied sampling strategies in (Swiss) routine river monitoring are monthly grab samples (also proposed by the WFD, EC 2000) and time-proportional composite samples in medium-sized rivers (Munz et al. 2012). Monthly grab samples are not appropriate for pesticide monitoring because concentration peaks are most likely missed. This is more pronounced the smaller the investigated river is (see **Figure 1.3**). Hence, especially in small and medium-sized rivers, interpretations from grab samples can only be used with care (Rabiet et al. 2010, Stehle et al. 2013, Wittmer et al. 2014a). **Figure 1.3** also clearly shows that in order to capture concentration peaks, especially in small rivers, event-triggered samples (with high temporal resolution) are needed. This sampling strategy has been used in many scientific investigations (e.g., Doppler et al. 2012, Leu et al. 2004, Rabiet et al. 2010, Shipitalo and Owens 2003), but is impossible in routine monitoring due to the large costs and time involved. Time-proportional composite samples (e.g. over a two week period) provide information about the long-term exposure to organisms and are therefore suitable to compare with AA-EQS (EFSA 2013). Taking two-week time proportional composite water samples was therefore also proposed for routine pesticide monitoring in Switzerland (Wittmer et al. 2014a). However, (cooled) automated

sampling devices with batteries are needed. This is not always practically feasible, especially in less developed countries.

As an alternative to composite water samples, the use of passive sampling for micropollutant monitoring has been tested in recent years (see **Box 3)**. Different types of samplers exist for detecting different substance classes. Most frequently used are POCIS (polar organic chemical integrative sampler) and Chemcatcher® (**Figure 1.4B)** for the detection of polar and semi-polar substances, as well as semipermeable membrane devices (SPMD), low density polyethylene (LDPE) and polydimethylsiloxane (PDMS) (**Figure 1.4C**) for the detection of non-polar substances (e.g. Harman et al. 2012, Namieśnik et al. 2005, Stuer-Lauridsen 2005, Vrana et al. 2005, Zabiegała et al. 2010). Polar and non-polar pesticides have often been detected by passive samplers, in particular by POCIS. Current studies have shown that the qualitative screening is very successful because the passive samplers are able to accumulate a broad range of substances (Harman et al. 2012). To derive time-weighted average aqueous concentrations from passive sampler data, the volume of water in liters sampled on the passive sampler over the deployment period has to be known (i.e. sampling rates). Methods that determine realistic sampling rates for a large number of substances at the same time, however, are missing and the capability for accurate quantification has not been tested yet under changing field conditions. It is therefore unclear which pesticides can be quantitatively monitored by passive sampling in surface waters.

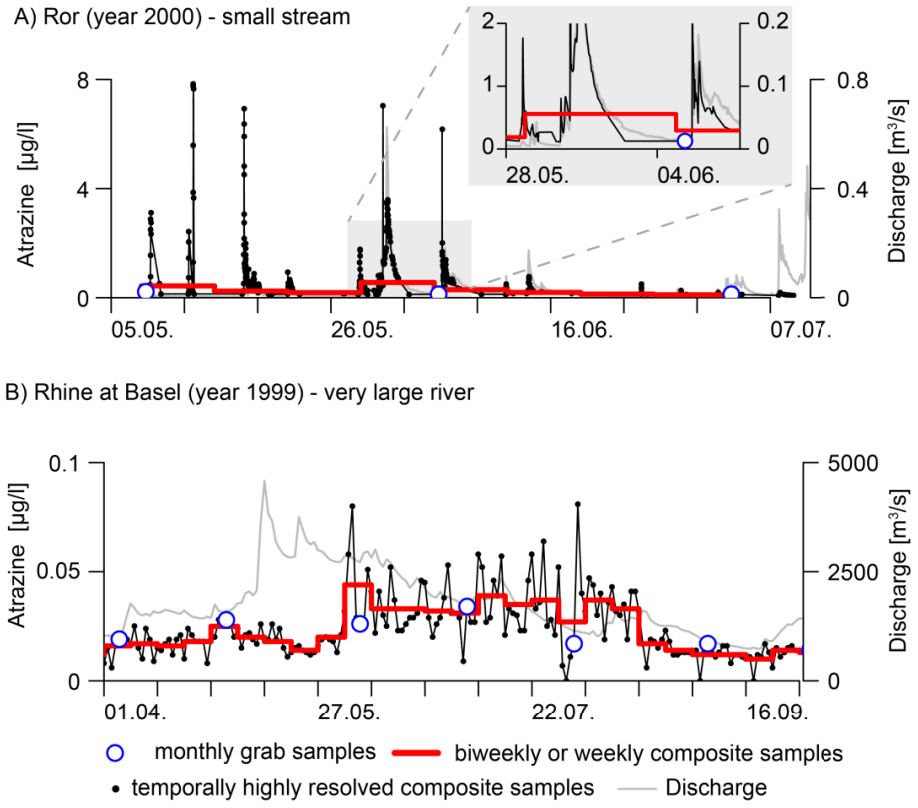

Figure 1.3. Influence of the sampling strategy on the measured concentrations in A) a small stream, B) a very large river. Adapted from Wittmer et al. (2014a).

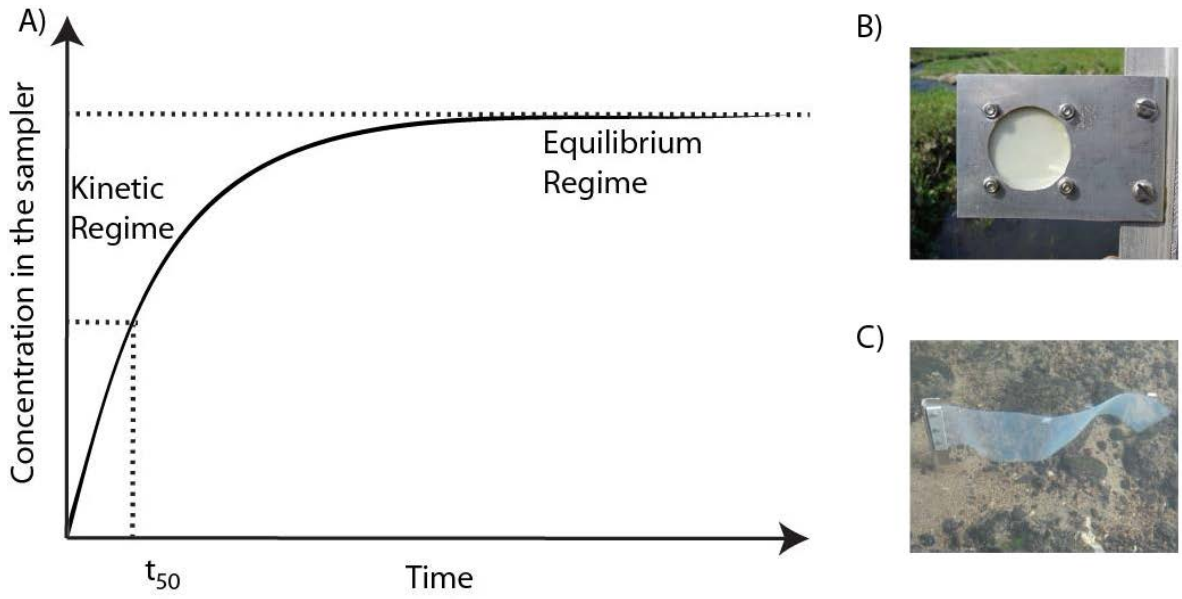

Figure 1.4. A) Principle of the uptake of substances by passive samplers (adapted from Vrana et al. 2005). t_{50} is the time at which 50% of the equilibrium concentration in the sampler is reached. B) SDB passive sampler (d=47mm) after deployment, C) PDMS passive sampler (30x10 cm^2) deployed in the river (pictures taken by Etienne Vermeirssen, Swiss Center for Applied Ecotoxicology Eawag-EPFL)

Passive samplers for non-polar substances have shown to have very high sampling rates in the range of 10-100 L/d for PCBs and PAHs (Rusina et al. 2010b, Smedes and Booij 2012). This resulted in very sensitive detection limits for these substance classes. These samplers have, however, rarely been used for the detection of pesticides. They are very promising for the detection of highly toxic non-polar pyrethroids and organophosphates for which currently no method exists that is able to detect the pesticides below their EQS (Loos 2012, Vorkamp et al. 2014).

Pesticide Analytics Based on Gas Chromatography and/or Liquid Chromatography Coupled to (Tandem) Mass Spectrometry

A lot of research has been done in developing new analytical methods to detect pesticides in surface waters. Common analytical devices that have been used for decades are based on gas chromatography electron impact (EI) ionization tandem mass spectrometry (GC-EI-MS/MS) or liquid chromatography electrospray ionization (ESI) tandem mass spectrometry (LC-ESI-MS/MS). In the last decade, the analytics shifted more and more from GC-MS to LC-MS (Alder et al. 2006) because most pesticide classes are polar and can be detected better by LC-ESI-MS/MS. A lot of research has also been put into the development of multi-residue methods that include several target substances in the same analytical run.

Box 3: Principle of Passive Sampling

Passive samplers are polymer membranes that are deployed in the water for several weeks and passively take up substances from the water phase (e.g. Allan et al. 2006, Harman et al. 2012, Vrana et al. 2005). In the ideal case (constant water concentrations and constant environmental conditions), the substances are taken up linearly in the beginning of the deployment (depending on the sampler type) (see **Figure 1.4A**). After longer deployment, equilibrium is achieved between the concentration in the sampler and the water concentration (e.g. Vrana et al. 2005). When the sampler is operated in the linear phase (kinetic regime), the uptake rate is constant. The kinetic regime is required for monitoring micropollutants in rivers. In this case, time weighted average water concentration (TWAC) over the deployment period can be calculated by the following equation:

$$TWAC = \frac{M_S}{R_S \cdot t} \quad , \qquad (1)$$

where M_s [ng] is the sampled mass, R_s [L/d] is the sampling rate and t [d] is the deployment time (e.g. Vrana et al. 2005). The crucial parameter is R_s. This number is dependent on the physico-chemical properties of the substance, on the properties of the sampler material and can change depending on environmental conditions (e.g. flow velocity, temperature, pH, salinity, degree of biofouling) (Harman et al. 2012).

Calibration of the sampler is usually done in laboratory experiments or flow channel systems where a constant water concentration and flow velocity is used (Harman et al. 2012). In the environment, however, the sampling rates can differ and be variable during the deployment time due to changes in environmental conditions. Methods to correct for these changes in-situ are the use of performance reference compounds (PRCs) that are spiked into the sampler before deployment (e.g. Huckins et al. 2002). These substances need to have similar properties as the investigated substances, but must not be present in the water (e.g. deuterated compounds). Data on the release rate of the PRC out of the sampler is used to correct the sampling rate of the substances. This approach was shown to be successful for the in-situ calibration of PCBs and PAHs that are sampled by SPMD and PDMS (e.g. Smedes and Booij 2012). For POCIS and Chemcatcher, their use has not been fully demonstrated (Mills et al. 2014).

Thereby, it is important to have a broad enrichment of chemicals (usually done by solid phase extraction (SPE), e.g. Kern et al. 2009, Richardson and Ternes 2011). Then, the column material and eluents of the chromatography have to be chosen in order to separate the chemicals accordingly, and the MS settings (e.g. transitions, collision energies) have to be selected carefully so that substance peaks are not overlapping or superimposed by background noise. Many scientific investigations have used LC-ESI-MS/MS for multi-residue studies, but only focus on a subset of 10-40 selected pesticides (e.g. Battaglin et al. 2011, Dujakovic et al. 2010, Herrero-Hernández et al. 2013, Kampioti et al. 2005, Schäfer et al. 2007, Vryzas et al. 2011). In routine monitoring in Switzerland, the same holds true (Munz et al. 2012). The selection of the substances is usually based on previous knowledge from the investigators. The set of monitored substances is often dominated by herbicides or legacy insecticides, because they normally have/had the highest application rates and they have often been found in high concentrations (e.g. Schulz 2004). Only a few modern insecticides, a few fungicides and a few TPs are regularly monitored. Although LC-ESI-MS/MS can provide fast and powerful analysis for nearly 100 substances in a single run (Jansson and Kreuger 2010), the drawback using low-resolution quadrupole instruments is that the number of substances is limited and the knowledge about fragmentation of the substances needs to be available a priori.

In the last few years, the development of high-resolution (HR) MS for the detection of all kinds of micropollutants was a major innovation (Richardson 2011). The instruments, based on time-of-flight (TOF) or orbitrap detection, provide both high mass accuracy (often < 5 ppm) and high resolution in full scan mode, which enables very sensitive detection of a theoretically unlimited number of substances. This even enables the screening for previously unknown chemicals (non-target screening) or for substances that are expected in the water but for which no reference standard is available (suspect screening) (Krauss et al. 2010). There are a few scientific studies that developed an automated qualitative target screening using LC-HR-MS with several hundred of polar or semi-polar pesticides using a customized database (e.g. Ibáñez et al. 2008, Mezcua et al. 2009, Mol et al. 2012). The set-up of these databases is, however, laborious because all reference standards have to be purchased in advance. In a non-target screening, theoretically all measurable substances can be detected, but data evaluation is very time consuming, because there is no information as a starting point. There is therefore a need for practicable, fast, and efficient screening tools that are able to detect as many substances as possible at trace-level concentrations, without the need for reference standards in advance. The suspect screening approach seems most promising for this purpose.

Nevertheless, some substances such as non-polar pyrethroids and organophosphates cannot be covered by such screening methods because they are not efficiently measurable by LC-MS. Even the extraction of 12 L of water and highly sensitive analytics based on GC-HR-MS did not allow for detection limits in the required pg/L range (Vorkamp et al. 2014). The main improvement to reduce detection limits is therefore to increase the enrichment factor together with optimized clean-up methods.

1.3. GOALS AND APPROACH

As discussed above, the large substance diversity, the low environmental quality standards and the complex input pattern of pesticides into surface waters set high demands on the analytical methods and sampling strategies. The currently used methods are not covering the complete pesticide spectrum and are therefore not sufficient to comprehensively assess the pesticide exposure and (consequently) the risk posed by pesticides.

Therefore, the first goal of this thesis was to develop a set of tools to comprehensively assess the exposure of pesticides in surface waters. Thereby, analytical methods and sampling strategies that cover almost the complete pesticide spectrum at (ultra)trace-level concentrations were developed and evaluated (chapters 2, 3, 4).

The second goal was to apply these comprehensive tools in a large, representative field study in order to assess the actual pesticide exposure and associated risk, and to identify blind spots in conventional monitoring strategies (chapter 5).

In **chapter2**, a combined target and suspect screening method by LC-HR-MS/MS for the detection of nearly all polar and semi-polar pesticides and TPs is described. The study tested the hypothesis of whether it is possible to efficiently identify suspected pesticides in water without having a reference standard; by only screening for the exact mass of the substance. This would open the door for the detection of new substances and also for TPs for which no reference standard is commercially available.

In **chapter 3**, the performance of the Chemcatcher® passive sampler was compared to ambient water samples for over 300 polar and semi-polar substances, analyzed by LC-HR-MS/MS. Besides pesticides, the selected substances also included pharmaceuticals and industrial chemicals in order to facilitate the comparison of the sampling methods. The hypothesis was that passive samplers for polar and semi-polar substances reach better detection limits than ambient water samples. This would especially be important for the detection of polar insecticides with expected low concentrations. In addition, it was evaluated how well sampling rates can be generated from in-situ calibration in the field, how strong environmental conditions affect sampling rates and if a model can predict sampling rates from physico-chemical properties of the substances.

Chapter 4 describes a method for the detection of highly-toxic non-polar insecticides at ultratrace-levels (substances that could not be covered in chapter 2). Thereby, silicon rubber (SR) based passive samplers and detection by GC-MS/MS were used. The hypothesis was that the uptake kinetics of non-polar pesticides on the SR are similar to other non-polar substances for which very high sampling rates have been reported. High sampling rates of target compounds

require a good clean-up method to get rid of the simultaneously sampled environmental matrix. With such a method, it should be possible to gain extremely low detection limits and to check compliance with EQS.

Chapter 5 applies the tools generated in chapters 2-4 and assesses the complete pesticide exposure in a large field study. Thereby, five agriculturally and urban influenced, medium-sized Swiss rivers with diverse land use in their catchments (40-105 km^2) were investigated. In each catchment, nine bi-weekly time-proportional composite water samples were taken between March and July 2012. Nearly the complete pesticide spectrum was analyzed in all samples, measured concentrations were compared with EQS and a mixture toxicity assessment was done. This was – to our knowledge - the most complete pesticide screening that was applied to a large field study. The evaluations from the nearly complete screening were compared with scenarios where only a subset of chemicals (e.g. the 30 most frequently monitored pesticides in Switzerland) was investigated. The hypothesis was that using a nearly complete screening has a large influence on the exposure assessment, and will therefore also change the risk assessment.

In **chapter 6**, the main conclusions from the thesis are drawn and an outlook for further research questions and further developments in routine pesticide monitoring are given.

2. ALLEVIATING THE REFERENCE STANDARD DILEMMA USING A SYSTEMATIC EXACT MASS SUSPECT SCREENING APPROACH WITH LIQUID CHROMATOGRAPHY - HIGH RESOLUTION MASS SPECTROMETRY

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ABSTRACT

In this study, the efficiency of a suspect screening strategy using liquid chromatography high resolution mass spectrometry (LC-HRMS) without the prior purchase of reference standards was systematically optimized and evaluated for assessing the exposure of rarely-investigated pesticides and their transformation products (TPs) in 76 surface water samples. Water soluble and readily-ionizable (electrospray ionization) substances, 185 in total, were selected from a list of all insecticides and fungicides registered in Switzerland and their major TPs. Initially, a solid phase extraction-LC-HRMS method was established using 45 known, persistent, high sales volume pesticides. Seventy percent of these target substances had LOQ < 5 ng/L. This compound set was then used to develop and optimize a HRMS suspect screening method using only the exact mass as a priori information. Thresholds for blank subtraction, peak area, peak shape, signal to noise, and isotopic pattern were applied to automatically filter the initially picked peaks. The success rate was 70%; false negatives mainly resulted from low intense peaks. The optimized approach was applied to the remaining 140 substances. Nineteen additional substances were detected in environmental samples - two TPs for the first time in the environment. Sixteen substances were confirmed with reference standards purchased subsequently, while three TP standards could be obtained from industry or other laboratories. Overall, this screening approach was fast and very successful and can easily be expanded to other micropollutant classes for which reference standards are not readily accessible such as TPs of household chemicals.

KEYWORDS

high resolution mass spectrometry, exact mass screening, suspect screening, target screening, insecticides, fungicides, transformation products

2.1. INTRODUCTION

The use of pesticides in agricultural practices may lead to release of both parent compounds and transformation products (TPs) into surface waters (Carter 2000, Leu et al. 2004), which can then threaten the health of aquatic organisms even at low concentrations (Schäfer et al. 2007, Schulz 2004). Therefore, appropriate analytical tools are necessary to detect residues of current-use pesticides and TPs in the low ng/L range. Multi-residue methods using solid-phase extraction (SPE) and LC-MS/MS (Petrovic et al. 2010, Huntscha et al. 2012, Jansson and Kreuger 2010) can provide fast and powerful target analysis for more than 100 chemicals at sensitivities in the low ng/L range. However, as the exposure of surface waters to pesticides is heavily dependent on local conditions (e.g. land use, application procedures), a single-run measurement of all pesticides potentially occurring in a sample is desirable to provide a holistic exposure estimate.

The use of high resolution mass spectrometers (HRMS) such as orbitrap and time-of-flight (TOF) instruments provide both high mass accuracy and resolution in full scan mode, enabling accurate mass screening of a theoretically unlimited number of polar organic pollutants (Richardson 2011). High-resolution mass spectrometers are not yet widespread in use due to higher costs, but seem to be one of the future MS trends (Petrovic et al. 2010). Krauss et al. (2010) introduced the three screening methods target analysis, suspect screening and non-target screening. Besides the classical quantitative target analysis approach (using reference standards), a qualitative suspect screening (exact mass as a priori information) approach or non-target screening (no previous information of the chemical available) can be pursued with high resolution mass spectrometers. In many cases, an automated qualitative target screening is performed using a customized database (with information of the exact mass, retention time, and fragments of tandem mass spectra) containing up to several hundred substances (Mezcua et al. 2009, Gómez et al. 2010, Ibáñez et al. 2008, Mol et al. 2012, Martínez Bueno et al. 2012, Diaz et al. 2013). Such databases are powerful for practical screening of compounds where reference standards are commercially available (Zedda and Zwiener 2012), mainly because of the knowledge of the retention time under the specific chromatographic conditions. However, the construction of such databases is a laborious and costly task, as all substances must be purchased and measured individually. New reference standards need to be purchased and integrated into the database as soon as the focus of the study changes. In addition, substances where reference standards are not easily accessible (e.g., many TPs) cannot be integrated in such a database. On the other hand, comprehensive non-target screening in its current state is very time consuming because many picked peaks at all masses and retention times (usually several thousands) must be evaluated irrespective of the focus in a study.

Suspect screening without reference standards, using only the information of the chemical structure a priori, is a very promising approach. The number of substances that can be screened qualitatively is theoretically unlimited but can be limited intentionally depending on the focus of the study and on the substances expected to be present in the sample. As there are currently

approximately 70 million chemicals registered in the Chemical Abstracts Service (CAS 2013) a screening based only on the ~~"e~~xact mass" could result in an unmanageable number of results with a large number of false positives. However, as opposed to non-target screening, expert knowledge regarding substances likely to occur in the surface water is necessary and should be used as a pre-filter for the analysis. In addition, compound-specific information such as molecular formula and structure is available for suspects (Krauss et al. 2010). Therefore, it is hypothesized that this concept is feasible for substance groups such as current-use pesticides and household chemicals, which usually contain polar functional groups (often electrospray-ionizable heteroatoms) and distinguishable isotopic patterns (e.g. Cl- or Br-containing molecular formula). If such a screening strategy is feasible, it alleviates the dilemma of requiring reference standards a priori and opens the door for the fast detection of compound classes for which reference standards are not easily accessible (e.g., TPs).

Segura et al. (2011) validated a suspect screening method with drinking water and surface water samples spiked with 17 substances. In a few other publications (Nurmi et al. 2012, Kern et al. 2009, Chiaia-Hernandez et al. 2012), suspects (pharmaceuticals, pesticides, or industrial products) were screened in this manner for a limited set of environmental samples. However, these approaches involved relatively laborious manual evaluation. A comprehensive strategy for an automated suspect screening for a whole substance class, systematically evaluated on a large number of environmental samples, is critically needed.

To test this hypothesis and to bring the proof of concept, a semi-automated, suspect screening approach based on LC-HRMS was developed and validated for 218 insecticides, fungicides and their major TPs. A list containing the exact mass of each suspect compound was thereby the only information required a priori. This brute force method, which includes a large number of known TPs that were not yet investigated in surface waters, was tested for the first time in composite surface water samples under realistic concentrations (ng/L range).

2.2. MATERIALS AND METHODS

2.2.1. Substance Selection

218 substances (55 insecticides, 72 fungicides, 14 various pesticides (e.g. acaricides) and 77 TPs) were chosen for the suspect screening (see **appendix A.1**). This includes the complete list of synthetic organic insecticides and fungicides registered in Switzerland between 2007 and 2013 (SR916.161 2010). Major TPs for the most commonly used insecticides and fungicides in Switzerland were also selected, as well as minor TPs for neonicotinoid insecticides, as they are an important insecticide class in terms of use quantity and known impacts on aquatic organisms (Nyman et al. 2013, Van Dijk et al. 2013) and bees (Henry et al. 2012, Whitehorn et al. 2012).

To begin, all substances were evaluated for their relevance to occur in water. All substances with log K_{ow} > 5 were excluded from the analysis (see step 1 in **Figure 2.1**). Log K_{ow} values were taken from the Footprint database (University of Hertfordshire 2013) or calculated using Jchem for Excel (Version 5.11.5.906) for the 68 substances where no data were available (**appendix A.1**). Then, the ionization efficiency of all remaining substances was estimated. Based on expert knowledge for over 400 diverse compounds analyzed with ESI, only substances containing following functional groups were set as readily-ionizable in the spray: a nitrogen atom (except cyano or nitrate functional groups); an oxygen or sulfur atom in a carboxylic/sulfonic acid or if the neighbors are very electron donating or withdrawing (e.g. phenolic group with halogen substitution on the ring); a phosphorous atom if in the form of an organophosphate. Substances that did not meet these criteria were excluded from the suspect screening (see **Figure 2.1**).

From the ~~i~~onizable" compounds, 45 substances (**appendix A.1**) were selected in order to establish a broad SPE-LC-HRMS method. This list included 19 insecticides (5 carbamates, 4 organophosphates, 4 neonicotinoids, 2 diacyl hydracines, 2 pyridines, 2 others), 18 fungicides (7 azole fungicides, 2 anilino pyrimidines, 2 carbamates, 2 morpholines, 5 others) and 8 TPs (7 insecticide TPs, 1 fungicide TP). The selection was based on the theoretical likeliness to be found in the water (sales amounts in Switzerland (internal document), physicochemical properties (University of Hertfordshire 2013), and predicted fate behavior (University of Hertfordshire 2013). In addition, the selected substances covered a wide range of physico-chemical properties and structures (log K_{ow}, pK_a, functional groups, see **appendix A.1**).

2.2.2. Field Study

The method was tested on a large field study, where five agriculturally-influenced streams were sampled over an entire application season (March-July 2012) (see **appendix A.2**). The catchments were selected based on different land use characteristics, so that all crops that are either present in high densities in Switzerland (cereals, corn, sugar beet) or have an intense pesticide application (oilseed rape, potatoes, vegetables, apple orchards, vineyards) are present at high density in at least one catchment. Twenty-eight bi-weekly (March, April and July), 40 weekly (May and June) time-proportional composite samples, and 8 grab samples (opportunistic samples during high-flow conditions) were collected. The composite samples were obtained by automatic sampling devices (Isco sampler) with a 60 minute sub-sampling interval. Subsamples were cooled during sampling; weekly or bi-weekly samples were stored at -20°C until preparation.

2.2.3. Sample Preparation

In order to enrich the analytes from all water samples, an offline solid phase extraction (SPE) method as described by Kern et al. (2009) was used. Briefly, the pH was set to 6.5-6.7 (using

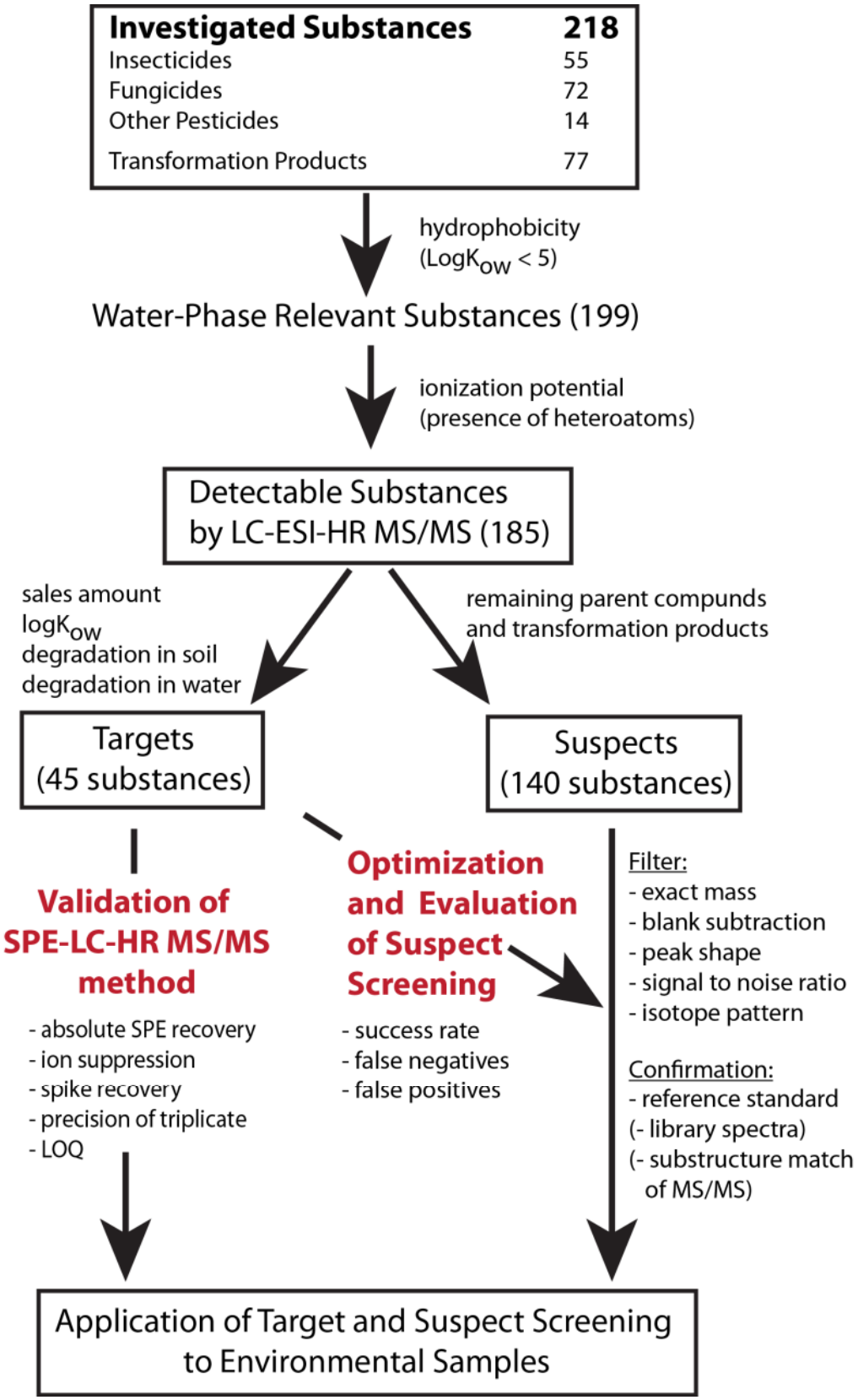

Figure 2.1. Scheme of the established suspect screening method.

formic acid or ammonia solutions), the sample was filtered (GF/F; 0.7 µm, Whatman, Amesham Place, UK) and 1 L of surface water was measured into a pre-rinsed glass bottle. Then, 200 ng of internal standard mix was added (see **appendix A.3**). The samples were passed over a multilayered cartridge containing Oasis HLB (Waters, Massachusetts, USA), Strata XAW, Strata XCW (both Phenomenex, Munich, Germany) and Isolute ENV+ (Biotage, Uppsala, Sweden), in order to enrich neutral, cationic and anionic species of a broad range of K_{ow} values. The elution of the analytes was achieved with 6 mL ethyl acetate/methanol 50:50 v:v with 0.5% ammonia and 3 mL ethyl acetate/methanol 50:50 v:v with 1.7% formic acid. The sample extracts were evaporated to 100 µL using a gentle nitrogen stream and reconstituted to 1 mL using nanopure water to give a final water:methanol ratio of 90:10 in the aliquot. The aliquots were stored at 4°C in a glass vial until analysis.

2.2.4. LC-HRMS/MS

Liquid Chromatography

20 µL of the aliquot was injected and separated on a reversed phase column (XBridge™ C18 column, 3.5 µm, 2.1 x 50 mm; Waters, Ireland). The following gradient of water (solvent A) and methanol (solvent B) both acidified with 0.1% formic acid (Merck KGaA, Darmstadt Germany) at a flow rate of 200 µL/min (Rheos 2200 pump, Flux Instruments, Switzerland) was used: 0 min 10% B, 0-4 min linear gradient to 50% B, 4-17 min linear gradient to 95% B, 17-25 min kept at 95% B, 25-25.1 min switch to 10% B, 25.1-29 min kept at 10% B. .

High Resolution Mass Spectrometry

Mass spectrometric analysis was performed on a high resolution mass spectrometer (QExactive, Thermo Fisher Scientific Corporation) with ESI. Each sample was run once each in positive and negative mode, with the following parameters. Ion source: HESI-II, spray voltage: 4000 V (+) / 3000 V (-), sheath gas flow: 40 AU, capillary temperature: 350° C, heater temperature: 40° C; Orbitrap full scan. Mass range: 100-1,000 m/z, mass resolution: 140,000, AGC target: 500,000, maximal injection time: 250 ms. Data dependent MS/MS (Top 5). Mass resolution: 17,500, microscan: 1, underfill ratio: 0.1%, isolation window: 1 m/z, dynamic exclusion: 8s. The mass accuracy was determined to be < 5 ppm for all measurements.

2.2.5. Analytical Method Validation with Target Substances

The 45 target analytes were purchased from several suppliers (see **appendix A.3**). For 13 compounds, a stable isotope-labeled analog was available for use as an internal standard. For the other compounds, an internal standard with a similar retention time was used (see **appendix A.3**). The method description for the determination of absolute SPE recovery, the ionization

suppression, the spike recovery, the precision (relative standard deviation (RSD%) of the concentration in triplicate measurements), the LOQ, and the optimized collision energy (CE) of the above described SPE-LC-HRMS method can be found in **appendix A.4.** For these evaluations, a mixture of grab samples from the five rivers was used.

2.2.6. Processing of Target Substances

All samples for the method validation and all 76 environmental samples were prepared and measured as described above. Processing of the 45 target substances was done manually using the quantitation method in ExactFinder V 2.0 (Thermo Fisher Scientific Corporation). The retention time and the isotope pattern of the targets were compared manually with a reference standard using the extracted ion chromatograms (5 ppm) and the full scan MS, respectively. Additionally diagnostic MS/MS fragments were matched with the MS/MS of reference standards. Quantification was performed with a calibration curve using internal standard calibration (in nanopure water, processed over the SPE, using an appropriate isotope labeled standard as internal standard) with following concentration levels: 0.1, 1, 2, 5, 5, 10, 25, 50, 100, 200, 500, 750 ng/L.

2.2.7. Optimization and Evaluation of the Suspect Screening with Artificial Suspects.

The efficiency of the suspect screening approach was optimized and validated with the 45 target substances, applied as artificial suspects (**Figure 2.1**). The exact mass, which was the only information a priori, was calculated from the chemical formula for the corresponding m/z of [M+H]+, [M+Na]+, [M+NH4]+, [M-H]-, [M+HCO2]- and [M+H3C2O2]-. Peak picking was performed using ExactFinder V 2.0 (Thermo Fisher Scientific Corporation) with an exact-mass filter of < 5 ppm. Blank subtraction (amplifier: 10) from a processed nanopure water sample spiked with the internal standard mix was mainly performed automatically. The optimized automatic filter criteria were: i) peak area > 5e6 (positive mode) / > 5e5 (negative mode), ii) peak score > 0.5, iii) signal to noise (S/N) > 100, isotope score > 50. ExactFinder V 2.0 fits peak shape (peak symmetry) and calculates a resulting peak score. For the calculation of the S/N, the signal height is baseline corrected whereas the noise height is the peak-to-peak- height of the baseline noise. The isotope score is a vector sum approach taking into account the deviation from the predicted intensity and exact mass of each expected isotope (ExactFinder V 2.0). The remaining peaks were checked manually for appropriate S/N and isotope pattern.

The positive findings from the suspect screening obtained for the 45 substances in the 76 composite water samples were compared to the manually-evaluated target screening results. Success rates, number of false negatives and false positives were estimated.

2.2.8. Application of Suspect Screening for Real Suspects.

The developed and validated suspect screening procedure was then applied to the remaining 140 substances. As an additional step - for further and/or unequivocal confirmation - the samples with positive findings were re-measured with a targeted MS/MS approach (HCD collision energies 15, 30, 45). If a library spectrum existed (Thermo Fisher Library Manager (Version 2.0) or MassBank, Horai et al. 2010), the MS/MS spectra of the suspects in the environmental samples were compared with those in the library. When the spectrum matched, a reference standard was purchased to unequivocally confirm the identity with MS/MS and retention time. If the spectrum did not match, no reference standard was purchased and the substance was considered a false positive. If no library spectra existed but a reference standard was commercially available, the reference standard was purchased in order to unequivocally confirm or exclude the identity of the substance. If neither a library spectrum nor a reference standard was commercially available, the MS/MS fragments were checked for their plausibility using the fragmentation prediction software MassFrontier (Version 6.0), MetFrag (Wolf et al. 2010) (settings: search ppm: 5, PubChem and ChemSpider search) or the Peak Search tool from MassBank (Horai et al. 2010) (search settings: relative intensity: 10, tolerance, 0.01, Instrument Type: ESI). For substances with a plausible MS/MS spectrum, a request was sent to the manufacturer or to other analytical laboratories.

2.3. RESULTS AND DISCUSSION

2.3.1. Substance Selection

Of the 218 investigated substances, 199 had a log K_{ow} < 5 and were therefore considered to be potentially water relevant (122 of 141 parents, 77 of 77 TPs, see **appendix A.1**). From the 199 substances with reasonable water solubility, 185 were evaluated as potentially ionizable by ESI (111 of 122 parents, 74 of 77 TPs, see **Figure 2.1**) based on the theoretical assessment of functional groups. Substances containing hetero atoms are often ionizable, as either a free electron pair is available to gain a proton to form a cation or the functional groups can lose a proton to form an anion. Pesticide TPs are expected to be detected using LC-ESI-MS with even higher efficiency than parent compounds, because functional groups such as hydroxyl- or carboxyl- groups are often added to the molecule during transformation, making them highly ionizable (Richardson and Ternes 2011). The investigated TPs are expected to be more often negatively ionizable than parents (35% and 11%, respectively) because they more often contain acidic groups after metabolism. This is in agreement with the experimental findings of Reemtsma et al. (2013b) for 150 TPs. With this careful validation step, the possibility of false negatives is reduced (Krauss et al. 2010) and only substances with a high probability of low detection limits in LC-ESI-MS are investigated. This theoretical assessment showed that within

this substance class, which covers a large structural diversity, the ionization of the majority of the substances with ESI is feasible. This is necessary for the suspect screening approach without prior purchased reference standards to be successful.

2.3.2. Validation of the Analytical Method

In order to prove that the SPE-LC-HRMS method is capable to enrich, separate and detect a broad range of polar compounds, the selected method was evaluated with 45 compounds. A summary of all method validation parameters is depicted in **Table 2.1** (all values for each substance are listed in **appendix A.5, Table A.2** and **Table A.3**, optimal HCD collision energies for the fragmentation are found in **Table A.4**, **Table A.5** and **Figure A.3**). 91% of the substances had absolute SPE recoveries in river water between 75% and 125%, independent of the substance class, showing the broad enrichment efficiency of the multilayered cartridge. For only four substances (fenpropidin, propamocarb, spiroxamine and 2-isopropyl-6-methyl-4-pyrimidinol), the recovery was between 65-75%. Ion suppression in river water was less than 50% for 87% of all substances and was between 50% and 75% for only six substances (aldicarb, clothianidin, flonicamide, methoxyfenozide, thiacloprid, 3,5,6-trichloro-2-pyridinol). Good spike recoveries between 75-125% were achieved for 87% of all compounds, showing that the method is also able to accurately quantify the substance concentrations. For cyproconazole, myclobutanil, methoxyfenozide, tebufenozide and fipronil-sulfone, spike recovery was 35-57%, and for flonicamide it was 150%. A good agreement in triplicate concentration (precision) of < 25% (RSD) was found for all substances except pymethrozine (38% RSD). All substances with a stable isotope-labeled analog showed precisions < 10%. The LOQs in river water were found to be < 5 ng/L for 70% of the analytes and > 20 ng/L for only 8 substances, indicating the high detection sensitivity for substances with a broad range of physico-chemical properties.

For chlorpyrifos, chlorpyrifos-methyl, prochloraz and diazinon, an isotope-labeled analog was used as internal standard in order to correct for the slow hydrolysis in the extract. However, as the LOQ of the substances are affected, it is necessary to either analyze them immediately after extraction or to store the extracts at -80°C to maintain the full sensitivity for those analytes. Degradation of the deuterated internal standards chlorpyrifos-D10, chlorpyrifos-methyl-D6 and diazinon-D10 led to the formation of the undeuterated TPs 3,5,6-trichloro-2-2-pyridinol and 2-isopropyl-6-methyl-4-pyrimidinol. This caused a high blank value of the two TPs in the samples. Thus, when the detection of these substances is in focus, an internal standard with a different labeling position should be used.

The developed method is thus selective and sensitive for the majority of the 45 compounds covering a large range of physico-chemical properties and can be expected to provide comparable performance characteristics with broad and efficient enrichment as well as low LOQs for the remaining 140 insecticides, fungicides, and TPs.

Table 2.1. Quality Parameters for the Target Analytes.

Parameter	Criteria	Fungicides (18)	Insecticides (19)	TPs (8)
SPE Recovery	75-125%	15	19	7
	<75%	3	0	1
	>125%	0	0	0
Ion Suppres-sion	<0%	0	2	0
	0-20%	1	2	2
	20-50%	17	10	5
	50-75%	0	5	1
Spike Recovery	75-125%	16	16	7
	<75%	2	2	1
	>125%	0	1	0
Precision (RSD %)	0-10%	15	13	5
	10-25%	3	5	3
	>25%	0	1	0
LOQ (ng/L)	0.3-1	6	3	1
	1-5	10	10	2
	5-20	0	2	3
	>20	2	4	2

TPs: transformation products, RSD: relative standard deviation

2.3.3. Suspect Screening in Real Surface Water Samples – A) Optimization using Artificial Suspects

As selectivity of the exact mass screening is essential for the success of such a strategy, a careful optimization and evaluation was performed using the 45 target substances (detected with concentrations of 0.4-660 ng/L in the 76 surface water samples) as a test set of artificial suspects. The goal was to establish the automated filter criteria to maximize the number of target detections, while minimizing the false positive peaks. Thereby, the right balance between false positives and false negatives has to be found (Mol et al. 2012). Peak picking (m/z < 5ppm) was carried out initially without any restrictions. Then, the automatic filters blank subtraction, peak area, peak score, signal to noise (S/N) and isotope score were applied in order to reduce the number of false positives. In the following, the optimized criteria are explained.

For the blank subtraction, an amplifier of 10 was found to be the optimum. However, the retention time window for the blank subtraction in the used software was very narrow (RT ± 0.1 min), and could not be adjusted. As experience showed that the retention time can shift up to 0.5 minutes from spiked nanopure samples to surface water samples during a longer sequence,

additional blank subtraction (RT ± 0.5 min with an amplifier of 10) was carried out manually in order to overcome this problem in the current study. Therefore, an adjustable retention time window for the blank subtraction or a peak alignment algorithm (using an internal standard as a reference RT) is recommended to integrate into an automatic and efficient suspect screening workflow.

The threshold for peak area filtering was optimized by applying different automated filters (1e5-1e8; see **Figure 2.2** for the results from the positive mode). We observed that 50% of the initially picked noise peaks (11,267 peaks from 45 artificial suspects in 76 surface water samples picked) could be reduced by a peak area filter of 5e6, while only 6% of the confirmed target peaks were lost (blue diamonds). As the number of false negatives is heavily biased by the concentration range of the analyzed samples, the effect on peaks close to the LOQ was investigated separately (green triangles). This showed again that 5e6 was the optimum filter criteria as only 10% of all peaks that were between LOQ and 3 times LOQ were lost. In the negative mode, 5e5 was the optimal parameter.

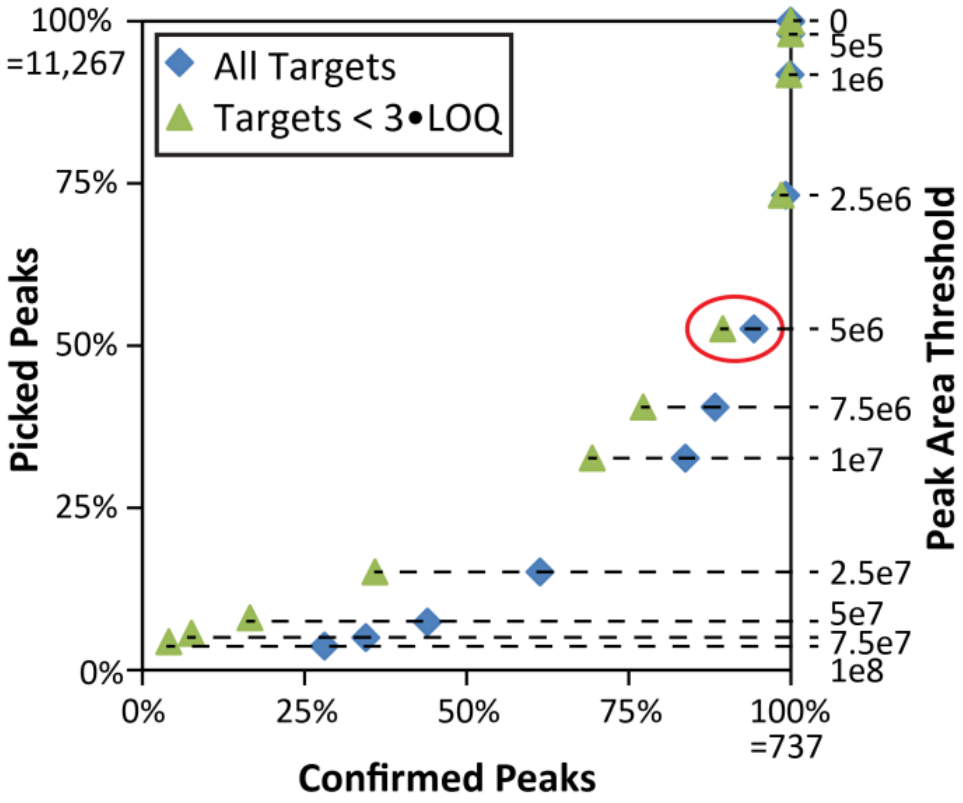

Figure 2.2. Losses of all picked peaks (45 artificial suspects in 76 surface water samples) as well as losses of all confirmed target peaks (blue diamonds) and low intense target peaks (green triangles), i.e. with signals between LOQ and 3 x LOQ, when applying different peak area thresholds in positive mode (1e5-1e8). The dots in the red circle were selected to result in the optimal parameter of 5e6.

The S/N value in the software is calculated by the ratio of the signal peak height and the peak-to-peak height of the background. The calculated S/N factor of 100 in the software seems to be an arbitrary value and corresponds to a visually derived S/N value of 10 (taking the peak-to-peak height of the background into account, see **Figure A.5A**). This value was therefore chosen as optimal parameter. However, S/N is difficult to estimate in HRMS data, especially Orbitrap data, where the noise level may be effectively zero for some masses due to automated noise subtraction during acquisition. In addition, the subtraction range of the background could not be adjusted in the software used. As a result of this difficulty, the used software algorithm could not score the S/N correctly all the time (see example in **Figure A.5B**). Therefore, some peaks had to be excluded manually afterwards.

The automatic filter criteria for the isotope score was set rather low to 50. For substances with a distinct isotopic pattern (e.g., thiacloprid, **Figure 2.3**), the isotope score was very valuable, even at trace concentrations (low ng/L range). However, the isotope score needs to address instrumental detection thresholds of the isotopes. At low intensities, it is possible that isotope peaks are missing because they fall below instrumental detection limits. The software algorithm used gave low isotope scores in such situations (see example in **Figure A.6**), although it is not possible that the isotope peak is present in this sample. More robust informatics tools are needed to address the problem of missing isotope peaks at low intensities. The score should incorporate mass accuracy, isotope intensity differences, abundance threshold and profile shape.

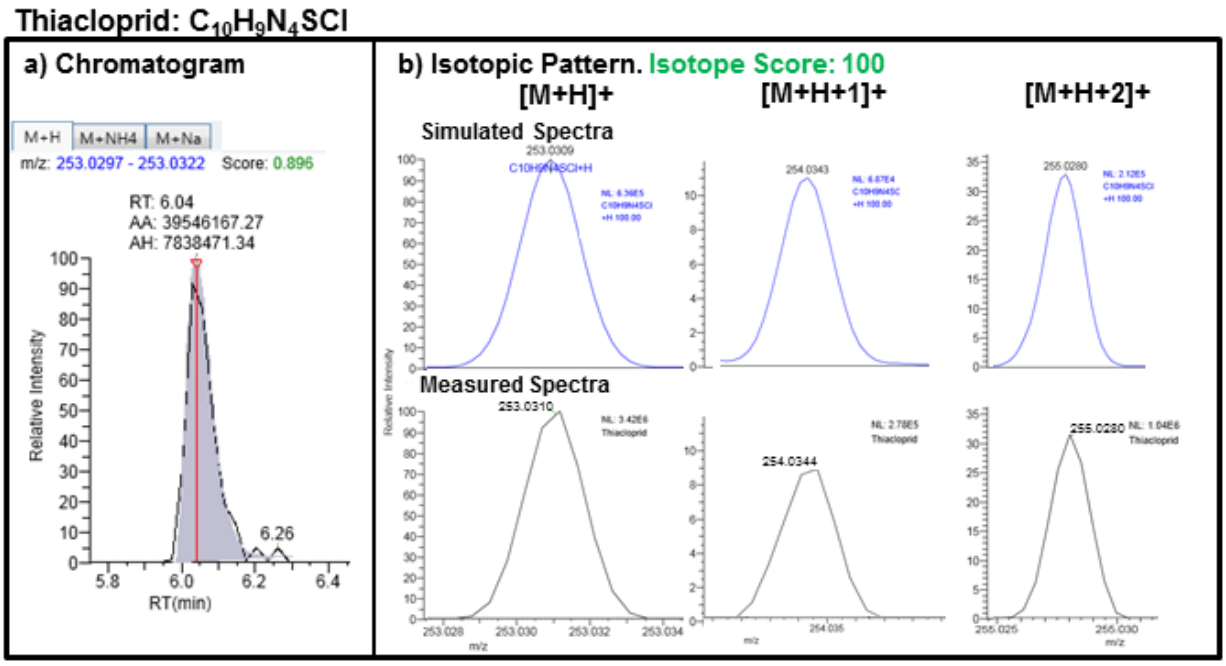

Figure 2.3. Example for a detected substance in the suspect screening: thiacloprid (15 ng/L) in the river Limpach. a) Measured chromatogram with peak fit by the software ExactFinder V 2.0 (gray shaded area). Score: peak score, RT: retention time, AA: peak area, AH: peak intensity b) isotopic pattern, blue: simulated spectra, gray: measured spectra.

2.3.4. Suspect Screening in Real Surface Water Samples – B) Evaluation Using Artificial Suspects

The optimized filter criteria were then used to validate the suspect screening method (see **Figure 2.4**) using the 45 artificial suspects in the 76 surface water samples. The blank subtraction reduced the number of initially picked peaks by 26%, and only resulted in the loss of 9% of the target peaks. Especially carbendazim, pirimicarb, fenpropidin, and pyrimethanil were affected. The high blank values of the four substances either resulted from a contamination of the internal standard or from cross-contamination of the analyte in the sequence. This problem may be avoided by improved syringe washing or the use of a higher purity internal standard and should be less important for real suspects where no analyte or internal standard is in the system. The peak area filter reduced the number of remaining peaks by 46%, resulting in only 6% false negatives. Thereby, the least sensitive pesticides at low concentrations are most affected (Mol et al. 2012). Two substances were no longer detected in samples as a result (difenoconazole and methomyl, both detected only twice in the target screening). However, all false negatives were at concentrations lower than 3 times the LOQ of the substance. With the very successful filter setting of the peak score, another 54% of the remaining peaks were reduced while only 8% of the confirmed peaks were lost. The peak score fit was good for most confirmed peaks down to the low ng/L range (see thiacloprid in **Figure 2.3**, left) and only isomeric substances with unresolved doublet peaks were missed. With the S/N criterion, only 20% of the remaining peaks were reduced automatically. The isotope score reduced 40% of the remaining peaks, while only leading to 8% false negatives. In total, of initially 15,821 picked peaks that were picked from the 45 artificial suspects in the 76 surface water samples (only exact mass as information), 89% were automatically excluded with the filtering procedure presented here (see **Figure 2.4**, large).

The remaining 1,347 peaks were checked manually for S/N (factor of 10, peak-to-peak height of background peaks was used as noise level) and isotope fit (see **Figure 2.4**). The manually inspected isotope pattern was considered to be correct when all isotopes with a theoretical intensity above 1e5 (instrument detection limit) were visible, with relative mass and intensity deviations between the theoretical and measured isotope pattern below 5 ppm and 25 %, respectively. Thereof, 570 peaks were confirmed target peaks and 700 peaks were manually excluded due to low effective S/N or isotope fit (4% of all peaks). Seventy-seven peaks (9% of all confirmed target peaks) fulfilled all filter criteria but were found to be false positive when comparing the measured retention time with reference standards. Summing up, although the manual effort is strongly reduced by the optimized parameter settings, there is still potential to reduce the number of manually checked peaks with improved software algorithms.

The overall success rate (number of detections in the suspect screening divided by the number of detections in the target analysis) was 70% (see **Figure 2.4**, large). To investigate the distribution of false negative peaks (using the optimized and validated filter criteria), the false negatives were divided into peak area categories and plotted together with the filter criteria that leaded to the

false negative peaks (**Figure 2.4**, small). Peaks with peak areas smaller than 5e6 were all false negatives due to the peak area filter criterion applied. This threshold is lower than twice the LOQ (target method) for most substances. Roughly 50% of the peaks with peak areas smaller than 1e7 were missed in the automatic screening. This was mainly due to the filter criteria peak shape, S/N and isotope score. The value 1e7 is a factor of 4 to 6 higher than the LOQ (target method) for most substances. Peaks lager than 1e7 that were missed in the automatic screening (roughly 20% of all target peaks) were to a large part missed due to the filter criterion blank subtraction. The fact that with an automated suspect screening, the LOQs are slightly higher compared to a manual target analysis was also shown by Segura et al. (2011) and Mol et al. (2012).

The parameterization of the filter criteria was shown to be optimal for the given analytical instrument (type, resolution, mass accuracy and detection response), the software used and the given sample matrix. If another instrument, software, or matrix (e.g. waste water) is used, the settings of the optimal parameters will differ and have to be re-evaluated accordingly.

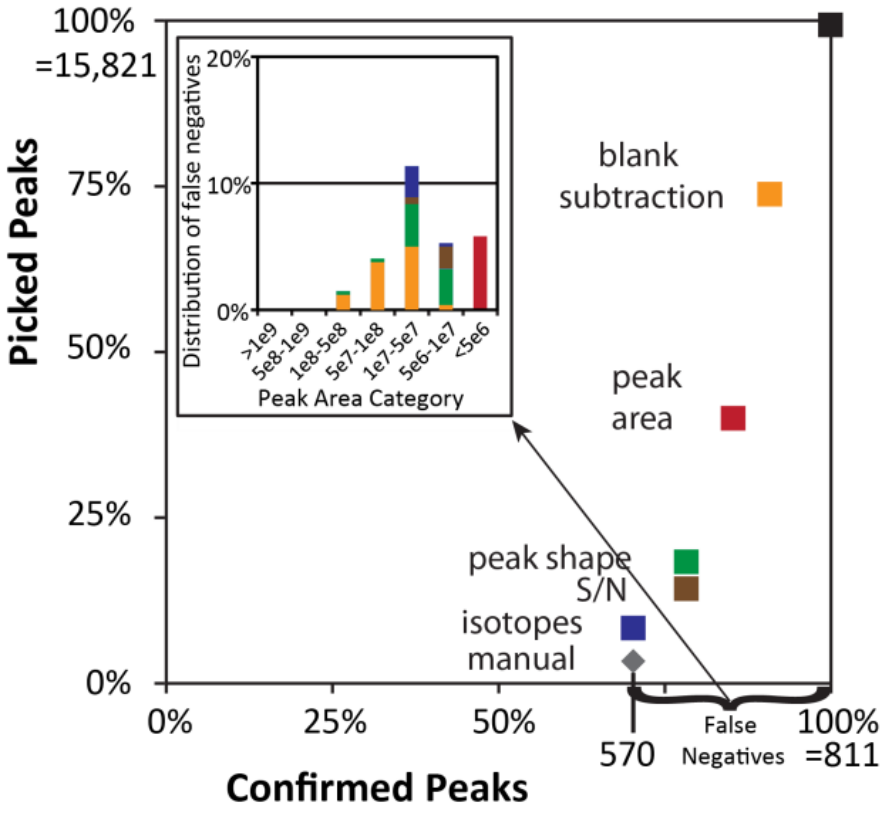

Figure 2.4. Large Figure: Reduction of all picked peaks (from 45 artificial suspects in 76 surface water samples) and losses of confirmed target peaks when applying the optimized automated filter criteria (squares) with subsequent manual check (diamond) of the remaining peaks. Small Figure: Distribution of the false negatives in the suspect screening divided into peak area categories. The percentage is relative to the total number of confirmed peak in the target method.

2.3.5. Suspect Screening in Real Surface Water Samples – C) Application with Real Suspects

In the 76 surface water samples, the optimized and validated suspect screening strategy was applied for the 140 real suspects without reference standards (74 parents, 66 TPs, see **Figure 2.1**). From initially roughly 60,000 peaks that were detected in all samples after peak picking, 90% were automatically reduced (as found in the validation).

By manually checking the remaining peaks for appropriate S/N and isotope pattern, 30 substances remained: 19 parent compounds and 11 TPs (see **Table A.6**, **Table A.7**, **Table A.8**). A library mass spectrum existed for all 19 parent compounds. Six parent compounds (30%) were found to be false positives due to non-matching MS/MS spectra (see **Table A.8**). For the other 13 parent compounds, a reference standard was purchased and all substances were unambiguously confirmed by matching retention time and MS/MS fragments (see **Table A.6**). For 3 TPs, a reference standard was commercially available and thus, purchased. Thereby, two substances were confirmed (chlorothalonil-4-hydroxy, imidacloprid-desnitro; see **Table A.6**) and one substance was found to be false positive (3-phenoxybenzoic acid; see **Table A.8**). For 8 TPs, neither a library spectra existed nor a reference standard was commercially available. Here, the obtained MS/MS spectra were compared with theoretical fragment predictions by software packages (MetFrag, MassFrontier) or the similarity of measured spectra (peak search tool in MassBank). Five substances did not show plausible fragments and were therefore set as false positives (see **Table A.8**). However, three substances showed plausible MS/MS fragments and were therefore considered as tentatively confirmed (**Table A.7**): i) 2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid (chlorothalonil TP R417888), ii) 3-(2-chlorothiazol-5-ylmethyl)-5-methyl-[1,3,5]oxadiazinan-4-ylidineamine (thiamethoxame TP NOA407475), iii) N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine (metalaxyl TP CGA62826).

In order to unambiguously confirm these three substances, for which no reference standard was commercially available, requests were sent to the manufacturer. NOA407475 and CGA62826 could be delivered free of charge by the industry (Syngenta Crop Protection, Münchwilen, Switzerland). The real identity of the substances could be confirmed by matching retention time and fragments (**Figure 2.5** for NOA407475 and **Figure A.7** for CGA62826). To our best knowledge, the MS/MS spectra of the two substances have not previously been reported in literature. The chlorothalonil TP R417888 was confirmed by matching retention time and two fragments (m/z 220, 284) with an authentic reference standard at another laboratory (Landeswasserversorgung Langenau).

These results show that instead of implementing a laborious and costly target analysis with reference standards for 140 substances, only 30 substances required manual verification. In total, only 16 commercially available reference substances were purchased to unambiguously confirm the substance identities. For TPs with plausible MS/MS spectra which were not easily accessible,

more effort could be devoted to search for or synthesis reference standards. In this case, three additional substances could be confirmed by reference standards from the industry or by the co-operation with other laboratories.

2.3.6. Unknown Identification of Frequently Detected False Positives

Attempts were made to identify the false positives that were detected frequently (see **Table A.9**), using non-target identification methods. The measured MS/MS spectra were evaluated using both MetFrag and MassBank for correct annotations and assignment of corresponding compound spectra with those fragments. The generated MS/MS of the suspected substance ―diethofencarb" in the environmental samples corresponded to the spectra of atenolol acid in the MassBank database. The presence of the pharmaceutical TP was confirmed with a reference standard. Both substances have the same molecular formula but different MS/MS fragments. Similarly, the suspect ―methiocarb-sulfone" was shown to be propachlor-ESA. The MS/MS spectra of the suspected ―pyrifenox" (M+NH4) matched with the spectra of an azole fungicide (MassBank), while in silico fragmentation with MetFrag showed that the TP prothioconazole-desethio had the best match (score 1.0, 2 explained fragments). The identity of this TP was finally confirmed with a reference standard (see **Figure A.8**).

Thus, with the additional knowledge of the MS/MS spectra of a substance, the real identity of frequently-occurring peaks can sometimes be assigned for known unknowns. Libraries with good quality MS/MS spectra containing sufficient compound information (Stravs et al. 2013) are essential to perform this search and it is crucial that such libraries are expanded to more substances in the future (Zedda and Zwiener 2012).

2.3.7. Findings in Swiss Surface Waters

Following the target analytical approach, 13 out of 19 insecticides, 17 out of 18 fungicides, and 3 out of 8 TPs were detected in at least one of the 76 composite surface water samples. The most frequently detected insecticides were pirimicarb (in 83% of the samples, 0.4-110 ng/L), diazinon (63%, 3.4-91 ng/L), fipronil (63%, 0.6-26 ng/L), thiamethoxam (58%, 3.0-57 ng/L), and thiacloprid (30%, 4.0-90 ng/L); the most detected fungicides were azoxystrobin (92%, 1.2-192 ng/L), cyproconazole (76%, 0.7-160 ng/L), carbendazim (72%, 5.0-65 ng/L), dimethomorph (70%, 2.1-130 ng/L), and propamocarb (70%, 0.4-240 ng/L). From the TPs, azoxystrobin-acid (91%, 2.4-190 ng/L) and thiacloprid-amide (20%, 1.5-9.7 ng/L) were frequently detected. The measured concentrations were generally low, 90% of all insecticide detections were below 20 ng/L, while 90% of all fungicide detections were below 50 ng/L.

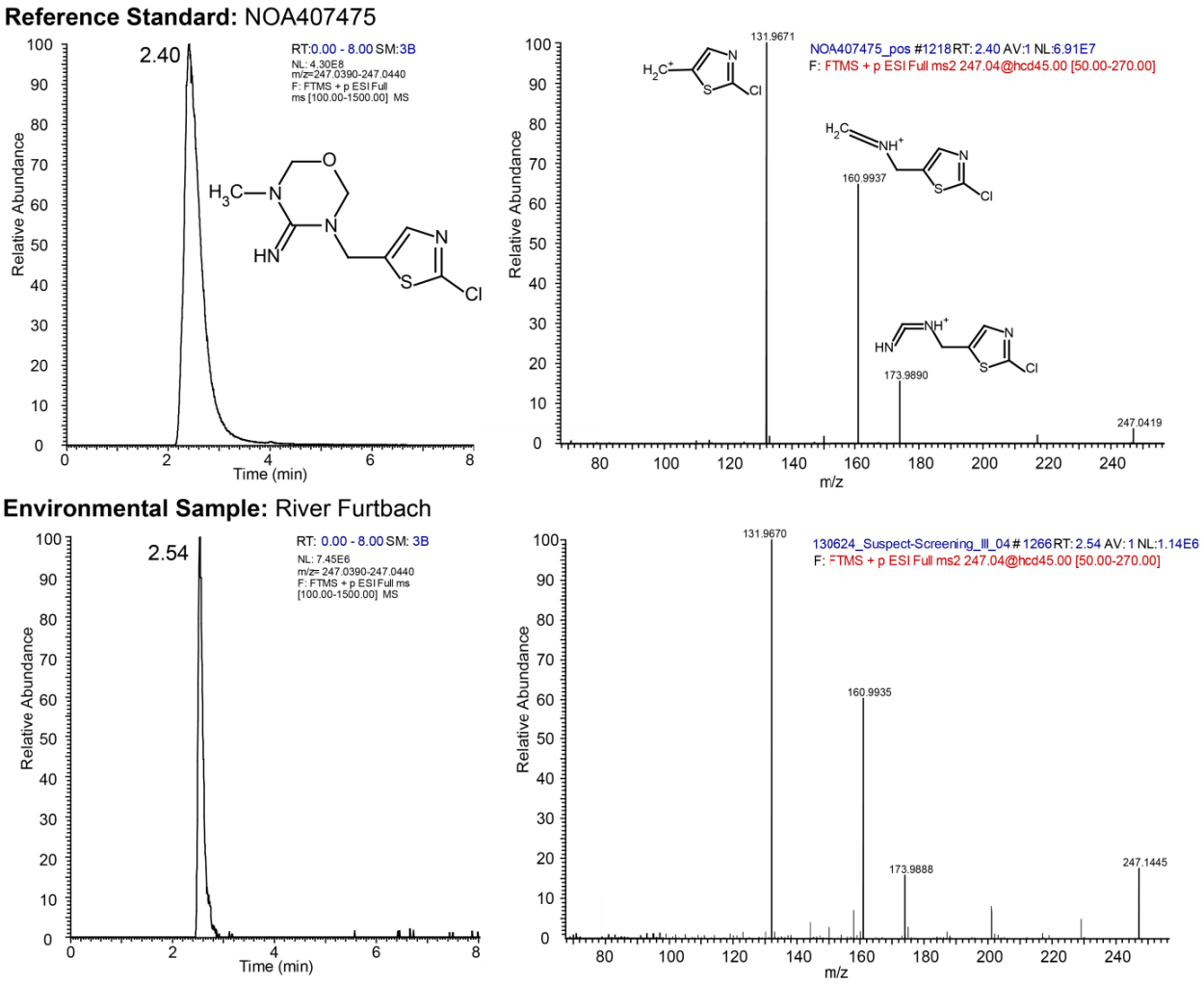

Figure 2.5. Chromatogram (left) and MS/MS (right) of the thiamethoxame TP NOA407475, in the positive ionization mode.

After applying the suspect screening approach, another 13 parent compounds (2 insecticides, 11 fungicides) and 5 TPs (2 insecticide TP, 3 fungicide TP) could be identified (see **appendix A.7**). The following substances were detected in more than 50% of the samples: i) metalaxyl (50%,), ii) chorothalonil-4-hydroxy (chlorothalonil TP R182281) (66%), and iii) 2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid (chlorothalonil TP R417888) (90%). Two other interesting TPs are imidacloprid-desnitro (in 10% of the samples) and (3-(2-chlorothiazol-5-ylmethyl)-5-methyl-[1,3,5]oxadiazinan-4-ylidineamine) (thiamethoxame TP NOA 40747, in 14% of the samples) which (to our best knowledge) have not been detected in surface water samples before. Prothioconazole-desethio, which was identified by the false positive unknown approach, was detected in 29% of all samples. This rigorous approach and careful validation has enabled the identification of many relevant parent compounds and their TPs.

2.4. CONCLUSION

A combination of non-selective enrichment/extraction together with selective and sensitive detection by high resolution mass spectrometry allowed the establishment of a suspect screening approach without the need of reference standards a priori, covering nearly all Swiss-registered insecticides, fungicides, and known TPs in surface water. The search for and purchase of reference standards was only necessary once it was quite certain that they were present in the samples investigated. Thus, the workflow presented alleviates the reference standard dilemma for suspect screening of hundreds of compounds. The hypothesis that the brute force approach to screen for compounds using only exact mass as a priori information is fast and effective was proven correct for polar pesticides and their TPs when accompanied by automatic and manual filters such as blank subtraction, intensity, peak shape, S/N and isotopic pattern. However, more sophisticated software tools for the blank subtraction, the signal to noise and the isotope score are desirable in order to reduce the subsequent manual effort. In this study, the concept is presented using Orbitrap data, but this approach should be applicable to other HRMS data with other (open access or vendor specific) software, after performing careful parameter optimization. The screening approach presented here provides fast and comprehensive results for a quantitative and qualitative assessment of insecticide and fungicide contamination in surface water samples. This approach can also be extended to other substance groups with similar chemical structures for which reference standards are not easily accessible, such as herbicides, biocides, pharmaceuticals, industrial chemicals and their transformation products.

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3. IN-SITU CALIBRATED FIELD SAMPLING RATES OF CHEMCATCHER® PASSIVE SAMPLERS FOR NEARLY 100 SUBSTANCES: RIVER CONCENTRATION DYNAMICS INFLUENCE THEIR ROBUSTNESS

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Submitted to *Water Research*

ABSTRACT

In a large field study, the performance of the Chemcatcher® passive sampler - styrenedivinylbenzene (SDB-RPS) covered by a polyether sulfone (PES) membrane - was investigated for 322 polar organic micropollutants. Five rivers with different agricultural and urban influences were monitored from March to July 2012 with two methods i) two-week time-proportional composite water samples and ii) two-week passive sampler deployment. All substances - from different substance classes with $\log K_{ow}$ -3 to 5, and neutral, anionic, cationic, and zwitterionic species - were analyzed by liquid-chromatography high-resolution tandem mass spectrometry. This study showed that SDB passive samplers are well-suited for the qualitative screening of polar micropollutants because the number of detected substances was similar (204 for SDB samples vs. 207 for composite water samples), limits of quantification were comparable (median: 1.3 ng/L vs. 1.6 ng/L), and the handling in the field and laboratory is fast and easy. In-situ calibrated sampling rates (field R_s) could be determined for 88 compounds where the R^2 from the regression (water concentration vs. sampled mass on SDB disk) was > 0.75. Substances with moderately fluctuating river concentrations such as pharmaceuticals showed much better correlations than substances with highly fluctuating concentrations such as pesticides ($R^2 > 0.75$ for 93% and 60% of the investigated substances, respectively). Flow velocity (0.05-0.8 m/s) and temperature (5-20°C) did not have a systematic influence on the field R_s. It was observed that ionic species had significantly lower field R_s than neutral species. However, a correlation between determined field R_s and $\log D_{ow}$ could only predict R_s with large uncertainties. We conclude that only substances with relatively constant river concentrations can be quantified accurately in the field by passive sampling if substance-specific R_s are determined. For that purpose, the proposed in-situ calibration is a very robust method and values can be used in future monitoring studies in rivers with similar environmental conditions.

KEYWORDS

styrenedivinylbenzene, pesticides, pharmaceuticals, liquid chromatography high resolution mass spectrometry, surface water, monitoring

3.1. INTRODUCTION

Passive sampling in the field has been shown to be an alternative to ambient water samples for monitoring polar organic micropollutants such as pesticides, pharmaceuticals, and industrial chemicals (e.g., Allan et al. 2006, Harman et al. 2012, Mills et al. 2014). Two general designs of passive samplers have been used to date for the detection of polar substances in water - the polar organic compound integrative sampler (POCIS) and the polar version of Chemcatcher®. Both types exist of a receiving material which is usually Oasis HLB for POCIS and styrenedivinylbenzene (SDB) for Chemcatcher®, often covered by a diffusive limiting membrane which is usually made of polyether sulfone (PES). Due to the relatively easy handling during deployment and extraction, passive samplers can serve as a cost-effective and robust monitoring tool. Over 300 compounds have been shown to accumulate in POCIS (e.g., >100 pesticides, >90 pharmaceuticals, >30 industrial chemicals, Harman et al. 2012). Most published work is about POCIS, with less information available about Chemcatcher® (Mills et al. 2014), although the sampler is much easier to handle. Due to the structural similarities of the receiving phases (Vermeirssen et al. 2012), it can be hypothesized that a similar number of substances can accumulate in SDB disks as in POCIS.

For a proper quantification, robust sampling rates (R_s) are critical for all sampler types (Harman et al. 2012). R_s are substance specific and there is an intense discussion underway about whether or not R_s can be predicted from physico-chemical properties. Different studies have investigated the relationship between R_s and $\log K_{ow}$ or $\log D_{ow}$, but have obtained very different results (e.g., Morin et al. 2013, Shaw et al. 2009, Vermeirssen et al. 2013).

Without a direct link to physico-chemical properties, many studies have focused on calibrating the passive samplers for single substances. Different methods exist in laboratory-scale (e.g., static renewal, static depletion, flow-through systems), but all methods yield different R_s and there is no standard calibration method yet (Mills et al. 2014, Morin et al. 2013). Because R_s are also dependent on water matrix properties such as temperature, pH, ionic strength, and dissolved organic matter (Harman et al. 2012), R_s calculated at laboratory conditions, usually done with nanopure or tap water, do not simulate field conditions very well (i.e., river water, wastewater).

To account for the influence of the water matrix, the use of flow channels which run with river water is a very good alternative (e.g., Vermeirssen et al. 2008). With this approach, different flow velocities can also be tested under controlled conditions, as flow velocities can have a large effect on R_s, too (Vermeirssen et al. 2009). However, determining R_s for a large number of substances under varying environmental conditions is time- and resource-consuming.

Methods exist that correct for varying environmental conditions such as flow velocity and biofouling in-situ, such as the use of performance reference compounds (PRCs), but their reliability for calibrating polar passive samplers has not yet been fully demonstrated (Harman et

al. 2012, Mills et al. 2014). Due to the fact that the POCIS and Chemcatcher normally have two phases (receiving phase and diffusive limiting membrane), an isotropic exchange cannot be expected, per se. Shaw et al. (2009) for example found that uptake and release is not isotropic when using SDB-RPS disks covered with a PES membrane. SDB disks alone have a two-phasic release, as shown in a previous study of our research group (Vermeirssen et al. 2013).

As an alternative to laboratory experiments or flow channel experiment that run under controlled conditions, R_s can also be calibrated in-situ by analyzing ambient water samples and passive samples taken at the same location during the same time. Harman et al. (2012) stated that when no PRC approach is possible, the calibration of R_s in-situ *"will provide the best possible approximation of time weighted average concentrations",* because it accounts for differences in water matrix and flow conditions. It is therefore hypothesized that if different rivers with varying water matrix and flow conditions are used for the calibration, all field differences will even out, so that the generated field R_s can be adapted to other rivers with similar environmental parameters.

The presented paper therefore approaches the different research gaps by a large field study that investigated a broad number of substances using SDB-RPS disks covered by a PES membrane (further referred as SDB passive sampler). The goals of the study were i) to check how many and which substances accumulate on the SDB passive sampler, ii) to compare the obtained limits of quantification (LOQ) by the SDB passive sampler with those in ambient water samples, iii) to determine field R_s for a large number of substances by in-situ calibration, iv) to assess the influence of environmental parameters on the quantity and robustness of the field R_s, and v) to test with a large data set (88 field R_s), whether $\log K_{ow}$ and $\log D_{ow}$ can predict R_s.

Using an extensive screening with liquid chromatography – high-resolution tandem mass spectrometry (LC-HR-MS/MS), 322 substances from different classes were investigated in five rivers over five months. Large temporal and spatial differences in flow velocities, temperatures, and micropollutant concentrations were present in the rivers, covering a broad range of environmental conditions. SDB disks covered by a PES membrane were used because they are easier to handle than POCIS and because the membrane increases the linear uptake window to 7-30 days for most substances (Shaw et al. 2009, Vermeirssen et al. 2012). The results will also be of further value because field R_s are provided for nearly 100 substances. These R_s can be used in future passive sampling studies in other rivers with similar environmental conditions.

3.2. MATERIALS AND METHODS

3.2.1. Field Study

A large field study investigating five medium-sized Swiss rivers (Furtbach, Limpach, Mentue, Salmsacher Aach, Surb; catchment size 38-105 km^2; stream order 3-4 after Strahler 1952) was carried out between March and July 2012 (see **Figure B.1**). The rivers had comparable sizes and were influenced by intense but varying agricultural and/or urban land use (details in **chapter 5**). In each catchment, from mid-March to mid-July 2012, nine two-week composite water samples were taken and nine Chemcatchers® (SDB-RPS disks covered by PES membranes) were deployed for two weeks. Composite water samples were taken time-proportionally by automatic sampling devices (Isco sampler), using a 60-min sub-sampling interval. The samples were cooled on-site, transported to the lab, and stored at -20°C until analysis.

Conditioned SDB passive samplers (see section 3.2.4) were deployed at the same locations during approximately the same time intervals by attaching the disks to an iron rod (see **Figure B.2**). For logistical reasons, shifts in the time intervals between the composite water samples and the passive sampler deployments were at most 1-2 days in all rivers except in the river Limpach, where it was 3-4 days. The SDB disk of the sampler was recovered after two weeks and put in 6 mL of acetone. The samples were brought to the lab and stored at -20°C until analysis. At the beginning and end of the deployment, the flow velocity was measured directly at the passive sampler. Temperature data and discharge data were provided by local authorities. Only one passive sampler was lost; therefore, 44 sample pairs were available for comparison. Additional field study information can be found in **Table B.1**.

3.2.2. Investigated Substances

In total, 322 polar to semi-polar organic micropollutants were investigated ($logK_{ow}$ values -3 to 5, neutral, anionic, cationic, and zwitterionic species). This consisted of 129 pesticides (plant protection products and biocides), 49 pesticide transformation products (TPs), 89 pharmaceuticals, 26 pharmaceutical TPs, and 29 compounds from various other classes (i.e., illicit drugs, industrial chemicals, corrosion inhibitors, artificial sweeteners, and personal care products) (see **appendix B.2**). The substances were selected due to previous detections in Swiss wastewater effluents (Schymanski et al. 2014) and included nearly all pesticides which were detected in these five rivers during a complete pesticide screening **(chapter 5)**.

3.2.3. Extraction of Composite Water Samples

Composite water samples were extracted by an offline solid phase extraction (SPE) method described in **chapter 2**. Briefly, one liter of water sample was adjusted to pH 6.5-6.7, filtered (0.7 µm pore size), and spiked with an internal standard mix containing roughly 150 different internal standards from all substance classes. The sample was enriched on a multi-layer cartridge containing Oasis HLB, Strata XAW, Strata XCW, and Isolute ENV+ in order to capture as many polar organic micropollutants as possible (neutral and ionic species). Elution was done by ethyl acetate / methanol (50% / 50%) with 0.5% ammonia followed by ethyl acetate / methanol (50% / 50%) with 1.7% formic acid. The combined extracts were evaporated to 0.1 mL by a gentle nitrogen stream and reconstituted to 1 mL using nanopure water.

3.2.4. Preparation and Extraction of Passive Sampler

Passive sampler were prepared according to Vermeirssen et al. (2009). Briefly, Empore™ SDB-RPS disks (47 mm diameter, Sigma Aldrich, Switzerland) and PES membranes (47 mm diameter, 0,45 µm pore size, Sigma Aldrich, Switzerland) were conditioned, first with methanol and then with nanopure water (30 min each) on a rotary shaker. The SDB disks were placed on a 70 by 100 mm steel plate, covered by a PES membrane, and closed by a 70 by 70 mm cover plate (see **Figure B.2**). The disks were stored in nanopure water at room temperature until deployment.

Extraction of the disks was done similar to the method described in Vermeirssen et al. (2013). Briefly, the recovered SDB disks (in acetone) were shaken on a rotary shaker for 30 min. The acetone was transferred to a new vial and 6 mL of methanol was added to the SDB disk and shaken for 30 min. The acetone fraction was reduced to roughly 1 mL using a vacuum rotator (Genevac® EZ-2, Genevac SP Scientific, UK) and the methanol fraction was added to the acetone. The solvent was filtered (PTFE, 0.45 µm pore size) and the internal standard mix was added. The extract was evaporated to 0.2 mL and reconstituted to 2 mL using nanopure water; thus, there was a dilution of factor two compared to the composite water samples.

3.2.5. Analysis

Extracts from both the composite water samples and SDB disks were measured by LC-HR-MS/MS using an XBridge C18 column for chromatographic separation and with electrospray ionization (ESI) on a QExactive MS (Thermo Fisher Scientific Corporation) for detection (details in **chapter 2**). Nanopure and methanol, both acidified with 0.1% formic acid, were used as eluents for the chromatographic gradient. The detection was done by full scan with resolution (R) of 140 000 and data-dependent MS/MS (R=17 500, Top 5) carrying out separate runs for positive and negative ionization.

3.2.6. Data Evaluation

For all substances, the number of detections in the composite water samples and the passive samplers were qualitatively checked with the *Target Screening* tool of TraceFinder 3.2 software (Thermo Fisher Scientific Corporation). In the composite water samples, all compounds were also quantified using the *Quan* tool of TraceFinder 3.2. Target compounds in the passive samplers were only quantitatively evaluated for the substances with more than ten detections in the 44 composite water samples (137 substances).

To have an environmentally representative and statistically robust dataset, only substances which fulfilled the following criteria were used for quantitative comparison of the two sampling methods: i) ≥ 10 detections in composite water samples and in the corresponding passive sampler, ii) concentration difference between maximum and minimum water concentration larger than factor three, iii) the differences in flow velocity between the samples at least 0.3 m/s, and iv) detection with both sample types in at least two rivers.

The LOQs in water sample extracts and passive sampler extracts were calculated by multiplying the LOQs determined from the calibration curve (i.e., the lowest calibration standard with signal to noise (S/N) >10 and more than five scans per peak) by the matrix factor (MF). The MF accounts for the ion suppression due to environmental matrix and was calculated from spiked samples by equation 1:

$$MF = \frac{A_{calibration\ standard}}{A_{spiked\ env.sample} - A_{unpiked\ env.sample}}, \quad (1)$$

where $A_{\text{spiked env. sample}}$ is the peak area of an environmental sample that was spiked with a certain concentration (200 ng/mL for water sample extracts, 100 ng/mL for passive sampler extracts), $A_{\text{unspiked env. sample}}$ is the peak area in the same unspiked sample, and $A_{\text{calibration standard}}$ is the peak area of a calibration standard in nanopure water with the same concentration as the spike.

Field sampling rates (field R_s, in L/d) were calculated from the slope of the regression between the average water concentration (c_w, in ng/L; from the composite water samples) and the sampled mass per day of the SDB passive sampler (m_{SDB}, in ng divided by the deployment time t, in days), see equation 2:

$$\frac{m_{SDB}}{t} = R_s \cdot c_w \quad (2)$$

3.3. RESULTS AND DISCUSSION

3.3.1. Broad Accumulation of Substances on SDB Passive Sampler

From the 322 investigated substances, 207 were detected at least once in a composite water sample and 204 were detected at least once on a SDB passive sampler. The range of substances detected was very similar in both sampling types (181 overlapping substances), but not identical. On the one hand, 23 substances had no detection in the composite water sample but at least one detection on the SDB passive sampler (e.g., diflufenican, climbazol, irbesartan, orbencarb, cocaine; see **appendix B.2**). Additionally, some substances had a much higher detection frequency on the passive sampler (e.g., difenoconazole, ketoprofen, methiocarb, metrafenone and flusilazole). Large matrix effects in the composite water sample extracts often reduced their detection frequency because of increases in the LOQs (see section 3.3.6 for comparison of LOQs). On the other hand, 26 substances were not detected on the passive sampler but had at least one detection in the composite water sample (e.g., caffeine, saccharin, terbuthylazin-desethyl-2-hydroxy, 2-naphthalinsulfonic acid). Other substances with significantly more detections in the composite water samples were eprosartan, fenpropidin, cyclamat, DMSA, and atrazine-desethyl-2-hydroxy. Many of these substances showed low accumulation on the SDB passive sampler or had high blank values in the passive sampler extract (see section 3.3.6).

These results verify the hypothesis that SDB-RPS material is able to take up a broad range of substances with large differences in physico-chemical properties. This data set - which contains the largest number of substances investigated with passive sampling to date - supports previous statements that passive sampling can successfully be used in the qualitative assessment of polar organic micropollutants in surface waters (Harman et al. 2012, Mills et al. 2014).

3.3.2. Correlation between Water Concentration and Sampled Mass on SDB Disk is Often Poor for Substances with Highly Fluctuating River Concentrations

In the next step, it was checked if a quantitative correlation could be established for those compounds which fulfilled the criteria for comparison (i.e., >10 detections, varying environmental conditions, see section 3.2.6). For these 114 substances, a regression between water concentration from the composite water samples (ng/L) and sampled mass on SDB disk (ng/d) was calculated (see **Figure 3.1** for nine examples, **appendix B.3** for all substances). For the majority of the substances (88 out of 114), either a good or fair correlation was found (R^2 > 0.9 or R^2 between 0.75-0.9, respectively, see **Figure 3.2B**).

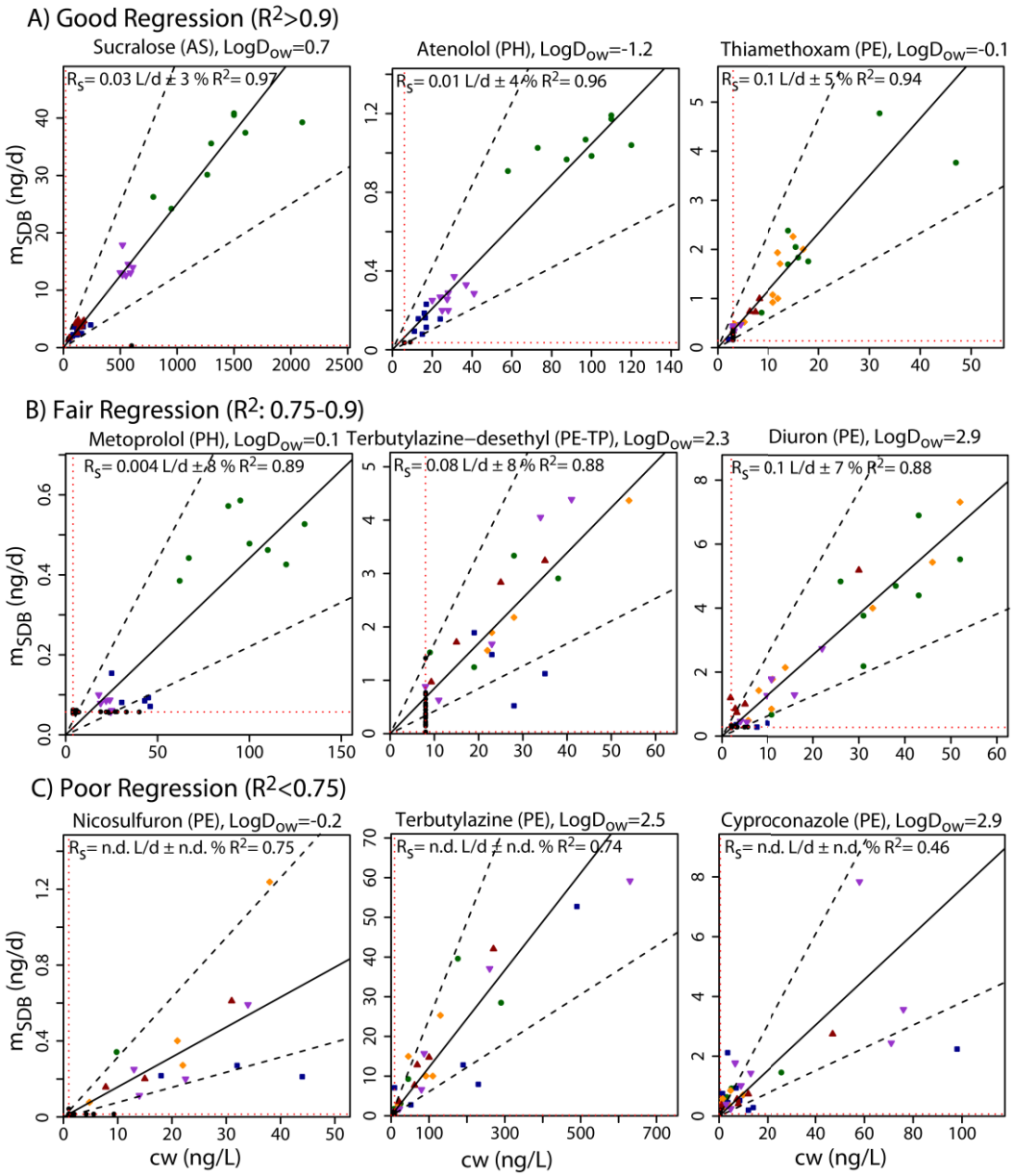

Figure 3.1. Correlation between water concentration (c_w, ng/L; from the composite water samples) and sampled mass on the SDB disk (m_{SDB}, ng/d) for nine exemplary substances with A) good regression (R^2>0.9), B) fair regression (R^2:0.75-0.9 and C) poor regression (R^2<0.75). Sampling rates (R_s) with their standard deviations were calculated from the slope of the regression for substances with R^2>0.75. Black, solid line: regression by least square method using $1/c_w$ as weighting factor, dashed lines: difference of factor two, red dotted lines: limits of quantification (LOQ) in water sample (vertical) and passive sampler extract (horizontal), see **Table 3.1**. Colors and shapes indicate different rivers (green dots: Furtbach, blue squares: Limpach, orange diamonds: Salmsacher Aach, red triangles: Mentue, purple triangles: Surb). Black dots: detections in either composite water sample or passive sampler was <LOQ. The non-detects are shown as LOQ but were not included into the regression. AS: artificial sweetener, PH: pharmaceutical, PE: pesticide, PE-TP: pesticide transformation product

It was hypothesized that substances with highly fluctuating concentrations would be more difficult to interpret because, depending on when the concentration peak occurs, the passive sampler will integrate the substances differently. For example, if the concentration peak is at the end of the deployment time, it is possible that the substance is still located in the PES membrane and has not yet diffused into the SDB material. This so called *lag-phase* can be on the order of several days, depending on the substance properties and probably also on the pore size of the membrane (Morin et al. 2013, Shaw et al. 2009, Vermeirssen et al. 2012).

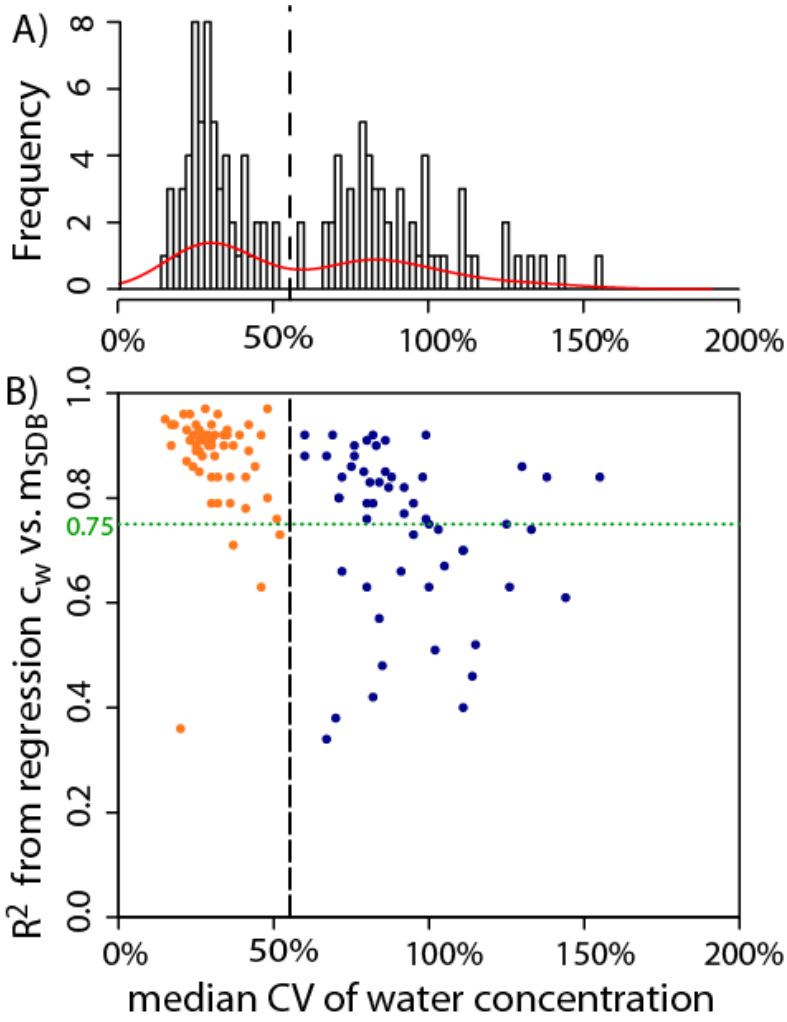

Figure 3.2. A) Distribution of the coefficient of variation (CV) (median value of the five rivers) of all 114 quantified substances. Red line is the density function, dashed line shows the division of the data set into two categories: left: moderately fluctuating substances, right: highly fluctuating substances. B) Influence of the CV on the R^2 from the regression between water concentration (c_w) and sampled mass on SDB disk (m_{SDB}, see **Figure 3.1** and **appendix B.3**). Orange dots: moderately fluctuating substances, blue dots: highly fluctuating substances. For substances below the green dotted line (R^2<0.75), no sampling rate was calculated.

The substances were therefore divided into two categories by looking at the coefficient of variation (CV) of the water concentrations in each river: „moderately fluctuating" substances and „highly fluctuating " substances (**Figure 3.2A**, **Table 3.1**). The histogram clearly indicates that the separation into these two categories at CV 53% is justified. As hypothesized, moderately fluctuating substances had significantly better regressions than highly fluctuating substances (see **Figure 3.2B**). Only four out of 59 moderately fluctuating substances had a $R^2 < 0.75$ (atrazine, chloridazone-desphenyl, thiacloprid-amide, D617). Moderately fluctuating substances with good regressions were mainly pharmaceuticals and other substances coming from wastewater effluents, but also pesticide TPs probably originating from groundwater. These substances are released into the river from a relatively constant source. In contrast, 22 out of 55 highly fluctuating substances had a poor R^2. These were mainly pesticides coming from sources showing highly dynamic concentration patterns caused by rainfall runoff events (e.g., azoxystrobin, propamocarb, thiacloprid, simeton). These results are in agreement with results from Shaw and Mueller (2009) who found in laboratory studies that it is difficult to interpret results from fluctuating concentrations.

3.3.3. Field R_s Could be Determined for 88 Substances

For all substances with an R^2 of the regression above 0.75 (55 moderately fluctuating substances and 33 highly fluctuating substances, see **Figure 3.2B**) a field R_s was calculated from the slope of the regression (**Figure 3.1**, **Table 3.1**). It has to be considered that the extrapolation of the determined values for highly fluctuating concentrations to other studies is less robust because the concentration dynamics will be different from this study (see section above).

Field R_s ranged from 0.0002 L/d (acesulfame) to 0.4 L/d (fenhexamid) with a median value of 0.07 L/d. The majority of the substances (90%) had field R_s from 0.01–0.1 L/d. This in-situ calibration is robust because it incorporates data pairs from five different rivers influenced by different land uses and with flow velocities from 0.05–0.8 m/s, temperatures from 5–20°C, and fluctuating discharge over the five month investigation period. The calibration showed that time-weighted average concentrations (TWAC) (ng/L) of the 88 substances calculated from the sampled amount and the determined field R_s showed agreement with concentrations from the composite water samples within a factor of two for 90% of all detections. In 5% of the cases, the TWAC was underestimated by more than a factor of two; in 5% it was overestimated.

Table 3.1. Determined field sampling rates (field R_s), limits of quantification (LOQ) in composite water samples and in the passive sampler extracts, as well as substance properties of all substances for which a quantitative correlation was possible (R^2>0.75).

substance name	CAS no.	substance class[b]	LOQ water (ng/L)	LOQ SDB (ng/disk)	concentration range water sample (ng/L)	detection frequency water / SDB	field R_s (L/d)[c]	standard deviation of R_s (%)	R^2 from regression	$logD_{ow}$[d] (at pH=8)	speciation (at pH=8)	input category[f]
2,4-D	94-75-7	PE	4	1	4.3-78	35/27	**0.02**	9	0.84	-1.0	anionic	HF
2,6-dichlorbenzamide	2008-58-4	PE-TP	5	0.5	7.5-48	44/44	**0.06**	4	0.95	0.4	neutral	MF
4-acetamidoantipyrin	83-15-8	PH-TP	5	1	3.2-710	38/42	**0.06**	5	0.90	-0.1	neutral	MF
4-formylaminoantipyrin	1672-58-8	PH-TP	1	0.5	1.9-210	37/41	**0.09**	6	0.90	0.5	neutral	MF
acesulfame	55589-62-3	AS	8	1.5	34-16 000	44/25	**0.0002**	6	0.94	-1.5	anionic	MF
amisulpride	71675-85-9	PH	2	0.5	2.3-47	26/24	**0.01**	7	0.88	1.1	neutral	MF
atenolol	29122-68-7	PH	6	0.5	8.9-120	26/25	**0.01**	4	0.96	-1.2	cationic	MF
atenolol acid	56392-14-4	PH-TP	6	0.5	27-480	36/33	**0.003**	5	0.93	-1.2	zwitterionic	MF
atrazine-2-hydroxy	2163-68-0	PE-TP	2	1	3.3-28	44/44	**0.03**	6	0.86	2.1	neutral	MF
atrazine-desethyl	6190-65-4	PE-TP	6	2	5-34	44/44	**0.1**	5	0.91	1.5	neutral	MF
azoxystrobin acid	1185255-09-7	PE-TP	2.5	2	2.4-140	43/44	**0.07**	8	0.78	0.3	anionic	MF
benzotriazole	95-14-7	CI	180	10	190-2 100	23/44	**0.04**	5	0.94	1.4	neutral	MF
benzoylecgonin	519-09-5	ID-TP	1	0.5	2.3-43	23/20	**0.03**	4	0.97	-0.6	zwitterionic	MF
bezafibrat	41859-67-0	PH	1	0.6	3.5-24	17/20	**0.05**	7	0.92	0.5	anionic	HF
bicalutamide	90357-06-5	PH	1	0.5	0.5-6.8	16/22	**0.1**	10	0.86	2.3	neutral	MF
candesartan	139481-59-7	PH	10	0.5	15-140	28/42	**0.05**	4	0.96	-0.5	anionic	MF
carbamazepine	298-46-4	PH	2	1	6-110	35/41	**0.1**	7	0.85	2.5	neutral	MF
carbamazepine-10,11-dihydro-10,11-dihydroxy	58955-93-4	PH-TP	5	5	9.7-200	35/33	**0.08**	6	0.90	-0.2	neutral	MF
carbamazepine-10,11-epoxide	36507-30-9	PH-TP	1	1	1.1-31	33/32	**0.1**	5	0.92	1.0	neutral	MF
carbendazime	10605-21-7	PE	5	1	2.9-65	36/44	**0.09**	7	0.86	1.5	neutral	HF
cetirizine	83881-52-1	PH	25	6	24-320	18/19	**0.03**	7	0.92	0.5	zwitterionic	MF
chloridazon-methyl-desphenyl	17254-80-7	PE-TP	7	0.5	50-180	44/44	**0.02**	5	0.91	-1.4	neutral	MF
chlortoluron	15545-48-9	PE	2	0.2	1.8-20	14/31	**0.09**	15	0.76	2.5	neutral	HF
clarithromycin	81103-11-9	PH	1	1.5	1.1-120	35/25	**0.05**	7	0.88	2.7	cationic/neutral[e]	HF
clindamycin	18323-44-9	PH	1	0.5	1.4-27	19/18	**0.06**	12	0.80	0.9	cationic/neutral[e]	MF
clopidogrel carboxylic acid	144457-28-3	PH	1	0.5	1.5-56	35/34	**0.03**	5	0.92	0.9	zwitterionic	MF
diazinon	333-41-5	PE	3	0.6	1.3-43	27/44	**0.1**	9	0.83	3.7	neutral	HF
diclofenac	15307-86-5	PH	2	2	1.4-320	38/39	**0.06**	4	0.93	0.9	anionic	MF
DEET (diethyltoluamide)	134-62-3	P	7	25	4.3-520	39/20	**0.1**	7	0.90	2.2	neutral	HF
dimethachlor	50563-36-5	PE	1	0.5	1.1-5.6	14/34	**0.1**	12	0.84	2.2	neutral	MF
dimethenamide	87674-68-8	PE	1	0.3	1.1-14	22/38	**0.1**	9	0.86	2.2	neutral	HF
dimethoat	60-51-5	PE	3	2	3.5-21	11/29	**0.1**	10	0.90	0.7	neutral	HF
dimethomorph	110488-70-5	PE	2	2	2.1-61	33/33	**0.08**	6	0.91	2.7	neutral	HF
diuron	330-54-1	PE	2	4	1.1-52	39/33	**0.1**	7	0.88	2.9	neutral	HF
EDDP (2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidin)	30223-73-5	ID-TP	2.5	0.1	1.7-33	16/28	**0.03**	9	0.89	3.0	cationic	MF
epoxiconazole	133855-98-8	PE	4	0.6	4.4-64	15/41	**0.08**	13	0.79	3.3	neutral	HF
ethofumesate	26225-79-6	PE	3	1.5	3.6-290	38/41	**0.08**	8	0.79	2.7	neutral	HF
fenamidone	161326-34-7	PE	1	1	0.5-18	20/21	**0.2**	10	0.84	2.8	neutral	HF
fenhexamid	126833-17-8	PE	3	3	1.1-23	12/15	**0.4**	8	0.92	4.1	anionic	HF
fenofibric acid	42017-89-0	PH-TP	1	0.5	0.7-3.4	22/21	**0.08**	9	0.85	0.8	anionic	MF
fipronil	120068-37-3	PE	0.5	0.6	0.5-14	29/36	**0.1**	11	0.76	3.8	neutral	MF
fluconazole	86386-73-4	PH	1	0.5	1.4-33	29/34	**0.09**	5	0.92	0.3	neutral	MF
flufenacet	142459-58-3	PE	3	0.5	3.6-290	23/36	**0.1**	9	0.84	3.2	neutral	HF
flufenacet-ESA	201668-32-8	PE-TP	3	0.5	1.6-38	27/32	**0.02**	10	0.79	-1.2	anionic	HF
gabapentin	60142-96-3	PH	90	2.5	60-390	17/35	**0.005**	5	0.96	-1.3	zwitterionic	MF
hydrochlorothiazide	58-93-5	PH	2	0.5	2.4-380	38/42	**0.05**	3	0.96	-0.1	neutral	MF

Table 3.1. continuation.

substance name	CAS no.	subtance class[b]	LOQ water (ng/L)	LOQ SDB (ng/disk)	concentration range water sample (ng/L)	detection frequency water / SDB	field R_s (L/d)[c]	standard deviation of R_s (%)	R^2 from regression	$logD_{ow}$[d] (at pH=8)	speciation (at pH=8)	input category[f]
indomethacine	53-86-1	PH	1	0.5	1.1-19	33/29	**0.07**	6	0.92	0.1	anionic	MF
isoproturon	34123-59-6	PE	1	1	1.1-350	44/44	**0.08**	6	0.86	2.5	neutral	HF
lamotrigine	84057-84-1	PH	2	0.5	6.1-220	35/36	**0.07**	5	0.91	1.0	neutral	MF
levamisol	14769-73-4	PH	1	0.5	0.6-8.7	15/13	**0.1**	7	0.93	1.8	neutral	MF
levetiracetam	102767-28-2	PH	15	1.5	9-95	31/32	**0.02**	5	0.93	-0.5	neutral	MF
lidocaine	137-58-6	PH	1	2	2.4-55	35/27	**0.09**	6	0.92	2.6	cationic/neutral[e]	MF
mecoprop	16484-77-8	PE	1	0.5	4.9-470	44/43	**0.03**	6	0.85	-0.5	anionic	HF
mefenamic acid	61-68-7	PH	4	1	2.2-95	31/37	**0.06**	7	0.86	2.0	anionic	MF
metamitron	41394-05-2	PE	10	2	48-1 500	28/44	**0.06**	8	0.84	0.9	neutral	HF
metamitron-desamino	36993-94-9	PE-TP	8	0.5	8.4-680	38/44	**0.05**	5	0.91	1.4	neutral	HF
metazachlor	67129-08-2	PE	2	0.5	1.4-180	23/30	**0.2**	6	0.92	2.5	neutral	HF
metazachlor-ESA	172960-62-2	PE-TP	7	0.5	11-520	44/43	**0.04**	5	0.92	-0.7	anionic	MF
metformin	657-24-9	PH	50	1	49-2 600	38/42	**0.004**	7	0.84	-5.4	cationic	MF
methyl-benzotriazole	136-85-6	CI	50	10	27-16 850	37/44	**0.05**	10	0.75	1.7	neutral	HF
metolachlor-ESA	171118-09-5	PE-TP	2	0.5	36-310	44/43	**0.04**	5	0.90	-0.3	anionic	MF
metolachlor-morpholinon	120375-14-6	PE-TP	1	0.5	2.2-10	15/32	**0.1**	12	0.82	2.5	neutral	HF
metolachlor-OXA	152019-73-3	PE-TP	9	1	9-130	36/43	**0.03**	8	0.83	-0.6	anionic	HF
metoprolol	37350-58-6	PH	4	0.8	2.3-130	35/19	**0.004**	8	0.89	0.1	cationic	MF
N4-acetyl-sulfamethoxazole	21312-10-7	PH-TP	3	2	3-26	22/21	**0.03**	8	0.88	-0.1	anionic	MF
napropamide	15299-99-7	PE	6	0.5	7-78	17/38	**0.1**	7	0.92	3.3	neutral	HF
naproxen	22204-53-1	PH	10	2.5	26-87	21/26	**0.07**	6	0.92	-0.4	anionic	MF
O-desvenlafaxine + tramadol[a]	93413-62-8 27203-92-5	PH	4	0.5	10.5-340	35/35	**0.009**	6	0.89	1.2 + 1.6	cationic + cationic	MF
oxazepame	604-75-1	ID	1	0.2	1.1-58	34/35	**0.1**	4	0.94	2.2	neutral	MF
pethoxamide	106700-29-2	PE	1	0.5	1.0-80	19/24	**0.1**	10	0.84	3.0	neutral	HF
phenazone (antipyrene)	60-80-0	PH	2	2	2.0-8.0	14/16	**0.08**	8	0.92	0.4	neutral	MF
pirimicarb	23103-98-2	PE	0.4	1	0.2-48	37/35	**0.1**	8	0.83	1.7	neutral	HF
prometryn + terbutryn[a]	7287-19-6 886-50-0	PE	2	2	1.4-34	17/19	**0.1**	13	0.79	3.5 + 3.7	neutral + neutral	MF
propachlor	1918-16-7	PE	1	2.5	1.4-220	13/13	**0.2**	15	0.76	1.6	neutral	HF
propazin-2-hydroxy+ terbutylazin-2-hydroxy[a]	7374-53-0 66753-07-9	PE-TP	4	0.7	2-45	35/43	**0.04**	8	0.83	0.4 + 0.3	neutral + neutral	MF
propiconazole	60207-90-1	PE	3	0.6	1.9-65	28/44	**0.1**	9	0.81	3.7	neutral	HF
sitagliptin	486460-32-6	PH	10	0.5	11-160	20/35	**0.09**	7	0.91	0.4	cationic	MF
S-metolachlor	87392-12-9	PE	1	1	2.6-960	44/44	**0.1**	8	0.77	3.1	neutral	HF
sotalol	3930-20-9	PH	7	0.5	4.1-78	27/34	**0.01**	7	0.87	-1.6	cationic	MF
sucralose	56038-13-2	AS	20	5	49-2 100	35/34	**0.03**	3	0.97	0.7	neutral	MF
sulfamethazine	57-68-1	PH	2	0.5	1.2-11	29/42	**0.1**	8	0.84	-0.1	anionic	MF
sulfamethoxazole	723-46-6	PH	6	2	5.5-82	28/35	**0.04**	6	0.90	-0.1	anionic	MF
sulfapyridine	144-83-2	PH	2	0.1	2.1-43	23/40	**0.1**	6	0.92	0.1	anionic	MF
tebuconazole	107534-96-3	PE	2	1	1.9-86	33/43	**0.09**	8	0.82	3.7	neutral	HF
terbutylazin-desethyl	30125-63-4	PE-TP	8	0.5	5-54	21/43	**0.08**	8	0.88	2.3	neutral	HF
thiamethoxame	153719-23-4	PE	3	2	2.2-47	26/40	**0.1**	5	0.94	-0.1	neutral	MF
trimethoprim	738-70-5	PH	2	0.2	1.5-33	24/19	**0.03**	7	0.92	0.9	neutral	MF
venlafaxine	93413-69-5	PH	2	0.5	2.4-94	35/24	**0.01**	7	0.91	1.8	cationic	MF

[a] due to the same parent mass and retention time, substances were quantified as the sum, [b] substance class: PE: pesticide, PH: pharmaceutical, PE-TP: pesticide transformation product, PH -TP: pharmaceutical transformation product, ID: illicit drug, ID-TP: illicit drug transformation product, CI: corrosion inhibitor, AS: artificial sweetener, [c] for highly fluctuating substances (see last column), adaptations to other rivers are less robust, see section 3.3.2, [d] for neutral species, experimental $logK_{ow}$ values were taken from www.chemspider.com, for ionic species, $logD_{ow}$ at pH 8 were predicted by Jchem for Excel (Version 5.11.5.906), [e] both species were considered when the minor species at pH=8 accounted for more than 25%, [f] MF: moderately fluctuating substances, HF: highly fluctuating substances, category selection, see **Figure 3.2**.

For 23 substances, the calculated field R_s from this study could be compared with R_s calculated from previous studies, including two previous investigations carried out by our research group, which were done in a flow channel using river water at 13 cm/s and 8 cm/s (Vermeirssen et al. 2009 and Vermeirssen et al. 2012, respectively), and two studies from another research group which used large calibration chambers with tap water at 14 cm/s (Shaw et al. 2009, Stephens et al. 2009). The comparison showed that the reported R_s agreed with the determined field R_s within a factor of two for 19 of the 23 substances (see **Figure B.4**). Only diazinon, diuron, sulfamethoxazole, and mecoprop showed larger differences. The significantly higher values for diazinon and diuron in our study can be explained by the use of a PES membrane with a larger pore size compared to the other studies (0.45 µm compared to 0.1 µm). Both substances have a long lag-phase because a large fraction is sorbed to the PES membrane (Vermeirssen et al. 2012). The differences for sulfamethoxazole and mecoprop can be explained by different deployment times in the experiments. Both substances have a short linear uptake phase of only eight to ten days (Vermeirssen et al. 2012).

The results show that the determined field R_s - at least for moderately fluctuating substances - can be used for passive sampling studies in other rivers that have similar environmental conditions (i.e., flow velocity, temperature, pH, salinity).

3.3.4. Flow Velocity and Temperature Have no Systematic Impact on the Field R_s

Next, we checked the influence of environmental parameters on the field R_s. Specifically, the average flow velocity (measured at the beginning and end of the deployment) and the mean temperature during each deployment were correlated with the ~~*local*~~ ~~R_s~~, i.e., the R_s that was calculated from each sample that had both a detection in the composite water sample and in the passive sampler.

No correlation between flow velocity and the ~~*local*~~" R_s was found for the majority of the substances (see **Figure B.5A**). This is in agreement with a previous study from our research group (Vermeirssen et al. 2009). There, we found that the increase in R_s from the flow velocity 0.1 m/s to 0.4 m/s is only 20% if the SDB disk is covered by a PES membrane. Only at lower flow velocities are the effects of flow on uptake more pronounced. Therefore if passive samplers are used in rivers where the flow velocities are usually below 0.1 m/s, changes in flow velocities will become important (Vermeirssen et al. 2009).

When only temperature was taken into account, no correlation could be found for most substances (see **Figure B.5B**). Because an increase in temperature should lead to a maximum increase in R_s of a factor of two (Harman et al. 2012), it can be expected that this effect is overshadowed by other environmental changes such as fluctuating concentrations or biofouling.

However, a slight systematic influence of the environmental conditions on R_s can be seen when all measured variables are taken into account using a principal component analysis (PCA). Samples with low flow velocities, low temperatures, and low discharge (category 1 from the PCA, see **Figure B.3**) had lower ~~"~~*local*" R_s compared to samples with high flow velocities, high temperatures, and high discharge (category 5) (see **Figure B.5C**). The trend is not very pronounced however and the variations between the substances and between the samples is very large. Thus, it can be concluded that although environmental factors have a large influence on the local R_s, the flow velocity and temperature showed no systamatic trend in the rivers investigated.

Other environmental factors such as dissolved organic matter and natural organic matter have previously been shown to have little or no effects on R_s (Harman et al. 2012) and were therefore not investigated. Although salinity and pH may have an influence on R_s (e.g., changing speciation, see next section), they could not be considered in this study because they were very similar between the five rivers.

3.3.5. $LogD_{ow}$ Can only Predict R_s with Large Uncertainties

It would be desirable to predict R_s from physico-chemical properties of the substances to eliminate the need for experimental determination of R_s in either laboratory or field studies. Many studies have tried to correlate R_s of POCIS or Chemcatcher® with $logK_{ow}$ or $logD_{ow}$, but with differing results. Shaw et al. (2009) found no influence at all, Gunold et al. (2008) found a large scattering, MacLeod et al. (2007), Thomatou et al. (2011) and Morin et al. (2013) found different non-linear regressions, and our research group recently found that a linear regression produces a reasonable fit (Vermeirssen et al. 2013). Several studies state that it is important to correct for the speciation of the substances. Unfortunately, most of these studies only included 8-22 substances in their analysis, which makes it difficult to generalize the respective findings. Because in this study field R_s were determined for 88 substances, this large data set was used to check the correlation between R_s and $logK_{ow}$ or $logD_{ow}$.

It was found that a linear regression of the field R_s with $logD_{ow}$ was slightly better than the linear regression with $logK_{ow}$, but still poor ($R^2 = 0.37$ vs. $R^2 = 0.10$, see **Figure 3.3** and **Figure B.6**). Polar ionic species with low $logD_{ow}$ had in general lower R_s than neutral species with higher $logD_{ow}$. Half of all neutral substances (at pH 8) had $R_s \geq 0.1$ L/d (**Table 3.1**, **Figure 3.3**). For the ionic species, the opposite trend was visible; 45% of all cationic substances, 64% of the anionic substances, and all zwitterionic species had $R_s < 0.05$ L/d. This is also in agreement with results from Li et al. (2011) who found higher R_s by POCIS for the neutral form of a substance compared to the ionic form. It is unclear why fenhexamid, which is mainly anionic at pH 8, had by far the highest R_s. One possible explanation is the high hydrophobicity (predicted logDow: 4.1) which might compensate for the charge effect.

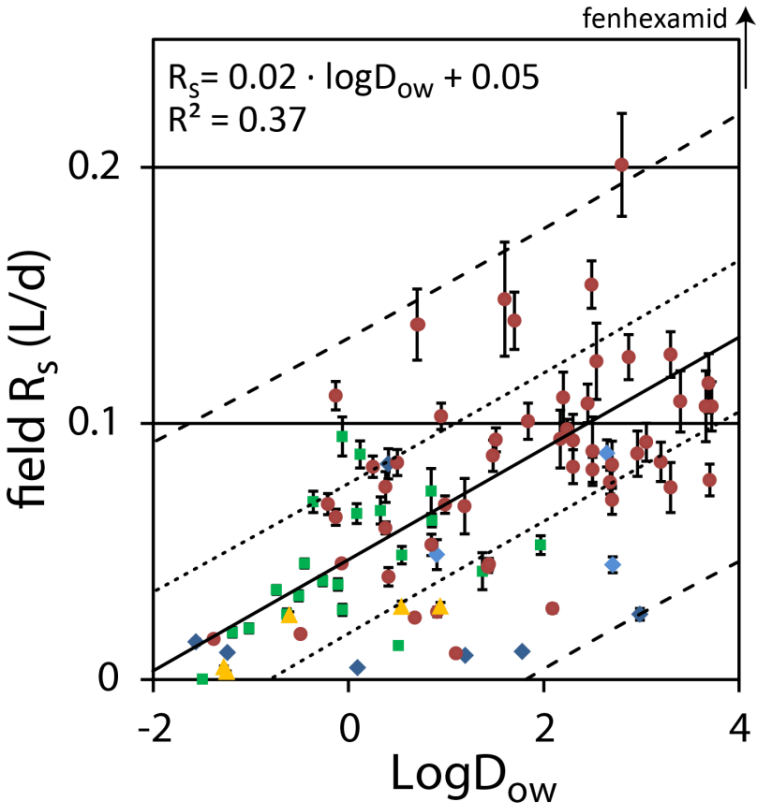

Figure 3.3. Correlation between $logD_{ow}$ and determined field sampling rates (field R_s, see **Table 3.1**) for the 88 substances. Different speciation at pH 8 are denoted in different colors (red dots: neutral species, green squares: anionic, dark blue diamonds: cationic, light blue diamonds: cationic/neutral, orange triangles: zwitterionic). If the minor species was <25%, only the major species at pH=8 is indicated. Black line shows the linear regression curve by least square method. Dashed line is the 95% prediction interval, dotted line the 50% prediction interval. The error bars show the uncertainties of R_s (see **Table 3.1**). Uncertainties from the $logD_{ow}$ predictions could not be quantified and were therefore not included.

Although it seems that some correlation with $logD_{ow}$ is possible, a prediction of R_s can only be done with large uncertainties (**Figure 3.3**, see 95% and 50% prediction intervals). It is also important to mention that $logD_{ow}$ values - especially for ionic species - inherently have large uncertainties, since they are calculated from the predicted speciation at the given pH based on the chemical structure. In addition, it has to be considered that the field R_s used for the correlation are influenced by the environmental conditions during the sampling period. Our previous studies, which were conducted under more controlled conditions (i.e., flow channels) gave a better correlation for 22 substances using the same sampler type (i.e., SDB-RPS covered with a PES membrane, Vermeirssen et al. 2012). We also previously found that the correlation was even better for SDB disks without PES membranes (Vermeirssen et al. 2013) for which no lag phase has to be taken into account.

Nevertheless, since there was only a poor correlation with $logD_{ow}$, the results clearly show that hydrophobicity is not the only parameter that determines R_s. Due to the diversity of functional groups of the substances and of the receiving phase as well as the additional transport mechanisms across the PES membrane, this is reasonable. It is therefore important to gain a better mechanistic understanding about the transport over the PES membrane and the sorption to the receiving phases for both neutral and ionic species under controlled conditions.

For practical implications, for new compounds with no experimentally derived R_s, we propose as first estimation to assume an average R_s of 0.05 L/d for very polar anionic substances and an average R_s of 0.1 L/d for semi-polar neutral substances, and to consider larger uncertainties (see **Figure 3.3**).

3.3.6. Detection Limits in Composite Water Samples and Passive Samplers Are Comparable

The availability of field R_s for 88 substances allowed for the calculation of an LOQ_{SDB} (in ng/L) and a comparison with the LOQ determined in the composite water samples (LOQ_w). The LOQ_{SDB} was calculated by dividing the LOQ from the analytics (in ng/disk, see section 3.2.6 and **Table 3.1**) by the determined field R_s and by an average deployment time of 14 days. A comparison with the LOQ_w showed that the average LOQs were comparable (median LOQ_{SDB}: 1.4 ng/L, median LOQ_w: 1.6 ng/L), but there were large differences between the single substances (**Figure 3.4**). For 51 substances the LOQ_{SDB} was lower, and for 37 substances the LOQ_w was lower.

The LOQs from both sampling types is mainly determined by the enrichment factor (EF) and the MF, if there is no blank value in the extracted chromatogram. The EF in the composite water sample extracts was 1000; in the passive sampler extracts it is determined by R_s. The median field R_s of the 88 substances was 0.07 L/d (see **Table 3.1** and **Figure B.7**), which corresponds to an EF of 500 (14 day deployment, dilution of factor two compared to water samples, see section 3.2.4). The average EF for substances measured in the composite water samples was therefore twice as high as for compounds measured in passive sampler extracts. At the same time, the MF in the water samples were on average also twice as high as in the passive sampler extracts (see **Figure B.8**). This counteracts the advantage of higher EF and therefore explains why, on average, the LOQs of both methods are quite similar.

Five substances had significantly higher LOQs in the water samples than in the passive sampling extracts. Candesartan, napropamide, and tebuconazole showed unusually high matrix effects in the water sample extracts (see **Figure B.8**); benzotriazole had a relatively high blank value in the water sample extracts; and diazinon was partially hydrolyzed in the water sample extracts during storage and extraction. On the contrary, the cationic beta-blockers atenolol, metoprolol, and

sotalol, as well as the anionic artificial sweetener acesulfame had much higher LOQs with the SDB passive sampler due to very low R_s (**Figure 3.4**).

Previous studies that compared the performance of POCIS with water samples came to the conclusion that better LOQs were achieved by the passive samplers (Alvarez et al. 2005, Lissalde et al. 2011). A comparison is always tricky because LOQs are also dependent on the method used for extracting and analyzing the water samples (e.g., the SPE material and the EF), as well as on the size and deployment time of the passive sampler. Our procedure for water sample enrichment included different SPE materials for the enrichment of neutral, anionic, and cationic substances whereas other analyses normally only use Oasis HLB which is mainly for the enrichment of neutral substances. In any case, it is possible that LOQs of POCIS are better than LOQs from SDB passive samplers because the surface area of POCIS is 3.6 times larger and uptake kinetics are similar to SDB (Vermeirssen et al. 2012). However, POCIS may also sample more matrix which would minimize this advantage. For an accurate comparison, the influence of the MF in POCIS and SDB extracts need to be systematically tested for a large number of substances.

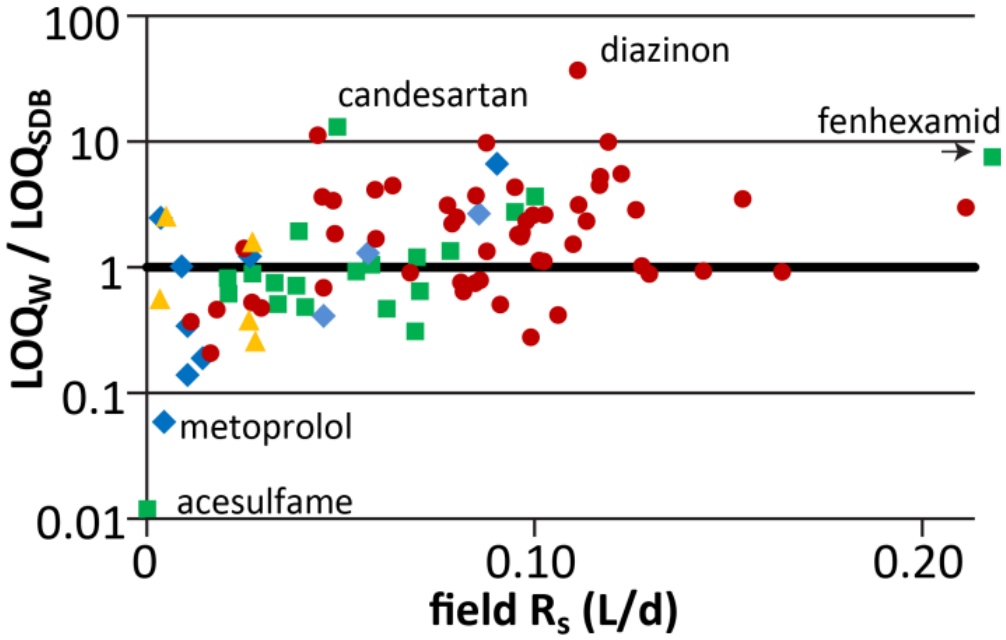

Figure 3.4. Comparison of the limits of quantification (LOQ) found in the composite water samples (LOQw, ng/L) and by the SDB passive sampler (LOQ_{SDB}, ng/L), depending on the determined field sampling rate (field R_s, see **Table 3.1**). Different speciation (at pH 8) are denoted in different colors (red dots: neutral species, green squares: anionic, dark blue diamonds: cationic, light blue diamonds: cationic/neutral, orange triangles: zwitterionic). Black solid line shows were the LOQs are equal. Dots above the black line are substances where the LOQ by the SDB passive sampler is lower than the LOQ in the water sample.

3.4. CONCLUSIONS

The large field study investigating 322 substances confirmed that the Chemcatcher® passive sampler (SDB-RPS disks covered by a PES membrane) are perfectly suitable for qualitative screening of polar micropollutants in river waters. Over 200 substances were accumulated and could be detected in at least one sample. The field deployment and analytics is easier and faster compared to water sampling with automated instrumentation, which is especially valuable in remote locations. The number of detections and LOQs for each substance were in general comparable, although some substances were better detected in the composite water samples, while others were better with the passive samplers.

The majority of the substances showed a good correlation between water concentration and sampled mass on the SDB disk. However, sampled mass of substances with highly fluctuating concentrations in the river often showed poor correlations. For this reason interpretation of passive sampler results for compounds which originate from sources with a changing release pattern (e.g., pesticides from agricultural fields) needs to be done with much more caution than for substances with a more consistent release pattern (e.g., pharmaceuticals originating from wastewater effluents).

This study showed that the in-situ calibration of passive samplers is feasible and field R_s were determined which are now available for use in other studies. The field R_s for the moderately fluctuating substances are robust because very diverse samples were used (different rivers, different temperatures, fluctuating discharge, etc.). Comparison with literature data supports the plausibility of the determined field R_s.

The study also showed that the R_s has to be determined for each single substance for the calculation of TWACs to be accurate, because an overall model to predict R_s from physico-chemical properties is (still) lacking. It was shown that the speciation has a large influence on R_s and that $\log D_{ow}$ indicates the trend of R_s, but the overall correlation was not satisfying. However, for a first estimation for unknown compounds, an average R_s of 0.05 L/d and 0.1 L/d can be assumed for polar and semi-polar substances, respectively.

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4. PICOGRAM PER LITER DETECTIONS OF PYRETHROIDS AND ORGANOPHOSPHATES IN SURFACE WATERS USING PASSIVE SAMPLING

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ABSTRACT

Pyrethroids and organophosphates are among the most toxic insecticides for aquatic organisms, leading to annual-average environmental quality standards (AA-EQS) in the picogram per liter range in surface waters. For monitoring purposes, it is therefore crucial to develop very sensitive analytical methods. Until now, it is very difficult to reach detection limits at or below given AA-EQSs. Here, we present a passive sampling method using silicone rubber (SR) sheets for the sampling of ten pyrethroids and two organophosphates in surface waters. An analytical method was developed, optimized and validated for the extraction of the insecticides from the SR sheets by accelerated solvent extraction followed by clean-up on C18 and silica gel and detection with GC-MS/MS in positive ionization mode. Good precision (<20%) and absolute recovery (>50%) was observed for all substances, accuracy was between 66% and 139%. Limits of detection between 6 and 200 pg/L were achieved for all substances in surface waters using average sampling rates for PCBs and PAHs. The lack of substance-specific sampling rates and missing performance reference compounds led to an uncertainty in the concentration estimation of factor three in both directions. In a large field study, comprising 40 environmental samples from nine Swiss rivers, eight out of 12 substances were detected (most frequently: chlorpyrifos, cypermethrin). Most of the estimated organophosphate concentrations were between 0.1-1 ng/L, most pyrethroid detections below 0.1 ng/L. Four substances (chlorpyrifos-methyl, cypermethrin, deltamethrin and lambda-cyhalothrin) showed exceedances of their respective AA-EQS in multiple samples, also when the uncertainties in the concentration estimation were considered. As pyrethroid and organophosphate detection by SR passive sampling is very practicable and allows sensitive analysis, it has the potential to become a new tool in the monitoring of non-polar pesticides.

KEYWORDS

insecticides, gas chromatography mass spectrometry, silicone rubber, analytics, surface water, monitoring

4.1. INTRODUCTION

Pesticides applied to agricultural fields or in urban areas can enter surface waters by different routes (e.g. runoff, spray drift, waste water treatment plants, storm water overflows, Carter 2000) and affect the aquatic ecosystem (Schäfer et al. 2007, Werner et al. 2004) Particularly insecticides have a high ecotoxicological potential (Schulz 2004). The by far most toxic insecticides towards aquatic organisms are pyrethroids. Acute EC-50 values for to the amphipod *Hyalella azteca* for four of five frequently applied pyrethroids in the US are between 1.7 and 3.3 ng/L (Weston and Lydy 2010). For cypermethrin, which is one of the new priority pollutants in the European Water Framework Directive (WFD) and which is the most frequently applied pyrethroid in Switzerland, an annual average environmental quality standard (AA-EQS) of 0.08 ng/L in surface waters was defined (EC 2013). Hence, it is essential that appropriate analytical methods are developed for the detection of pyrethroids in the picogram per liter range in surface waters. Non-polar organophosphates are also toxic towards aquatic organisms; for chlorpyrifos, for example, the AA-EQS is 30 ng/L (EC 2013).

Because most of these substances are highly non-polar ($\log K_{ow}$ 4-8), dissolved concentrations in the water are expected to be very low, as the compounds quickly sorb to sediments or suspended particles. Thus, pyrethroid monitoring studies have often focused on the measurement in the sediment and in the sediment pore water (Budd et al. 2007, Weston et al. 2004). Although only 0.4-1% of the pyrethroids in river water are expected to be present in the freely dissolved form (Liu et al. 2004), this fraction is bioavailable (Yang et al. 2006) and thus responsible for a large part of the toxicity. There are only studies in California and in Spain investigating dissolved pyrethroids (Feo et al. 2010c, Hladik and Kuivila 2009, Weston and Lydy 2010) with focus on peak concentrations in small creeks or drains from agricultural or residential sites (concentrations in the range of 5-50 ng/L). Predicted pyrethroid concentrations in small to medium sized rivers in Switzerland are between 0.001 and 0.01 ng/L, predicted organophosphate concentrations between 2-20 ng/L. These values were calculated using a runoff scenario with the model Exposit (Exposit 2.01 2011) by taking into account site specific application rates, degradation in soil, polarity-dependent emission to surface waters and dilution in the stream.

Most pyrethroid analytics are carried out by gas chromatography (GC) coupled to electron-caption detection (ECD) or mass spectrometry (MS). Newer technologies include GC coupled to tandem MS (MS/MS) or two-dimensional GC coupled to high-resolution (HR)MS (Feo et al. 2010a). Extraction of the water samples is normally done by liquid-liquid extraction (LLE) or solid phase extraction (SPE) (Feo et al. 2010a). A recent review by Loos (2012) stated that it is *"extremely difficult, if not impossible with current methods"* to reach detection limits of cypermethrin in the low picogramm per liter range in ambient water samples. For example, Vorkamp et al. (2014) showed that, despite extraction of 12 L of water combined with very sensitive HRMS, the AA-EQS value for cypermethrin could not be reached. There are only two studies which reached detection limits in the sub-ng/L range for some pyrethroids using SPE

followed by detection on GC-electron ionization (EI)-MS (Hladik and Kuivila 2009) and ultrasound-assisted emulsification-extraction (UAEE) followed by GC-negative chemical ionization (NCI)-MS/MS, respectively (Feo et al. 2011).

Recently, we found with a comprehensive pesticide screening performed by liquid chromatography-HR-MS/MS, that pyrethroids and non-polar organophosphates were the only substance classes which cannot be adequatly measured (see **chapter 5**). This can lead to a considerable underestimation of the insecticidal toxicity of environmental samples.

One way to overcome this problem is the use of passive sampling (e.g., Huckins et al. 2006, Namieśnik et al. 2005, Stuer-Lauridsen 2005, Vrana et al. 2005), a sampling tool that is under discussion for regulatory compliance monitoring (Allan et al. 2006). Passive sampling for non-polar substances has been established with semipermeable membrane devices (SPMD) (e.g., Stuer-Lauridsen 2005), low density polyethylene (LDPE, e.g., Rusina et al. 2007) and more recently with silicone rubber sheets (SR), also known as polydimethylsiloxane (PDMS) (e.g., Smedes and Booij 2012). For non-polar PCBs and PAHs, the use of SR has been investigated intensively during the last years (Rusina et al. 2007, Rusina et al. 2010b, Smedes and Booij 2012, Smedes et al. 2009). The main advantage of passive sampling is that non-polar substances have very high sampling rates, in the range of liters per day, which drastically reduces the detection limits (Smedes and Booij 2012). Another advantage is that sorption to sampling equipment such as collection tubes and storage containers is avoided. Compared to water samples, where pyrethroids sorbed to dissolved organic carbon are also measured (Liu et al. 2004), only truly dissolved substances sorb to passive samplers. It is currently under discussion if passive sampling can be used in regulatory monitoring within the WFD, because EQS are defined for the whole water concentration and thus passive sampling is not in compliance with the WFD approach (Mills et al. 2014). Challenges in the quanitification of water concentrations remain because the PMDS sampling rate is dependent on a number of parameters such as flow rate, temperature, salinity, and biofouling (Smedes and Booij 2012). Because hardly any sensitive ambient water sampling methods exist for pyrethroids, passive sampling is a promising strategy nevertheless (Loos 2012, Mills et al. 2014).

The goals of this study were (i) to develop a practicable, selective and sensitive SR based passive sampling method for the detection of highly toxic pyrethroids and organophosphates in surface waters with LODs at or below their respective AA-EQS values (often picogramm per liter range), and (ii) to apply the method in surface water monitoring of nine streams in Switzerland.

4.2. MATERIALS AND METHODS

4.2.1. Analytes and Solvents

Following solvents were used for the development and application of the analytical method: ethyl acetate (purity ≥99.7%, Sigma-Aldrich, Buchs, Switzerland), acetonitrile (99.99% Acros Organics), hexane (≥96% Merck), methanol (purity ≥99.9%, Fisher Scientific), propanol (≥99%, Scharlau) and nanopure water (ultra purity water device Milli-Q gradient A10, Millipore AG, Zug, Switzerland). All investigated substances (12 target substances, five substances used as performance reference compounds (PRCs)) and four internal standards (see **Table 4.1**) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Information about substance properties are listed in the supplementary data (**Table C.1**).

4.2.2. Preparation of SR Sheets

SR was chosen as passive sampler type because it is more robust than LDPE and SPMD and because higher sampling rates are expected due to higher diffusion coefficients compared to LDPE (Rusina et al. 2010a). SR sheets were purchased from Altecweb (UK) (AlteSil^{TM} translucent, 0.5±0.05 mm thickness, initial size 60x60 cm^2). The SR sheets were cut to the appropriate size, washed with tap water, dried and pre-extracted by Soxhlet in ethyl acetate for 100 h in order to remove oligomers and other impurities (Rusina et al. 2007). Afterwards, SR sheets were dried and stored in methanol at room temperature until use.

4.2.3. Environmental Monitoring in Nine Rivers

Forty environmental samples were taken in six medium-sized rivers and in three small streams with diverse agricultural and urban land use in their catchments (**Figure C.6**). Sampling was done between March and July 2012 in the six medium-sized rivers and between April and May 2013 in the small streams. Each SR sheet (10 x 30 cm^2) was deployed for two weeks. At six time points, a blank sample was brought to the field which was not deployed in the water. Flow velocity was measured exactly at the location of the sheet at the beginning and at the end of the deployment (**Table C.3**). After deployment, SR sheets were slightly brushed in order to get rid of biofilm and other living organisms, and stored at -20°C until extraction and analysis. One third of each sheet (10 x 10 cm^2) was extracted and processed with the developed analytical method (next section).

4.2.4. Final Extraction and Clean-Up Procedure

After exposure, SR sheets were extracted using accelerated solvent extraction (ASE, Dionex ASE 350) in stainless steel cells (10 mL) using the following optimized parameters: five extraction cycles using methanol as solvent at 120°C with a static time of 10 min and a rinse volume of 75%. After extraction, 60 µL of the internal standard mix (1 mg/L) was added. The extract was evaporated to 0.5 mL on a vacuum rotator (Genevac® EZ-2, Genevac SP Scientific, Ipswich, UK) and finally evaporated to complete dryness under a gentle nitrogen stream. The completely evaporated glass vial was reconstituted with 0.5 mL hexane.

Clean-up was performed over a combined column using 500 mg of silica gel (Silicagel 60, 0.063-0.2 mm, Merk KGaA, Darmstadt, Germany, activated at 130°C for five days) on top and 500 mg of C18 (Separis, Genzach-Wyhlen, Germany) on the bottom. The materials were packed into a Pasteur pipette (Brand Gmbh, Wertheim, Germany) and were separated by a frit. The column was conditioned with 6 mL of hexane, the extract was run over the column and the column was rinsed with an additional 2 mL of hexane. The complete solvent was discarded. Elution was done with 10 mL of acetonitrile. The eluate was evaporated to 0.5 mL with the Genevac®, evaporated to complete dryness under a gentle nitrogen stream and reconstituted with 0.3 mL hexane. The aliquot was transferred into a small GC-MS vial (BGB Analytik, Böckten, Switzerland) and measured by GC-MS/MS.

4.2.5. Analysis by GC-MS/MS

The extracts were measured on a GC-MS/MS instrument (Trace GC Ultra™ gas chromatograph, coupled to a Thermo Scientific TSQ Quantum, positive EI mode). The used column was a Zebron ZB-5MS (15m, 0.225 mm inner diameter, film thickness 0.25 µm). The temperature program was run for 59.8 min in order to separate all target substances and interferences from the remaining matrix. It started at 55°C for 1 min and included a two-step temperature increase: i) +30°C/min to 140°C, ii) +2°C/min to 252°C. Further instrument parameters are listed in **Table C.2**.

GC-MS/MS transitions and collision energies of all analytes and internal standards were optimized by applying different collision energies on the most intense masses in the full scan. All transitions were optimized and validated using a spiked environmental sample. The best transition was used as quantifier, the second best transition as confirmation ion (qualifier). Substances were quantified over the area ratio between analyte and internal standard. Following internal standards were used: chlorpyrifos-methyl D6 (for tefluthrin, chlorpyrifos-methyl, chlorpyrifos, allethrin, imiprothrin), trans-cypermethrin D6 (for bifenthrin, tetramethrin, fenpropathrin, phenothrin, lambda-cyhalothrin, acrinathrin, permethrin, cypermethrin), etofenprox D5 (for etofenprox), fenvalerate D7 (for esfenvalerate, fluvalinate, deltamethrin). If an analyte or internal standard had a double peak due to the presence of diastereomers, the more

intense peak was used for quantification in all optimization, validation and kinetic experiments. In the environmental samples, the sum of both peaks was used for quantification, in order to account for possible photo-isomerization of the substances.

4.2.6. Optimization of the Extraction

Pre-extracted SR sheets of the size of 10x10 cm^2 were dried under the hood, spiked with 300 ng of the analyte mix and dried overnight. The sheets were extracted with ASE using different parameters in order to optimize the extraction efficiency: number of cycles (three, five), solvent (methanol, propanol), temperature (80°C, 100°C, 120°C), static time (5 min, 10 min, 15 min) and rinse volume (50%, 75%, 100%). After extraction, internal standard mix (150 ng) was added to the extracts. Clean-up was only done with a C18 column and measurement was performed by a normal GC-MS device (see **Table C.2** for instrumental details).

4.2.7. Optimization of the Clean-Up

Clean-up was tested using C18 material and silica gel for the reduction of silica oligomers and environmental matrix, respectively. SR sheets were deployed in the nearby Chriesbach river (Dübendorf, Switzerland) for two weeks, in February 2013, cut into pieces of 10 x 10 cm^2, and extracted with the optimized ASE parameters (see section 4.2.4). Analyte mix (300 ng) was spiked to the extracts. The extracts were evaporated to complete dryness and reconstituted in the appropriate solvent (see below).

Six column arrangements (always 500 mg packed into a Pasteur pipette) and solvents (conditioning 6 mL, elution 10 mL) were tested and checked for the efficiency of matrix reduction and recovery of analytes: A) C18 column (solvent: acetonitrile), B) silica gel column (hexane), C) C18 column (acetonitrile) followed by a silica gel column (hexane), D) silica gel column (hexane) followed by a C18 column (acetonitrile), E) combined C18 (top) / silica gel (bottom) column (acetonitrile), F) combined silica gel (top) / C18 (bottom) column (conditioned with hexane, elution with acetonitrile). In the arrangements C and D, the eluted solvent from the first clean-up was evaporated to complete dryness (Genevac® and nitrogen) and the substances were reconstituted in the second solvent. Internal standard mix (150 ng) was spiked at the end of the procedure. The extracts were measured on the normal GC-MS device (see **Table C.2**). A duplicate of each column arrangement was tested.

4.2.8. Validation of the Analytical Procedure

The optimized procedure was validated for the following parameters: precision of triplicates, absolute recovery of the extraction and clean-up procedure, accuracy, limit of detection (LOD)

and limit of quantification (LOQ) of the whole analytical method. Validation experiments were measured on the GC-MS/MS. To check the precision and the absolute recovery, surface water exposed SR sheets with environmental matrix (deployed in the nearby Chriesbach river for two weeks in June, 2013) were cut into pieces of 10 x 10 cm^2 and measured with the optimized procedure (see section 4.2.4). Six samples were spiked with the analyte mix before ASE (three times 300 ng, three times 30 ng), six samples were spiked at the end of the procedure (three times 300 ng, three times 30 ng) and three samples were not spiked with the analyte mix. Internal standard mix (60 ng) was spiked in each sample at the end of the procedure.

LODs and LOQs of the whole analytical method were determined from calibration standards (1 - 1000 ng/mL in the final extract) spiked on SR sheets (10 x 10 cm^2), which were run over the whole procedure described in section 4.2.4. A signal-to-noise (s/n) factor of three was used for determining LOD and ten for determining LOQ of the whole method. If a peak in one of the blank samples existed, the LOQ was defined as ten times the maximal blank value. The influence of environmental matrix was checked by comparing the s/n in a spiked environmental sample with the s/n in a calibration standard. The accuracy was calculated by the relative recovery of a spiked environmental sample.

4.2.9. Estimation of Aqueous Concentrations for Pyrethroids and Organophosphates

To estimate aqueous concentrations (C_W; in ng/L) from the passive sampler data, the mass (m, in ng) of insecticide sampled per SR sheet was divided by a sampling rate (R_S, in L/d) and sampling duration (t, in days): $C_W = m / (R_S * t)$. For sampling rates, we used R_S-values published for PCBs and PAHs that have similar $logK_{ow}$ values to the investigated insecticides (Rusina et al. 2010b, Smedes and Booij 2012). The sampling rates from the literature were corrected to a surface area of 300 cm^2. Because no substance-specific sampling rates were available for pyrethroids and organophosphates, we considered an uncertainty of the concentrations of factor three in both directions, i.e. for an average value of 100, the considered concentration range was 33 to 300.

To check whether this approach is justified (i) an experiment for estimating the elimination of pyrethroids and organophosphate from SR to water was carried out in a flow channel system and (ii) 28 out of the 40 SR sheets that were deployed in the rivers were spiked with five performance reference compounds (PRCs) prior exposure (**Table C.3**). Detailed descriptions are given in **appendix C.2**.

4.3. RESULTS AND DISCUSSION

4.3.1. Optimized Extraction and Clean-Up Procedure

First, the SR extraction, clean-up of the received extracts and GC-MS/MS analysis were optimized. Optimized extraction parameter settings of the ASE were found to be five extraction cycles using methanol as solvent at 120°C with a static time of 10 min and a rinse volume of 75%. Although five cycles increased the extraction time from 45 to 60 min and solvent volume from 20 to 30 mL, it significantly improved the extraction efficiency for all pyrethroids and organophosphates. This is in contrast to results reported for soils in the review of Albaseer et al. (2010), who observed no further increase in extraction between three and five cycles. However, for the extraction of soils, stronger solvents such as acetone/dichloromethane are normally used (compared to methanol for the extraction of SR). Extraction at 120°C led to significantly improved recoveries compared to 100°C, which is in agreement with Albaseer et al. (2010). Temperatures >120°C were not tested because of the risk of extracting more matrix and possible degradation of the analytes (see review of Albaseer et al. 2010). The extraction efficiency with propanol was in the same range as with methanol, but evaporation of propanol required much more time or higher temperatures. More non-polar solvents such as ethyl acetate or hexane were not tested, because it causes significant swelling of the SR sheets and extraction of more oligomers (Smedes and Booij 2012). Static time and rinse volume did not have an effect on extraction efficiency, therefore intermediate values were used. Compared to classical soxhlet extraction, about 15-20 times less solvent volume is needed with the ASE (Albaseer et al. 2010). Because extraction can be done batch-wise, ASE is a fast and efficient method for extracting pyrethroids and organophosphates from SR and could be a good alternative to the classical soxhlet extraction of other non-polar compounds from SR sheets.

The comparison of **Figure 4.1A** (only C18) and **Figure 4.1B** (C18 and silica gel) shows that a silica gel column is highly efficient in reducing environmental matrix. Especially long-chain hydrocarbons were efficiently eliminated (see arrows in **Figure 4.1A**). Florisil, which has similar properties as silica gel, has already been used for the reduction of environmental matrix in the pyrethroid analysis in sediments (Feo et al. 2011, You et al. 2004), meat (Barbini et al. 2007, Stefanelli et al. 2009) and vegetables (López-López et al. 2001), but has not been applied to SR before. The comparison between **Figure 4.1C** (only silica gel) and **Figure 4.1D** (silica gel and C18) clearly shows that the C18 column is needed to reduce siloxane oligomers from the sample (see arrows in **Figure 4.1C**), as has already been reported by Smedes and Booij (2012). Shorter oligomers, however, are not fully retained on the C18 material (see arrows in **Figure 4.1D**).

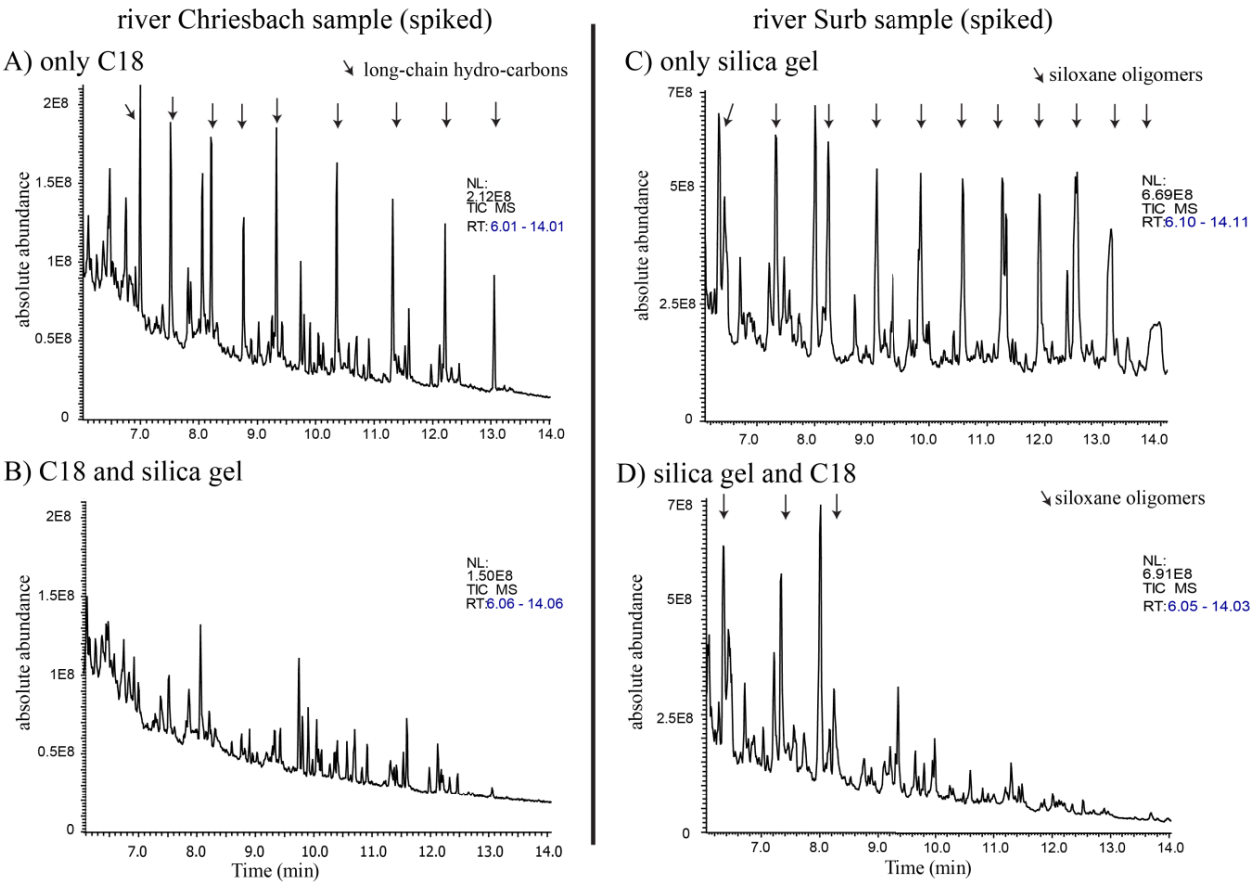

Figure 4.1. Matrix reduction by the two columns, visible in the total ion chromatograms (TIC): Left: reduction of environmental matrix by the silica gel column: A) only C18, B) C18 and silica gel in a river Chriesbach sample. Right: reduction of the siloxane oligomers by the C18 column: C) only silica gel, D) silica gel and C18 in a river Surb sample. Long-chain hydro-carbons and siloxane oligomers assigned by NIST database search are indicated with arrows. Note that measurement was performed on a normal GC-MS device with different chromatographic settings as for the GC-MS/MS (see **Table C.2**). Therefore, the retention times in **Figure 4.1** and **Figure 4.2** are not comparable.

The combined silica gel (top) / C18 (bottom) column (set-up E, 4.2.7) had the same effect on matrix and oligomer reduction as when the two steps were performed sequentially with a solvent change in between (set-up D). Because the clean-up procedure using all column arrangements showed 100% recovery for all substances, the combined column was selected as optimal procedure. Rinsing the column with 2 mL of hexane after loading the extract further reduced the matrix without eluting pyrethroids from the silica gel column, as also observed by Barbini et al. (2007).

Table 4.1. Optimized analytical parameters and quality control parameters for the analysis of pyrethroids and organophosphates in SR sheets.

	Optimized Analytical Parameters				Quality Control Parameters				
Substance name	**Quantifier transition**	**CE[b]**	**Qualifier transition**	**CE[b]**	**Precision[c]**	**Absolute Recovery[c]**	**Accuracy[e]**	**LOD method (ng/300 cm² SR)**	**LOQ method (ng/300 cm² SR)**
Target Analytes									
Bifenthrin	181→166	15	181→141	22	2%	66±2%	74%	3	10
Chlorpyrifos	314→258	15	197→169	15	5%	67±8%	66%	-[g]	10
Chlorpyrifos-methyl	286→93	20	286→271	25	4%	63±3%	-[f]	30	90
Cypermethrin (alpha)	163→127	5	163→91	10	3%	76±8%	107%	4	12
Deltamethrin[a]	253→93	18	181→152	20	11%	85±12%	139%	-[g]	50
Esfenvalerate	167→125	10	167→89	30	11%	78±12%	111%	-[g]	50
Etofenprox	163→135	10	163→107	16	4%	75±2%	103%	-[g]	15
Lambda-Cyhalothrin	181→152	20	197→141	15	4%	68±4%	109%	50	150
Permethrin	183→165	15	183→168	15	1%	68±5%	76%	-[g]	30
Phenothrin	123→81	12	183→153	18	17%[d]	94±16%[d]	106%	60	200
Tefluthrin	177→127	20	197→141	10	15%	80±14%	96%	-[g]	100
Tetramethrin	164→107	17	164→135	10	3%	63±3%	107%	-[g]	40
Performance Reference Compounds (PRC)									
Acrinathrin	208→181	8	181→152	25	8%	53±8%	-[f]	6	20
Allethrin	123→95	11	123→81	10	15%[d]	84±7%[d]	102%	-[g]	600
Fenpropathrin	181→152	26	265→210	15	1%	71±3%	-[f]	5	15
Fluvalinate (tau)	250→200	20	250→208	20	16%	80±22%	-[f]	-[g]	75
Imiprothrin	123→56	20	123→81	10	17%[d]	90±15%[d]	111%	-[g]	30
Internal Standards (ISTD)									
Chlorpyrifos-methyl D6	292→274	20	292→242	20					
Cypermethrin D6	169→96	15	169→133	10					
Etofenprox D5	168→136	10	168→108	10					
Fenvalerate D7	174→126	15	174→91	25					

[a] deltamethrin cannot be distinguished from tralomethrin because under commonly used GC conditions, tralomethrin breaks down to deltamethrin (Feo et al. 2010b), [b] CE: collision energy [eV], [c] spike level 100 ng/mL unless otherwise stated, [d] values were taken from samples spiked with 1000 ng/mL because LOQ is above 100 ng/mL. Note that for imiprothrin, the values were taken from the qualifier transition (123→81) because the quantitation transition was improved later, [e] spike level: 200 ng/mL, [f] could not be evaluated because initial concentration was above 200 ng/mL, either due to environmental concentrations or previous spike of PRCs, [g] if a signal was present in the blank samples, only LOQ was determined as ten times the intensity of the blank value.

4.3.2. Optimized GC-MS/MS Analysis

Most optimized transitions for the quantifier and qualifier fragment (**Table 4.1**) were also reported in the literature (Feo et al. 2011, Frenich et al. 2008, Hladik and Kuivila 2009, Pihlström et al. 2007, You et al. 2010). Only for imiprothrin and etofenprox, other tansitions than reported in the literature were found as optimum. The optimized chromatographic run in the GC-MS/MS analysis lasted 60 min. Thereby, all substances investigated were separated without interferences from the remaining matrix. **Figure 4.2** shows the selected reaction monitoring (SRM) chromatograms of all substances for their optimized transitions (quantification ion, see **Table 4.1**). It is well known that for pyrethroids, multiple peaks are observed due to the

separation of diastereomers (chirality centers at cyclopropyl ring and/or on the α-carbon connected to the cyano group as well as *cis/trans*-isomerization) (Feo et al. 2010a). Indeed, nine substances showed a double peak in their chromatograms (see **Figure 4.2**). Lambda-cyhalothrin and acrinathrin are structurally very similar so that all optimized transitions are visible for both substances (see **Figure 4.2**).

4.3.3. Validation of the Final Analytical Method

The optimized procedure was validated with different quality control parameters. **Table 4.1** lists the results for precision, absolute recovery, accuracy, LOD and LOQ of the whole analytical method. All parameters were determined with environmental matrix. The precision was very good with <10% for ten substances and 10-20% for seven substances. The absolute recovery for the entire procedure (ASE and clean-up) was between 75-100% for half of the substances and between 50-75% for all other substances. The absolute recovery corresponds to the extraction efficiency of the ASE as no analyte loss was detected during the clean-up procedure. Method accuracy was good (75-125%) for most substances. Only values for chlorpyrifos (66%) and deltamethrin (139%) were outside this range. The method LOQ in the environmental matrix was ≤100 ng/300cm^2 SR sheet for 14 substances. Out of them, six substances had a LOQ even below 20 ng/300cm^2, five substances between 20 and 50 ng/300cm^2 and three substances between 50 and 100 ng/300cm^2. For ten substances, low blank values were observed (present in similar range in all six blank samples). Most probably, these low blank values are coming from remaining impurities in the matrix which have the same retention time and the same fragment ions. To ensure that the concentrations in environmental samples are not artifacts, a factor of ten above the maximum blank value was chosen as LOQ for these substances (see section 4.2.8).

The results show that the optimized procedure to extract pyrethroids and organophosphates from SR sheets together with the measurement by GC-EI-MS/MS is robust, selective and sensitive and can be applied to environmental samples.

4.3.4. Estimation of Sampling Rates

To investigate the suitability of the passive sampling approach, some preliminary kinetic experiments were carried out and some PRCs were used (see **appendix C.2** for detailed information). An exponential elimination of semi-polar substances from spiked SR sheets was observed, supporting the applicability of the chosen approach. However, as no distribution coefficients between SR and water (K_{pw}) are available for the investigated insecticides and for the used SR material, no sampling rates could be calculated.

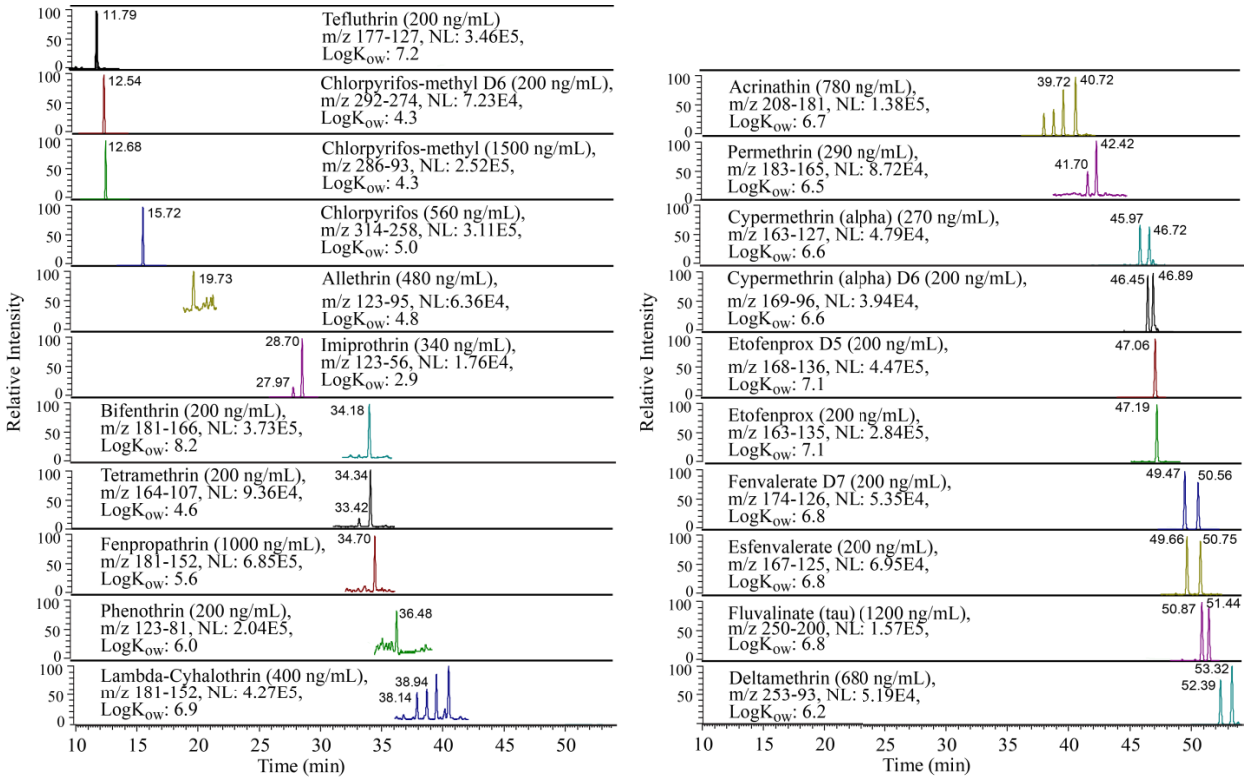

Figure 4.2. Selected reaction monitoring (SRM) chromatograms (quantifier transition) of all investigated substances (including internal standards and performance reference compounds (PRCs)) in a spiked river Furtbach sample (spike level: 200 ng/mL) sorted by their retention time. Note that effective concentrations can be higher than the spike level because of substances taken up from the river or spiked PRCs. For allethrin and phenothrin, the LOQ is higher than the spiked amount, thus peaks are not very pronounced. $LogK_{ow}$ values were taken from Feo et al. (2010a) except for chlorpyrifos, chlorpyrifos-methyl and etofenprox (Chemspider: www.chemspider.com, experimental value of EPI Suite).

Thus, average literature values determined for PCBs and PAHs were used as a proxy in this study. Both substance classes have $logK_{ow}$ values that are in the same range as pyrethroids and organophosphates ($logK_{ow}$ values 3-7). Smedes and Booij (2012) determined sampling rates for PCBs and PAHs between 30-60 L/d (normalized to 600 cm^2) in turbulent marine water. Rusina et al. (2010b) determined sampling rates of 10-25 L/d (normalized to 100 cm^2) for PAHs ($logK_{ow}$ values 3-6) at a flow velocity of 0.09 m/s under laboratory conditions. Overall, sampling rates normalized to 300 cm^2 ranged between 15-75 L/d. Differences in sampling rates between PCBs and PAHs with similar $logK_{ow}$ values are small (factor two), although they have a different structure (Rusina et al. 2010b). Only a weak correlation between K_{pw} and the sampling rate was observed (Rusina et al. 2010b). It can thus be hypothesized that pyrethroids and organophosphates with similar $logK_{ow}$ values have sampling rates in the same range. For the estimation of environmental concentrations, an average sampling rate from the literature of 35 L/d was therefore used for all substances.

There are various uncertainties in the sampling rate due to differences in physico-chemical properties of the substances and environmental uncertainties such as water temperature, degree of biofouling, potential photolysis in the SR and water flow velocities. Effects of water temperatures on the sampling rates are expected to be small. For SPMDs, Booij et al. (2002) determined a two-fold difference for a 20°C temperature change. Water temperature in three of the rivers investigated in this study (Mentue, Furtbach, Surb) ranged from 5 to 20°C during the study period (March to July 2012). Therefore, variability can be expected to be lower than a factor of two. Little biofouling was observed. Thus, its effect on sampling is considered negligible. Photolysis of pyrethroids might also be relevant. The photolysis half-lives are in the range of half-lives of PAHs, for which a significant effect was shown in SPMDs (Komarova et al. 2009). The largest uncertainties are expected to result from differences in flow velocities. Flow velocities during the deployment in the rivers ranged from 0.05 to 0.8 m/s, up to almost tenfold higher than in the study of Rusina et al. (2010b). The relationship between flow velocity and substances uptake on SR in this high flow velocity range has not been investigated yet.

In order to incorporate the uncertainties described above (substance properties, temperature, flow velocity), an overall uncertainty of factor three in both directions (i.e. one order of magnitude in total) was defined in this study. PRCs could be used to calculate in-situ sampling rates to partly correct for these uncertainties (Booij and Smedes 2010, Huckins et al. 2002). However, the only candidates for pyrethroid PRCs to date are imiprothrin, allethrin, acrinathrin, fenpropathrin and fluvalinate because these pyrethroids are not in use in Switzerland. Their $\log K_{ow}$ values are much lower compared to the target pyrethroids or so high that no release could be observed within the sampling period. Thus, it needs to be checked in future studies if additional pyrethroids or organophosphate PRCs can be made available or if PRCs from other substance classes (such as PCBs or PAHs) could be reasonable alternatives. In addition, experiments that determine the duration of linear uptake of pyrethroids and organophosphates would advance the understanding of the kinetic behavior of the investigated substances. It is possible that smaller substances are already in equilibrium after a two week deployment in the river (personal communication Kees Booij, NIOZ, The Netherlands).

In summary, the preliminary experiments (see **appendix C.2** for detailed information) together with the knowledge from literature showed that sampling rates of pyrethroids should be in the same range as sampling rates for PCBs and PAHs. Thus, a concentration estimation with large uncertainties can be reported. In future studies, exact K_{pw} values need to be determined, possible photolysis of the substances in the SR sheet has to be experimentally tested, appropriate PRCs have to be found and the duration of linear uptake has to be checked for all substances to decrease the uncertainties of the passive sampling method. This was not the main focus of the current study and will require a lot of effort before the passive sampling approach can be implemented into routine monitoring programs.

Table 4.2. Estimation of limit of detection (LOD) and limit of quantification (LOQ) in environmental samples and comparison with the annual-average environmental quality standards (AA-EQS).

Substance name	LOD surface water (pg/L)		LOQ surface water (pg/L)		AA-EQS (pg/L)
	average	range[a]	average	range[a]	
Bifenthrin	**6**	2-18	**20**	7-60	95[c]
Chlorpyrifos	**-**	-	**20**	7-60	30,000[d]
Chlorpyrifos-methyl	**60**	20-180	**200**	67-600	200[e]
Cypermethrin (alpha)	**8**	3-24	**20**	7-60	80[d]
Deltamethrin	**-**	-	**100[b]**	33-300	3[f]
Esfenvalerate	**-**	-	**100**	33-300	100[e]
Etofenprox	**-**	-	**30**	10-90	5,400[g]
Lambda-Cyhalothrin	**100[b]**	33-300	**300[b]**	100-900	20[h]
Permethrin	**-**	-	**60**	20-180	1,000[i]
Phenothrin	**100[b]**	33-300	**400[b]**	130-1200	1[k]
Tefluthrin	**-**	-	**200[b]**	67-600	16[k]
Tetramethrin	**-**	-	**80**	27-240	290[k]

[a] taking uncertainties of factor three in both directions into account, [b] LOD and LOQ in surface water above annual-average environmental quality standard (AA-EQS), [c] ESIS 2010, [d] EC 2013, [e] RIVM 2014c, [f] RIVM 2008a, [g] ESIS 2007, [h] RIVM 2008b, [i] WFD-UKTAG 2012, [k] RIVM 2014a

4.3.5. Resulting Detection Limits

The resulting LODs in surface waters calculated with the average sampling rate of 35 L/d ranged from 6 pg/L to 200 pg/L (**Table 4.2**). Given the various uncertainties, we also reported the range of LODs and LOQs. The LODs in surface waters were for most substances lower than LODs reported in the literature so far. For eight substances, the LOD was lower than its reported AA-EQS value (**Table 4.2**).

4.3.6. Results of the Field Study

Of 12 investigated substances, eight were detected in at least one of 40 environmental samples collected (see **Figure 4.3**). The detections of all substances were correlated with the specific land use patterns in the catchments. Chlorpyrifos (37) and cypermethrin (24) were the most frequently detected substances. Chlorpyrifos was detected in all nine rivers which is in agreement with its very diverse application spectrum (permitted in vegetables, orchards, vineyards, sugar beet, forestry and in private gardens). Cypermethrin which is registered for pest control on vegetable

crops, oilseed rape, forestry and private gardens, was detected in four rivers (Furtbach catchment: high vegetable density and residential areas; Surb, Mentue and Limpach catchment: high oilseed rape density). Chlorpyrifos-methyl which is only permitted for use on vegetables and orchards was detected in the rivers Furtbach and Salmsacher Aach; deltamethrin and lambda-cyhalothrin (permitted for use on vegetables and oilseed rape, in private gardens and as a biocide in residential areas) in the river Furtbach; and permethrin (permitted as a biocide in residential areas) in the rivers Furtbach and Surb. It appears that the application of deltamethrin and lambda-cyhalothrin on oilseed rape is of minor importance, because they were not detected in catchments with high oilseed rape densities.

With two exceptions, all pyrethroid concentration estimates were below 1 ng/L, 50% of all detections even below or equal to 0.1 ng/L (**Figure 4.3**, all concentration estimates in **Table C.4**). Most organophosphate detections (63%) were between 0.1 and 1 ng/L, roughly 20% were below 0.1 ng/L and 20% between 1 and 10 ng/L. As mentioned above, we cover the lack of substance-specific sampling rates and missing performance reference compounds by reporting an uncertainty in the concentration estimation of a factor of three in both directions. The concentration range of the detected substances are within the expected concentration range from theoretical calculations (see introduction). This indicates that the applied PMDS sampling rate is in the correct range. Highest pyrethroid concentrations were found for deltamethrin (up to 2 ng/L); highest organophosphate concentrations ranged up to 10 ng/L (chlorpyrifos) and 8 ng/L (chlorpyrifos-methyl).

Measured pyrethroid concentration estimates in this study were an order of magnitude lower than concentrations measured in California, where several pyrethroids were found in concentrations between 5-25 ng/L (Ensminger et al. 2013, Hladik and Kuivila 2009, Weston and Lydy 2010.) Reported cypermethrin and deltamethrin concentrations in Spain were up to 60 ng/L (Feo et al. 2010c). However, it has to be kept in mind that concentrations from our study are average concentrations over two weeks in medium sized streams. In the reported studies, small creeks or drains from agricultural or residential areas were sampled by grab samples or composite samples during rain events. The discrepancy between the measured concentrations in the studies can therefore be explained. In addition, the application of pyrethroids in California and Spain are different to the application pattern in Switzerland due to different climatic conditions. The risk of pyrethroids by short-term pulses after runoff events are therefore very important to consider, too.

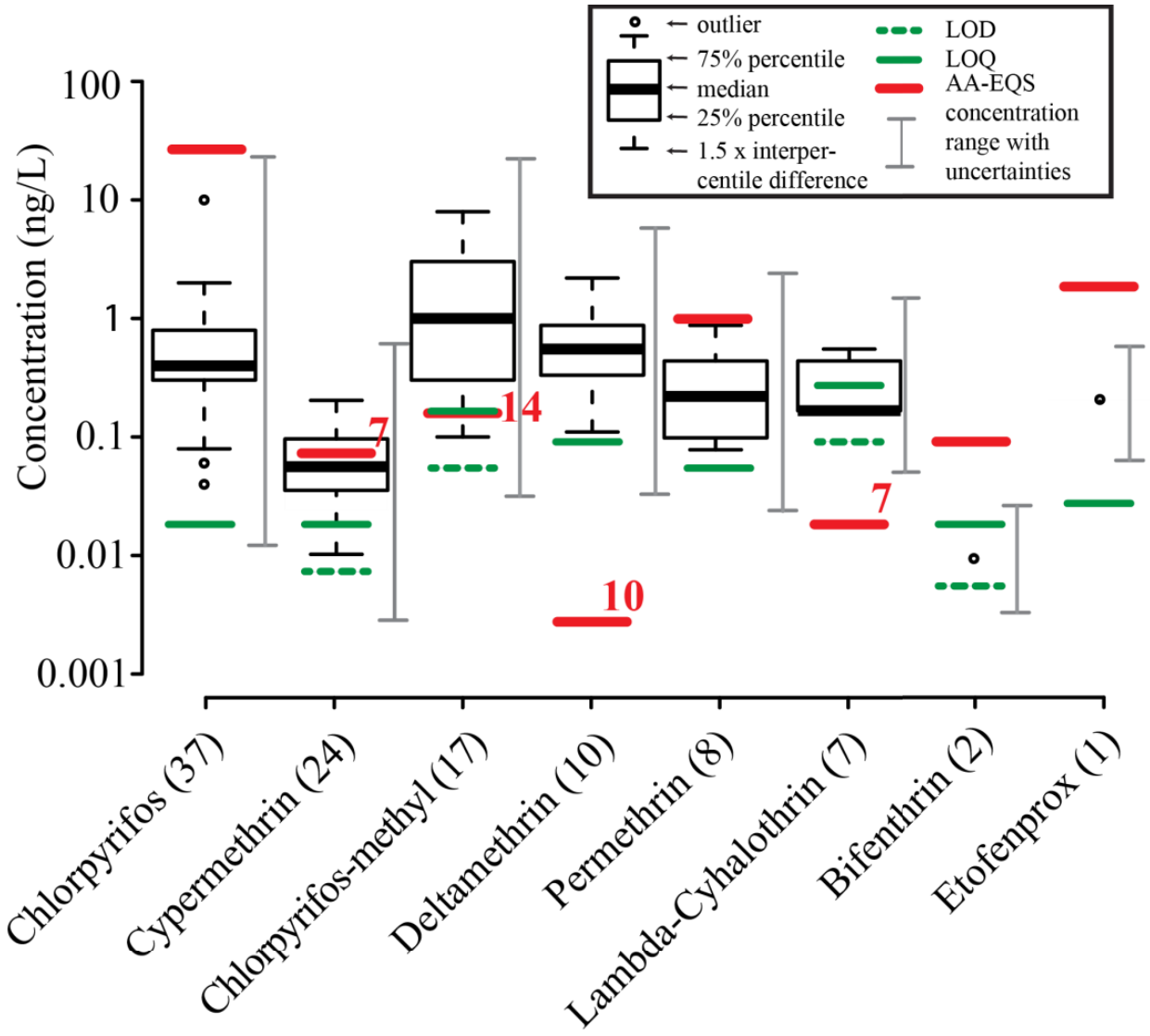

Figure 4.3. Boxplots with the estimated concentration of all positive detections of the investigated pyrethroids and organophosphates in the 40 environmental samples and comparison with their annual-average environmental quality standards (AA-EQS). Values below limit of quantification (LOQ) but above limit of detection (LOD) are depicted as 0.5 times LOQ. In parentheses, the number of detections are shown. The red numbers are the number of exceedances of AA-EQS taking into account average sampling rates. Note that the uncertainty of the concentrations is a factor of three in both directions which is indicated by the gray arrows.

4.3.7. Comparison with AA-EQS

Although reported concentrations are estimations and have appreciable uncertainties, they can be used as indicators of the risk of AA-EQS exceedances in surface waters. When comparing the estimated water concentrations with the AA-EQS of each substance, four substances (chlorpyrifos-methyl, cypermethrin, deltamethrin and lambda-cyhalothrin) showed exceedances in at least one sample (**Table 4.2** and **Figure 4.3**). Especially chlorpyrifos-methyl (14 exceedances up to a factor of 40) and deltamethrin (ten exceedances up to a factor 700) had numerous exceedances. For deltamethrin and lambda-cyhalothrin, the AA-EQS is still lower than the environmental LOD. This means that the risk for these two substances might be underestimated.

A sensitivity analysis showed that the number of AA-EQS exceedances of most substances is little affected by the uncertainties. Most detections were either clearly below the AA-EQS or clearly above the AA-EQS. For deltamethrin, for example, we found ten exceedances, irrespective of whether the lowest concentration estimation or the highest concentration estimation was taken. For chlorpyrifos-methyl, the number of exceedances would increase from 11 to 17. However, for cypermethrin, the uncertainties have a considerable impact on the number of exceedances because all cypermethrin concentration estimates were within a small concentration range which was close to its AA-EQS. Therefore, the lowest concentration estimates resulted in zero exceedance, while with the highest concentration estimates resulted in 23 exceedances. For substances whose AA-EQS was never exceeded (chlorpyrifos, permethrin), the comparison would not change at all or only slightly, when uncertainties are taken into account.

4.4. CONCLUSIONS

The study showed that the detection of pyrethroids and organophosphates by SR passive sampling followed by analysis on GC-MS/MS is very efficient: i) deployment of the samplers in the river is easy and provides composite data from which time-weighted average concentrations can be estimated, ii) the extraction with the ASE and clean-up with the combined C18/silica gel column is fast and reliable, iii) the analysis uses a GC-MS/MS device which is already available in many laboratories.

The biggest advantage of passive sampling by SR is the tremendous uptake capacity of non-polar substances from the water. For estimated sampling rates, the sampled chemical amount collected on a SR sheet (30 x 10 cm^2) within two weeks is equal to the extraction of approximately 500 liters of water. Due to the lack of substance-specific sampling rates and because appropriate PRCs are missing, the uncertainties of the water concentration estimations are still large. The calculation of exact K_{pw} values and the investigation of the duration of linear uptake are

(amongst others) important parameters for reducing these uncertainties and need to be determined in future studies.

Small and medium-sized rivers in Switzerland contain various pyrethroids and organophosphates. Effects from these insecticides on aquatic organisms cannot be ruled out as their corresponding AA-EQS values were exceeded several times, also when the uncertainties in the quantification are taken into account.

As the EQS values in the WFD are defined for the whole water matrix, it needs to be discussed whether and how SR passive sampling of dissolved non-polar insecticides can be successfully implemented in routine surface water monitoring.

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5. HOW A COMPLETE PESTICIDE SCREENING CHANGES THE ASSESSMENT OF SURFACE WATER QUALITY

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ABSTRACT

A comprehensive assessment of pesticides in surface waters is challenging due to the large number of potential contaminants. Most scientific studies and routine monitoring programs include only 15–40 pesticides, which leads to error-prone interpretations. In the present study, an extensive analytical screening was carried out using liquid chromatography, high-resolution mass spectrometry, covering 86% of all polar organic pesticides sold in Switzerland and applied to agricultural or urban land (in total 249 compounds), plus 134 transformation products; each of which could be quantified in the low ng/L range. Five medium-sized rivers, containing large areas of diverse crops and urban settlements within the respective catchments, were sampled between March and July 2012. More than 100 parent compounds and 40 transformation products were detected in total, between 30–50 parent compounds in each two-week composite sample in concentrations up to 1500 ng/L. The sum of pesticide concentrations was above 1000 ng/L in 78% of samples. The chronic environmental quality standard was exceeded for 19 single substances; using a mixture toxicity approach, exceedances occurred over the whole measurement period in all rivers. With scenario calculations including only 30–40 frequently measured pesticides, the number of detected substances and the mixture toxicity would be underestimated on average by a factor of two. Thus, selecting a subset of substances to assess the surface water quality may be sufficient, but a comprehensive screening yields substantially more confidence.

KEYWORDS

micropollutants, insecticides, fungicides, herbicides, biocides, plant protection products, transformation products, mixture toxicity, high resolution mass spectrometry, agriculture

5.1. INTRODUCTION

Surface waters in agriculturally and urban influenced catchments contain a large number of pesticides (e.g., Herrero-Hernández et al. 2013, Kreuger 1998) and their transformation products (TPs) (e.g., Kern et al. 2011a, Reemtsma et al. 2013a), which can pose risks to aquatic organisms even at low ng/L concentrations (e.g., Schäfer et al. 2007, Schulz 2004). The exposure of surface waters to pesticides is heavily dependent on local conditions (e.g., land use, pesticide application, weather conditions, soil type, topography, sewer type) and therefore can be spatially and temporally variable. In the Swiss and European legislation, there is a distinction between active ingredients in plant protection products (further referred as PPPs) and active ingredients in biocide products (further referred as biocides). PPPs are used to protect plants and are therefore allowed to be used in agriculture and private gardens. Biocides are used to protect materials, such as wood, building facades, roofs, or for in-house applications and are therefore used for domestic, industrial, and/or commercial applications. The main transport pathways of PPPs are diffuse via surface runoff, leaching to field drains and spray drift from agricultural fields (e.g., Brown and van Beinum 2009); the main sources for biocides are effluents from wastewater treatment plants (WWTPs), rain gutters, and combined sewer overflows (Wittmer et al. 2010). A considerable number of active ingredients can function both as a PPP and as a biocide.

Due to the high number of compounds and their high spatial and temporal variability, it is difficult to design a proper monitoring campaign to assess the exposure and risk to aquatic organisms in surface waters which will provide a high level of confidence. The results of any monitoring program are dependent, to a large part, on the sampling location, sampling time, and sampling strategy.

Moreover, a crucial factor in any monitoring program is the selection of the substances which are to be investigated. Routine analysis usually focuses on just 15-40 analytes (Munz et al. 2012); analysis is mostly carried out by liquid chromatography mass spectrometry (LC-MS/MS) using triple quadrupole instruments. The selection of the substances is normally done based on expert knowledge and analytical feasibility. Until now, surface water monitoring programs have usually focused on selected herbicides (e.g., Huntscha et al. 2012, Kreuger 1998), in general because herbicide concentrations were expected to be higher than insecticide or fungicide concentrations. This assumption is based on the interpretation of previous monitoring (e.g., Kreuger 1998, Munz et al. 2012) and sales data (BLW 2010), as well as environmental fate properties (University of Hertfordshire 2013). Modern insecticides (e.g., neonicotinoids, Starner and Goh 2012, Yamamoto et al. 2012), fungicides (e.g., azoles, Battaglin et al. 2011, Kahle et al. 2008, Reilly et al. 2012), and also TPs (e.g., Kern et al. 2009, Reemtsma et al. 2013b) have only rarely been included in monitoring programs. However, insecticides often show ecotoxicological effects at lower concentrations than herbicides (University of Hertfordshire 2013). This implies that, despite their low concentrations, the ecotoxicological relevance of insecticides cannot be overlooked (Schulz 2004).

With continuously shifting pesticide management practices and authorization, the relevant substances change over time and may even be regionally different. A full assessment of all registered pesticides and TPs would be highly desirable. Recent advances in LC-high-resolution-MS/MS and appropriate software tools allow efficient screening of an almost unlimited number of polar organic substances in a single run (Krauss et al. 2010, **chapter 2**). Our hypothesis is that using a comprehensive analytical screening has a large influence on the exposure assessment, and will therefore change the risk assessment of surface waters. In fact, we postulate that only by conducting a full analytical assessment of all potentially occurring pesticides together with the relevant ecotoxicological data, a complete mixture toxicity estimation can be done. Due to the advancement of analytical instrumentation, the need for mixture toxicity assessments (Backhaus and Faust 2012, Belden et al. 2007, Junghans et al. 2006, Price et al. 2012) may become even more important than in the past.

To test this hypothesis, we carried out a comprehensive pesticide screening of almost all authorized, polar, organic PPPs (*i.e.,* herbicides, fungicides, insecticides) and biocides, as well as a large number of pesticide TPs by using LC-high-resolution-MS/MS. The aim was to gain an overview of the diversity of pesticides in medium-sized Swiss rivers, to determine spatial and temporal differences due to land use and application season, and to comprehensively assess the ecotoxicological risk in the rivers. Compliance with environmental quality standards (EQS) values for single substances was investigated, as well as mixture toxicity assessments. Finally, it was possible to evaluate how exposure and risk assessments change when pesticide screening is less complete, i.e.by carrying out different assessments with only a subset of analytes.

5.2. MATERIALS AND METHODS

5.2.1. Sampling Site

Five river catchments distributed over the Swiss plateau (see map in **Figure 5.1**) were selected in order to monitor the large diversity of PPPs and biocides occurring in Switzerland. The catchments were between 38 and 105 km^2 and differed widely regarding arable crop densities, densities of special crops, urban areas, and WWTP discharges (see bar charts in **Figure 5.1**). Hence, most potential sources of pesticide contamination in Switzerland were covered. The five rivers were classified as medium-sized (stream order 3-4 after Strahler 1952).

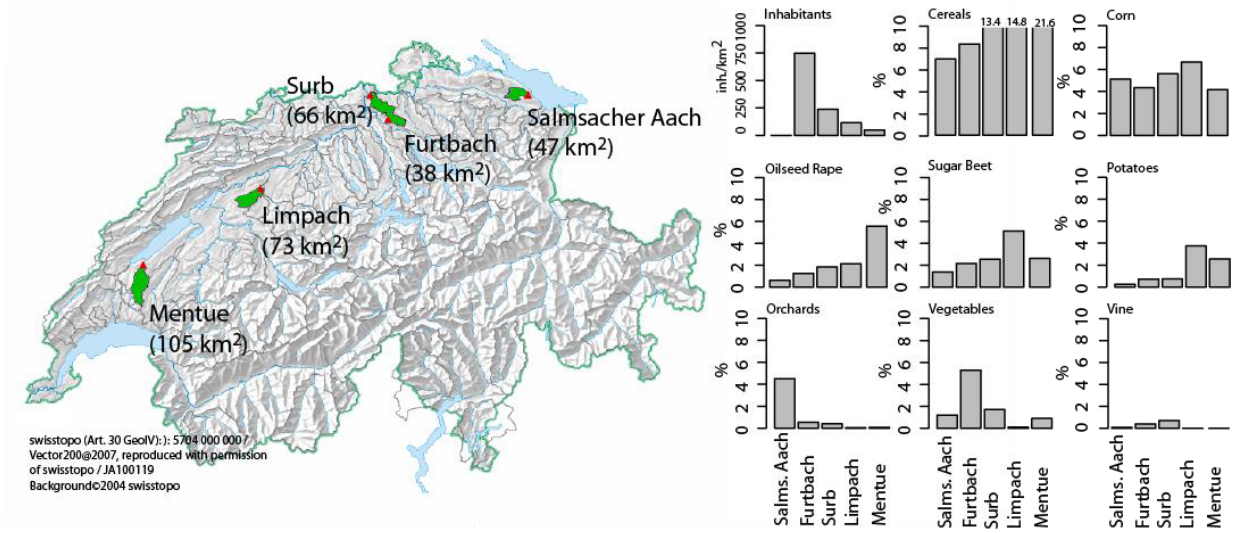

Figure 5.1. Location and characteristics of the five investigated catchments. Green: catchment area, red: sampling location. Bar charts show the densities of the most important crops (%) and the number of inhabitants connected to WWTPs in the catchments (BAFU 2013).

5.2.2. Sampling

Nine bi-weekly (March 19–July 23, 2012) time-proportional composite water samples were collected from each river with automatic sampling devices (Isco sampler) with 60 minute sub-sampling intervals. Weekly composites of one liter were taken (cooled on-site) and transported to the laboratory. Two weekly composites were mixed to bi-weekly samples in the laboratory, and stored at -20°C until analysis. During the sampling period, there were six to ten rainfall events (see **Figure 5.2**, top). Overall, a relatively dry spring (discharge in the river was 30-60% less than the average of the previous 12 years) was followed by a summer with an average river discharge (see **Figure D.1**).

5.2.3. Substance Selection

At the outset of substance selection for this monitoring, all polar, synthetic, organic PPPs (*i.e.,* herbicides, fungicides, insecticides) that have been registered and sold in Switzerland between 2005 and 2011 (220 substances, BLW 2012) and all polar, synthetic, organic substances listed as biocides in Switzerland (109 substances, BAG 2012) were included in the study (**Table 5.1**, see **Table D.1** for all substances). Forty of the selected compounds were registered both as a PPP and as a biocide. Only substances that were expected in the water phase were considered. Substances with $\log K_{ow} > 5$, including pyrethroid insecticides as well as quaternary ammonia cations, were excluded due to their sorption to organic matter. For the biocides, substances with

low half-lives in water (< 1d, University of Hertfordshire 2013) were also excluded. In addition to the parent compounds, 134 TPs, covering a variety of pesticide classes, taken from the footprint database (University of Hertfordshire 2013), were included in the analysis (see **Table D.1**).

5.2.4. Analytics

136 out of 289 measurable pesticides and 54 out of 136 TPs were analyzed with an offline solid phase extraction (SPE) LC-electrospray-ionization-high-resolution-MS/MS method and quantified with target screening using reference standards and isotope-labeled internal standards **(chapter 2)**. In brief, one liter of sample was passed over a multilayered cartridge containing Oasis HLB, Strata XAW, Strata XCW, and Isolute ENV+ in order to enrich a broad spectrum of substances. Elution was done subsequently by ethyl acetate/methanol (50%/50%) with 0.5% ammonia and ethyl acetate/methanol (50%/50%) with 0.5% formic acid. Combined neutral extracts were evaporated to 0.1 mL and reconstituted with 0.9 mL of nanopure water. The chromatographic separation was carried out with a XBridge™ C18 column using nanopure and methanol acidified with 0.1% formic acid as eluents. High-resolution MS and MS/MS data were generated on a QExactive (Thermo Fisher Scientific Corporation). Full scan with resolution (R) of 140,000 and data-dependent MS/MS (R=17,500, Top 5) with separate run for positive and negative ionization were acquired.

The presence of the remaining parent compounds and TPs was checked by suspect screening using a recently developed approach **(chapter 2)**. In comparison to non-target screening, the information about the chemical structure is available a priory in the suspect screening (Krauss et al. 2010). Briefly, after an automatic peak picking of the exact masses of all theoretically measurable substances from the MS full scan, different filter criteria (blank subtraction, peak area, signal to noise, peak symmetry and isotopic pattern) were applied to reduce the number of false positives. For confirmation and quantification of the filtered peaks, reference standards were purchased and the retention times and MS/MS spectra were compared. The automated suspect screening method led to slightly higher LOQs than the target method and thus, approximately 30% of low-intensity peaks close to the LOQs were missed. All detected suspects were confirmed by a reference standard and subsequently quantified in the samples.

5.2.5. Risk Assessment

For each detected pesticide, a chronic environmental quality standard (AA-EQS), derived in line with the Technical Guidance Document (TGD) (see EC 2011a) of the Water Framework Directive (WFD) of the European Union, was searched for in the literature (values are listed in **Table D.2**). For 22 substances, AA-EQS values were derived in-house (Swiss Center for Applied Ecotoxicology Eawag/EPFL 2013). For 14 substances, where no AA-EQS value was available,

an *ad hoc* EQS value was derived using a limited data set (see **Table D.3**). Only parent compounds were considered in the ecotoxicological assessment because not enough is known about the toxicity of TPs.

Risk quotients (RQs, i.e., measured concentrations in the composite samples divided by the AA-EQS, EFSA 2013) were calculated for each substance in each sample. Initially, risk assessment was based on single substances. Subsequently, mixture toxicity was assessed in a tiered process. First, as a worst case estimation of the mixture toxicity, the RQ of each detected substance was summed in a sample (concentration addition model, Backhaus and Faust 2012, Belden et al. 2007, Price et al. 2012). Second, the risk was categorized into the three pesticide classes herbicides, fungicides, and insecticides. Thereby, only RQs of substances from the same pesticide class were summed. This realistic worst-case approach was done in order to determine which substance class most affects the total risk.

5.2.6. Scenario Calculations

The results from the comprehensive screening were evaluated based on the number of detected substances, the sum of pesticide concentrations, the single substance toxicity, and the mixture toxicity in each sample. Then, three scenarios were created which included only a subset of compounds and the same evaluations were done with these results. In the first scenario, a ~~"~~Swiss Monitoring" scenario, only the 32 most frequently measured pesticides by Swiss authorities were included (selected substances, see **Table D.1**). In the second scenario, twenty studies were selected from international scientific literature which included multi-residue methods for pesticide measurements in surface waters and which were from various countries with agricultural practices similar to Switzerland. The 36 most frequently investigated pesticides in those studies were used for the evaluation (~~"~~International Studies" scenario, see **Table D.1**). Although this literature search was not complete, it gives a clear overview of which pesticides are considered to be most important in surface waters based on the knowledge of the international scientific community. In the third scenario, the pesticides that are listed as priority substances in the WFD (EC 2013) and have been registered in Switzerland (15 pesticides) were considered (~~"~~WFD Pesticides" scenario, see **Table D.1**).

5.3. RESULTS AND DISCUSSION

5.3.1. Analytical Coverage

With the SPE LC-high-resolution-MS/MS analysis (including target and suspect screening), 91% of polar organic PPPs registered in Switzerland and 81% of potentially-relevant biocides were

covered (**Table 5.1**). Thus, this comprehensive screening allows for a thorough exposure and risk assessment of pesticides in Swiss surface waters.

The advantages of this method are threefold: the non-specific enrichment on the multi-layer cartridge, together with a good chromatographic separation and very specific and sensitive detection on the high-resolution MS. Thereby, substances with very broad physico-chemical properties (e.g., $\log K_{ow}$ -2 to 5) can be detected to the low ng/L range in one run. With the target method, 125 of 136 target pesticides could be measured with LOQs below their specified AA-EQS values. Another 158 polar pesticides were covered by the suspect screening, from which additionally 25 pesticides could be detected in at least one sample.

Substances like carbamates (aldicarb), organophosphates (chlorpyrifos, chlorpyrifos-methyl), or amino acid derivatives (glyphosate, glufosinate) were not covered by the analytical method because they are not well-ionized in the mass spectrometer due to the lack of a hetero-atom or because they are hydrolyzed during preparation. Further, non-polar substances with $\log K_{ow}>5$ could not be detected with this method. Due to strong sorption to organic matter, the freely dissolved water concentrations for these compounds are expected to be very low. Nevertheless, pyrethroid insecticides, for which AA-EQS values in the sub-ng/L range are proposed (e.g., cypermethrin, EC 2013), can still pose a risk. Analytical methods covering such low detection limits are very challenging. The risk from insecticides may therefore be underestimated in this study.

Table 5.1. Number of investigated and analytically covered pesticides, separated into plant protection products (PPPs, divided into the classes herbicides, fungicides, and insecticides) and biocides.

	Pesti-cides[a]	**PPPs**	Herbi-cides	Fungi-cides	Insecti-cides	**Bio-cides**
Investigated Substances	**289**	**220**[b]	105	73	42	**109**[c]
Measurable	**249 (86%)**	**200 (91%)**	99	70	31	**88 (81%)**
Targets[d]	116	113	63	33	17	27
Suspects	133	87	36	37	14	61
Analytically not covered	**40**	**20**	6	3	11	**21**

[a] substances that are registered both as PPP and biocide are displayed in both columns so that the sum of PPPs and biocides is not equal to the total number of pesticides. [b] PPPs: all organic synthetic pesticides that have been sold at least in one year between 2005-2011, excluding non-polar substances ($\log K_{ow}>5$). [c] biocides: all organic synthetic biocides, excluding non-polar substances ($\log K_{ow}>5$) and quaternary ammonia cations; excluding fast degradable substances (half-life water < 1 d). [d] the 25 substances that were confirmed in the suspect screening, are included in the targets.

5.3.2. Screening Results – Parent Compounds

Concentrations and Detection Frequency

From the 249 measurable parent compounds, 104 substances (42%) were detected in at least one of the 45 samples (see **Table 5.2**, **Table D.4**, and **Table D.5** for detailed results of detected substances in all catchments). They consisted of 82 PPPs (not additionally registered as biocides), 2 biocides (not additionally registered as PPPs), and 20 substances registered as both PPP and biocide. In total, 54 herbicides, 31 fungicides, and 17 insecticides were detected. Three main reasons were identified why a substance was not detected: i) low sales data, ii) fast degradation in water or soil, iii) high LOQ in the analytical method. As expected, herbicides had the highest detection frequencies (58%, compared to 43% and 34% for fungicides and insecticides, respectively) and highest concentrations (95^{th}-percentile concentration for all detected substances in the 45 samples: 100 ng/L, compared to 35 ng/L and 16 ng/L for fungicides and insecticides, respectively). This corresponds to the differences in sales data. Kreuger (1998) also found herbicides most frequently and generally in highest concentrations.

Three herbicides had concentrations above 1000 ng/L, while 20 herbicides, five fungicides and three biocides had concentrations above 100 ng/L (**Table 5.2**, **Table D.4** and **Table D.5**). It has to be noted that the measured concentrations are average concentrations over two weeks in medium-sized rivers and that maximum concentrations, especially in smaller streams, can be much higher. Forty percent of herbicide detections were below 10 ng/L, while for fungicides 52% and for insecticides 67% of the detections were below 10 ng/L. This shows that it is very important to have low LOQs for all substances, especially for insecticides where in general the EQS values are also lower.

Catchment Differences and Seasonal Trends

In spite of the different land uses in the five catchments, differences in the number of detected substances and concentration ranges were less pronounced than expected (see **Figure 5.2**). Between 64 (Salmsacher Aach river) and 76 (Surb river) pesticides were detected at least once. The most substances were detected in May and June (45 on average), while numbers were slightly lower in March/April (30) and July (40) (**Figure 5.2A**). This result is easily explained as the main agricultural pesticide application period is between May and June. In contrast, there is no clear seasonal trend of the sum of concentrations (**Figure 5.2B**) and often a few herbicides dominated the total pesticide concentration sum. Interestingly, which substances had the highest concentrations did change over the season. In the Furtbach catchment for example, metamitron and metolachlor concentrations accounted for 75% of the total herbicide concentration in March. At the end of May, terbuthylazine and metolachlor summed up to more than 60% of the total herbicide concentration.

The sum of pesticide concentrations exceeded 1 µg/L in 78% of samples and was on average 1.6 to 2.5 µg/L in each river (**Figure 5.2B**). Substantially lower concentrations were measured in the Salmsacher Aach river, with concentration sums below 2 µg/L at all time points (average: 0.8 µg/L). This is due to lower herbicide concentrations probably caused by smaller relative densities of arable crops.

Frequently Detected Pesticides

In total, 33 pesticides (17 herbicides, 4 fungicides, 2 insecticides, 1 biocide, and 9 substances with double registration) were detected in all five rivers (**Table 5.2**). These substances are expected to be ubiquitous in Swiss rivers with agricultural and urban influence. A large number of these frequently measured substances were also included in many of the international studies considered, indicating their known surface water relevance. However, 8 of the 53 most frequently detected substances in **Table 5.2** were never or only once included in any of the investigated international studies and are therefore potentially overlooked compounds.

Herbicides detected in the five rivers are mainly applied to widespread arable crops such as cereals (e.g., mecoprop, isoproturon), corn (e.g., metolachlor, terbuthylazine), sugar beet (e.g., chloridazone, metamitrone), or potatoes (e.g., metribuzine), all of which are present in each of the catchments. Metamitron, metolachlor, mecoprop, and chloridazone were also the substances with the highest maximum concentrations (**Table 5.2**). This corresponds well with sales data of the substances in Switzerland. The herbicide diuron was also detected in all rivers. It is, however, not applied to large field crops but is used in orchards and vineyards and is additionally registered as biocide. Wittmer et al. (2011) frequently detected diuron as a result of the biocide application in catchments with a high urban land use. But in the Salmsacher Aach, diuron detections were most likely a result of application to apple orchards, since there is no WWTP located within the catchment.

Fungicides detected in all rivers (**Table 5.2**) also mainly originated from arable crops such as cereals (e.g., cyproconazole, tebuconazole) or potatoes (e.g., dimethomorph, propamocarb). Three of the seven fungicides are also authorized as biocides and can therefore be attributed to multiple land use types, complicating source identification. Fungicides with the highest sales numbers, such as chlorothalonil, folpet, captan, and mancozeb, are all non-stable (half-life in water or soil < 1 d) and were accordingly never detected.

Footnotes **Table 5.2**: # only substances that were detected in more than three rivers are shown. [a] also registered as biocide, [b] also registered as veterinary pharmaceutical, [c] AA-EQS: annual average environmental quality standard, see **Table D.2** for references, [d] dicamba, 5-Chloro-2-methyl-4-isothiazolin-3-on (CMI) and metosulam are the only additional substances with EQS exceedances, [e] Letters indicate literature reference: A: Battaglin et al. 2011, B: Dujakovic et al. 2010, C: Gómez et al. 2010, Mezcua et al. 2009, D: Herrero-Hernández et al. 2013, E: Jansson and Kreuger 2010, F: Huntscha et al. 2012, G: Reilly et al. 2012, H: Schäfer et al. 2011, I: Tanabe et al. 2001, K: Belmonte Vega et al. 2005, L: Vryzas et al. 2011, M: Hladik et al. 2008, N: Kampioti et al. 2005, O: Rodrigues et al. 2007, P: Wode et al. 2012, Q: Tankiewicz et al. 2013, R: Finizio et al. 2011, S: Schäfer et al. 2007, T: Lissalde et al. 2011, U: Phillips and Bode 2004, - not included in the 20 analyzed studies

Table 5.2. Detection frequency and maximum concentrations of the most frequently detected pesticides in the five investigated rivers and comparison with international monitoring studies (for Footnotes see page 98) [#]

substance name	LOQ (ng/L)	AA-EQS (ng/L)[c]	detection frequ-ency	maximum concent-ration	no. of EQS excee-dances[d]	measured in international monitoring studies[e]	no. of rivers with detec-tions	pesticide class
s-metolachlor	1	270	100%	960 ng/L	9	C D E F G H L M N P R T U	5	herbicides
mecoprop-P	1	3 600	100%	470 ng/L	0	C E F H N P		
isoproturon[a]	1	320	100%	350 ng/L	1	C D E F H K N O P T		
bentazon	1	73 000	89%	490 ng/L	0	E F H N P		
diuron[a]	2	20	89%	52 ng/L	13	C D E F H K N O P R T U		
ethofumesate	3	22 000	87%	290 ng/L	0	D E H L P		
chloridazon	2	10 000	82%	670 ng/L	0	C D E F P		
2,4-D	4	200	80%	78 ng/L	0	E F N P U		
MCPA	7	1 340	78%	270 ng/L	0	E H F N P U		
atrazine	8	600	71%	345 ng/L	0	B C D E F G H I K L M N P R T U		
ioxynil	1	130	71%	41 ng/L	0	C P		
metribuzin	1	120	69%	120 ng/L	0	C D E H P		
terbuthylazine[a]	9	220	64%	630 ng/L	6	C D E F H K M N P R T		
metamitron	25	4 000	62%	1 500 ng/L	0	C D E H P		
flufenacet	3	137	53%	290 ng/L	3	C		
nicosulfuron	1	35	53%	44 ng/L	2	-		
dimethenamide	1	130	49%	14 ng/L	0	F		
pethoxamid	1	79	44%	80 ng/L	1	-		
sulcotrion	3	5 000	29%	91 ng/L	0	F		
tepraloxydim	1	110 000	22%	4.9 ng/L	0	-		
propyzamide	1	6 000	73%	1 400 ng/L	0	E	4	
cycloxydim	2	464 000	62%	160 ng/L	0	-		
metazachlor	2	20	53%	180 ng/L	12	C E F H P T		
prosulfocarb	10	600	44%	690 ng/L	1	C E		
linuron	9	260	38%	270 ng/L	1	B C D E H I K N O R S T		
tembotrione	0.5	320	31%	50 ng/L	0	-		
triflusulfuron-methyl	0.4	150	31%	10 ng/L	0	E F		
dimethachlor	1	46	31%	5.6 ng/L	0	F		
foramsulfuron	2	7	22%	61 ng/L	4	-		
mesosulfuron-methyl	1	4 000	22%	8.7 ng/L	0	-		
mesotrione	10	80	18%	61 ng/L	0	F		
azoxystrobin	1	950	98%	120 ng/L	0	A C D E F G H F M S T	5	fungicides
cyproconazole[a]	0.5	18 900	82%	98 ng/L	0	A C D M Q		
carbendazim[a]	5	340	82%	65 ng/L	0	B C D F K O T		
tebuconazole[a]	2	1 200	76%	86 ng/L	0	A C D M O S		
dimethomorph	2	5 600	76%	61 ng/L	0	C D G T		
propamocarb	0.3	1 030 000	73%	160 ng/L	0	C E		
metalaxyl-M	1	120 000	71%	380 ng/L	0	A C D E H P R U		
propiconazole[a]	3	1 800	64%	65 ng/L	0	A C E L M	4	
fenamidone	1	1 250	47%	18 ng/L	0	-		
pencycuron	3	1 340	44%	160 ng/L	0	I		
cyprodinil	5	160	38%	330 ng/L	1	C D E G K S		
boscalid	2	11 600	36%	55 ng/L	0	A G P		
epoxiconazole	4	190	33%	64 ng/L	0	C		
pirimicarb	0.4	90	84%	48 ng/L	0	C D E H S T	5	insecticides
fipronil[a,b]	0.5	12	67%	14 ng/L	1	G M		
diazinon[a,b]	3	15	62%	43 ng/L	8	C D G H I L M N R U		
thiamethoxam[a]	3	140	60%	47 ng/L	0	C E		
dimethoate	3	70	27%	21 ng/L	0	B C D E H I L N O R T		
thiacloprid	4	10	36%	65 ng/L	6	C E	4	
pymetrozine	5	500	27%	54 ng/L	0	K		
carbofuran	10	20	22%	45 ng/L	4	B C D E G H K L M O S T		
diethyltoluamide (DEET)	7	41 000	89%	520 ng/L	0	C F	5	biocide

Four of five insecticides (pirimicarb, diazinon, thiamethoxame, and dimethoate) (**Table 5.2**) that were detected in all five rivers have the highest insecticide sales numbers, are permitted to be used in many different crops, and are also applied in private gardens. Neonicotinoids, whose relevance has been heavily discussed in recent years due to their effects on bees (Henry et al. 2012, Whitehorn et al. 2012) and aquatic organisms (Goulson 2013, Van Dijk et al. 2013), were also frequently detected. Especially the sprayed PPPs thiamethoxame (applied in orchards, vegetables, and private gardens) and thiacloprid (applied in potatoes, cereals, and oilseed rape) were frequently found. Seed dressings (imidacloprid, clothianidin) were only detected sporadically in relatively low concentrations (< 20 ng/L), although sales data are in comparable ranges to the sprayed neonicotinoids. The detections of imidacloprid in the rivers Furtbach and Surb are most likely a result of spray application on vegetables.

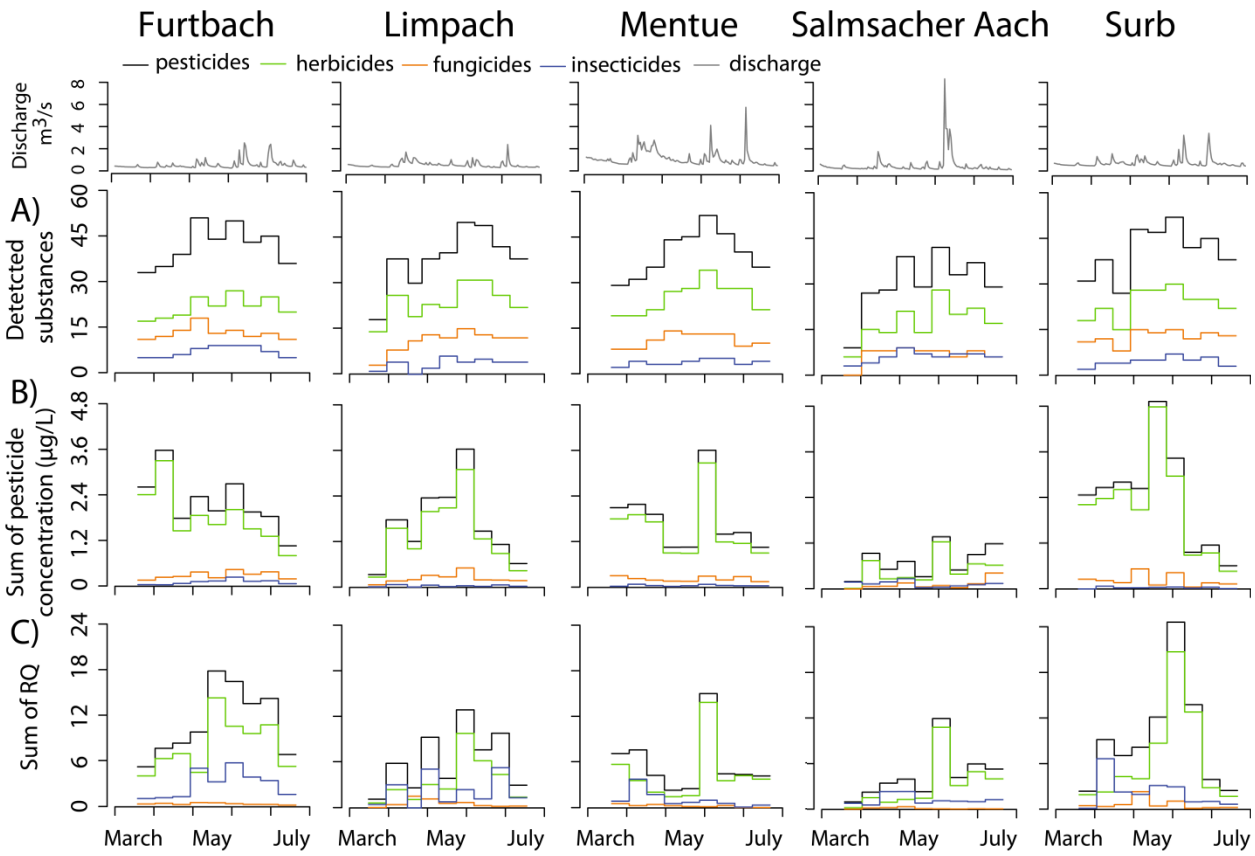

Figure 5.2. Number of detected substances (A), sum of pesticide concentrations (µg/L) (B), and sum of risk quotients (C) in the five rivers during the sampling period in 2012 (parent compounds of all herbicides, insecticides, and fungicides considered; biocides that are not registered as PPPs are not included). In addition, the discharge during the sampling period is shown (top).

To summarize, the PPPs that were detected in all rivers were substances with high sales numbers and either applied in arable crops which were present in all catchments or substances with a very broad agricultural application.

Biocides have been investigated only sporadically in previous years and the pervasiveness of biocides in surface waters has not yet been fully assessed. Interestingly, in this comprehensive screening, besides the well-known diethyltoluamide (DEET), diuron, carbendazim, azole fungicides, and diazinon (Kahle et al. 2008, Wittmer et al. 2011), no other biocides were frequently detected. The fact that the wastewater amount was variable in the five catchments (from 0% in the Salmsacher Aach up to 80% in the Furtbach river at baseline discharge) leads to the conclusion that there are no other important biocides in Swiss surface waters.

Some substances were frequently detected in just one or two catchments. Examples of such site-specific substances are myclobutanil and methoxyfenozide (both registered for orchards and vineyards), which were only detected in the orchard-dense Salmsacher Aach catchment. Benthiavalicarb-isopropyl (applied on potatoes) and dimefuron (applied on oilseed rape) were only found in the Mentue catchment. This shows that a list of relevant compounds on a national scale is, in many cases, not sufficient. Either very detailed usage data for the investigation site needs to be available, or a complete screening for all potentially present pesticides has to be carried out in order to get the full exposure picture.

5.3.3. Screening Results – Transformation products (TPs)

Out of the 134 investigated TPs, 40 were detected at least once (31 herbicide, 4 fungicide, 4 insecticide, and 1 biocide TPs) (see **Table D.6**). In particular, TPs of chloroacetanilide herbicides (e.g., metolachlor-ESA and metazachlor-ESA), chloridazone, atrazine, and azoxystrobin were detected in nearly every sample. These TPs were already frequently detected in other studies in Switzerland (Kern et al. 2011a) and Germany (Reemtsma et al. 2013a). Between 15 and 25 TPs were detected in each sample. Fifteen percent of all TP detections were above 100 ng/L. The concentration sum of the TPs exceeded 1 µg/L in 35% of samples and was dominated by herbicide TPs. Interestingly, the median concentration sum of the detected TPs in this study was 860 ng/L, which is 2.6 times higher than the median concentration found in German rivers (Reemtsma et al. 2013a). For six substances, only the TP was detected but not the parent compound (bifenox, chlorothalonil, dichlobenil, dichlofluanid, fluazifop-butyl, prothioconazole). Either the parent compound of these TPs has a short half-live in water or soil (e.g., bifenox, prothioconazole) or the parent compound could not be measured by the analytical method (chlorothalonil and dichlobenil). Information about the application of the parent compounds can consequently be inferred from TP monitoring. It can be concluded that herbicide TPs are present in concentrations comparable to the parent compounds while fungicide and insecticide TPs seem to have less relevance in surface waters.

5.3.4. Risk Assessment - Single Substances

For each of the 104 detected parent substances, an AA-EQS value could be found in or derived from the literature (see **Table D.2**). This means that in addition to the broad analytical coverage, a full risk assessment could be performed for all detected pesticides.

First, the risk of single substances was investigated, which was considered the least conservative risk assessment scenario. In total, 19 substances contributed at least once to an exceedance of an AA-EQS in the 45 composite samples (**Table 5.2**). These substances consisted of 13 herbicides, 4 insecticides, 1 fungicide, and 1 biocide (not registered as a PPP). The most critical substances were diuron (13 exceedances), metazachlor (12), metolachlor (9), diazinon (8), terbuthylazine (6), and thiacloprid (6). Six substances (diuron, metolachlor, foramsulfuron, diazinon, terbuthylazine, and carbofuran) had exceedances in more than three rivers; thus, they are probably relevant substances on a national scale. In 31 of 45 surface water samples (70%), at least one exceedance was registered. In nearly half of the samples, more than one exceedance was found (14 times 2-3 exceedances, 6 times 5-7 exceedances). The most exceedances (6-7) were in the Furtbach and Surb rivers in the beginning of June. Thus, when applying the least conservative scenario, already two-thirds of the water samples exceeded critical concentrations.

5.3.5. Risk Assessment - Mixture Toxicity

The fact that 104 different pesticides were measured in the five rivers shows that in the future more focus should be on mixture toxicity approaches. When applying the worst-case scenario (summation of all RQs), 44 out of 45 surface water samples exceeded the RQ of 1, up to an RQ of 25 (**Figure 5.2C**, black line). It can be clearly seen that the Furtbach and Surb rivers show the highest risks (average exceedances by a factor of 11 and 9, respectively), while the other three rivers also had average exceedances of a factor of 4 to 6. Highest risks were found at the end of May and beginning of June in all rivers (the main agricultural pesticide application season). However, samples in March already had mixture RQs of more than two in nearly all catchments.

Herbicides (**Figure 5.2C**, green line) were responsible for the largest part of the mixture toxicity risk, accounting for 60-80% (median) of the total risk in the catchments. Second contributor to the risk were insecticides (6-20%, blue line). It has to be noted that the risk of the highly toxic pyrethroids was not included. Although expected concentrations are very low (sub-ng/L), these substances could still substantially contribute to the overall risk from insecticides. In contrast, the risk from fungicides and biocides was very low. In classical risk assessment, however, only three organism groups (*i.e.,* plants, vertebrates, and invertebrates) are considered. Fungicides obviously target fungi, which are normally not considered in risk assessments. Thus, there might be a blind spot in the current risk assessment and the risk of fungicides may be underestimated (Reilly et al. 2012).

5.3.6. Scenario Analysis

A comprehensive screening as described here has not been feasible until now, especially for routine monitoring, due to the labor-intensive analysis and the need for a high-resolution mass spectrometer. Therefore, we analyzed how the exposure and risk assessment is different if only a subset of substances is considered as compared to a complete screening. The three scenarios „Swiss Monitoring", „International Studies", and „WFD Pesticides" were considered (see Materials and Methods). In all scenarios, a much lower number of substances would be detected per sample: 15-20 substances in the „Swiss Monitoring" and „International Studies" scenarios, and only 4 substances in the „WFD Pesticides" scenario, compared to roughly 40 substances in the complete screening (see **Figure 5.3A** and **Figure D.2A** for the temporal dynamic). Thus, about half to two-thirds of the detected substances were missed in the two scenarios investigating 35-40 substances. When looking at the concentration sums, the two scenarios „Swiss Monitoring" and „International Studies" covered 50-60% (**Figure 5.3B** and **Figure D.2**). The results of the concentration sums matched better with the complete screening than the results of the number of detections because the pesticides accounting for the highest concentrations were included in these scenarios (e.g., metamitron, metolachlor, terbuthylazin).

With regard to single substance toxicity, in the two scenarios „Swiss Monitoring" and „International Studies", 30-35% of the AA-EQS exceedances of single substances were missed, mainly because the relevant substances flufenacet, foramsulfuron, nicosulfuron, prosulfocarb, thiacloprid, and carbofuran were not included. In the „WFD Pesticides" scenario, more than 80% of the exceedances were missed. The only pesticide in the „WFD Pesticides" scenario that had multiple EQS exceedances in the current screening study was diuron. In the WFD, it is written that river-basin specific substances should be selected in addition to the priority list (EC 2013). This study confirms that for a proper risk assessment, this is essential. When considering mixture toxicity, it can be seen that on average 55-65% of the total risk (65-70% of the herbicide risk, 10-50% of the fungicide risk, and 35-55% of the insecticide risk) can be detected by the scenarios „Swiss Monitoring" and „International Studies" (**Figure 5.3C-F**, **Figure D.2C**). There are, however, large differences between the catchments. In the Furtbach river, nearly all of the risk was captured by the scenarios (80-85%), while in the Limpach river it was only 40-50% (**Figure D.3**). In four to eight of the 45 river samples, it would have been concluded that there was no risk from herbicides when only investigating the substances from the scenarios „Swiss Monitoring" and „International Studies", although a risk was detected by the complete screening. For insecticides, 14–18 of the samples (30-40%) would have been interpreted incorrectly. This shows that especially insecticides are still underrepresented in analytical methods and consequently in routine pesticide monitoring.

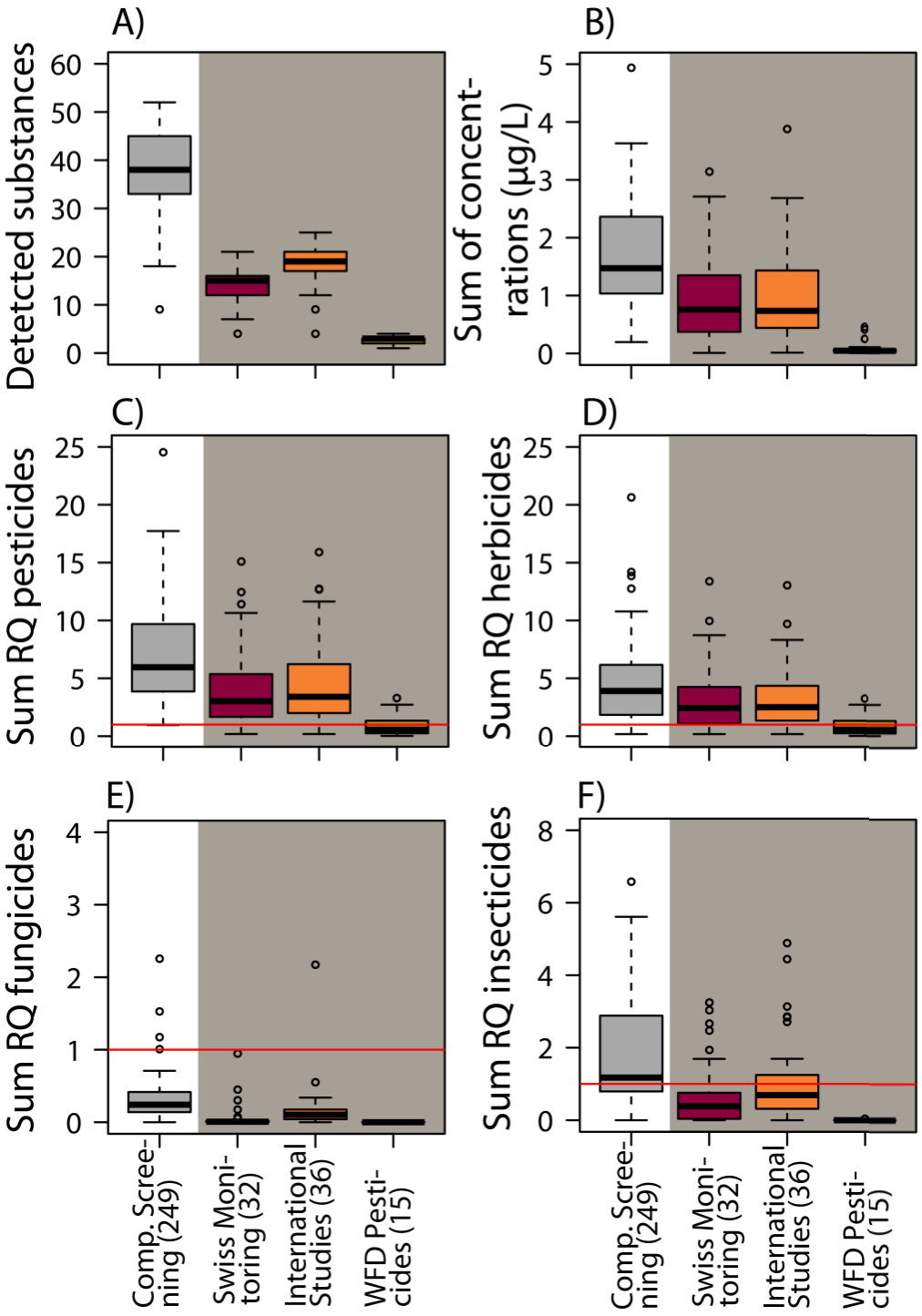

Figure 5.3. Number of detected pesticides (A), sum of pesticide concentrations (B), sum of risk quotients (RQs) for pesticides (C), for all herbicides (D), for all fungicides (E), and for all insecticides (F) in the 45 samples in the five catchments. Left boxplot (gray): complete screening, right boxplots (gray shaded area): three scenarios for which only a subset of substances were selected. Number in parentheses corresponds to the number of investigated substances in each scenario.

5.3.7. Implications for Routine Monitoring

The results of this study show that the most frequently measured pesticides by the scientific community and by Swiss authorities may allow a reasonable assessment of surface water quality in medium-sized Swiss rivers. The risk to surface waters from the mixture toxicity assessment was in most cases underestimated by a factor of two, and in extreme cases the underestimation was up to a factor of ten. The addition of some substances (e.g., flufenacet, foramsulfuron, thiacloprid, carbofuran) to the current substance selection would improve the surface water assessment. Nevertheless, when not all substances are monitored, there is always the probability that an important substance has been missed. This is especially true for monitoring of rivers in smaller catchments where a site-specific substance (that is not relevant on the broader scale) can be the dominant pesticide. Without a comprehensive screening, the only way to overcome this problem is detailed knowledge of the applied substances in the catchment, which is often hard to achieve in practice.

The risk assessment based on the complete screening showed that herbicides and insecticides dominate the risk in Swiss surface waters and exceedances of critical concentrations were found over the whole investigation period in all catchments. The fact that over 100 pesticides were detected in the five rivers demonstrates the importance of a refined mixture toxicity approach. It is also critical that relevant insecticides (e.g., neonicotinoids) are included in routine monitoring programs carried out by authorities. Furthermore, it is essential to use analytical methods with LOQs below 10 ng/L, in order to agree with EQS values. Finally, practically accessible methods are needed with which very toxic pyrethroids can be detected down to the sub-ng/L range.

Most of the relevant pesticides defined here can be measured after proper sample extraction on low-resolution LC-MS/MS (e.g., triple quadrupoles). Nevertheless, in the near future, sensitive high-resolution mass spectrometers and more automated software tools will most likely become accessible for routine analysis, too. Thereby, screening of the whole pesticide spectrum may become possible and perhaps even more cost-effective than defining the most relevant substances beforehand and analyzing them specifically. As the relevant pesticides will change over time and can be regionally different, a comprehensive screening is in either case the optimal way to do a proper pesticide exposure and risk assessment in surface waters.

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6. CONCLUSIONS AND OUTLOOK

6.1. CONCLUSIONS AND OPEN QUESTIONS

Two Trace-Level Mass Spectrometry Techniques and Complementary Sampling Strategies for the Complete Assessment of Pesticides

The first goal of this thesis was to develop a set of tools to comprehensively assess the exposure of pesticides in surface waters. The results showed that with only two analytical methods, almost the complete pesticide spectrum — from very polar to very non-polar substances, neutral and ionic species, parent compounds and transformation products (TPs) — can be covered. For most compounds (ultra)trace-level detection limits were reached which were needed to check for compliance with environmental quality standards (EQS). For polar to semi-polar substances, automated composite water samples and the detection by liquid chromatography high-resolution tandem mass spectrometry (LC-HR-MS/MS) is optimal (**chapter 2**) and gives representative average concentrations with low uncertainties. For non-polar pesticides, passive sampling by silicon rubber (SR) and detection by gas chromatography tandem mass spectrometry (GC-MS/MS) is optimal (**chapter 4**). Although quantification from passive samplers is currently rather uncertain due to limited knowledge of sampling rates, it is possible to detect the substances at (ultra)trace levels, which would not be possible with ambient water samples. The main conclusions of the method development (analytical and sampling) are highlighted below:

Majority of polar pesticides and TPs are detectable by LC-high resolution-MS/MS

The application of an LC-HR-MS/MS method using a combination of target screening and exact mass screening (suspect screening) showed that 86% of all polar to semi-polar pesticides and most of their known transformation products (TPs) can be efficiently screened for in surface waters (**chapter 2**). For such a broad and sensitive analytical method, it is crucial to have i) a non-selective enrichment by solid phase extraction (SPE, done by a multi-layer cartridge), ii) a good chromatographic separation, and iii) a selective and sensitive detection (achieved by a high resolution MS with mass accuracy <5 ppm, resolution of 140 000, and specific fragmentation in the MS/MS).

Exact mass screening is an efficient method for substances without reference standards

The hypothesis that pesticides can be screened efficiently with only the exact mass as initial information could be verified. In addition, only information that is available from the chemical structure such as the isotopic pattern and predicted fragmentation ions in the MS/MS is needed for further filtering. This semi-automated suspect screening opens the door for the detection of TPs for which reference standards are not easily available **(chapter 2**). Furthermore, the method can be adapted to other substance groups with similar properties such as pharmaceuticals, industrial chemicals and their TPs. Although the

semi-automated suspect screening method is already very efficient, more sophisticated software tools to reduce the manual effort in the peak filtering are still desired.

Passive sampling is less suitable for quantifying polar pesticides than ambient water samples

Passive sampling by Chemcatcher® devices was investigated as an alternative to ambient water samples in monitoring polar pesticides (**chapter 3**). From previous literature, it was hypothesized that more substances can be detected on the passive sampler compared to the composite water samples. This could not be verified for Chemcatcher® passive samplers. Detection limits and the number of detected substances were in the same range for the two sampling procedures. The field study set-up employed here could be used to calibrate the passive samplers in-situ, and sampling rates (R_s) were determined for nearly 100 substances from different substance classes. The study also showed that for membrane covered SDB disks, R_s is only slightly correlated with $logD_{ow}$ so that a prediction remains with large uncertainties. Therefore, a better understanding of both the chemical interactions between substance and sampling material and of the transport mechanism over the diffusive limiting membrane is needed. Unfortunately, sampling rates of substances with fluctuating river concentrations — which is the case for most pesticides — could often not be calculated. The adaptation of R_s for highly fluctuating substances to other rivers is therefore only possible with large uncertainties. As the sampling and extraction of the SDB passive samplers is easy, very fast and requires a minimum amount of resources, it can be concluded that passive sampling is perfectly suitable for qualitative screening. In remote areas, where an automated sampler cannot easily be installed due to a lack of electricity, passive sampling is still much better compared to taking grab samples, where concentration peaks are often missed completely.

Toxic non-polar insecticides are detectable in ultratrace levels by passive sampling

Important substances that could not be measured by LC-HR-MS/MS are the extremely toxic non-polar insecticides (pyrethroids and organophosphates). Previous studies have shown that it is nearly impossible to reach the requested detection limits for compliance with environmental quality standards (EQS) with ambient water samples (pg/L range), even when highly sensitive GC-HR-MS devices are used. Therefore, passive sampling using SR sheets was tested as an alternative (**chapter 4**). It was hypothesized that extremely low detection limits could be obtained due to very high sampling rates of the SR material (10-100 L/d). To that end, it was necessary to develop a fast and efficient extraction method (done by accelerated solvent extraction (ASE)), to optimize the clean-up of the environmental matrix (achieved by a combined C18/silica gel column) and to obtain a sensitive detection (done by GC-MS/MS). Thereby, it was possible to reach the required detection limits in the pg/L range for highly toxic non-polar pesticides, confirming the hypothesis and demonstrating that

passive sampling is a suitable method to measure these compounds. However, many open questions remain concerning the accurate quantification because no substance specific sampling rates could be determined and no correction methods for varying environmental factors (e.g., flow velocity) are available. For this, exact measurements of the distribution coefficient between sampler and water (K_{pw}) are needed and appropriate performance reference compounds (PRCs) need to be selected.

Complete Assessment of Pesticides Shows Real Contamination of Surface Waters

The second goal of this thesis was to apply the previously described comprehensive analytical and sampling tools in a large, representative field study in order to assess the actual pesticide exposure and associated risk, and to identify blind spots in conventional monitoring strategies. Therefore, a large field study comprising five medium-sized rivers distributed over the Swiss Plateau was carried out. The selected catchments had different land uses and were representative of agriculturally and urban influenced rivers in Switzerland. Two week time-proportional water samples were used to assess the chronic exposure of pesticides in medium-sized rivers (**chapter 5**). These samples reflected the average concentration that an organism has been exposed to within this period. In addition, SR passive samplers were deployed for the same two week sampling interval for the detection of non-polar insecticides (**chapter 4**). The main conclusions of the comprehensive exposure and risk assessment are highlighted below:

104 substances detected with concentration sums > 1 µg/L

The extensive screening provided a more comprehensive overview of the pesticide contamination of Swiss rivers. The results showed that the pesticide exposure is higher than previously identified: more than 100 parent compounds and 40 TPs were detected in total, between 30–50 parent compounds and 15–25 TPs were detected per water sample, and the sum of pesticide concentration was above 1 µg/L in nearly 80% of samples (**chapter 5**). From the 104 detected pesticides, 82 were registered only as plant protection products (PPP), which highlights the importance of the agricultural contribution. As expected, herbicides clearly dominated the exposure while insecticides were found in the lowest concentrations - which does not mean that they were less relevant (see below). In all catchments, a similar number of substances was detected, but the substance spectrum was highly variable and reflected the land use in the catchments. In a future study, it would be interesting to define the importance of the different sources of each pesticide (e.g., point-source vs. diffuse source, emissions from different crops). To achieve this, smaller catchments need to be investigated in more detail. Such studies might also reveal the dimension of maximum pesticide concentrations in rivers and can measure the degree to which maximum pesticide concentrations exceed the acute (MAC-) EQS.

Risk assessment suggests negative effects over the whole investigation period (March-July)

When comparing the measured pesticide concentrations with chronic (AA-)EQS values, at least one exceedance was detected in 70% of the samples (**chapter 5**). In total, 19 polar to semi-polar pesticides showed at least one exceedance. Most critical substances were the herbicides diuron, metazachlor and terbuthylazine, as well as the insecticides diazinon and thiacloprid. With the concentration estimates from the passive samplers, chlorpyrifos-methyl, cypermethrin, deltamethrin and lambda-cyhalothrin clearly indicated exceedances of AA-EQS, for deltamethrin this was up to a factor 700 (**chapter 4**). The high number of simultaneously occurring substances clearly shows that the assessment of mixture toxicity is very crucial. A risk assessment was carried out based on concentration addition and clearly indicated that a risk to aquatic organisms cannot be excluded during the whole investigation period (March–July 2012) in all catchments (**chapter 5**). In some cases, exceedances up to factor 25 were found. Main contributors were herbicides and insecticides which shows that aquatic plants and invertebrates were at highest risk. Investigations of diatoms and macroinvertebrates in the five catchments during three time points in the year 2012 support these results (AquaPlus 2013). It was shown that the aquatic communities in all five rivers were impacted, which may partly be explained by the presence of pesticides in the rivers.

Many open questions in the field of risk assessment remain

In the field of risk assessment, there are many open questions. First, EQS may change when new data become available. Because part of the derivation of EQS values is based on expert judgment, EQS derived by different countries are not necessarily equal, even if they were based on the same data. Second, for fungicides, the ecotoxicological evaluation is unsatisfactory because aquatic fungi are normally not included in the set of ecotoxicological studies (EC 2011a). It can be expected that fungi are the most sensitive species for fungicides and a first study to look into this supports this assumption (Dimitrov et al. 2014). Third, there is the question how long the sampling period has to be before pesticide concentrations can meaningfully be compared with AA-EQS values. And finally, more refined methods that address the issue of mixture toxicity need to be investigated. Therefore, more knowledge about the exact modes of action of each substance may become important.

Classical monitoring could miss large part of the risk

If exactly the same field study had been carried out, but only the 30–40 most frequently investigated substances (in Swiss routine monitoring or by scientific investigations) were analyzed, the number of detected substances would on average be underestimated by a factor of two (**chapter 5**). One third of all AA-EQS exceedances of single substances would be missed and on average half of the mixture toxicity as well. In extreme cases, mixture toxicity would even be underestimated by a

factor of ten, because one or several relevant substances would not be incorporated into the analysis. In particular, the risk from insecticides would not be covered well, because only a few substances are included in current pesticide monitoring. In 30–40% of cases for which an exceedance was found with the complete screening (even without non-polar insecticides), no risk would have been determined in the scenarios.

6.2. PRACTICAL IMPLICATIONS

Improvements in Routine Monitoring Required

The results show that although the currently used monitoring strategies are very important, they are not sufficient to comprehensively assess the pesticide exposure and risk. It is therefore important to include more and the most relevant pesticides into analytical methods. In particular, insecticides (e.g., neonicotinoids) and fungicides are very much underrepresented to date. In Switzerland, a project from the Federal Office for the Environment (FOEN), which had been running in parallel to this dissertation, aimed at selecting the 40 most important substances from diffuse sources (Wittmer et al. 2014a). In the FOEN project, theoretical considerations (sales numbers, application pattern, physico-chemical properties, persistence in soil and water) and results from former Swiss monitoring studies were used to pre-select important substances. Then, the results from the described complete screening study were compared with the pre-selection and adjustments were made if necessary. The final list will be proposed to the Cantonal authorities so that future routine monitoring is harmonized. It is important that such a list is adapted at least once every five years in order to account for changes in the pesticide regulation and market.

Nevertheless, even with an up-to-date list of nationally relevant substances, there is still the chance that locally important substances are missed. Therefore, a complete pesticide screening is desirable. This is in particular true in smaller catchments where the application behavior of local farmers can be the main driver for the pesticide exposure. Such a screening may even be valuable in routine monitoring in the near future, since LC-HR-MS/MS instrumentation will get cheaper and may soon be affordable to local authorities. Larger cantons in Switzerland have already bought such high-resolution devices. Also when software tools for the automated screening get more sophisticated, the manual effort will be reduced substantially. This trend can already be seen today, as data evaluation software from commercial vendors include more and more features to automate and speed up data processing.

Passive sampling is another option which cantonal authorities might be able to use to reduce workloads while (qualitatively) monitoring a broad range of compounds. This method could potentially also be very important for monitoring non-polar insecticides such as pyrethroids and organophosphates which cannot be measured in ambient samples at low enough levels for

accurate risk assessment. Further validation of this sampling method is still needed, but should certainly be pursued. Hopefully with more knowledge about sampling rates of different compounds and the influence of environmental factors on those sampling rates, passive sampling can officially be accepted as a monitoring tool, for example also for monitoring priority pollutants (e.g., cypermethrin, chlorpyrifos) for EQS compliance in the EU.

Actions for Pesticide Reduction Are Needed

The complete pesticide screening showed that the contamination of surface waters by pesticides is larger than previously identified. Several pesticides exceeded ecotoxicological thresholds, and for many substances also the numerical requirement for pesticides in Switzerland (0.1 µg/L) was exceeded (Wittmer et al. 2014b). From today's legislation (SR 814.20 1991), it is clear that actions are needed to reduce the pesticide load into surface waters. Although many improvements have already been made, more effort is required. This has also been acknowledged by the Swiss parliament, which recently (May 21, 2014) agreed on a national action plan for reducing the risks by pesticides (Schweizerische Eidgenossenschaft 2014b). One option is the ban of critical pesticides, as was the case for diazinon in the EU and in Switzerland. However, it has to be guaranteed that the alternatives provided are safe. If diazinon is replaced by highly toxic neonicotinoids and pyrethroids, then environmental risk is likely not decreased. Actions to decrease usage at the source may be more effective and include the encouragement of more integrated agricultural practices such as spraying only at certain pest pressure or even organic farming. Another approach is to prevent the applied substances from entering surface waters, e.g., by increasing distance requirements (between application area and water body) for certain substances or by the introduction of vegetated buffer strips in vulnerable areas, as well as the improved education of farmers and private gardeners for the safe handling and use of pesticides. The list presented here is not conclusive.

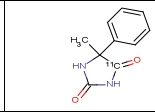
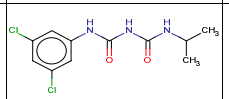
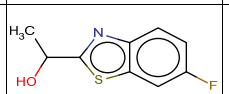
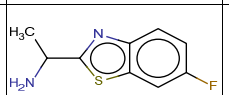
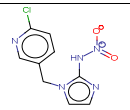
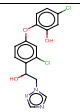
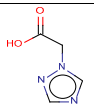
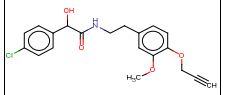
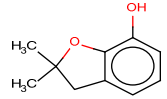
It is important to include ecotoxicologically-based water quality guidelines into the Swiss Water Protection Law (SR 814.20 1991). The ecotoxicologically-based EQSs of the different pesticides span several orders of magnitude. Therefore, a general threshold for all substances is not meaningful. For example, the numerical requirement of 0.1 µg/L is not conservative enough for 30% of all pesticides because EQS are below this value. The Swiss Federal Council has recently (August 20, 2014) reported that the introduction of such substance specific values for the assessment of the water quality is being considered for micropollutants (Schweizerische Eidgenossenschaft 2014a).

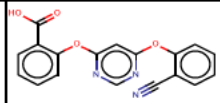
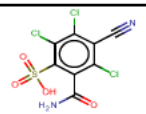
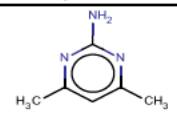
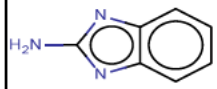
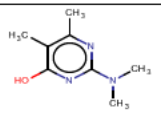
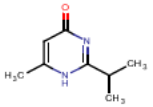
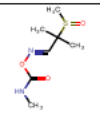
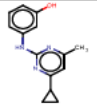
It is clear that only by incorporating diverse measures to reduce the pesticide load and through intensive discussions with all stakeholders can successful results be achieved. It is thereby important that the different goals of the stakeholders (e.g., surface water quality, food security, degree of self-sufficiency in food production) are balanced and a sound compromise found. The results from this dissertation clearly indicate that such measures are essential for improving the quality of Swiss surface waters.

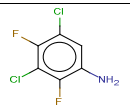
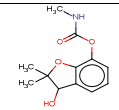
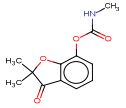
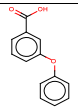
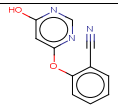
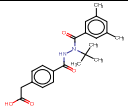
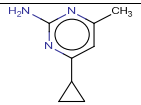
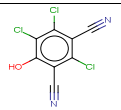
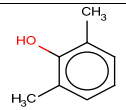
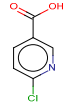
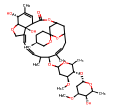
APPENDIX

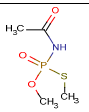
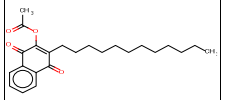
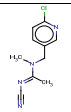
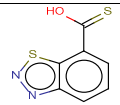
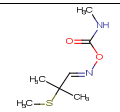
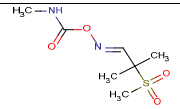
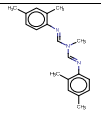
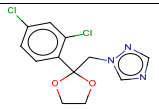
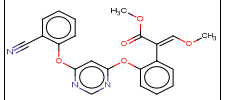
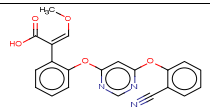
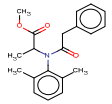
APPENDIX A SUPPPORTING INFORMATION TO CHAPTER 2

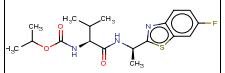
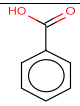
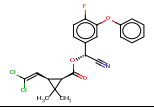
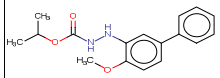
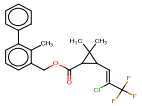
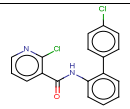
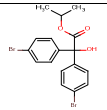
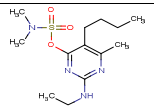
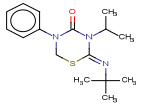
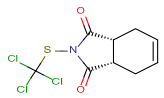
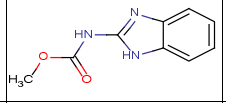
A.1. Substance Details

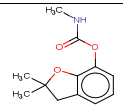
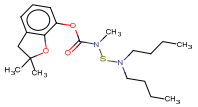
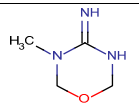
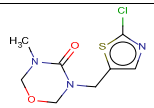
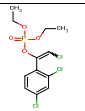
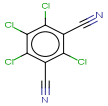
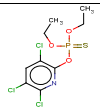
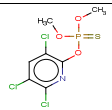
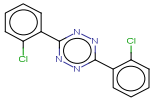
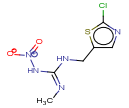
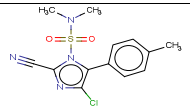
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
(S)-5-methyl-5-phenylimidazolidine-2,4-dione	TP (Fenamidone)	C9[11C]H10N2O2	6843-49-8		0.9	likely	Suspect
1-(3,5-dichlorophenyl)-5-isopropyl biuret	TP (Iprodione)	C11H13Cl2N3O2	63637-88-7		2.7	likely	Suspect
1-(6-fluoro-2-benzothiazol-2-yl)ethanol	TP (Benthiavalicarb-isopropyl)	C9H8FNOS	782480-72-2		2.1	likely	Suspect
1-(6-fluoro-2-benzothiazolyl)ethylamine	TP (Benthiavalicarb-isopropyl)	C9H9FN2S	177407-12-4		2.0	likely	Suspect
1-[(6-chloro-3-pyridinyl)methyl]N-nitro-1H-imidazol-2-amine	TP (Imidacloprid)	C9H8ClN5O2	115086-54-9		1.5	likely	Suspect
1-[2-[2-chloro-4-(4-chloro-phenoxy)-phenyl]-2-1H-[1,2,4]triazol-yl]-ethanol	TP (Difenoconazole)	C16H13Cl2N3O3	-[a]		**3.8**	likely	Suspect
1H-1,2,4-triazol-1-ylacetic acid	TP (Azoles)	C4H5N3O2	4314-22-1		-1.3	likely	Suspect
2-(4-chlorophenyl)-2-hydroxy-N-[2-(3-methoxy-4-prop-2-ynyloxy-phenyl)-ethyl]-acetamide	TP (Mandipropamid)	C20H20ClNO4	282720-26-7		**2.6**	likely	Suspect
2,3.dihydro-2,2-diemethyl-7-benzofuranol	TP (Cabofuran)	C10H12O2	1563-38-8		2.2	not likely	not included

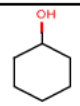
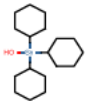
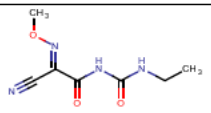
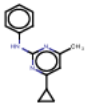
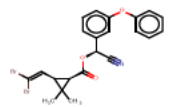
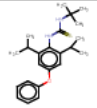
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]benzoic acid	TP (Azoxystrobin)	C18H11N3O4	951009-69-1		3.8	likely	Suspect
2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid	TP (Chlorothalonil)	C8H3Cl3N2O4S	1418095-02-9		-0.7	likely	Suspect
2-amino-4,6-dimethylpyrimidine	TP (Pyrimethanil)	C6H9N3	767-15-7		**1.0**	likely	Suspect
2-aminobenzimidazole	TP (Carbendazim)	C7H6N3	934-32-7		**0.9**	likely	Suspect
2-dimethylamino-5,6-dimethylpyrimidin-4-ol	TP (Pirimicarb)	C8H13N3O	40778-16-3		1.8	likely	Suspect
2-isopropyl-6-methyl-4-pyrimidinol	TP (Diazinon)	C8H12N2O	2814-20-2		**0.7**	likely	Taget
2-methyl-2-(4-(2-methyl-3-piperidin-1-yl-propyl)-phenyl)-propionic acid	TP (Fenpropidin)	C13H17F3N4O4	29091-21-2		4.4	likely	Suspect
2-methyl-2-(methylsulfinyl)propanal O-((methylamino)carbonyl)oxime	TP (Aldicarb)	C7H14N2O3S	1646-87-3		**-0.8**	likely	Suspect
3-(2-((1H-1,2,4-triazol-1-yl)methyl)-2-(2,4-dichlorophenyl)-1,3-dioxolan-4-yl)propan-1-ol	TP (Propiconazole)	C15H17Cl2N3O3	104390-58-1		2.9	likely	Suspect
3-(4-cyclopropyl-6-methylpyrimidin-2-ylamino)phenol	TP (Cyprodinil)	C14H15N3O	694520-26-8		2.9	likely	Suspect
3,5,6-trichloro-2-pyridinol	TP (Chlorpyrifos, Chlorpyrifos-methyl)	C5H2Cl3NO	6515-38-4		**3.2**	likely	Taget

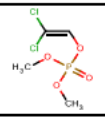
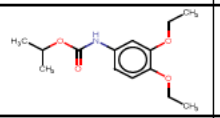
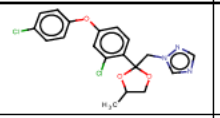
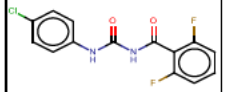
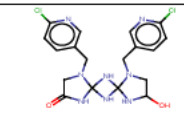
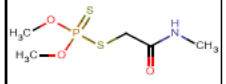
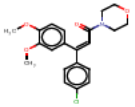
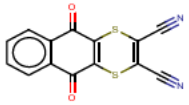
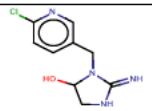
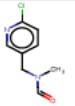
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
3,5-dichloro-2,4-difluoroaniline	TP (Teflubenzuron)	C6H3Cl2F2N	83121-15-7		2.6	likely	Suspect
3-hydroxycarbofuran	TP (Carbofuran)	C12H15NO4	16655-82-6		**1.5**	likely	Suspect
3-Ketocarbofuran	TP (Carbofuran)	C12H13NO4	16709-30-1		1.6	likely	Suspect
3-phenoxybenzoic acid	TP (Cypermethrin)	C13H10O3	3739-38-6		3.1	likely	Suspect
4-(2-cyanophenoxy)-6-hydroxypyrimidine	TP (Azoxystrobin)	C11H7N3O2	240802-59-9		2.3	likely	Suspect
4-(N'-(3,5-dimethylbenzoyl-N-(1,1-dimethylethyl)hydrazinocarbonyl)phenyl acetic acid	TP (Tebufenozide)	C22H26N2O4	163860-35-3		4.0	likely	Suspect
4-cyclopropyl-6-methyl-pyrimidine-2-ylamine	TP (Cyprodinil)	C8H11N3	92238-61-4		0.9	likely	Suspect
4-hydroxy-2,5,6-trichloroisophtalonitrile	TP (Chlorothalonil)	C8HCl3N2O	28343-61-5		3.2	likely	Suspect
5,6-dimethyl-2-(methylamino)pyrimidin-4-ol	TP (Pirimicarb)	C8H10O	1300-71-6		**2.6**	not likely	not included
6-chloronicotinic acid	TP (Imidacloprid)	C6H4ClNO2	5326-23-8		1.2	likely	Suspect
abamectin	I	C44H66O14	71751-41-2		**4.4**	not likely	not included

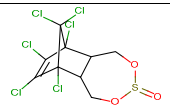
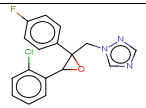
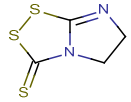
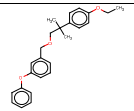
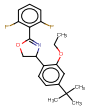
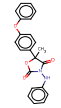
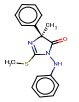
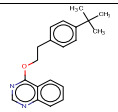
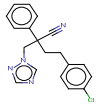
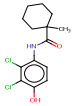
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
acephate	I	C4H10NO3PS	30560-19-1		**-0.9**	likely	Suspect
acequinocyl	A	C24H32O4	57960-19-7		**6.2**	-	not included
acetamiprid	I	C10H11ClN4	135410-20-7		**0.8**	likely	Suspect
acibenzolar-S-methyl	P	C7H4N2OS2	135158-54-2		**3.1**	likely	Suspect
aldicarb	I	C7H14N2O2S	116-06-3		**1.2**	likely	Taget
aldoxycarb	TP (Aldicarb)	C7H14N2O4S	1646-88-4		**-0.6**	likely	Suspect
amitraz	I	C19H23N3	33089-61-1		**5.5**	likely	not included
azaconazole	F	C12H11Cl2N3O2	60207-31-0		**2.4**	likely	Suspect
azoxystrobin	F	C22H17N3O5	131860-33-8		**2.5**	likely	Taget
azoxystrobin free acid	TP (Azoxystrobin)	C21H15N3O5	1185255-09-		3.8	likely	Taget
benalaxyl	F	C20H23NO3	71626-11-4		**3.5**	likely	Suspect

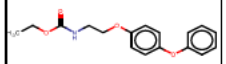
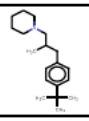
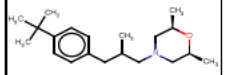
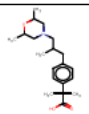
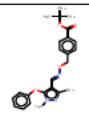
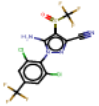
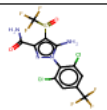
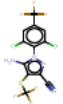
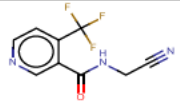
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
benthiavalicarb	F	C18H24FN3O3S	177406-68-7		**2.6**	likely	Suspect
benzoic acid	I	C7H6O2	65-85-0		**1.9**	likely	Suspect
beta-cyfluthrin	I	C22H18Cl2FNO3	68359-37-5		**5.9**	-	not included
bifenazate	I	C17H20N2O3	149877-41-8		**3.4**	likely	Suspect
bifenthrin	I	C23H22ClF3O2	82657-04-3		**7.3**	-	not included
boscalid	F	C18H12Cl2N2O	188425-85-6		**3.0**	likely	Taget
bromopropylate	A	C17H16Br2O3	18181-80-1		**5.4**	-	not included
bupirimate	F	C13H24N4O3S	41483-43-6		**3.7**	likely	Suspect
buprofezin	I	C16H23N3OS	69327-76-0		**4.9**	likely	Suspect
captan	F	C9H8Cl3NO2S	133-06-2		**2.5**	likely	Suspect
carbendazim	F	C9H9N3O2	10605-21-7		**1.5**	likely	Taget

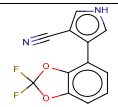
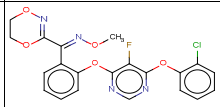
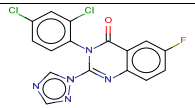
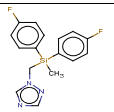
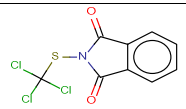
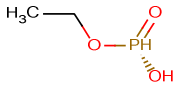
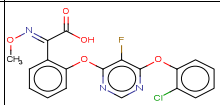
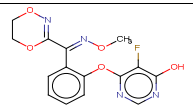
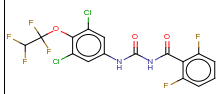
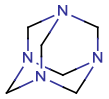
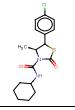
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
carbofuran	I	C12H15NO3	1563-66-2		**1.8**	likely	Suspect
carbosulfan	I	C20H32N2O3S	55285-14-8		**7.4**	likely	not included
CGA 353042	TP (Thiamethoxame)	C4H9N3O	915125-06-3		-0.4	likely	Suspect
CGA 355190	TP (Thiamethoxame)	C8H10ClN3O2S	902493-06-5		1.0	likely	Suspect
chlorfenvinphos	I	C12H14Cl3O4P	470-90-6		**3.8**	likely	Suspect
chlorothalonil	F	C8Cl4N2	1897-45-6		**2.9**	not likely	not included
chlorpyrifos	I	C9H11Cl3NO3PS	2921-88-2		**4.7**	likely	Taget
chlorpyrifos-methyl	I	C7H7Cl3NO3PS	5598-13-0		**4.0**	likely	Taget
clofentezine	A	C14H8Cl2N4	74115-24-5		**3.1**	likely	Suspect
clothianidin	I	C6H8ClN5O2S	210880-92-5		**0.9**	likely	Taget
cyazofamid	F	C13H13ClN4O2S	120116-88-3		**3.2**	likely	Suspect

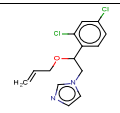
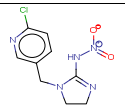
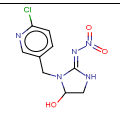
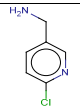
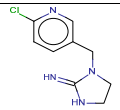
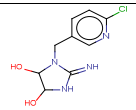
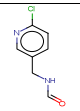
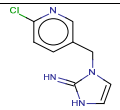
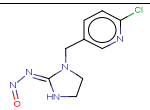
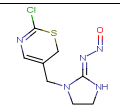
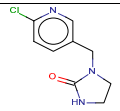
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
Cyclohexanol	I	C6H12O	108-93-0		1.3	not likely	not included
cyflufenamid	F	C20H17F5N2O2	180409-60-3		**4.7**	likely	Suspect
cyhexatin	I	C18H34OSn	13121-70-5		**4.8**	not likely	not included
cymoxanil	F	C7H10N4O3	57966-95-7		**0.7**	likely	Suspect
cypermethrin	I	C22H19Cl2NO3	52315-07-8		**5.3**	-	not included
cyproconazole	F	C15H18ClN3O	94361-06-5		**3.1**	likely	Taget
cyprodinil	F	C14H15N3	121552-61-2		**4.0**	likely	Taget
dazomet	I	C5H10N2S2	533-74-4		**0.6**	likely	Suspect
deltamethrin	I	C22H19Br2NO3	52918-63-5		**4.6**	not likely	not included
diafenthiuron	I	C23H32N2OS	80060-09-9		**5.8**	likely	not included
diazinon	I	C12H21N2O3PS	333-41-5		**3.7**	likely	Taget

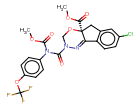
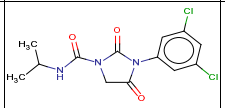
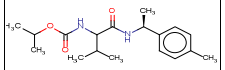
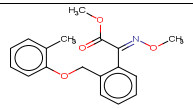
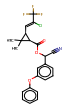
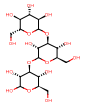
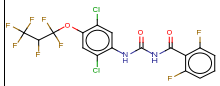
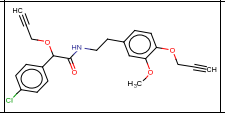
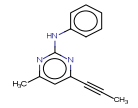
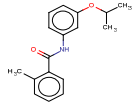
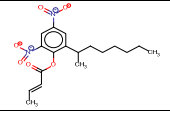
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
dichlorvos	I	C4H7Cl2O4P	62-73-7		**1.9**	likely	Suspect
diethofencarb	F	C14H21NO4	87130-20-9		**2.9**	likely	Suspect
difenoconazole	F	C19H17Cl2N3O3	119446-68-3		**4.4**	likely	Taget
diflubenzuron	I	C14H9ClF2N2O2	35367-38-5		**3.9**	likely	Suspect
dimer imidacloprid	TP (Imidacloprid)	C18H20Cl2N8O2	-[b]		2.5	likely	Suspect
dimethoate	I	C5H12NO3PS2	60-51-5		**0.7**	likely	Taget
dimethomorph	F	C21H22ClNO4	110488-70-5		**2.7**	likely	Taget
dithianon	F	C14H4N2O2S2	3347-22-6		**3.2**	not likely	not included
dodine	F	C13H29N3	2439-10-3		**1.3**	likely	Suspect
DPB[a]	TP (Imidacloprid)	C9H11ClN4O	-[b]		0.4	likely	Suspect
DPC (ring-open-guanidin)	TP (Imidacloprid)	C8H9ClN2O	-[b,c]		0.7	likely	Suspect

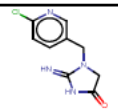
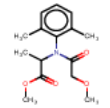
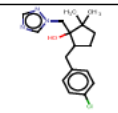
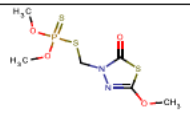
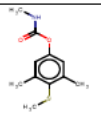
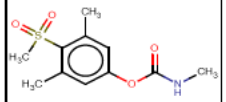
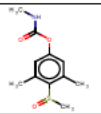
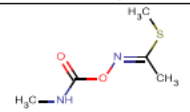
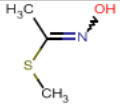
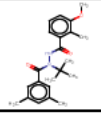
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$ [2]	Ionisation in ESI[3]	Screening Type
endosulfan	I	C9H6Cl6O3S	115-29-7		**4.8**	not likely	not included
epoxiconazole	F	C17H13ClFN3O	133855-98-8		**3.3**	likely	Taget
ethylene bisisothiocyanate sulphide	TP (Dithiocarbamates)	C4H4N2S3	33813-20-6		2.3	likely	Suspect
ethylenethiourea	TP (Dithiocarbamates)	C3H6N2S	96-45-7		-0.2	likely	Suspect
etofenprox	I	C25H28O3	80844-07-1		**6.9**	-	not included
etoxazole	A	C21H23F2NO2	153233-91-1		**5.5**	likely	not included
famoxadone	F	C22H18N2O4	131807-57-3		**4.8**	likely	Suspect
fenamidone	F	C17H17N3OS	161326-34-7		**2.8**	likely	Suspect
fenazaquin	I	C20H22N2O	120928-09-8		**5.5**	likely	not included
fenbuconazole	F	C19H17ClN4	114369-43-6		**3.8**	likely	Suspect
fenhexamid	F	C14H17Cl2NO2	126833-17-8		**3.5**	likely	Suspect

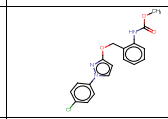
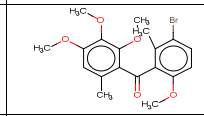
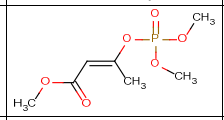
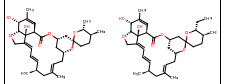
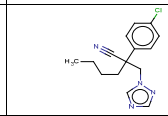
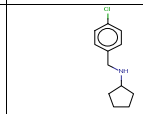
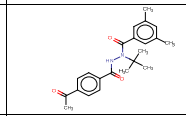
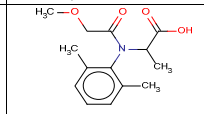
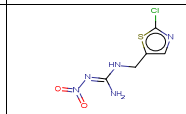
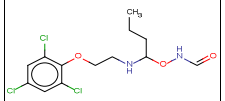
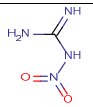
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
fenoxycarb	I	C17H19NO4	79127-80-3		**4.1**	likely	Taget
fenpropidin	F	C19H31N	67306-00-7		**2.6**	likely	Taget
fenpropimorph	F	C20H33NO	67564-91-4		**4.5**	likely	Suspect
fenpropimorph carboxylic acid	TP (Fenpropimorph)	C20H31NO3	121098-45-1		**4.9**	likely	Suspect
fenpyroximate	A	C24H27N3O4	134098-61-6		**5.0**	likely	not included
fipronil	I	C12H4Cl2F6N4OS	120068-37-3		**3.8**	likely	Taget
fipronil amide	TP (Fipronil)	C12H6Cl2F6N4O2S	205650-69-7		3.5	likely	Suspect
fipronil sulfide	TP (Fipronil)	C12H4Cl2F6N4S	120067-83-6		4.85 (EPI Suite)	likely	Taget
fipronil sulfone	TP (Fipronil)	C12H4Cl2F6N4O2S	120068-36-2		4.6	likely	Taget
flonicamid	I	C9H6F3N3O	158062-67-0		**-0.2**	likely	Taget
fluazinam	F	C13H4Cl2F6N4O4	79622-59-6		**4.0**	likely	Suspect

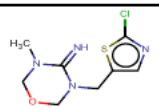
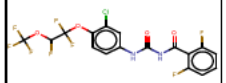
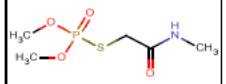
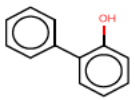
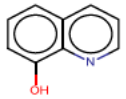
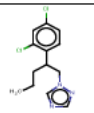
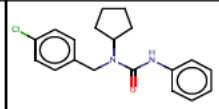
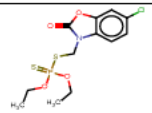
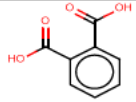
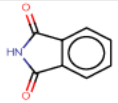
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
fludioxonil	F	C12H6F2N2O2	131341-86-1		**4.1**	likely	Suspect
fluoxastrobin	F	C21H16ClFN4O5	361377-29-9		**2.9**	likely	Suspect
fluquinconazole	F	C16H8Cl2FN5O	136426-54-5		**3.2**	likely	Suspect
flusilazole	F	C16H15F2N3Si	85509-19-9		**3.9**	likely	Taget
folpet	F	C9H4Cl3NO2S	133-07-3		**3.0**	not likely	not included
fosetyl	F	C2H7O3P	15845-66-6		**-0.7**	likely	Suspect
HEC-5725-carboxylic acid	TP (Fluoxastrobin)	C19H13ClFN3O5	-[a]		4.9	likely	Suspect
HEC-5725-des-chlorophenyl	TP (Fluoxastrobin)	C15H13FN4O5	-[a]		2.8	likely	Suspect
hexaflumuron	I	C16H8Cl2F6N2O3	86479-06-3		**5.7**	likely	not included
Hexamethylentetramin	A	C6H12N4	100-97-0		0.4	likely	Suspect
hexythiazox	A	C17H21ClN2O2S	78587-05-0		**2.7**	likely	Suspect

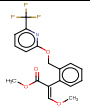
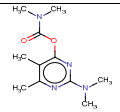
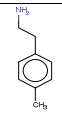
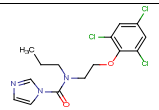
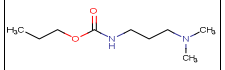
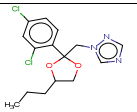
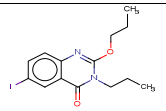
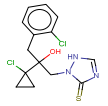
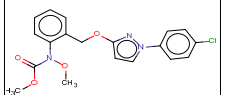
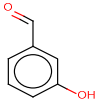
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
imazalil	F	C14H14Cl2N2O	35554-44-0		**2.6**	likely	Suspect
imidacloprid	I	C9H10ClN5O2	138261-41-3		**0.6**	likely	Taget
Imidacloprid-5-hydroxy	TP (Imidacloprid)	C9H10ClN5O3	-[b,c]		0.4	likely	Suspect
Imidacloprid-AMCP	TP (Imidacloprid)	C6H7ClN2	-[c]		0.7	likely	Suspect
Imidacloprid-desnitro	TP (Imidacloprid)	C9H11ClN4	115970-17-7		0.7	likely	Suspect
Imidacloprid-dihydroxy-guanidin	TP (Imidacloprid)	C9H11ClN4O2	-[c]		0.0	likely	Suspect
Imidacloprid-formyl-AMCP	TP (Imidacloprid)	C7H7ClN2O	-[c]		0.5	likely	Suspect
Imidacloprid-desnitro-olefin	TP (Imidacloprid)	C9H9ClN4	-[b,c]		1.1	likely	Suspect
Imidacloprid-nitrosimine	TP (Imidacloprid)	C9H10ClN5O	-[c]		0.9	likely	Suspect
Imidacloprid-nitroso	TP (Imidacloprid)	C8H10ClN5OS	-[d,e]		1.0	likely	Suspect
Imidacloprid-urea	TP (Imidacloprid)	C9H10ClN3O	120868-66-8		0.5	likely	Taget

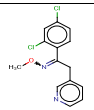
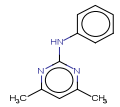
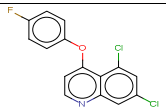
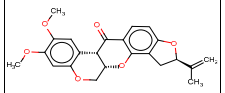
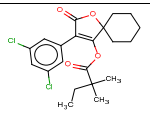
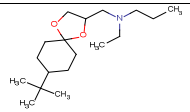
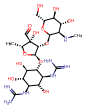
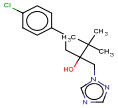
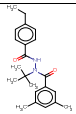
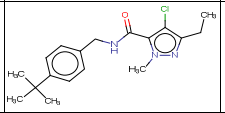
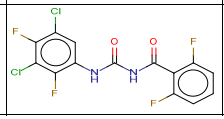
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
indoxacarb	I	C22H17ClF3N3O7	173584-44-6		**4.7**	likely	Suspect
iprodione	F	C13H13Cl2N3O3	36734-19-7		**3.1**	likely	Suspect
iprovalicarb	F	C18H28N2O3	140923-17-7		**3.2**	likely	Taget
kresoxim-methyl	F	C18H19NO4	143390-89-0		**3.4**	likely	Suspect
lambda-cyhalothrin	I	C23H19ClF3NO3	91465-08-6		**6.9**	not likely	not included
laminarin	F	C18H32O16	9008-22-4		**-1.6**	not likely	not included
lufenuron	I	C17H8Cl2F8N2O3	103055-07-8		**5.1**	likely	not included
mandipropamid	F	C23H22ClNO4	374726-62-2		**2.1**	likely	Suspect
mepanipyrim	F	C14H13N3	110235-47-7		**3.3**	likely	Suspect
mepronil	F	C17H19NO2	55814-41-0		4.2	likely	Suspect
meptyldinocap	F	C18H24N2O6	131-72-6		**6.6**	-	not included

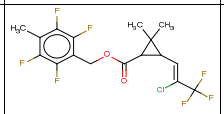
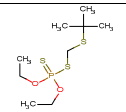
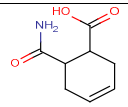
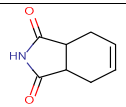
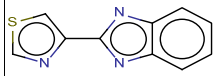
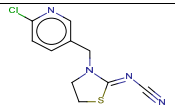
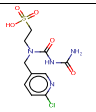
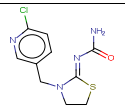
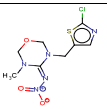
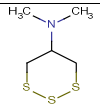
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
Met. 3 (imidacloprid)	TP (Imidacloprid)	C9H8ClN5O3	-[d]		0.3	likely	Suspect
Met. 4 (imidacloprid) / DPD	TP (Imidacloprid)	C9H9ClN4O	-[d,b]		0.3	likely	Suspect
metalaxyl	F	C15H21NO4	57837-19-1		**1.7**	likely	Suspect
metconazole	F	C17H22ClN3O	125116-23-6		**3.9**	likely	Suspect
methidathion	I	C6H11N2O4PS3	950-37-8		**2.6**	likely	Suspect
methiocarb	I	C11H15NO2S	2032-65-7		**3.2**	likely	Taget
Methiocarb sulfone	TP (Methiocarb)	C11H15NO4S	2179-25-1		1.3	likely	Suspect
methiocarb sulfoxide	TP (Methiocarb)	C11H15NO3S	2635-10-1		1.2	likely	Taget
methomyl	I	C5H10N2O2S	16752-77-5		**1.2**	likely	Taget
methomyl oxime	TP (Methomyl)	C3H7NOS	13749-94-5		**1.1**	likely	Suspect
methoxyfenozide	I	C22H28N2O3	161050-58-4		**3.7**	likely	Taget

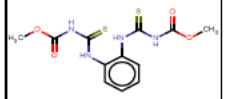
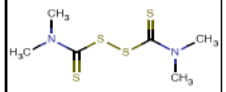
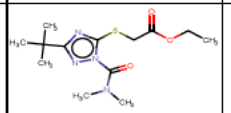
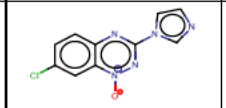
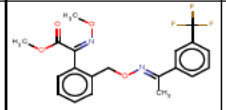
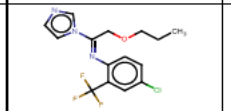
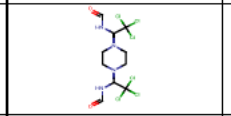
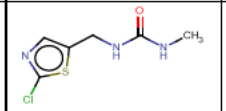
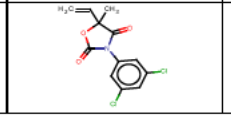
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
methyl N-(2{[1-(4-chlorophenyl)-1H-pyrazol-3-yl] oxymethyl} phenyl)carbamate	TP (Pyraclostrobin)	C18H16ClN3O3	512165-96-7		4.7	likely	Suspect
metrafenone	F	C19H21BrO5	220899-03-6		**4.3**	likely	Suspect
mevinphos	I	C7H13O6P	7786-34-7		**0.1**	likely	Suspect
Milbemectin	A	C63H90O14	-[a]		4.5	not likely	not included
myclobutanil	F	C15H17ClN4	88671-89-0		**2.9**	likely	Taget
N-((4-chlorophenyl)-methyl)-N-cyclopentylamide	TP (Pencycuron)	C12H16ClN	66063-15-8		**0.9**	likely	Suspect
N-(1,1-dimethyethyl)-N-(4-acetylebenzoyl)-3,5-dimethylbenzohydrazine	TP (Tebufenozide)	C22H26N2O3	166547-60-0		4.0	likely	Suspect
N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine	TP (Metalaxyl)	C14H19NO4	8764-37-2		2.0	likely	Suspect
N-(2-chlorothiazol-5-ylmethyl)-N'-nitroguanidine	TP (Clothianidin)	C5H6ClN5O2S	1155875-72-1		0.5	likely	Suspect
N-formyl-N'-propyl-N'-2(2,4,6-trichlorophenoxy)ethylurea	TP (Prochloraz)	C13H17Cl3N2O3	-[a]		3.7	likely	Suspect
Nitroguanidin	TP (Thiamethoxame)	CH4N4O2	556-88-7		-0.8	likely	Suspect

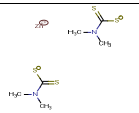
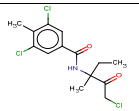
Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
N-methyl-N-nitroguanidine	TP (Clothianidin)	C2H6N4O2	4245-76-5		-0.6	likely	Suspect
NOA 407475	TP (Thiamethoxame)	C8H11ClN4OS	868542-26-1		1.3	likely	Suspect
novaluron	I	C17H9ClF8N2O4	116714-46-6		**4.3**	likely	Suspect
omethoate	TP (Dimethoate)	C5H12NO4PS	1113-02-6		**-0.7**	likely	Suspect
Orthophenylphenol	P	C12H10O	90-43-7		3.3	not likely	not included
Oxychinolin	F	C9H7NO	1322-20-9		1.8	likely	Suspect
penconazole	F	C13H15Cl2N3	66246-88-6		**3.7**	likely	Suspect
pencycuron	F	C19H21ClN2O	66063-05-6		**4.7**	likely	Suspect
phosalone	I	C12H15ClNO4PS2	2310-17-0		**4.0**	likely	Suspect
phthalic acid	TP (Folpet)	C8H6O4	88-99-3		1.3	likely	Suspect
phthalimide	TP (Captan)	C8H5NO2	85-41-6		**1.2**	likely	Suspect

Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
picoxystrobin	F	C18H16F3NO4	117428-22-5		**3.6**	likely	Suspect
pirimicarb	I	C11H18N4O2	23103-98-2		**1.7**	likely	Taget
p-methyl-phenethylamine	TP (Iprovalicarb)	C9H13N	3261-62-9		**1.8**	likely	Suspect
prochloraz	F	C15H16Cl3N3O2	67747-09-5		**3.5**	likely	Taget
propamocarb	F	C9H20N2O2	24579-73-5		**0.8**	likely	Taget
propiconazole	F	C15H17Cl2N3O2	60207-90-1		**3.7**	likely	Taget
proquinazid	F	C14H17IN2O2	189278-12-4		**5.5**	likely	Suspect
prothioconazole	F	C14H15Cl2N3OS	178928-70-6		**3.8**	likely	Suspect
pymetrozine	I	C10H11N5O	123312-89-0		**-0.2**	likely	Taget
pyraclostrobin	F	C19H18ClN3O4	175013-18-0		**4.0**	likely	Suspect
pyridin-3-carbaldehyde	P	C7H6O2	100-83-4		1.4	likely	Suspect

Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
pyrifenox	F	C14H12Cl2N2O	88283-41-4		**3.4**	likely	Suspect
pyrimethanil	F	C12H13N3	53112-28-0		**2.8**	likely	Taget
quinoxyfen	F	C15H8Cl2FNO	124495-18-7		**4.7**	likely	Suspect
Rotenon	A	C23H22O6	12679-58-2		3.3	not likely	not included
spirodiclofen	I	C21H24Cl2O4	148477-71-8		**5.8**	likely	not included
spiroxamine	F	C18H35NO2	118134-30-8		**2.9**	likely	Taget
streptomycin	P	C21H39N7O12	57-92-1		**-7.5**	likely	Suspect
tebuconazole	F	C16H22ClN3O	107534-96-3		**3.7**	likely	Taget
tebufenozide	I	C22H28N2O2	112410-23-8		**4.3**	likely	Taget
tebufenpyrad	A	C18H24ClN3O	119168-77-3		4.1	likely	Suspect
teflubenzuron	I	C14H6Cl2F4N2O2	83121-18-0		**4.3**	likely	Taget

Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	LogK$_{ow}$[2]	Ionisation in ESI[3]	Screening Type
tefluthrin	I	C17H14ClF7O2	79538-32-2		**6.4**	-	not included
terbufos	I	C9H21O2PS3	13071-79-9		**4.5**	likely	Suspect
tetrahydrophthalamic acid	TP (Captan)	C8H11NO3	2028-12-8		-0.1	likely	Suspect
tetrahydrophthalimide	TP (Captan)	C8H9NO2	85-40-5		**0.2**	likely	Suspect
thiabendazole	F	C10H6N3S	148-79-8		**2.4**	likely	Suspect
thiacloprid	I	C10H9ClN4S	111988-49-9		**1.3**	likely	Taget
thiacloprid sulfonic acid	TP (Thacloprid)	C10H13ClN4O5S	-[f]		-3.1	likely	Suspect
thiacloprid-amide	TP (Thacloprid)	C10H11ClN4OS	676228-91-4		1.1	likely	Taget
thiamethoxam	I	C8H10ClN5O3S	153719-23-4		**-0.1**	likely	Taget
thiocyclam hydrogen oxalate	I	C5H11NS3	31895-22-4		**-0.1**	likely	Suspect

Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$[2]	Ionisation in ESI[3]	Screening Type
thiophanate-methyl	F	C12H14N4O4S2	23564-05-8		**1.5**	likely	Suspect
thiram	F	C6H12N2S4	137-26-8		**1.7**	likely	Suspect
triadimenol	F	C14H18ClN3O2	55219-65-3		**3.2**	likely	Suspect
Triazamate	I	C13H22N4O3S	112143-82-5		**2.7**	likely	Suspect
triazoxide	F	C10H6ClN5O	72459-58-6		**2.0**	likely	Suspect
trifloxystrobin	F	C20H19F3N2O4	141517-21-7		**4.5**	likely	Suspect
triflumizole	F	C15H15ClF3N3O	99387-89-0		**4.8**	likely	Suspect
triforine	F	C10H14Cl6N4O2	26644-46-2		**2.4**	likely	Suspect
TZMU	TP (Clothianidin)	C6H8ClN3OS	634192-72-6		0.5	likely	Suspect
vinclozolin	F	C12H9Cl2NO3	50471-44-8		**3.0**	likely	Suspect

Susbstance Name	Pesticide Type[1]	Chemical Formula	CAS-Nr.	Structure	$LogK_{ow}$ [2]	Ionisation in ESI[3]	Screening Type
ziram	F	C6H12N2S4Zn	137-30-4		**1.7**	likely	Suspect
zoxamide	F	C14H16Cl3NO2	156052-68-5		**3.8**	likely	Suspect

[1] I: insecticide, F: fungicide, A: acaricide, P: various pesticides, TP: transformation product, (parent compund)

[2] in bold: taken from footprint database (http://sitem herts ac uk/aeru/iupac/), normal: calculated with Jchem for Excel (Version 5 11 5 906)

[3] guidelines for estimation of ionization potential: see main text

[a] University of Hertfordshire (2013), [b] Ding et al (2011), [c] DAR (2006), [d] Liu et al (2011), [e] Pandey et al (2009), [f] FAO (2006)

A.2. Field Study Site

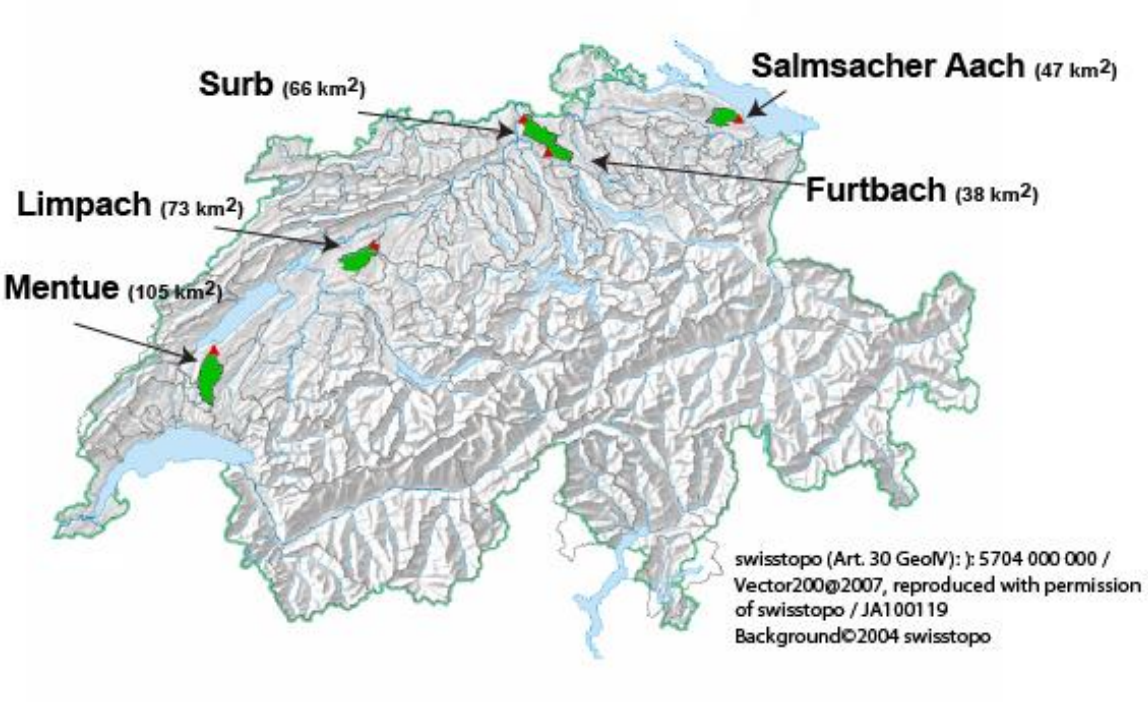


Figure A.1. Field Study site with the five catchments. In brackets are the catchment sizes.

A.3. Supplier Information Reference Standards

Table A.1. Supplier information of reference standards and corresponding internal standards.

Standard CAS number	Producer	Polarity	Assigned Internal Standand Producer
2-Isopropyl-6-methyl-4-pyrimidinol	Dr Ehrenstorfer (Augsburg, Germany)	+	**Carbendazim.D4**
2814-20-2			Dr Ehrenstorfer (Augsburg, Germany)
3,5,6-Trichloro-2-pyridinol	Dr Ehrenstorfer (Augsburg, Germany)	+	**Propazin-D6**
6515-38-4			Dr Ehrenstorfer (Augsburg, Germany)
		-	**Bicalutamid-D4**
			Toronto Research Chemicals (North York, ON,Canada)
Aldicarb (Na adduct)	Dr Ehrenstorfer (Augsburg, Germany)	+	**Clozapin-D8**
116-06-3			Toronto Research Chemicals (North York, ON,Canada)
Azoxystrobin	Dr Ehrenstorfer (Augsburg, Germany)	+	**Dimethenamid-D3**
131860-33-8			Toronto Research Chemicals (North York, ON,Canada)
Azoxystrobin free acid	High Purity Compounds (Cunnersdorf, Germany)	+	**Isoproturon-D6**
1185255-09-7			Dr Ehrenstorfer (Augsburg, Germany)
		-	**Clofibrin acid-D4**
			Toronto Research Chemicals (North York, ON,Canada)
Boscalid	Dr Ehrenstorfer (Augsburg, Germany)	+	**Dimethenamid-D3**
188425-85-6			Toronto Research Chemicals (North York, ON,Canada)
		-	**Clofibrin acid-D4**
			Toronto Research Chemicals (North York, ON,Canada)
Carbendazim	Dr Ehrenstorfer (Augsburg, Germany)	+	**Carbendazim-D4**
10605-21-7			Dr Ehrenstorfer (Augsburg, Germany)
Chlorpyrifos	Dr Ehrenstorfer (Augsburg, Germany)	+	**Chlolrpyrifos-D10**
2921-88-2			Dr Ehrenstorfer (Augsburg, Germany)
Chlorpyrifos-methyl	Dr Ehrenstorfer (Augsburg, Germany)	+	**Chlorpyrifos-methyl-D6**
5598-13-0			Dr Ehrenstorfer (Augsburg, Germany)
Clothianidin	Dr Ehrenstorfer (Augsburg, Germany)	+/-	**Clothianidin-D3**
210880-92-5			Dr Ehrenstorfer (Augsburg, Germany)
Cyproconazole	Dr Ehrenstorfer (Augsburg, Germany)	+	**Tebutam-D4 (Validation)**
94361-06-5			Solvias AG (Basel, Switzerland)
		+	**Tebuconazole-D6 (Environmental sample)**
			Dr Ehrenstorfer (Augsburg, Germany)
Cyprodinil	Dr Ehrenstorfer (Augsburg, Germany)	+	**Diuron-D6**
121552-61-2			Dr Ehrenstorfer (Augsburg, Germany)
Diazinon	Ultra Scientific (North Kingstown, RI, USA)	+	**Diazinon-D10**
333-41-5			Cambridge Isotope Laboratories (Andover, MA, USA)
Difenoconazole	Dr Ehrenstorfer (Augsburg, Germany)	+	**Chlorpyrifos-methyl-D6 (Validation)**
119446-68-3			Dr Ehrenstorfer (Augsburg, Germany)
		+	**Tebuconazole-D6 (Environmental sample)**
			Dr Ehrenstorfer (Augsburg, Germany)
Dimethoat	Riedel de Häen GmbH (Seelze, Germany)	+	**Dimethoat-D6**
60-51-5			Dr Ehrenstorfer (Augsburg, Germany)
Dimethomorph	Dr Ehrenstorfer (Augsburg, Germany)	+	**Dimethenamid-D3**
110488-70-5			Toronto Research Chemicals (North York, ON,Canada)
Epoxiconazole	Dr Ehrenstorfer (Augsburg, Germany)	+	**Metolachlor-D6 (Validation)**
133855-98-8			Dr Ehrenstorfer (Augsburg, Germany)
		+	**Tebuconazole-D6 (Environmental sample)**
			Dr Ehrenstorfer (Augsburg, Germany)
Fenoxycarb	Dr Ehrenstorfer (Augsburg, Germany)	+	**Prochloraz-D7 (Validation)**
79127-80-3			Dr Ehrenstorfer (Augsburg, Germany)
		+	**Diclofenac-D4 (Environmental sample)**
			Toronto Research Chemicals (North York, ON,Canada)
Fenpropidin	Riedel de Häen GmbH (Seelze, Germany)	+	**Terbutryn-D5**
67306-00-7			Dr Ehrenstorfer (Augsburg, Germany)
Fipronil	Dr Ehrenstorfer (Augsburg, Germany)	+	**Diazinon-D10**
120068-37-3			Cambridge Isotope Laboratories (Andover, MA, USA)
		-	**Diclofenac-D4**
			Toronto Research Chemicals (North York, ON,Canada)
Fipronil-sulfide	Dr Ehrenstorfer (Augsburg, Germany)	+	**Prochloraz-D7**
120067-83-6			Dr Ehrenstorfer (Augsburg, Germany)
		-	**Diclofenac-D4**
			Toronto Research Chemicals (North York, ON,Canada)
Fipronil-sulfone	Dr Ehrenstorfer (Augsburg, Germany)	+	**Ritonavir-D6**
120068-36-2			Toronto Research Chemicals (North York, ON,Canada)
		-	**Diclofenac-D4**
			Toronto Research Chemicals (North York, ON,Canada)

Table A.1 (continuation).

Standard CAS number	Producer	Polarity	Assigned Internal Standand Producer
Flonicamid	Dr Ehrenstorfer (Augsburg, Germany)	+	**Carbendazim-D4**
158062-67-0			Dr Ehrenstorfer (Augsburg, Germany)
		-	**Imidacloprid-D4**
			Dr Ehrenstorfer (Augsburg, Germany)
Flusilazole	Dr Ehrenstorfer (Augsburg, Germany)	+	**Diclofenac-D4 (Validation)**
85509-19-9			Toronto Research Chemicals (North York, ON,Canada)
		+	**Tebuconazole-D6 (Environmental sample)**
			Dr Ehrenstorfer (Augsburg, Germany)
Imidacloprid		+/-	**Imidacloprid-D4**
138261-41-3			Dr Ehrenstorfer (Augsburg, Germany)
Imidacloprid-urea	Dr Ehrenstorfer (Augsburg, Germany)	+	**Atrazin-Desisopropyl-D5**
120868-66-8			Dr Ehrenstorfer (Augsburg, Germany)
Iprovalicarb	Dr Ehrenstorfer (Augsburg, Germany)	+	**Octhilinon-D17**
140923-17-7			Toronto Research Chemicals (North York, ON,Canada)
Methiocarb	Dr Ehrenstorfer (Augsburg, Germany)	+	**Methiocarb-D3**
2032-65-7			Dr Ehrenstorfer (Augsburg, Germany)
Methiocarb-sulfoxide	Dr Ehrenstorfer (Augsburg, Germany)	+	**Imidacloprid-D4**
2635-10-1			Dr Ehrenstorfer (Augsburg, Germany)
Methomyl	Dr Ehrenstorfer (Augsburg, Germany)	+	**2,6-Dichlorbenzamid-3,4,5-D3**
16752-77-5			CDN-Isotopes (Pointe-Claire, Canada)
Methoxyfenozid	Dr Ehrenstorfer (Augsburg, Germany)	+	**Dimethenamid-D3**
161050-58-4			Toronto Research Chemicals (North York, ON,Canada)
		-	**Dichloprop-D6**
			Dr Ehrenstorfer (Augsburg, Germany)
Myclobutanil	Dr Ehrenstorfer (Augsburg, Germany)	+	**Metolachlor-D6 (Validation)**
88671-89-0			Dr Ehrenstorfer (Augsburg, Germany)
		+	**Tebuconazole-D6 (Environmental sample)**
			Dr Ehrenstorfer (Augsburg, Germany)
Pirimicarb	Dr Ehrenstorfer (Augsburg, Germany)	+	**Pirimicarb-D6**
23103-98-2			Dr Ehrenstorfer (Augsburg, Germany)
Prochloraz	Dr Ehrenstorfer (Augsburg, Germany)	+	**Prochloraz-D7**
67747-09-5			Dr Ehrenstorfer (Augsburg, Germany)
Propamocarb	Dr Ehrenstorfer (Augsburg, Germany)	+	**Chloridazon-methyl-desphenyl-D3**
24579-73-5			High Purity Compounds (Cunnersdorf, Germany)
Propiconazole		+	**Propiconazol-D5**
60207-90-1			Dr Ehrenstorfer (Augsburg, Germany)
Pymetrozine	Dr Ehrenstorfer (Augsburg, Germany)	+	**Chloridazon-desphenyl-$^{15}N_2$ (Validation)**
123312-89-0			Toronto Research Chemicals (North York, ON,Canada)
		+	**Chloridazon-methyl-desphenyl-D3 (Environmental sample)**
			High Purity Compounds (Cunnersdorf, Germany)
Pyrimethanil	Dr Ehrenstorfer (Augsburg, Germany)	+	**Chlortoluron-D6**
53112-28-0			Dr Ehrenstorfer (Augsburg, Germany)
Spiroxamine	Dr Ehrenstorfer (Augsburg, Germany)	+	**Methiocarb-D3**
118134-30-8			Dr Ehrenstorfer (Augsburg, Germany)
Tebuconazole	Dr Ehrenstorfer (Augsburg, Germany)	+	**Tebuconazole-D6**
107534-96-3			Dr Ehrenstorfer (Augsburg, Germany)
Tebufenozide		+	**Metolachlor-D6**
112410-23-8			Dr Ehrenstorfer (Augsburg, Germany)
		-	**Mecoprop-D6**
			Dr Ehrenstorfer (Augsburg, Germany)
Teflubenzuron	Dr Ehrenstorfer (Augsburg, Germany)	+	**Fenofibrate-D6**
83121-18-0			Toronto Research Chemicals (North York, ON,Canada)
		-	**Atorvastatin-D5**
			Toronto Research Chemicals (North York, ON,Canada)
Thiacloprid	Dr Ehrenstorfer (Augsburg, Germany)	+	**Atrazin-desethyl-$^{15}N_3$**
111988-49-9			
Thiacloprid-amide	Dr Ehrenstorfer (Augsburg, Germany)	+	**Atrazin-desisopropyl-D5**
676228-91-4			Dr Ehrenstorfer (Augsburg, Germany)
Thiamethoxam	Dr Ehrenstorfer (Augsburg, Germany)	+	**Thiamethoxam-D3**
153719-23-4			Sigma-Aldrich (Buchs, Switzerland)

A.4. Detailed Method Description for the Validation of the SPE-LC-HRMS/MS Method

For the quality control of the analytical method, two different experiments were performed in order to assess **absolute SPE recoveries, the spike recovery, the ion suppression, the precision** (relative standard deviation (RSD) in the concentration of triplicate measurements) and **the limit of quantification (LOQ)** in river water for each analyte. For both experiments, a mixture of grab samples from the five rivers was used. **Figure A.2** illustrates the spike scheme for the two different setups. Analytes and internal standards were spiked with an absolute amount of 200 ng in 1 liter of water. All samples were run in triplicates.

Absolute SPE Recovery

In order to calculate the absolute SPE recovery, three samples were spiked with analyte before the SPE, whereas three other samples were spiked with the analyte at the end (after evaporation). In addition to this, three samples was processed without spiking analytes to determine the background concentration. The internal standard was always added at the end (see **Figure A.2**). The SPE recoveries were calculated with the following equations:

$$A_{\mathrm{Rec}}\ in\ river\ \ water = \frac{Area\ \ Ratio_{\ Analyte\ spiked before} - Area\ \ Ratio_{\ No Analyte spiked}}{Area\ \ Ratio_{\ Analyte spiked after} - Area\ \ Ratio_{\ No Analyte spiked}}$$

, where

$$Area\ Ratio = \frac{Area_{Analyte}}{Area_{Istd}}$$

Ion Suppression

The ion suppression in the river water was calculated using the following equation:

$$Ion suppression = \frac{Area_{\ Analyte spiked after SPE\ and\ N_2\ in RW} - Area_{\ No\ Analyte spiked in RW}}{Area_{\ Analyte spiked after SPE\ and\ N_2\ in n.p.H_2O}}$$

RW indicates the river water, n.p. H_2O indicates nanopure water. All samples were spiked with 200 ng of analyte and internal standard.

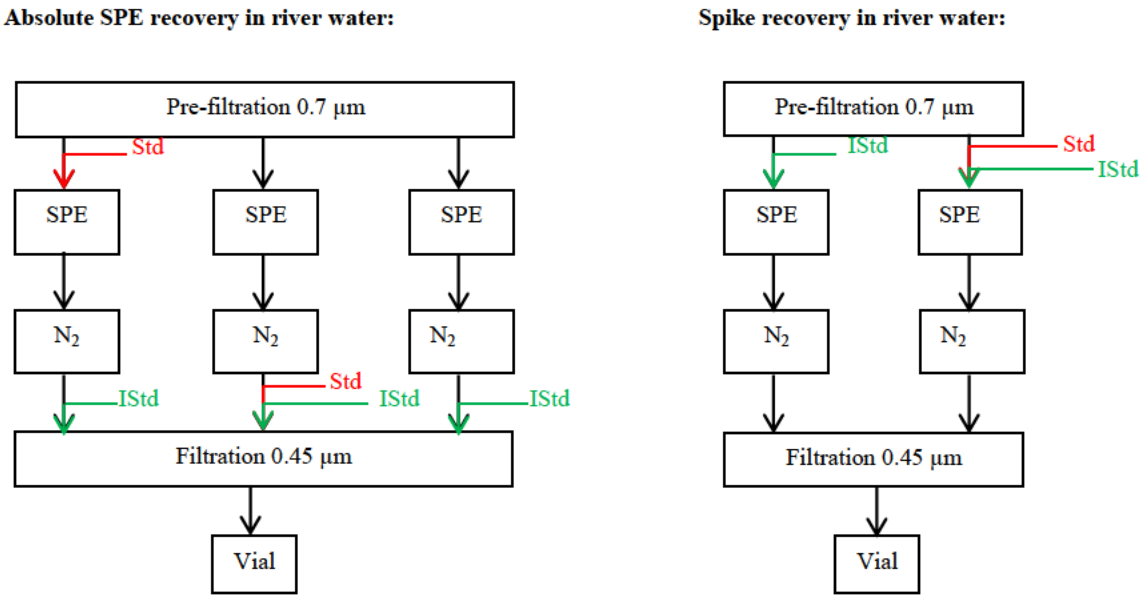


Figure A.2. Spike scheme for the absolute SPE recovery and spike recovery determination in river water. N_2 refers to the evaporation step with N_2. Red: Addition of analyte standard (200 ng), green: addition of internal standard (200 ng)

Spike Recovery And Limit of Quantification

In order to calculate the recovery of the spiked analyte amounts (spike recovery) and to determine the limit of quantification (LOQ) of the method, a calibration curve (processed over the SPE) was measured using following concentrations: 0.1, 1, 5, 10, 25, 50, 100, 200, 500, 750 ng/L. The spike recovery (R_{Rec}) was calculated with the following equation:

$$R_{Rec} \text{ in river water} = \frac{C_{spiked} - C_{No\ Std\ spike}}{Spiked\ \ amount}$$

Where C_{Spiked} is the determined concentration in the spiked sample whereas $C_{No\ Std\ spike}$ is the concentration in the sample without any standard spike. The spiked amount was 200 ng (see **Figure A.2**).

For a reliable determination of the LOQ in nanopure water, a minimum of five full scan sticks and a correct MS/MS spectrum was the criteria. LOQ in river water was determined by dividing the LOQ in nanopure water by the matrix factor:

$$LOQ_{RW} = \frac{LOQ_{n.p.H_2O}}{MF}$$, where $$MF(MatrixFactor) = \frac{Area_{Analyt\,espikedbeforeSPE\,inRW} - Area_{No\,analyt\,espikeinRW}}{Area_{200\,ng/L\,Standard}}$$

Precision of Triplicate Analysis

The precision of the measurement was determined by calculating the relative standard deviation (RSD%) in a triplicate of spiked environmental samples. Each of the three samples was thereby prepared separately.

Quality Control

In each sequence, the calibration curve was measured at the beginning and at the end of the sequence. Additionally, the 200ng/L and the 10 ng/L standards were measured several times in the middle of the sequence. Solvent blanks were used, generally every 6-8 samples in order to avoid any carry over. The spike recovery was checked using three spiked samples (twice 200 ng/L, once 10 ng/L).

A.5. Detailed Results of the Validation of the SPE-LC-HRMS/MS Method

Table A.2. Validation parameter of all target insecticides and transformation products in the river water (RW) matrix. Values in bold indicate the ionization mode that was finally used for the quantification in the environmental samples

Analyte CAS number	Polarity	SPE Recovery (%)	Ion Suppression [%]	Spike Recovery	LOQ_{RW} [ng/L]	Precision (RSD%)
2-Isopropyl-6-methyl-4-pyrimidinol[1] 2814-20-2	+ -	72%	49 ± 5	100%	-[c] -[c]	4%
3,5,6-Trichloro-2-pyridinol[2] 6515-38-4	**+** -	**98%** 99%	**53 ± 7** 38 ± 2	**75%** 100%	-[c] -[c]	**6%**
Aldicarb (Na adduct) 116-06-3	+	91%	60 ± 21	92%	200 00	13%
Chlorpyrifos 2921-88-2	+	82%	0 ± 0 3	120%[a]	200	10%
Chlorpyrifos-methyl 5598-13-0	+	85%	4 ± 1	110%[a]	200	7%
Clothianidin 210880-92-5	+ **-**	103% **103%**	49 ± 6 **76 ±7**	100%[a] **97%[a]**	5 0 **4.0**	**7%**
Diazinon 333-41-5	+	83%	-70 ± 29	100%[a]	10	5%
Dimethoat 60-51-5	+	98%	30 ± 2	110%[a]	3 0	4%
Fenoxycarb 79127-80-3	+	86%	41 ± 8	100%	14	25%
Fipronil 120068-37-3	+ **-**	114% **99%**	48 ± 11 **30 ± 5**	83% **72%**	44 **0.6**	**2%**
Fipronil-sulfide[3] 120067-83-6	+ **-**	115% **114%**	48 ± 19 **48 ± 12**	120% **82%**	41 **10**	**15%**
Fipronil-sulfone[3] 120068-36-2	+ **-**	129% **119%**	43 ± 19 **35 ± 9**	620% **110%**	11 **6.0**	**12%**
Flonicamid 158062-67-0	+ **-**	81% **93%**	40 ± 1 **52 ± 4**	84% **150%**	1 7 **2.3**	**5%**
Imidacloprid 138261-41-3	**+** -	**91%** 80%	**47 ± 6** 79 ± 9	**100%[a]** 89%[a]	**4.5** 23	**3%**
Imidacloprid-urea[4] 120868-66-8	+	94%	29 ± 1	99%	1 3	5%
Methiocarb 2032-65-7	+	98%	30 ± 4	110%[a]	1 0	10%
Methiocarb-sulfoxide[5] 2635-10-1	+	86%	17 ± 3	120%	10	17%
Methomyl 16752-77-5	+	100%	31 ± 2	100%	10	12%
Methoxyfenozid 161050-58-4	+ **-**	103% **109%**	36 ± 5 **58 ± 4**	95% **72%**	1 5 **2.8**	**6%**
Pirimicarb 23103-98-2	+	95%	32 ± 2	94%[a]	0 4	6%
Pymetrozine 123312-89-0	+	96%	-25 ± 6	120%	5 0	38%
Tebufenozide 112410-23-8	+ **-**	103% **109%**	29 ± 5 **49 ± 6**	100% **81%**	7 5 **2.0**	**4%**
Teflubenzuron 83121-18-0	**+** -	**110%** 92%	**41 ± 11** 32 ± 13	**93%** 34%	**50** 12	**6%**
Thiacloprid 111988-49-9	+	97%	53 ± 7	77%	4 4	15%
Thiacloprid-amide[6] 676228-91-4	+	98%	39 ± 6	93%	2 5	9%
Thiamethoxam 153719-23-4	+	95%	32 ± 1	93%[a]	3 0	9%

[a] Analytes with identically structured internal standards for the quantification, [b] for the determination of the LOQ_{RW}, the Na-Adduct was additionally taken into account, [c] could not be determined due to the high blank value, [1] TP of diazinon; [2] TP of chlorpyrifos; [3] TP of fipronil; [4] TP of imidacloprid; [5] TP of methiocarb; [6] TP of thiacloprid. RSD: relative standard deviation

Table A.3. Validation parameter of all target fungicides and transformation products in the river water (RW) matrix. Values in bold indicate the ionization mode that was finally used for the quantification in the environmental samples

Analyte CAS number	Polarity	SPE Recovery (%)	Ion Suppression [%]	Spike Recovery	LOQ_{RW} [ng/L]	Precision (RSD%)
Azoxystrobin 131860-33-8	+	103%	20 ± 2	100%	1 0	6%
Azoxystrobin free acid[1]	+	**104%**	**14 ± 2**	**100%**	**1.0**	
1185255-09-7	-	103%	63 ± 8	67%	2 5	6%
Boscalid	+	**98%**	**43 ± 4**	**88%**	**1.7**	**3%**
188425-85-6	-	113%	54 ± 2	94%	12	
Carbendazim 10605-21-7	+	96%	27 ± 1	97%[a]	5 0	3%
Cyproconazole 94361-06-5	+	118%	43 ± 6	51%	0 6	4%
Cyprodinil 121552-61-2	+	106%	44 ± 12	120%	5 0	16%
Difenoconazole 119446-68-3	+	110%	21 ± 3	100%	200	21%
Dimethomorph 110488-70-5	+	101%	35 ± 1	87%	2 1	5%
Epoxiconazole 133855-98-8	+	103%	24 ± 5	76%	4 1	5%
Fenpropidin 67306-00-7	+	71%	33 ± 2	81%	0 8	1%
Flusilazole 85509-19-9	+	104%	39 ± 14	100%	4 2	21%
Iprovalicarb 140923-17-7	+	95%	29 ± 2	82%	1 4	1%
Myclobutanil 88671-89-0	+	114%	43 ± 6	57%	0 8	5%
Prochloraz 67747-09-5	+	93%	40 ± 16	100%[a]	200 0	4%
Propamocarb 24579-73-5	+	73%	12 ± 1	91%	0 3	2%
Propiconazole 60207-90-1	+	108%	44 ± 10	98%[a]	3 0	2%
Pyrimethanil 53112-28-0	+	98%	48 ± 4	91%	1 0	3%
Spiroxamine 118134-30-8	+	65%	30 ± 2	96%	2 0	7%
Tebuconazole 107534-96-3	+	109%	45 ± 15	100%[a]	6 0	3%

a Analytes with identically structured internal standards for the quantification, b for the determination of the LOQRW, the Na-Adduct was additionally taken into account, 1 TP of azoxystrobin, RSD: relative standard deviation

Table A.4. Retention time (RT), normalized collision energy (NCE) and mass of the precursor ion and formed fragments for the analyzed insecticides and their TPs. Values in bold indicate the ionization mode that was finally used for the quantification in the environmental samples

Analyte CAS number	Formula	RT [min]	Precursor Ion [m/z][a]	Polarity	NCE [%][c]	Fragment I [m/z][d]	Fragment II [m/z][d]	Fragment III [m/z][d]
2-Isopropyl-6-methyl-4-pyrimidinol[1] 2814-20-2	$C_8H_{12}N_2O$	3 34	153 1022	+	60	84 0452	70 066	
3,5,6-Trichloro-2-pyridinol[2] 6515-38-4	$C_5H_2Cl_3N_1O$	9 71	**197.9275** 195 9129[b]	**+** -	**60** 80	**179.9617**	**133.9562**	**106.9456**
Aldicarb (Na adduct) 116-06-3	$C_7H_{14}O_2N_2S$	6 11	213 0668	+	30	116 0531	89 0425	70 0658
Chlorpyrifos 2921-88-2	$C_9H_{11}Cl_3NO_3PS$	16 03	349 9336	+	45	197 9274	114 9616	
Chlorpyrifos-methyl 5598-13-0	$C_7H_7Cl_3NO_3PS$	13 94	321 9023	+	30	289 8756	142 9926	
Clothianidin 210880-92-5	$C_6H_8ClN_5O_2S$	4 71	250 016 **248.0014**[b]	+	30 **30**	169 0538 **165.0229**	131 9668 **57.974**	
Diazinon 333-41-5	$C_{12}H_{21}N_2O_3PS$	12 98	305 1083	+	45	169 0797	153 1025	114 9618
Dimethoat 60-51-5	$C_5H_{12}NO_3PS_2$	5 13	230 0069	+	15	198 9645	170 9696	142 9925
Fenoxycarb 79127-80-3	$C_{17}H_{19}NO_4$	12 52	302 1387	+	30	256 0965	116 0709	88 0399
Fipronil 120068-37-3	$C_{12}H_4Cl_2F_6N_4OS$	12 63	436 946 **434.9314**[b]	+	30 **15**	367 9513 **329.9597**	289 9765 **249.9583**	
Fipronil-sulfide[3] 120067-83-6	$C_{12}H_4Cl_2F_6N_4S$	12 97	420 9511 **418.9365**[b]	+	45 **15**	316 9874 **382.9604**	**313.965**	**261.9586**
Fipronil-sulfone[3] 120068-36-2	$C_{12}H_4Cl_2F_6N_4O_2S$	13 51	452 9409 **450.9263**[b]	+	45 **15**	334 9715 **414.9502**	243 9782 **281.9928**	
Flonicamid 158062-67-0	$C_9H_6F_3N_3O$	3 65	230 0536 **228.0390**[b]	+	45 **15**	203 0421 **146.0207**	174 0157 **81.0078**	148 0365
Imidacloprid 138261-41-3	$C_9H_{10}ClN_5O_2$	4 73	**256.0596** 254 045[b]	**+** -	**60** 30	**209.0592** 153 0214	**175.0981** 85 9979	
Imidacloprid-urea[4] 120868-66-8	$C_9H_{10}ClN_3O$	4 52	212 0585	+	60	128 0263	126 0107	99 0558
Methiocarb 2032-65-7	$C_{11}H_{15}NO_2S$	10 17	226 0896	+	15	169 0683	121 0652	93 0705
Methiocarb-sulfoxide[5] 2635-10-1	$C_{11}H_{15}NO_3S$	4 97	242 0845	+	45	185 0631	170 0395	122 0728
Methomyl 16752-77-5	$C_5H_{10}N_2O_2S$	3 5	163 0536	+	30	106 0325	88 0221	
Methoxyfenozid 161050-58-4	$C_{22}H_{28}N_2O_3$	10 88	369 2173 **367.2027**[b]	+	15 **30**	313 1545 **149.0597**	149 0598 **105.0694**	
Pirimicarb 23103-98-2	$C_{11}H_{18}N_4O_2$	4 98	239 1503	+	45	182 1292	72 0452	
Pymetrozine 123312-89-0	$C_{10}H_{11}N_5O$	1 44	218 1036	+	60	105 0449		
Tebufenozide 112410-23-8	$C_{22}H_{28}N_2O_2$	12 29	353 2224 **351.2078**[b]	+	15 **30**	297 1595 **149.0597**	133 0648 **105.0695**	
Teflubenzuron 83121-18-0	$C_{14}H_6Cl_2F_4N_2O_2$	15 8	**380.9815** 378 967[b]	**+** -	**45** 15	**158.0412** 338 955	**141.0146** 195 9534	
Thiacloprid 111988-49-9	$C_{10}H_9ClN_4S$	5 63	253 0309	+	45	126 0107		
Thiacloprid-amide[6] 676228-91-4	$C_{10}H_{11}ClN_4OS$	4 54	271 0415	+	30	254 0147	228 0355	126 0106
Thiamethoxam 153719-23-4	$C_8H_{10}ClN_5O_3S$	3 89	292 0266	+	30	211 0647	181 0541	131 967

[a] If nothing mentioned the $[M+H]^+$ mass is shown, [b] represents the $[M-H]^-$ mass, [c] NCEs in negative ionization were determined only when the ion intensities were higher or in the same range as the ones in positive mode, [d] fragments masses determined by experimental data, [1] TP of diazinon; [2] TP of chlorpyrifos; [3] TP of fipronil; [4] TP of imidacloprid; [5] TP of methiocarb; [6] TP of thiacloprid.

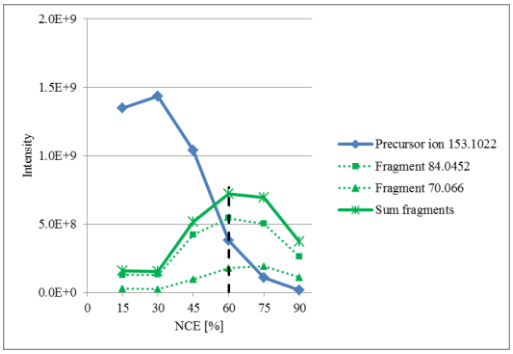
Table A.5. Retention time (RT), normalized collision energy (NCE) and mass of the precursor ion and formed fragments for the analyzed fungicides and their TPs Values in bold indicate the ionization mode that was finally used for the quantification in the environmental samples

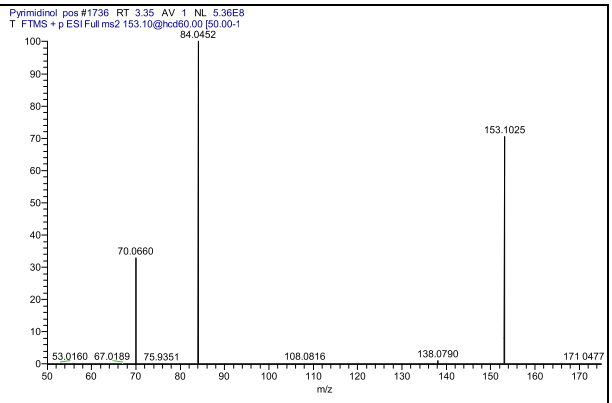
Analyte CAS number	Formula	RT [min]	Precursor Ion [m/z][a]	Polarity	NCE [%][c]	Fragment I [m/z][d]	Fragment II [m/z][d]	Fragment III [m/z][d]
Azoxystrobin 131860-33-8	$C_{22}H_{17}N_3O_5$	9 9	404 1241	+	15	372 0986	344 1037	172 0397
Azoxystrobin free acid[1]	$C_{21}H_{15}N_3O_5$	8 78	**390.1085**	**+**	**15**	**372.0985**	**344.1035**	**172.0394**
1185255-09-7			388 0939[b]	-	15	312 0783	212 0461	142 0398
Boscalid	$C_{18}H_{12}Cl_2N_2O$	10 38	**343.0399**	**+**	**30**	**307.0625**	**271.0858**	**139.9894**
188425-85-6			341 0254[b]	-	30	111 9945		
Carbendazim 10605-21-7	$C_9H_9N_3O_2$	3 31	192 0768	+	60	160 0509	132 056	
Cyproconazole 94361-06-5	$C_{15}H_{18}ClN_3O$	10 91/11 46*	292 1211	+	30	125 0157	70 0409	
Cyprodinil 121552-61-2	$C_{14}H_{15}N_3$	9 28	226 1339	+	100	93 0578		
Difenoconazole 119446-68-3	$C_{19}H_{17}Cl_2N_3O_3$	14 05/14 19*	406 072	+	60	251 0024	188 0388	
Dimethomorph 110488-70-5	$C_{21}H_{22}ClNO_4$	10 10/10 69*	388 1310	+	30	301 0615	165 0542	
Epoxiconazole 133855-98-8	$C_{17}H_{13}ClFN_3O$	11 79	330 0804	+	30	121 0453		
Fenpropidin 67306-00-7	$C_{19}H_{31}N$	9 14	274 2529	+	60	147 1169	86 0971	
Flusilazole 85509-19-9	$C_{16}H_{15}F_2N_3Si$	12 37	316 1076	+	30	187 059	165 0703	
Iprovalicarb 140923-17-7	$C_{18}H_{28}N_2O_3$	11 22/11 40*	321 2173	+	30	203 1391	119 0858	
Myclobutanil 88671-89-0	$C_{15}H_{17}ClN_4$	11 2	289 1215	+	60	125 0155	70 0408	
Prochloraz 67747-09-5	$C_{15}H_{16}Cl_3N_3O_2$	12 2	376 0381	+	15	308 0012	265 9542	
Propamocarb 24579-73-5	$C_9H_{20}N_2O_2$	2 37	189 1598	+	45	144 102	102 0555	74 0245
Propiconazole 60207-90-1	$C_{15}H_{17}Cl_2N_3O_2$	13 05/13 21*	342 0771	+	60	158 9767	69 0708	
Pyrimethanil 53112-28-0	$C_{12}H_{13}N_3$	7 56	200 1182	+	60	183 0922	107 061	82 0659
Spiroxamine 118134-30-8	$C_{18}H_{35}NO_2$	9 87/10 08*	298 2741	+	45	144 1386	100 1128	
Tebuconazole 107534-96-3	$C_{16}H_{22}ClN_3O$	12 98	308 1524	+	45	70 0409		

[a] If nothing mentioned the $[M+H]^+$ mass is shown, [b] represents the $[M-H]^-$ mass, [c] NCEs in negative ionization were determined only when the ion intensities were higher or in the same range as the ones in positive mode, [d] fragments masses determined by experimental data, [1] TP of azoxystrobin, * substances with chromatographic doublet peaks; the two values represent the elution time of the two maximum points

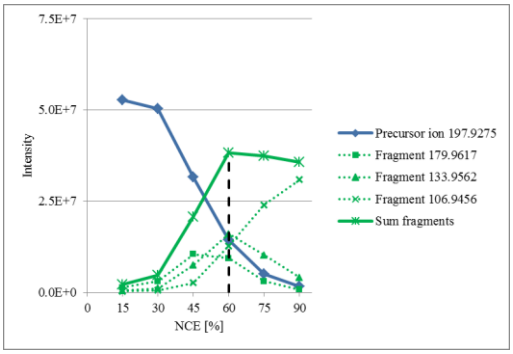
Figure A.3. Left: Breakdown curves (left) of the HCD normalized collision energy (NCE) with major fragments and optimal NCE (- - -). The better ionization mode (M+H) or (M-H) is shown. Right: spectra at the optimized NCE.

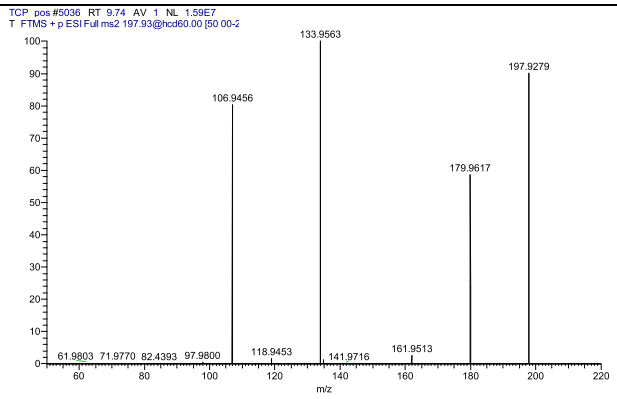
2-Isopropyl-6-methyl-4-pyrimidinol (M+H)



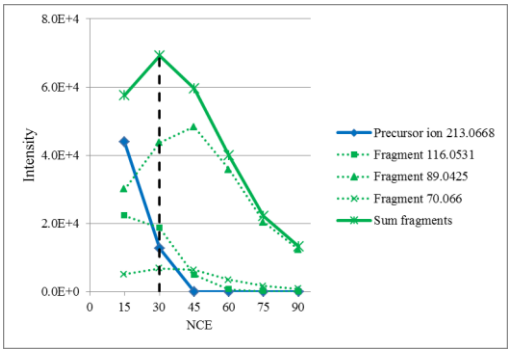


3,5,6-Trichloro-2-pyridinol (M+H)





Aldicarb (M+Na)



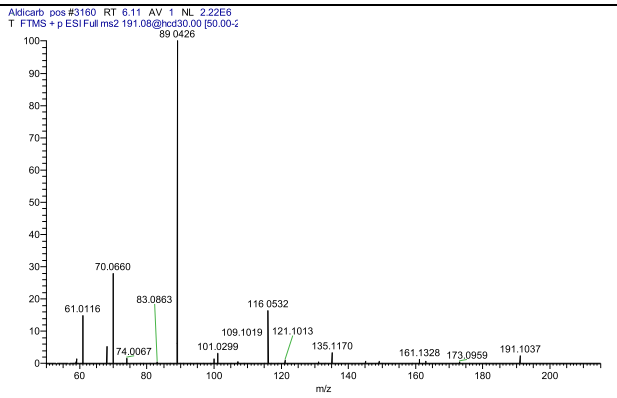
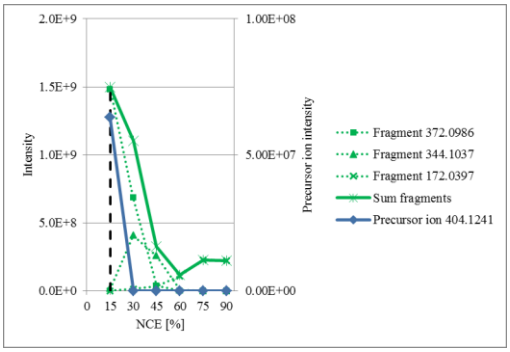
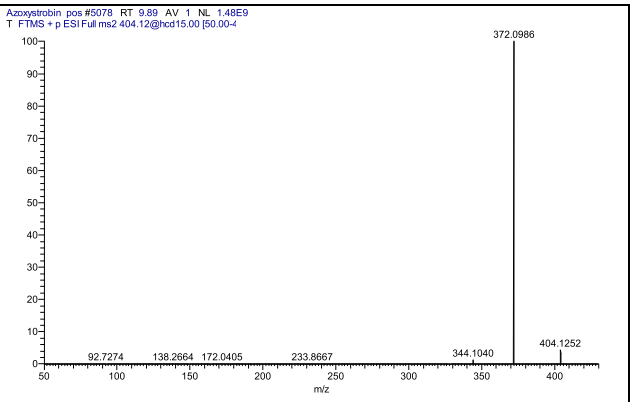


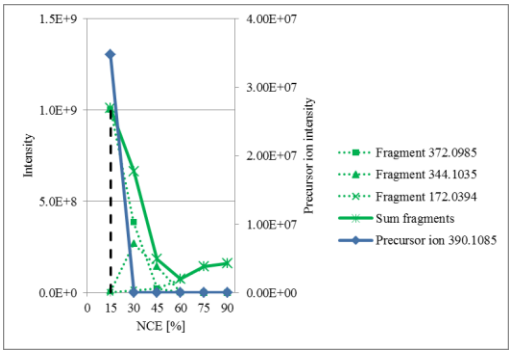
Figure A.3. Continuation

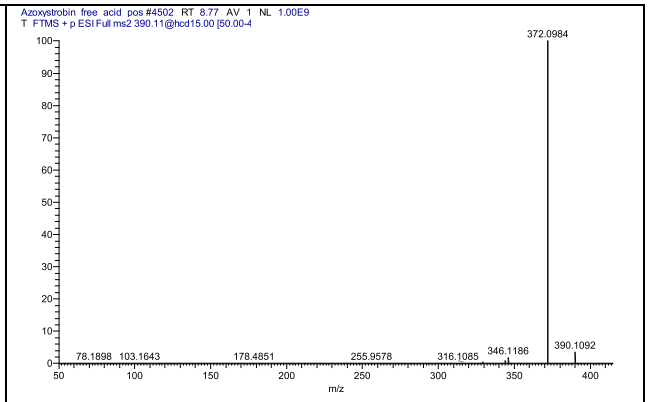
Azoxystrobin (M+H)



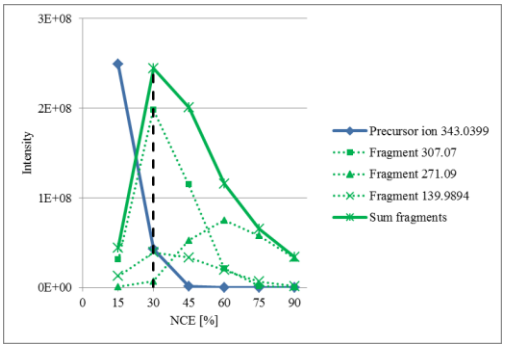


Azoxystrobin free acid (M+H)





Boscalid (M+H)



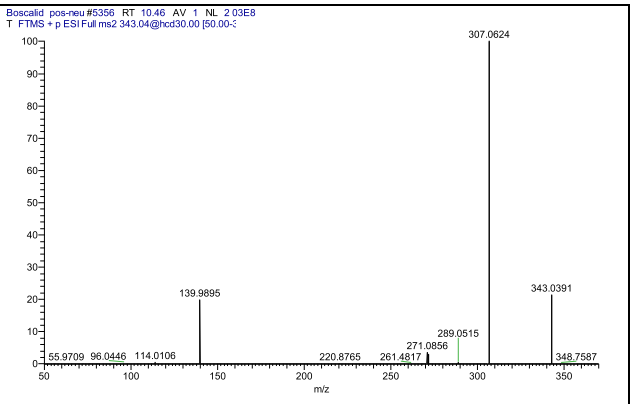
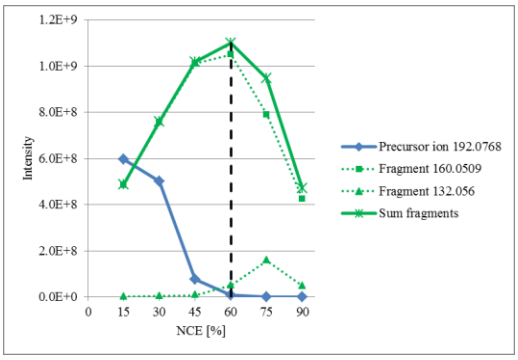
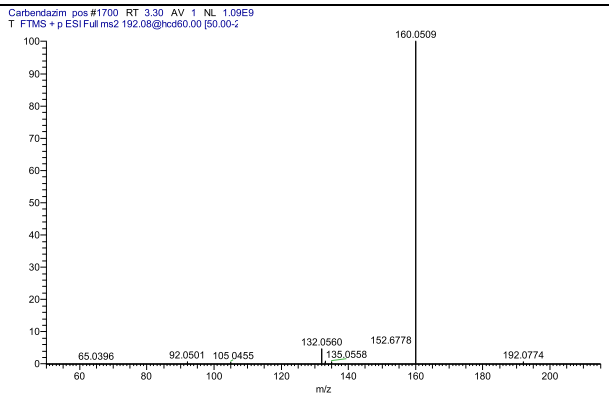


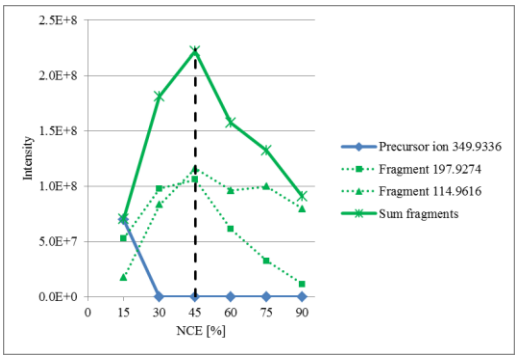
Figure A.3. Continuation

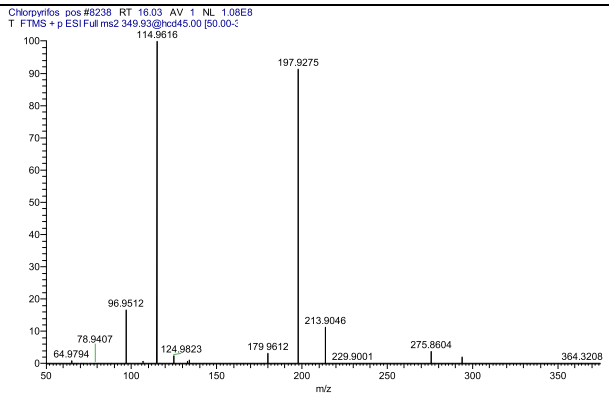
Carbendazim (M+H)



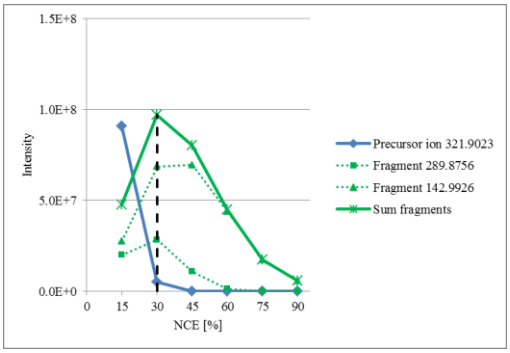


Chlorpyrifos (M+H)





Chlorpyrifos-methyl (M+H)



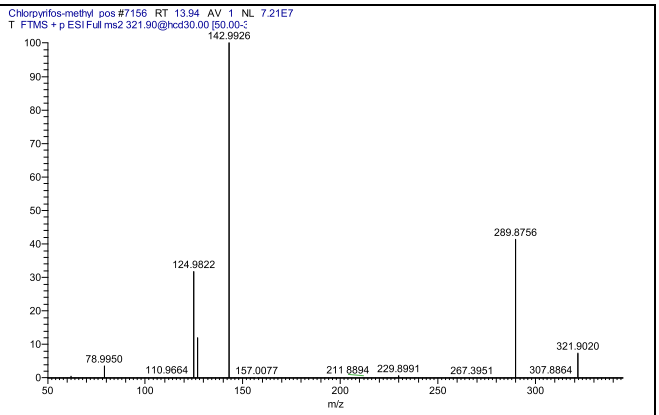
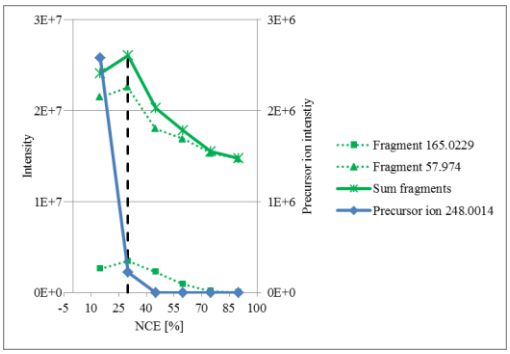
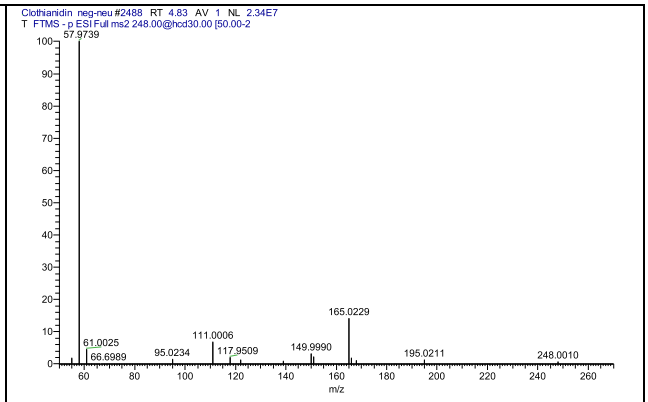


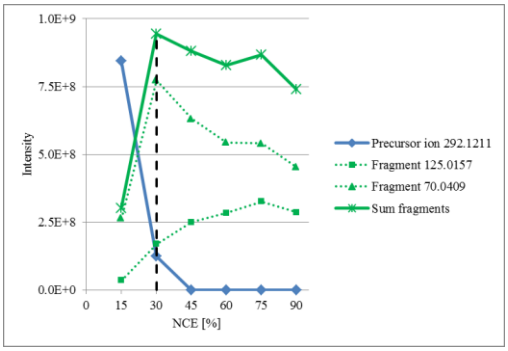
Figure A.3. Continuation

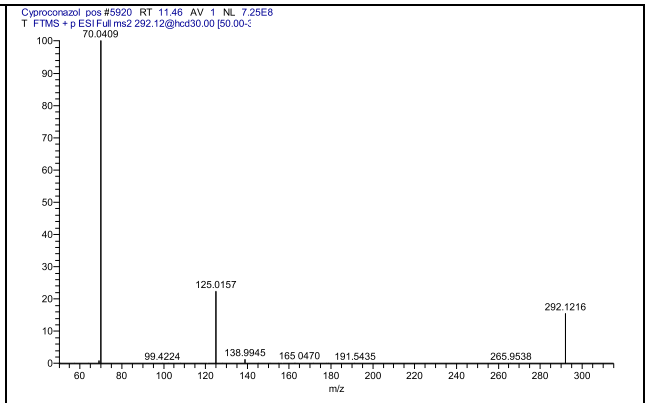
Clothianidin (M-H)



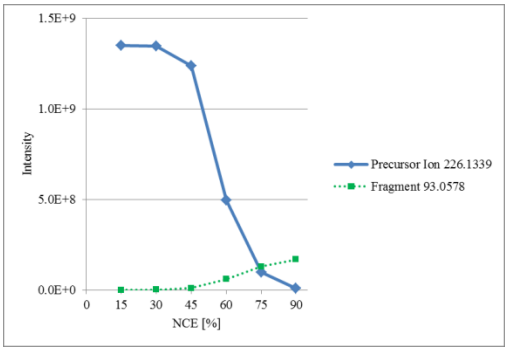


Cyproconazole (M+H)





Cyprodinil (M+H)



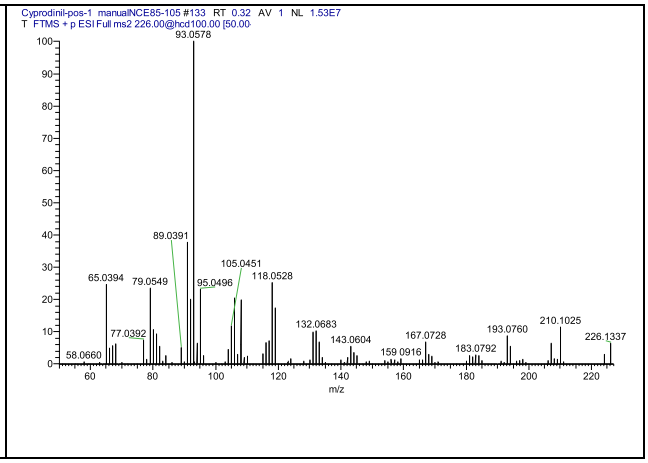
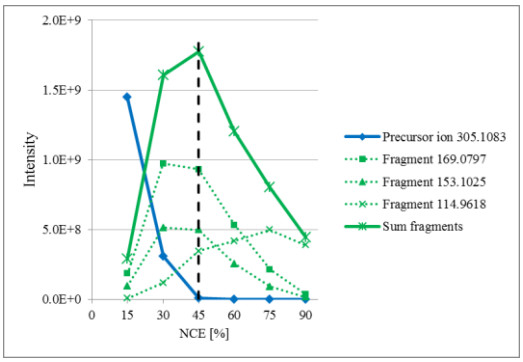
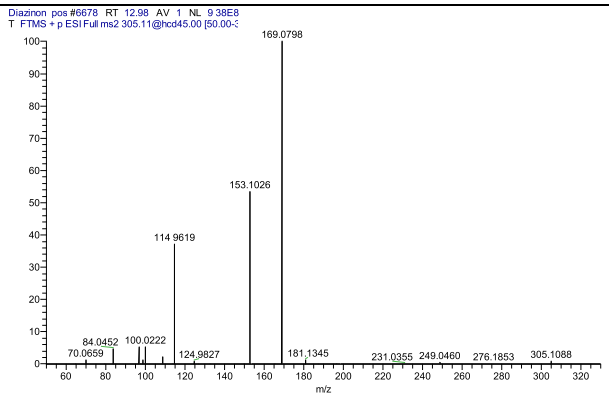


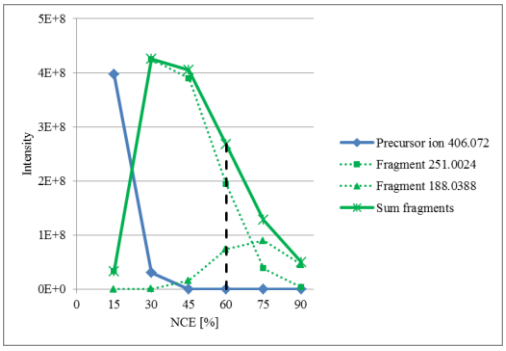
Figure A.3. Continuation

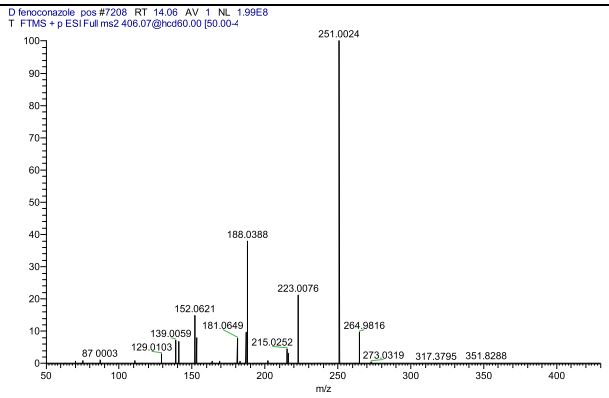
Diazinon (M+H)



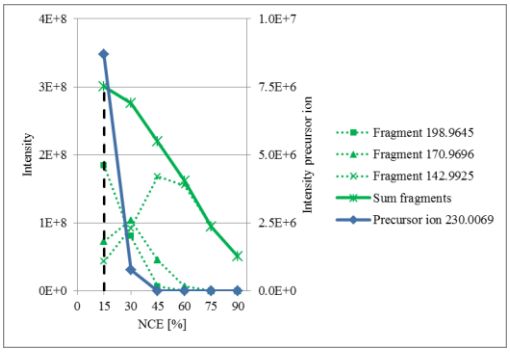


Difenoconazole (M+H)





Dimethoat (M+H)



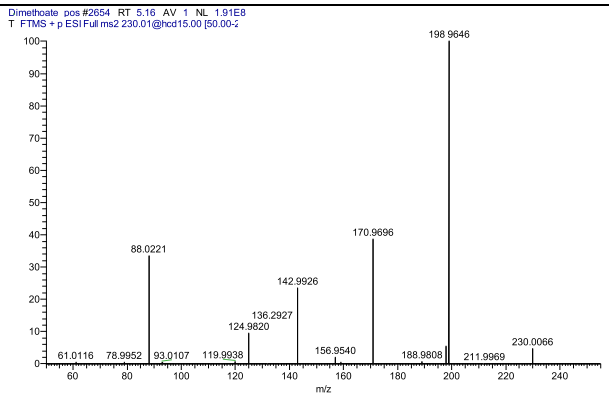
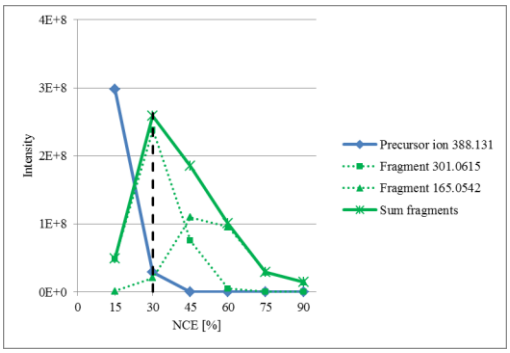
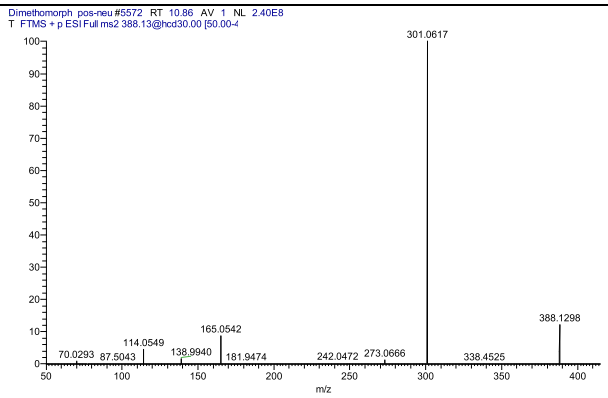


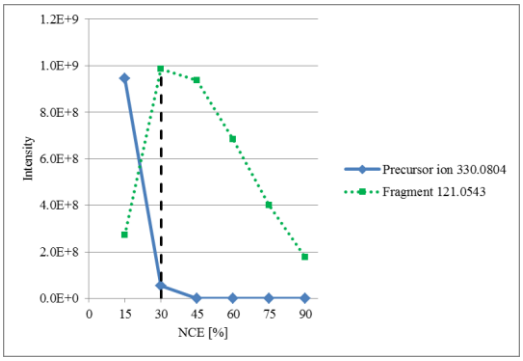
Figure A.3. Continuation

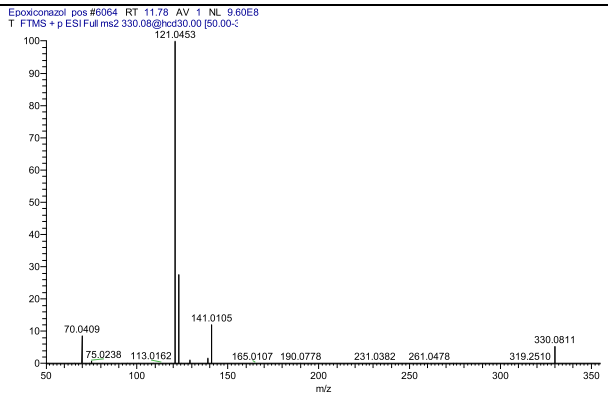
Dimethomorph (M+H)



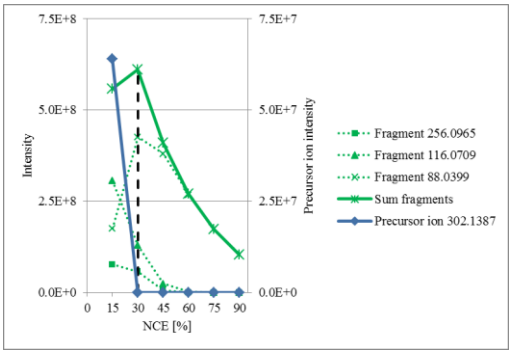


Epoxiconazole (M+H)





Fenoxycarb (M+H)



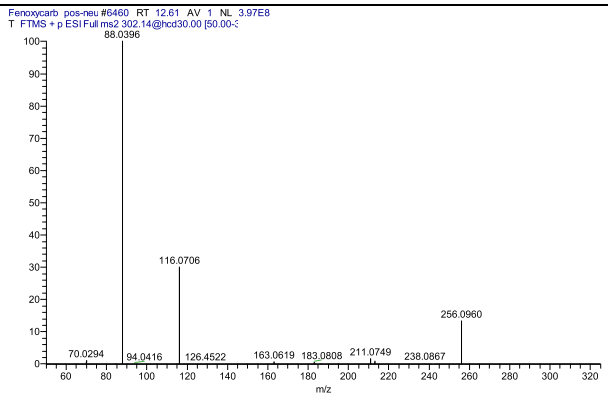
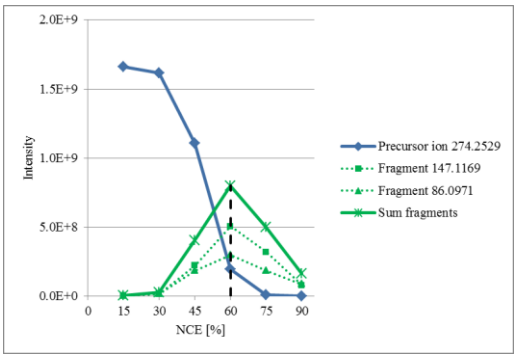
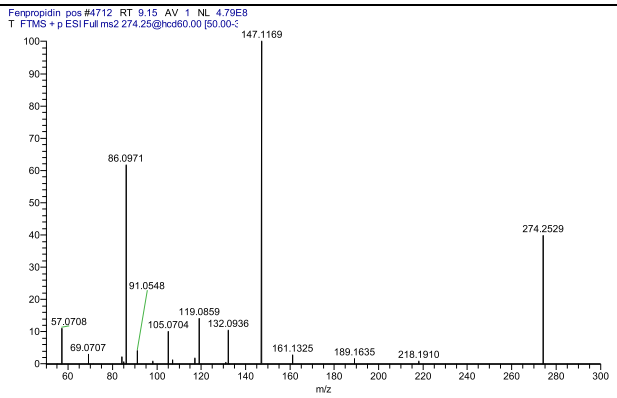


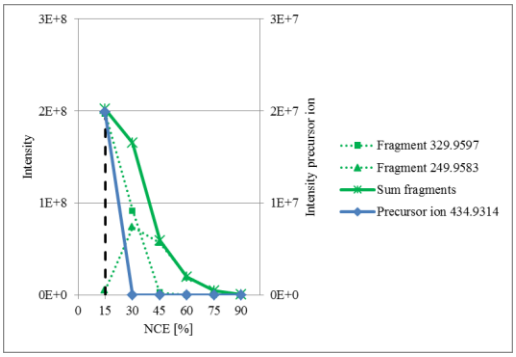
Figure A.3. Continuation

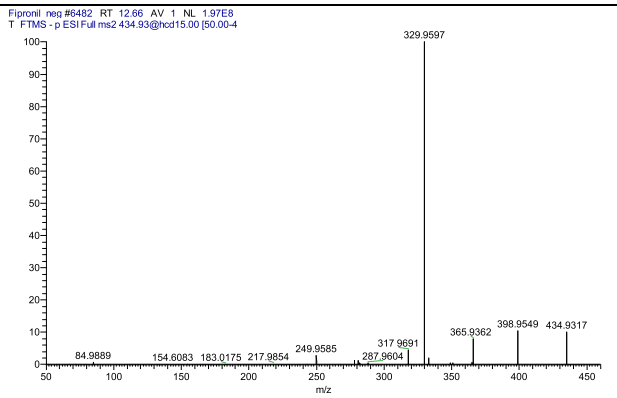
Fenpropidin (M+H)



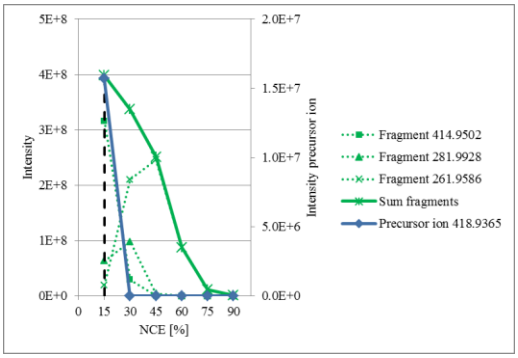


Fipronil (M-H)





Fipronil-sulfide (M-H)



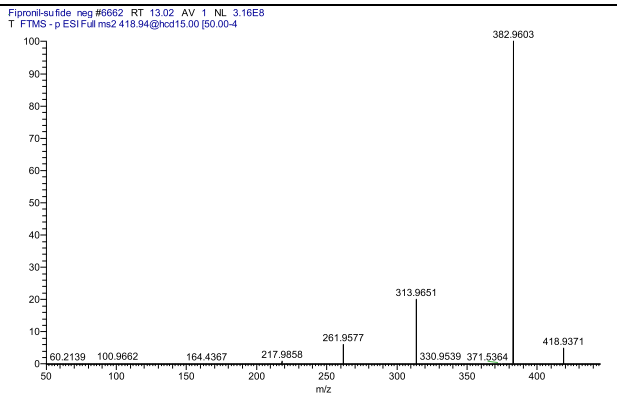
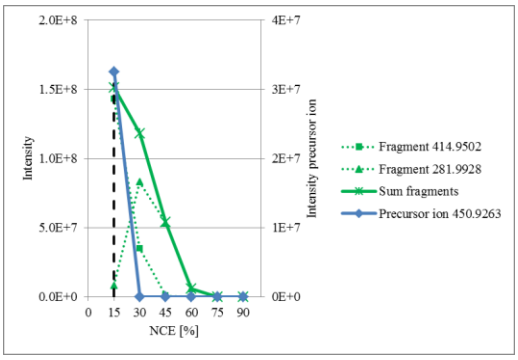
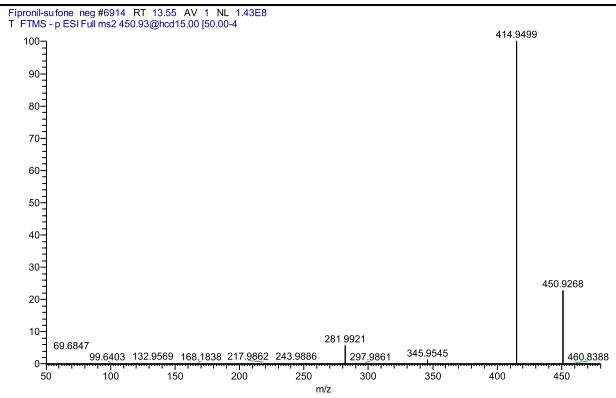


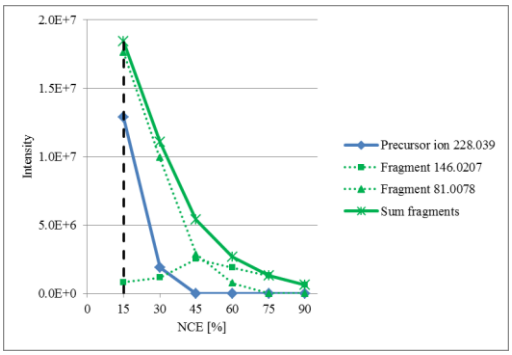
Figure A.3. Continuation

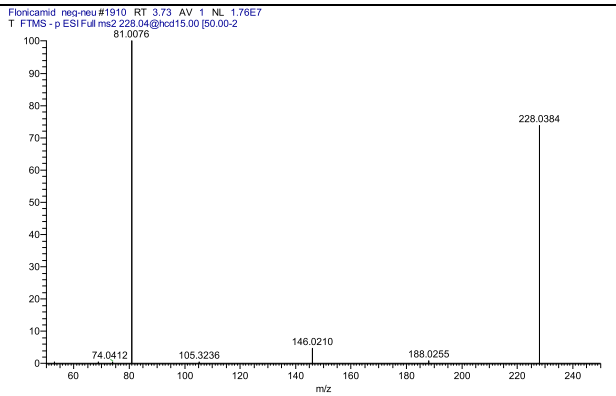
Fipronil-sulfone (M-H)



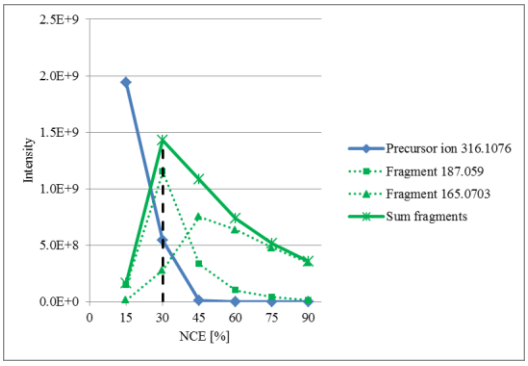


Flonicamid (M-H)





Flusilazole (M+H)



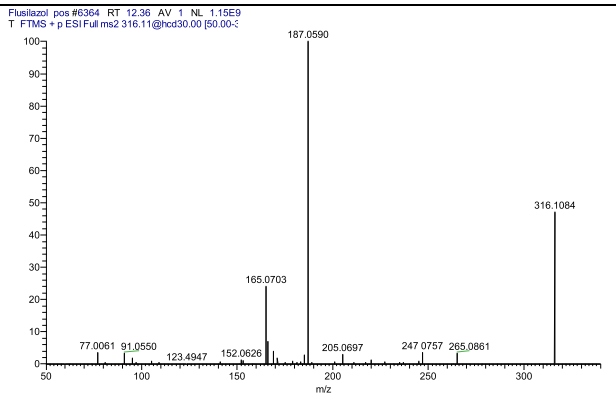
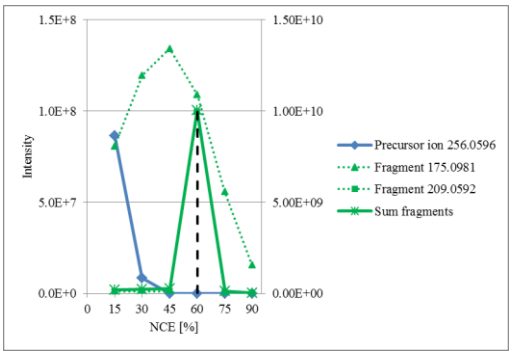
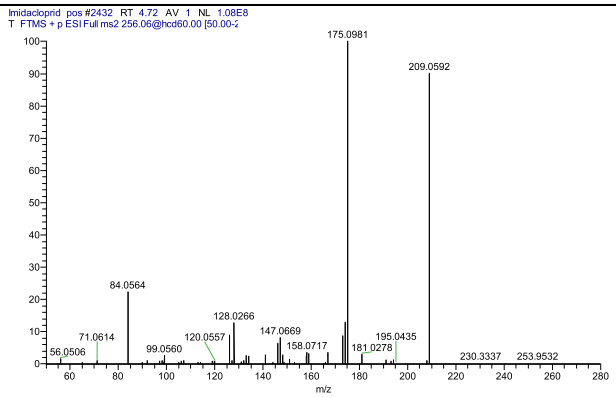


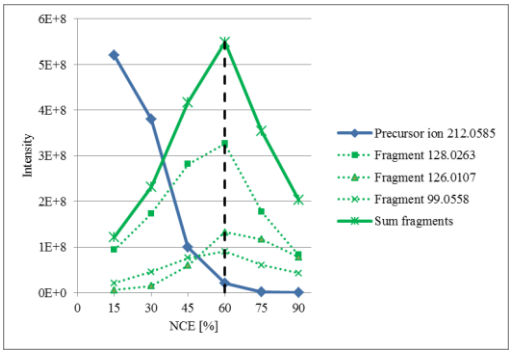
Figure A.3. Continuation

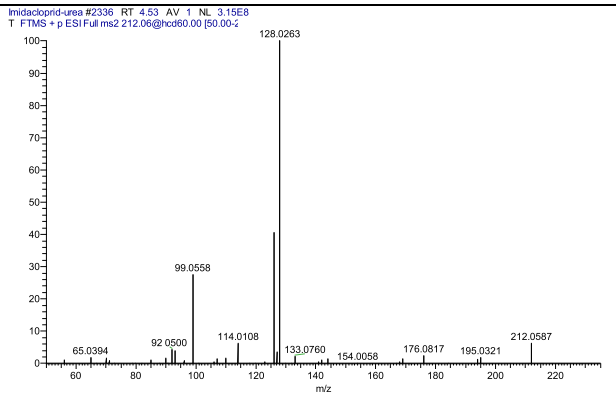
Imidacloprid (M+H)



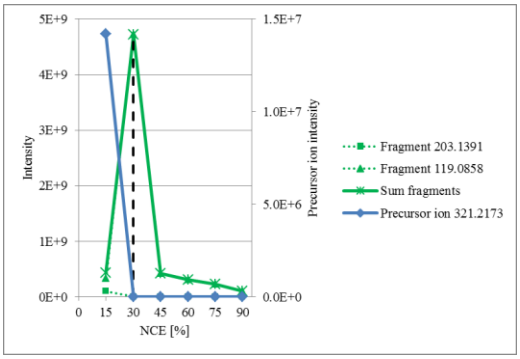


Imidacloprid-urea (M+H)





Iprovalicarb (M+H)



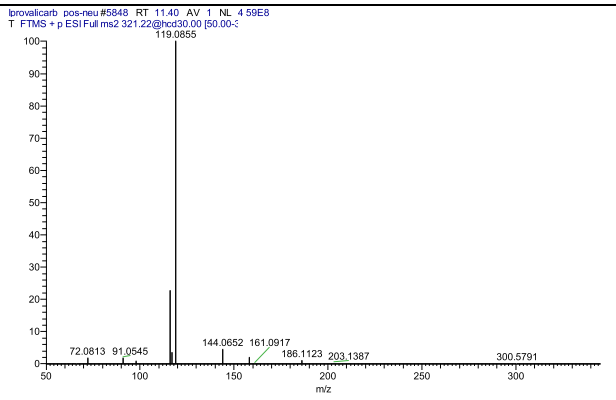
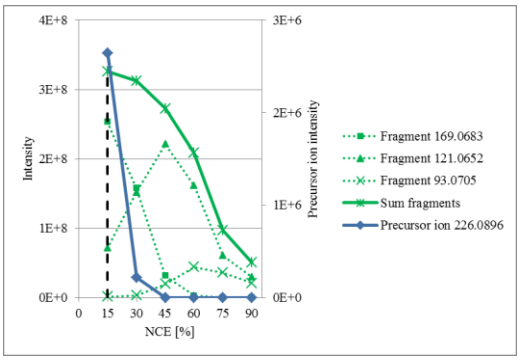
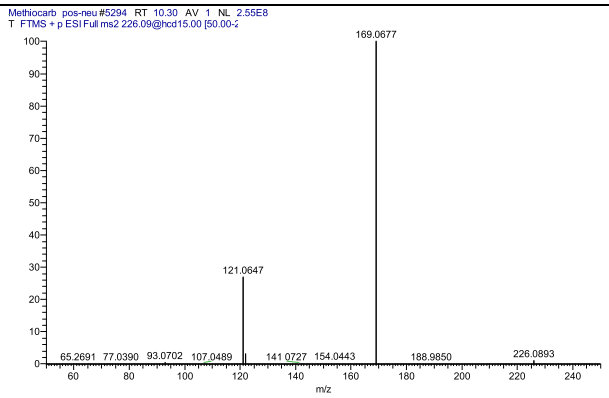


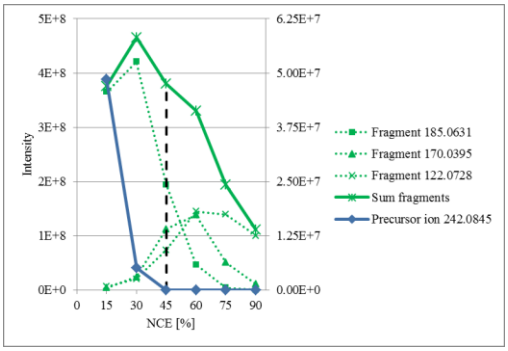
Figure A.3. Continuation

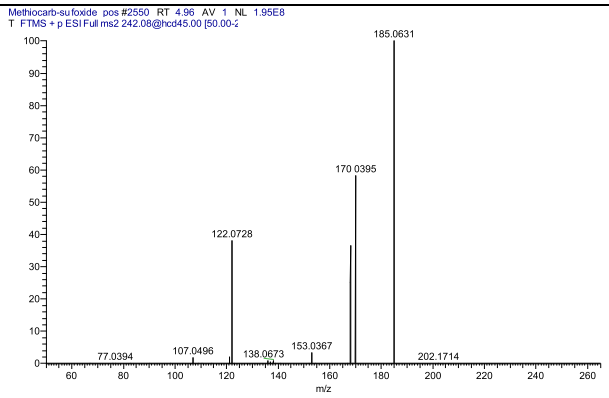
Methiocarb (M+H)



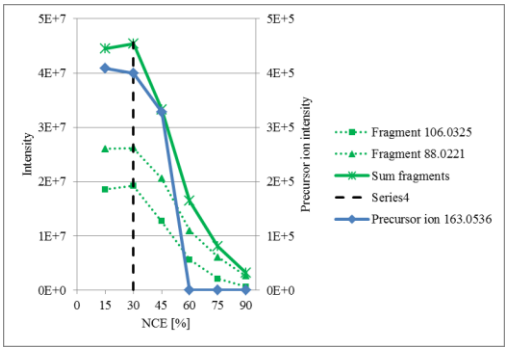


Methiocarb-sulfoxide (M+H)





Methomyl (M+H)



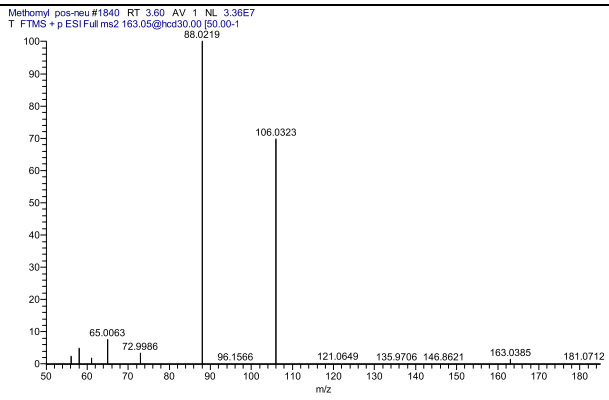
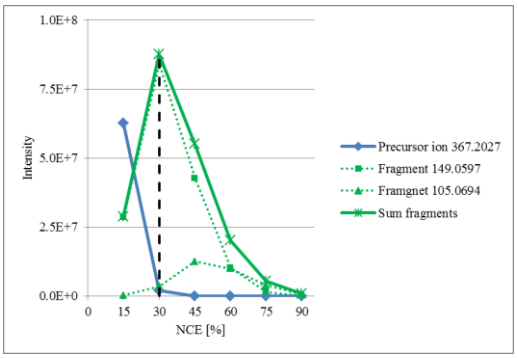
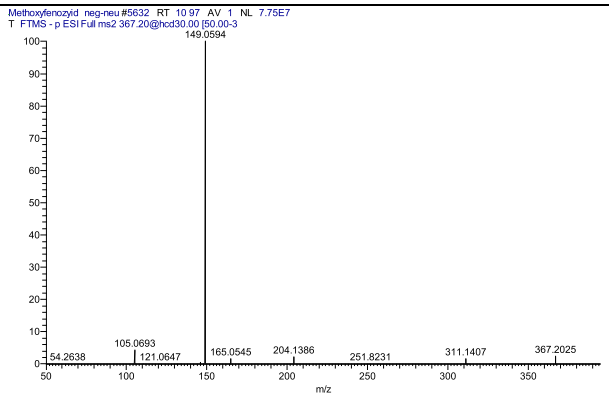


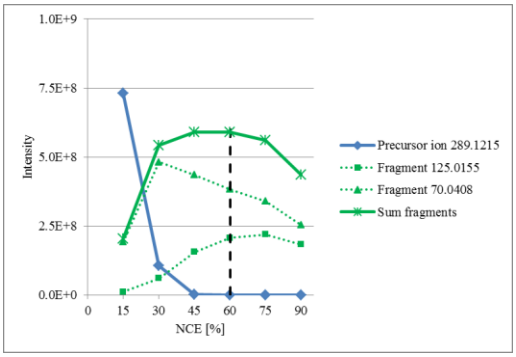
Figure A.3. Continuation

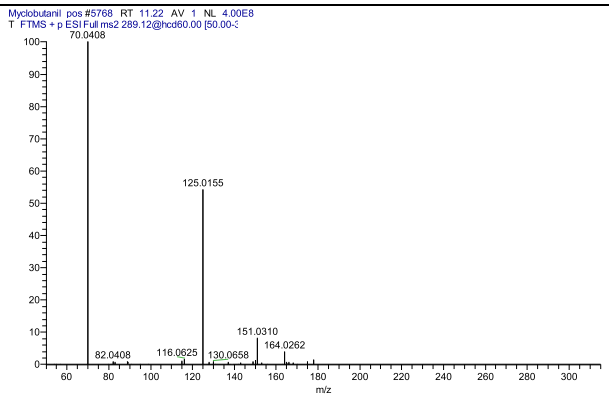
Methoxyfenozid (M-H)



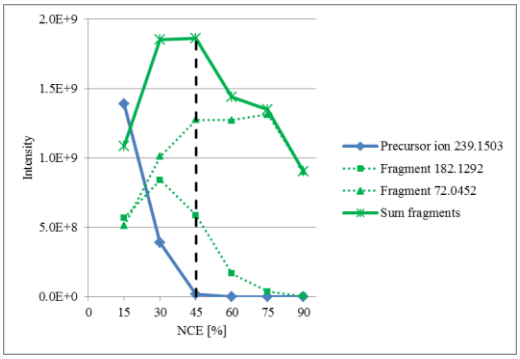


Myclobutanil (M+H)





Pirimicarb (M+H)



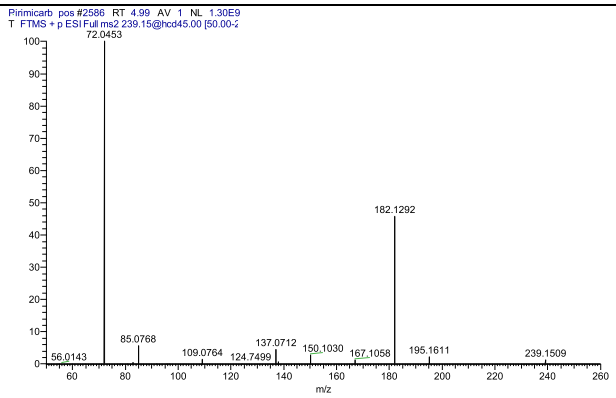
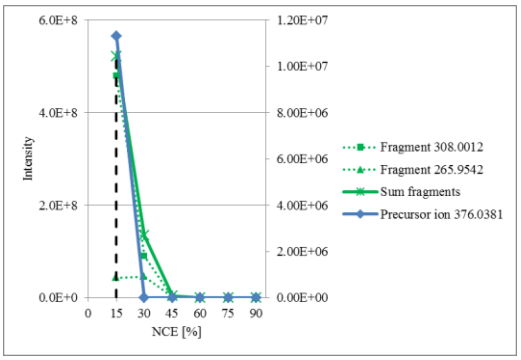
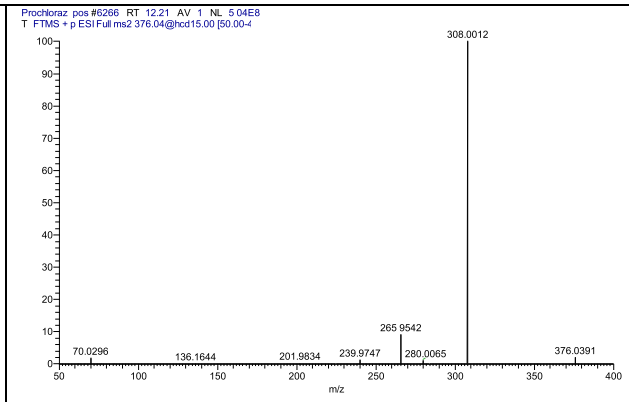


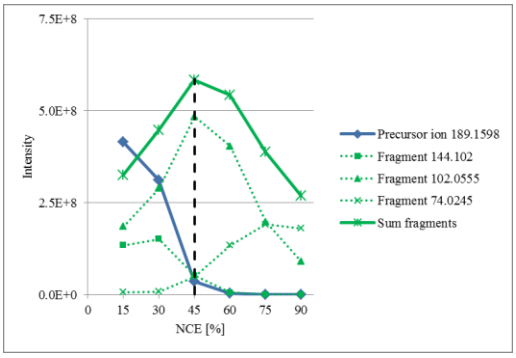
Figure A.3. Continuation

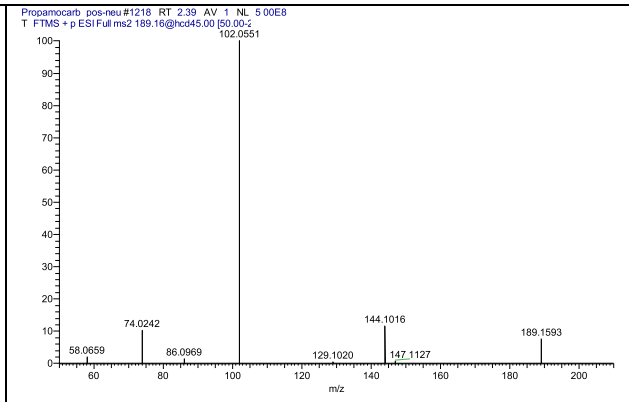
Prochloraz (M+H)



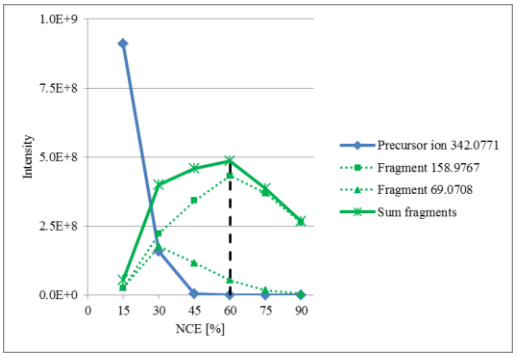


Propamocarb (M+H)





Propiconazole (M+H)



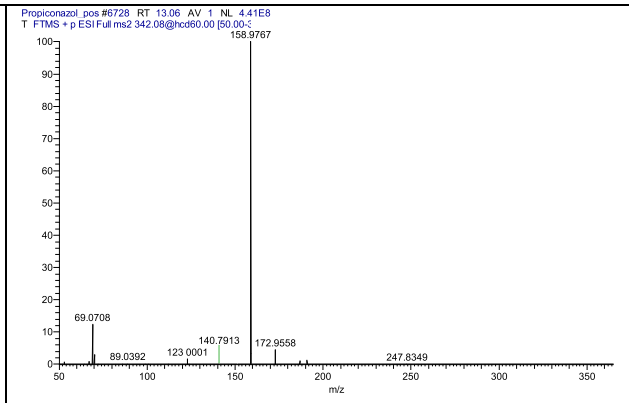
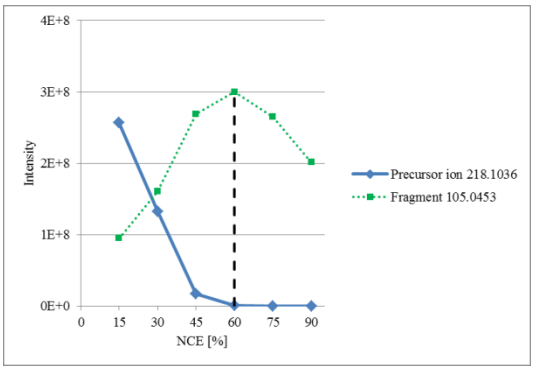
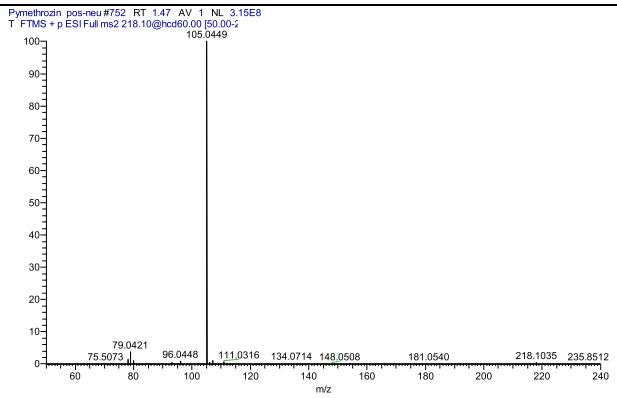


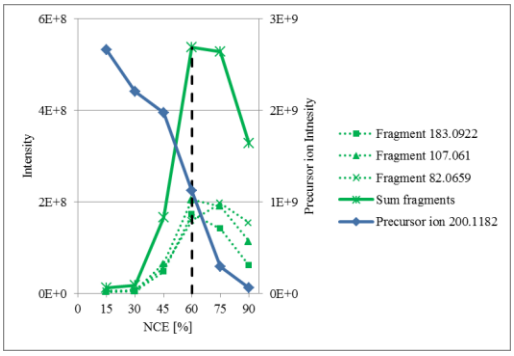
Figure A.3. Continuation

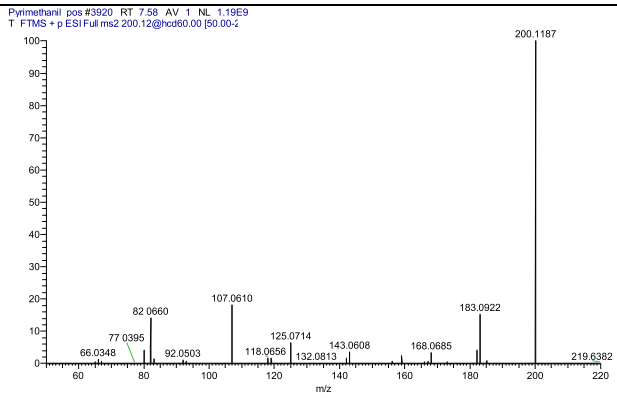
Pymetrozine (M+H)



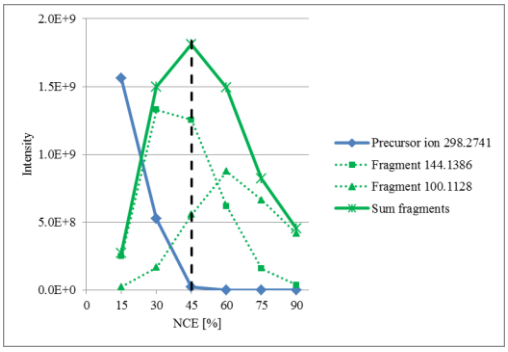


Pyrimethanil (M+H)





Spiroxamine (M+H)



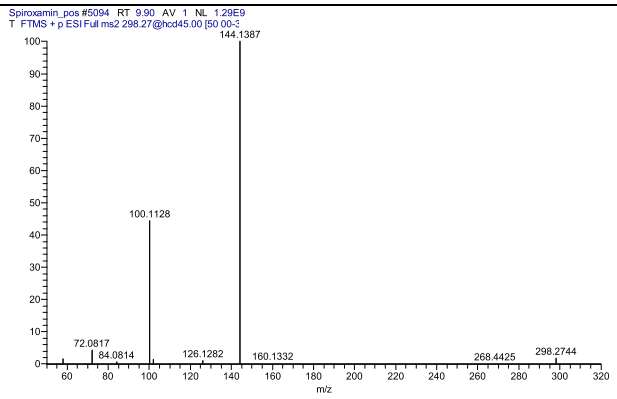
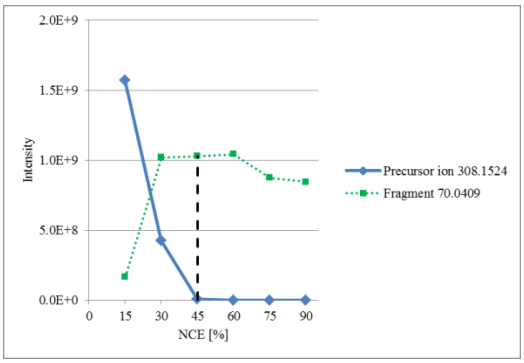
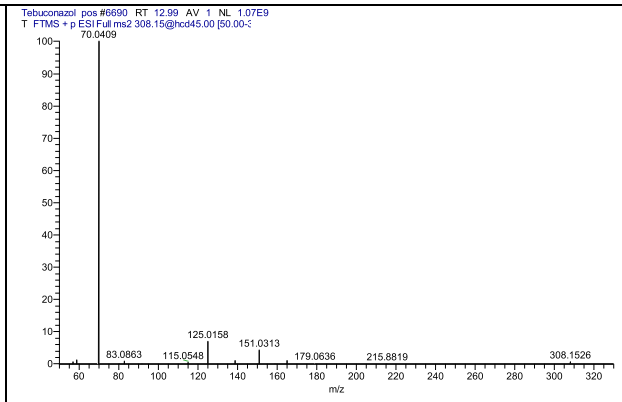


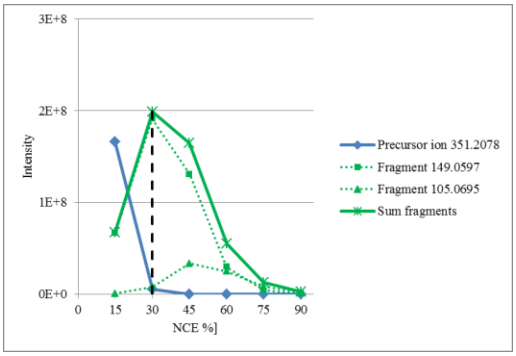
Figure A.3. Continuation

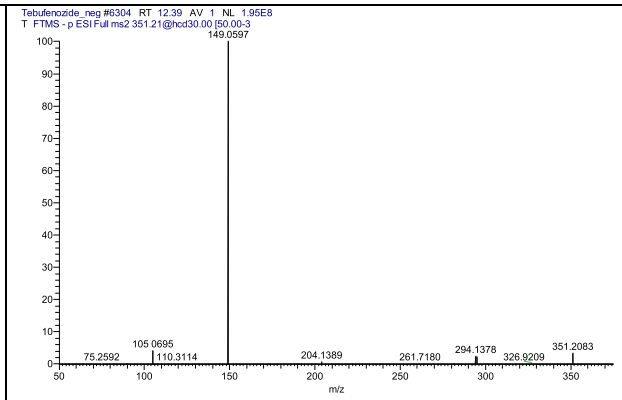
Tebuconazole (M+H)



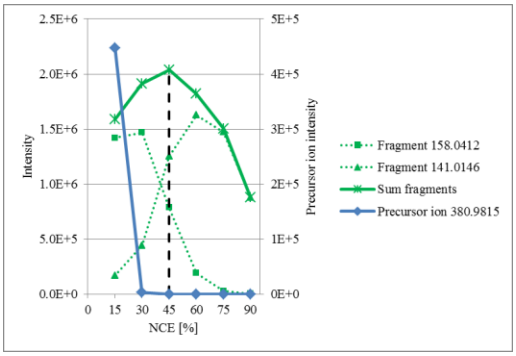


Tebufenozide (M-H)





Teflubenzuron (M+H)



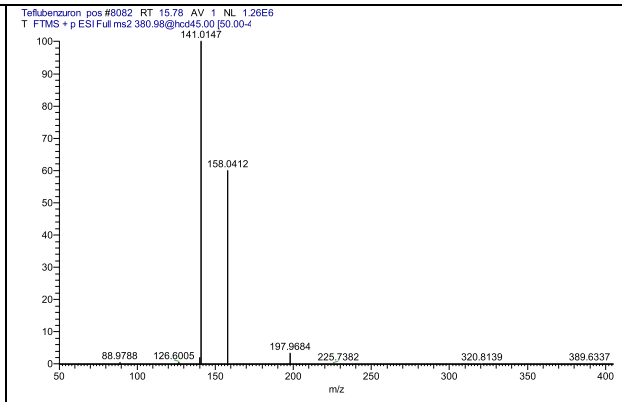
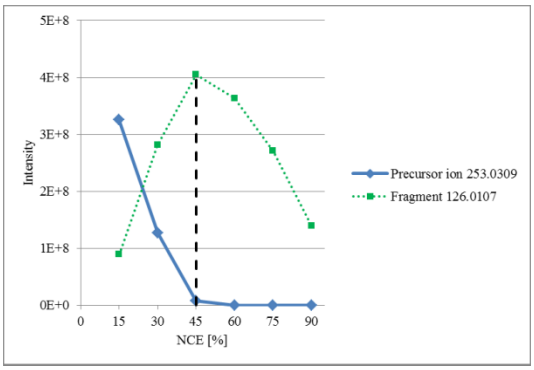
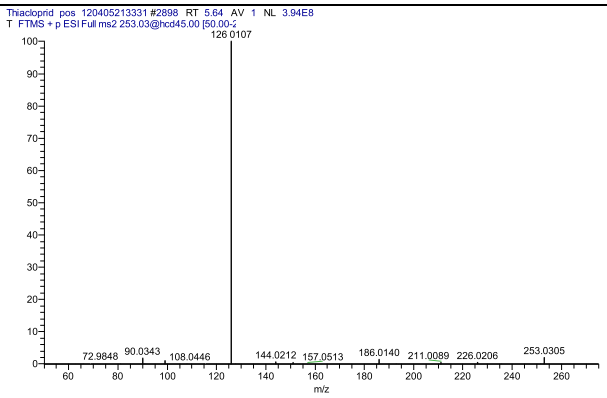


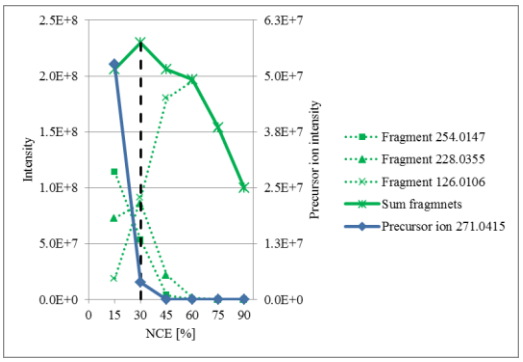
Figure A.3. Continuation

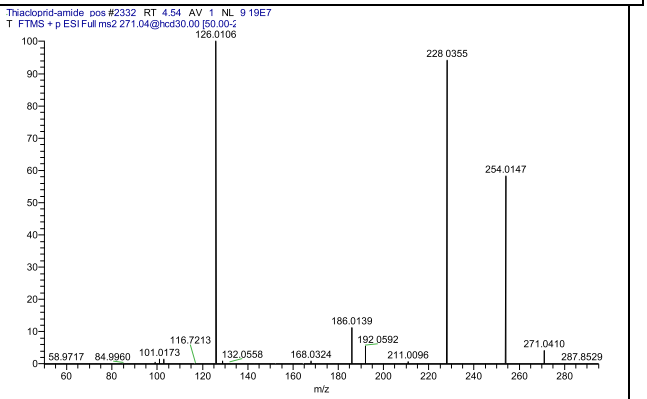
Thiacloprid (M+H)



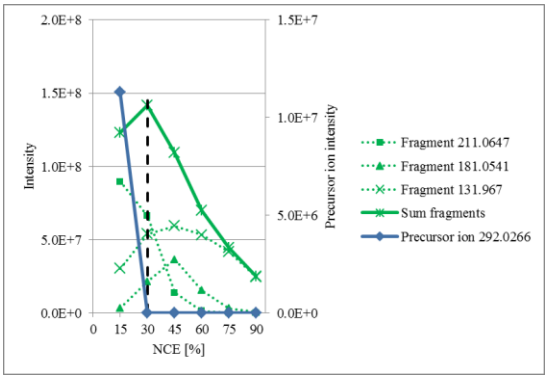


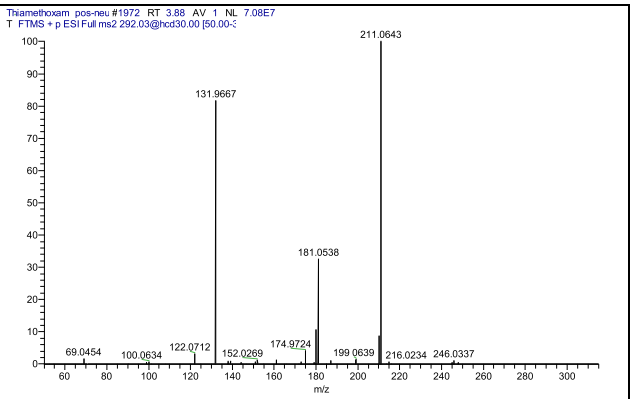
Thiacloprid-amide (M+H)





Thiamethoxam (M+H)





A.6. Automatic Filter Examples

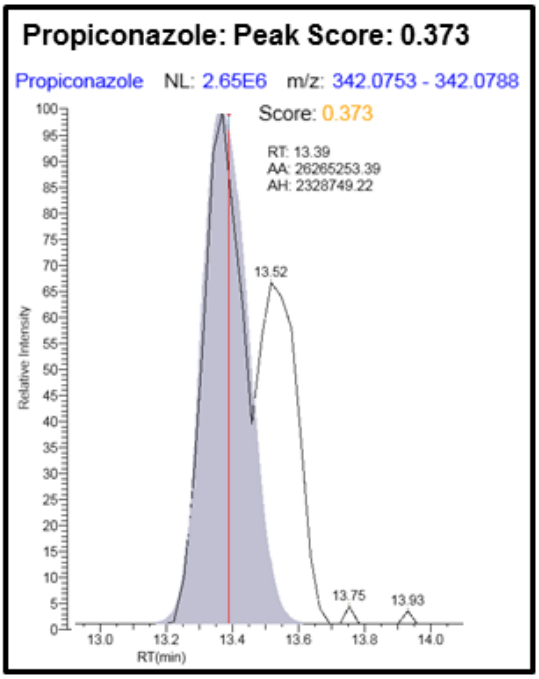


Figure A.4. Example of a low peak score due to unresolved doublet peak with ExactFinder V.2.0: Chromatogram of the two isomeric peaks of propiconazole (retention time: 13.39/13.52, intensity: 3.8e6). Peak Score = 0.375.

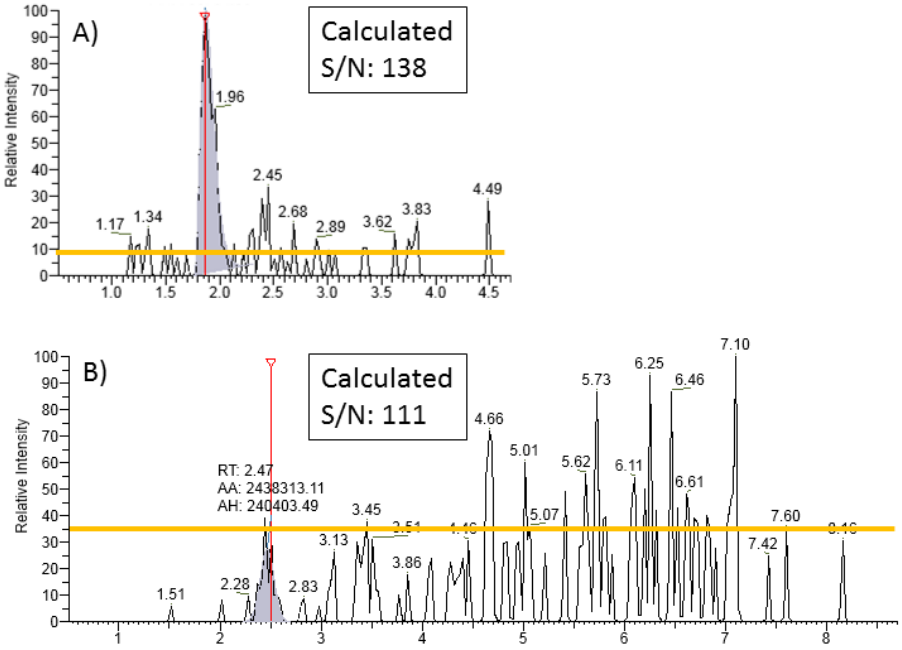


Figure A.5. Examples of a calculated S/N with the software ExactFinder (V.2.0. A) Pymethrozine in an environmental sample. B) False positive of tebuconazole in an environmental sample. The orange line represents the effective S/N (visual check).

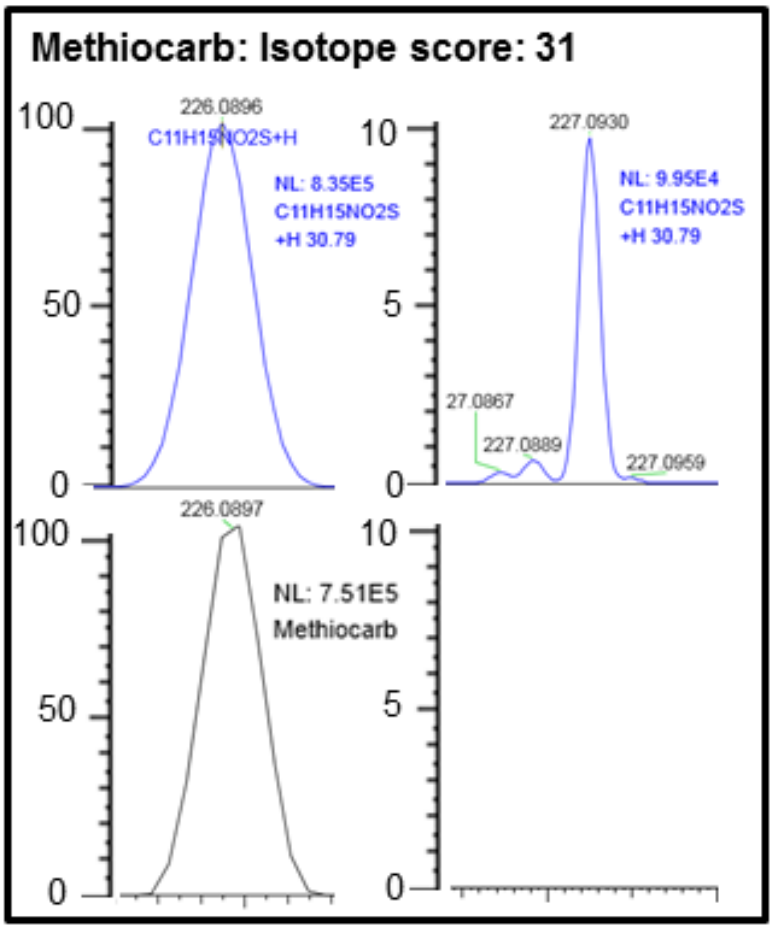


Figure A.6. Example of a low isotope score with ExactFinder V.2.0: Theoretical (top) and measured (bottom) isotope pattern of methiocarb. The M+1 isotope (^{13}C-peak) is missing because the expected intensity is slightly below the limit of detection of the instrument (1e5). The peak was automatically excluded due to an isotope score of 31. The theoretical intensity of the M+2 isotope is even lower than the M+1 and was not detected, either.

A.7. Confirmed Substances and False Positives from the Application of the Suspect Screening

Table A.6. Confirmed substances(with commercially available reference standards) by the applied suspect screening

Suspect Name	Ionization mode	RT (min)	m/z	Fragment 1[b]	Fragment 2[b]	Fragment 3[b]	NCE[c]
Benthiavalicarb-isopropyl	+	10.80	382.1595	180.0275 (100)	116.0705 (55)	72.0814 (45)	45
Carbofuran	+	7.18	222.1125	123.0440 (100)	165.0909 (40)	137.0596 (10)	45
Chlorfenvinphos	+	13.27/13.87	358.9768	98.9846 (100)	204.9378 (45)	169.9688 (40)	45
Chlorothalonil-4-hydroxy *(R182281; TP of chlorothalonil)*	-	9.60	244.9082	174.9705 (100)	146.9758 (80)	197.9400 (25)	75
Fenamidone	+	10.28	312.1165	92.0498 (100)	236.1183 (30)	103.0713 (20)	45
Fenhexamid	+/-	11.65	302.0709	55.0551 (100)	97.1016 (95)	143.0135 (55)	90
Fluoxastrobin	+	11.54	459.0866	188.0380 (100)	138.0105 (40)	306.0672 (35)	45
Imidacloprid-desnitro *(TP of imidacloprid)*	+	2.45	211.0745	126.0106 (100)	84.0561 (15)	175.0979 (10)	60
Kresoxim-methyl	+	12.86	314.1387	222.0915 (100)	235.0758 (40)	116.0499 (20)	30
Mandipropamid	+	10.70	412.1310	328.1099 (100)	125.0153 (75)	204.1020 (40)	30
Mepanipyrim	+	11.12	224.1182	106.0653 (100)	79.0547 (35)	206.0839 (30)	75
Metalaxyl	+	9.00/9.43	280.1543	160.1125 (100)	192.1387 (60)	220.1337 (20)	45
Penconazole	+	13.14	284.0716	158.9766 (100)	70.0407 (80)	122.9998 (10)	45
Pencycuron	+	13.91	329.1415	125.0153 (100)	218.0732 (10)	261.0789 (10)	30
Trifloxystrobin	+	14.66	409.1370	186.0521 (100)	116.0492 (20)	206.0808 (10)	45

[a] reference standard purchased at Dr. Ehrenstorfer, Augsburg, Germany, [b] m/z (relative intensity), [c] NCE: normalized collision energy

Table A.7. Confirmed substances(with commercially not available reference standards) by the applied suspect screening

Suspect Name	Ionization mode	Confirmation by
2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid *(R417888; TP of chlorothalonil)*	-	laboratory of the Landeswasser-versorgung Langenau[a]
3-(2-chlorothiazol-5-ylmethyl)-5-methyl-[1,3,5] oxadiazinan -4-ylidineamine *(NOA 407475; TP of thiamethoxame)*	+	Reference standard from Syngenta (see spectra in Fig. 5, main text)
N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine *(CGA 62826; TP of metalaxyl)*	-	Reference standard from Syngenta (see spectra in SI-7.3)

a: confirmed by matching retention time and two matching fragments (m/z 220, 284) of an authentic reference standard at the laboratory of the Landeswasserversorgung Langenau. Fragments 220 and 284 also found in Reemtsma et al. (2013b)

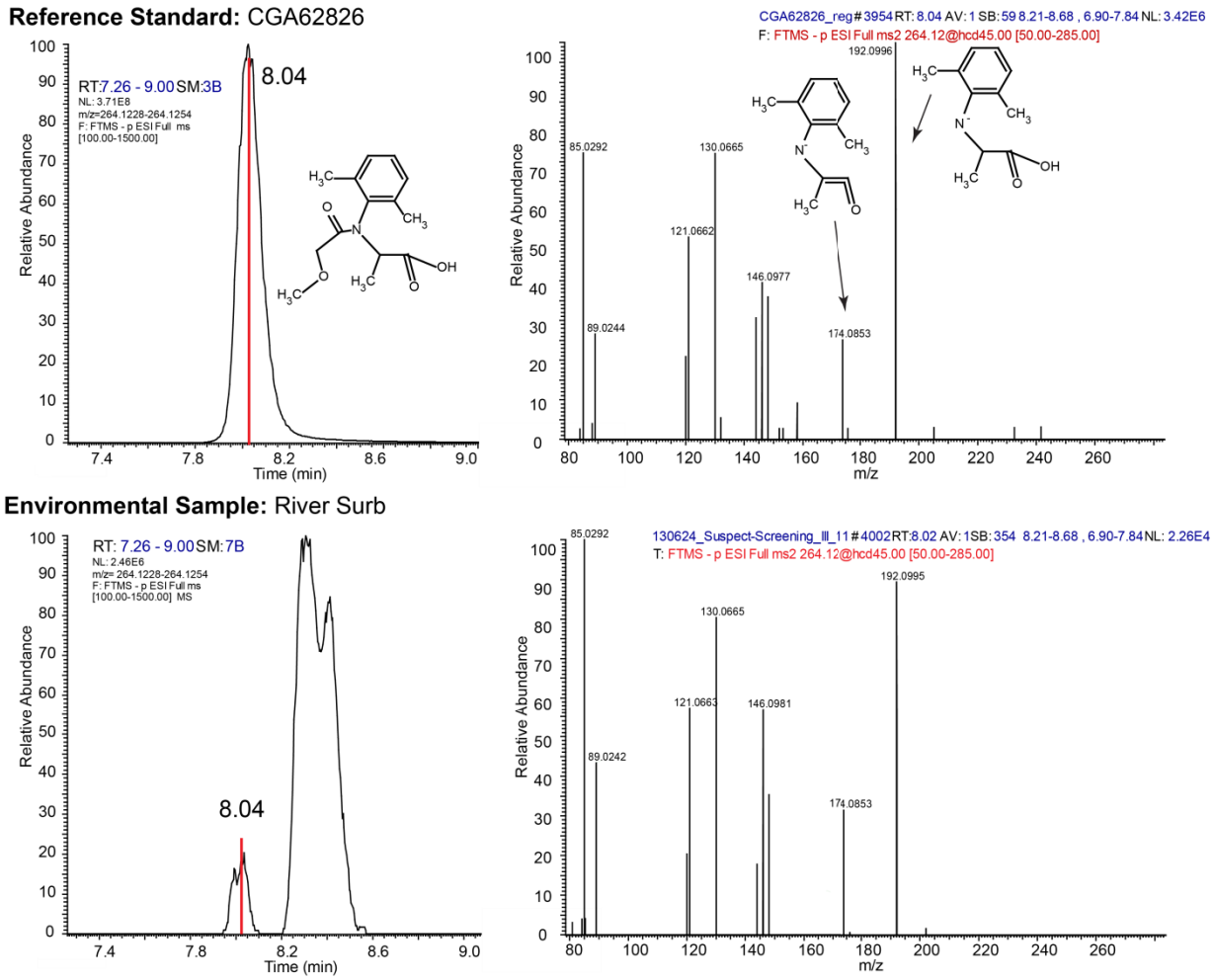


Figure A.7 Chromatogram (left) and MS/MS (right) of the metalaxyl TP CGA 62826, in the negative ionization mode. The red line in the chromatogram is the scan where the shown MS/MS was taken. The large unresolved doublet peak in the environmental sample was not picked by the automatic software because of a low peak score.

Table A.8. Excluded substances from the applied suspect screening

Suspect Name	Ionization mode	Reason for Exclusion
3-phenoxybenzoic acid *(TP of cypermethrin/permethrin)*	-	Comparison with Reference Standard (Dr. Ehrenstorfer, Augsburg, Germany)
4-(N'-(3,5-dimethylbenzoyl-N-(1,1-dimethylethyl)hydrazinocarbonyl)phenyl acetic acid *(TP of tebufenozid)*	+	Massfrontier: no matching fragments, MassBank and MetFrag: no matching annotations
Bifenazat	+	Comparison with MS/MS Spectra (Library Manager 2.0)
Diethofencarb*	+	Comparison with MS/MS Spectra (Library Manager 2.0)
Dodine	+	Comparison with MS/MS Spectra (Library Manager 2.0)
Famoxadone	+	Comparison with MS/MS Spectra (Library Manager 2.0)
Iprodione	+	Comparison with MS/MS Spectra (Library Manager 2.0)
Methiocarb-sulfone *(TP of methiocarb)**	-	Massfrontier: no matching fragments, MassBank and MetFrag: no matching annotations
Tetrahydrophthalamic acid *(TP of captan)*	+	Massfrontier: no matching fragments, MassBank and MetFrag: no matching annotations
Imidacloprid-dihydroxy-guanidin *(TP of imidacloprid)*	+	Massfrontier: no matching fragments, MassBank and MetFrag: no matching annotations
Imidacloprid-formyl-AMCP *(TP of imidacloprid)*	+	Massfrontier: no matching fragments, MassBank and MetFrag: no matching annotations
Pyrifenox*	+	Comparison with MS/MS Spectra (Library Manager 2.0)

[a] real identity confirmed. See **Table A.9**

Table A.9. Unknown identification of three false positives

Suspect Name	Ionization mode	Real Identity	Search Criteria / Definite Confirmation
Diethofencarb	+	Atenolol acid	Massbank search / Reference Standard of Atenolol-acid (Dr. Ehrenstorfer, Augsburg, Germany)
Methiocarb-sulfone	-	Propachlor-ESA	Massbank search / Reference Standard of Propachlor-ESA (Dr. Ehrenstorfer, Augsburg, Germany)
Pyrifenox	+	Prothioconazole -desethio	Massbank search, MetFrag search (score 1.0) / Reference Standard of Prothioconazole-desethio (Dr. Ehrenstorfer, Augsburg, Germany) (see Figure SI-7.6)

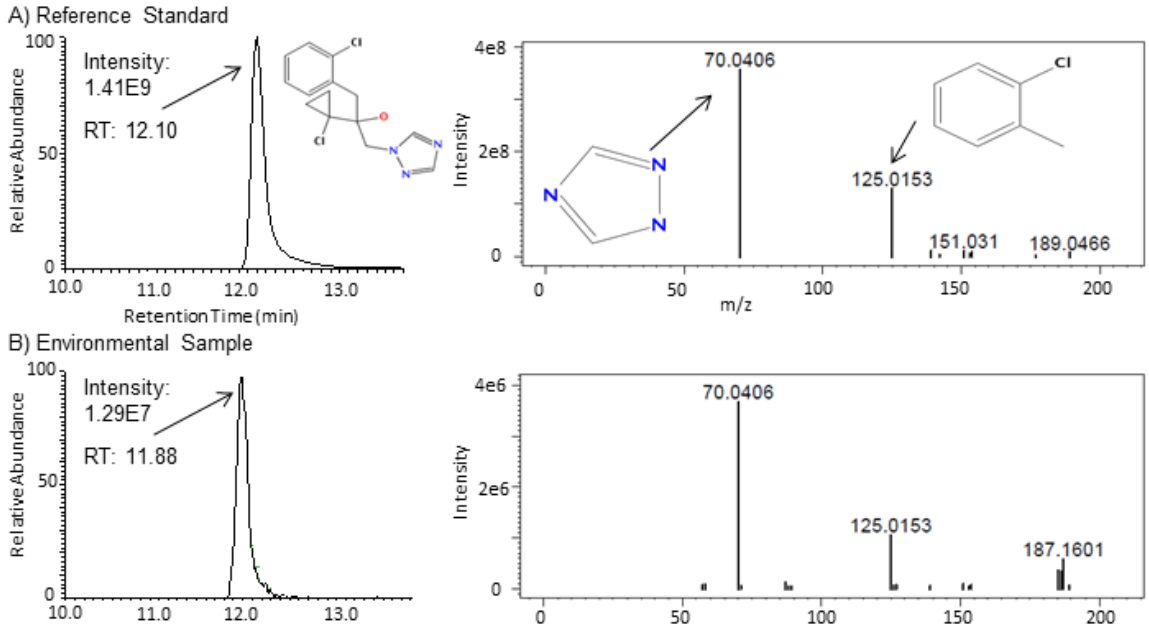


Figure A.8. Chromatogram (left) and MS/MS (right) of prothioconazole-desethio. A) Reference Standard. B: Environmental sample (river Mentue), The shift in retention time (RT) of 0.22 min is due to the use of a pre-column in the second measurement.

APPENDIX B SUPPORTING INFORMATION TO CHAPTER 3

B.1. Additional Field Study Information

Sampling Locations and Catchment Information

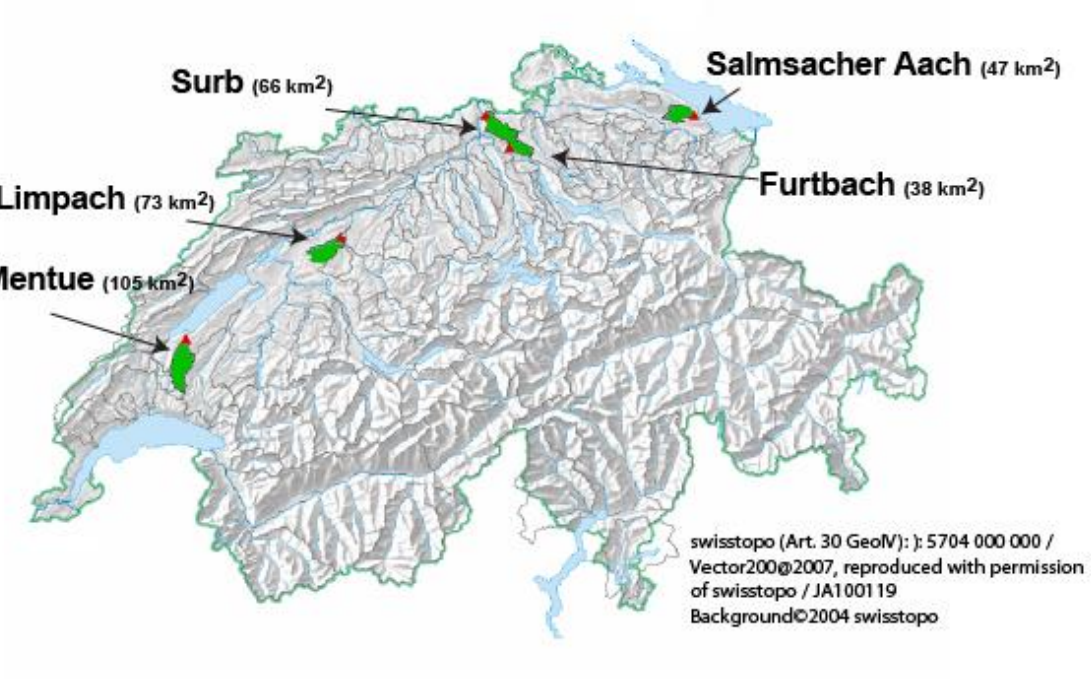


Figure B.1. Catchments (green) and sampling locations (red) of the five investigated rivers.

Land use characteristics:

i) intensive agricultural and/or urban impact due to relatively large densities of field crops
ii) one or two special crops (orchards, vineyards, vegetables) with high densities per catchment
iii) variable waste water amount (0-80% at dry weather conditions)
iv) few impact from forests and alpine areas
v) comparable catchment sizes (40-105 km^2).

Pictures from Sample Preparation and Deployment

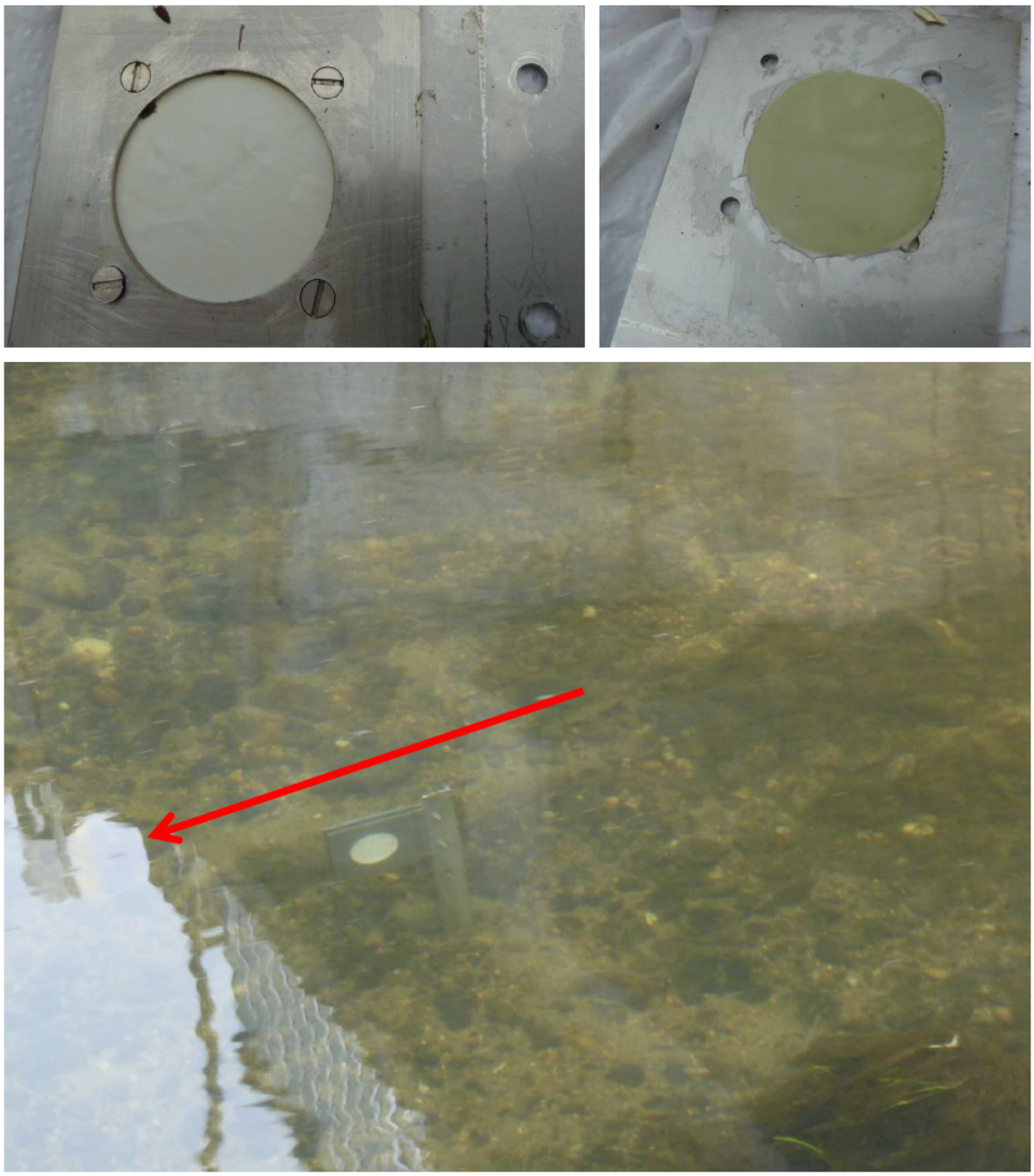


Figure B.2. Top left: prepared and conditioned passive sampler (SDB-RPS disk covered by a PES membrane). Top right: recovered SDB-RPS disk (PES membrane already removed). Bottom: deployed passive sampler in the river (iron rod was hammered roughly 30 cm into the river bed). The red arrow indicates the flow direction. All pictures were taken by one of the authors (Christoph Moschet).

Environmental Parameter in Each Sample

Table B.1. Environmental parameters in each sample.

sample No.	river name	date deployment	date recovery	flow velocity (m/s) at deployment	flow velocity (m/s) at recovery	average discharge (m^3/s)	minimal discharge (m^3/s)	maximal discharge (m^3/s)	no. of days with discharge peak	average tempe-rature (°C)	remarks	category from PCA[a]
1	Furtbach	20.03.2012	03.04.2012	0.60	0.45	0.29	0.26	0.39	0	10		1
2	Furtbach	03.04.2012	17.04.2012	0.45	0.75	0.43	0.31	0.75	2	9		3
3	Furtbach	17.04.2012	30.04.2012	0.75	0.50	0.36	0.27	0.48	0	11	aquatic plants at iron rod	1
4	Furtbach	30.04.2012	15.05.2012	0.50	0.30	0.56	0.27	1.17	10	12		2
5	Furtbach	15.05.2012	29.05.2012	0.60	0.65	0.38	0.26	0.65	3	15		5
6	Furtbach	29.05.2012	11.06.2012	0.65	0.85	0.52	0.23	1.86	5	14	colonized by invertebrates	3
-	Furtbach	14.06.2012	26.06.2012	-	-	-	-	-	-	-	sampler lost	-
7	Furtbach	26.06.2012	10.07.2012	0.75	0.80	0.87	0.31	2.38	10	16		5
8	Furtbach	10.07.2012	23.07.2012	0.80	0.70	0.56	0.39	0.94	5	16		5
9	Limpach	19.03.2012	03.04.2012	0.30	0.25	0.26	0.22	0.39	0	9		1
10	Limpach	03.04.2012	17.04.2012	0.20	0.05	0.60	0.22	1.57	4	9		1
11	Limpach	17.04.2012	30.04.2012	0.60	0.60	0.74	0.48	1.11	6	10	aquatic plants at iron rod	3
12	Limpach	30.04.2012	15.05.2012	0.35	0.05	0.47	0.39	0.64	0	13		2
13	Limpach	15.05.2012	29.05.2012	0.25	0.20	0.41	0.33	0.89	1	13		2
14	Limpach	29.05.2012	11.06.2012	0.20	0.60	0.46	0.20	1.06	3	15	rod moved due to flooding	2
15	Limpach	11.06.2012	26.06.2012	0.50	0.50	0.36	0.19	0.88	2	16	aquatic plants at iron rod	2
16	Limpach	26.06.2012	10.07.2012	0.30	0.05	0.52	0.17	2.25	4	18	aquatic plants at iron rod	4
17	Limpach	10.07.2012	23.07.2012	0.30	0.05	0.27	0.21	0.39	0	18	aquatic plants at iron rod	4
18	Mentue	19.03.2012	03.04.2012	0.35	0.05	0.59	0.48	0.98	0	8		1
19	Mentue	03.04.2012	17.04.2012	0.40	0.15	1.56	0.49	3.08	11	9		3
20	Mentue	17.04.2012	30.04.2012	0.70	0.10	1.76	1.11	2.64	12	10	aquatic plants at iron rod	3
21	Mentue	30.04.2012	15.05.2012	0.75	0.35	0.91	0.64	1.22	0	13		2
22	Mentue	15.05.2012	29.05.2012	0.40	0.35	0.65	0.47	1.42	1	13		2
23	Mentue	29.05.2012	11.06.2012	0.40	0.50	1.12	0.44	3.98	7	15		5
24	Mentue	11.06.2012	26.06.2012	0.75	0.15	0.91	0.49	1.84	3	16		2
25	Mentue	26.06.2012	10.07.2012	0.40	0.30	1.10	0.42	5.61	3	18		4
26	Mentue	10.07.2012	23.07.2012	0.50	0.10	0.53	0.39	0.76	0	16	aquatic plants at iron rod	4
27	Salmsacher A.	20.03.2012	04.04.2012	0.30	0.30	0.19	0.12	0.46	1	9		1
28	Salmsacher A.	04.04.2012	18.04.2012	0.50	0.50	0.39	0.11	1.67	4	9		3
29	Salmsacher A.	18.04.2012	02.05.2012	0.50	0.15	0.37	0.16	0.76	3	12		2
30	Salmsacher A.	02.05.2012	16.05.2012	0.15	0.15	0.21	0.08	0.68	3	11	aquatic plants at iron rod	2
31	Salmsacher A.	16.05.2012	30.05.2012	0.20	0.10	0.24	0.10	0.80	2	12		2
32	Salmsacher A.	30.05.2012	14.06.2012	0.10	0.75	1.73	0.09	8.23	10	14		5
33	Salmsacher A.	14.06.2012	27.06.2012	0.75	0.20	0.42	0.12	1.32	4	15		5
34	Salmsacher A.	27.06.2012	11.07.2012	0.20	0.35	0.22	0.11	0.52	2	17		4
35	Salmsacher A.	11.07.2012	24.07.2012	0.35	0.10	0.14	0.06	0.30	0	16		4
36	Surb	20.03.2012	04.04.2012	0.30	0.30	0.49	0.39	1.23	1	10		1
37	Surb	04.04.2012	18.04.2012	0.35	0.35	0.75	0.49	1.48	2	9		1
38	Surb	18.04.2012	02.05.2012	0.45	0.10	0.62	0.44	0.79	0	11		2
39	Surb	02.05.2012	16.05.2012	0.30	0.35	0.84	0.43	1.38	7	12		3
40	Surb	16.05.2012	30.05.2012	0.30	0.20	0.50	0.39	0.77	1	14		2
41	Surb	30.05.2012	13.06.2012	0.20	0.65	0.93	0.36	3.15	8	17		5
42	Surb	13.06.2012	27.06.2012	0.65	0.05	0.69	0.41	2.21	3	17		4
43	Surb	27.06.2012	10.07.2012	0.20	0.05	0.99	0.38	3.32	4	16		4
44	Surb	10.07.2012	23.07.2012	0.20	0.05	0.50	0.39	0.62	0	16	aquatic plants at iron rod	4

[a] see **Figure B.3**

Determination of Sample Classification by Principle Component Analysis (PCA)

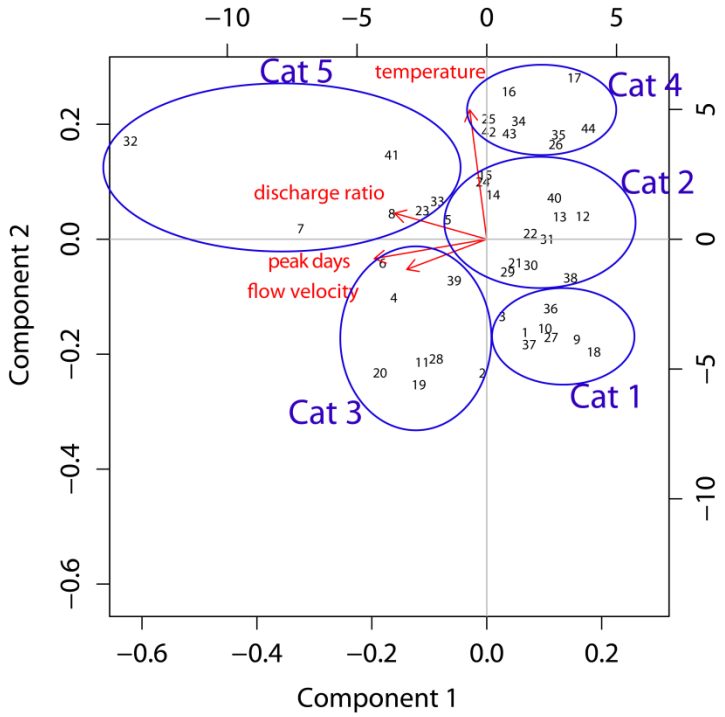


Figure B.3. Principle component analysis (PCA) for the classification of the surface water samples. Average flow velocity (measurement at beginning and end of deployment), average temperature, difference between maximum and minimum discharge (discharge ratio) and number of days with discharge peaks were taken into account (see **Table B.1**). Thereby, flow velocity and temperature have a direct influence on the sampling rate and the discharge has an indirect influence on sampled amount, because during high discharge, concentration peaks of diffuse pollutants are expected. Component 1 (mainly temperature) explains 37% of the variability, component 2 (mainly discharge, flow velocity) explains 25% of the variation. Numbers correspond to the samples (see **Table B.1**), categories (cat) were defined by following criteria: 1: low temperatures and low discharge, 2: medium temperature and medium discharge, 3: low temperature, but high discharge, 4: high temperature, but low discharge, 5: high temperature and high discharge.

B.2 Additional substance information

Substances with Quantitative Comparison

Table B.2. Substances with quantitative comparison

compound name	CAS No.	subs-tance class[b]	LOQw (ng/L)	LOQ SDB (ng/SDB)[c]	no. of detections in water	no. of detections in SDB	minimal concent-ration (ng/L)[d]	maximal concent-ration (ng/L)[d]
2,4-D	94-75-7	PE	4	1	35	27	4.3	78
2,6-Dichlorbenzamide	2008-58-4	PE-TP	5	0.5	44	44	7.5	48
4-Acetamidoantipyrine	83-15-8	PH-TP	5	1	38	42	3.2	710
4-Formylaminoantipyrine	1672-58-8	PH-TP	1	0.5	37	41	1.9	210
Acesulfame	55589-62-3	AS	8	2	44	25	34	(16 000)[e]
Amisulpride	71675-85-9	PH	2	0.5	26	24	2.3	47
Atenolol	29122-68-7	PH	6	0.5	26	25	8.9	120
Atenolol acid	56392-14-4	PH-TP	6	0.5	36	33	27	480
Atrazine	1912-24-9	PE	8	1	31	44	6.0	350
Atrazine-2-hydroxy	2163-68-0	PE-TP	2	1	44	44	3.3	28
Atrazine-desethyl	6190-65-4	PE-TP	6	2	44	44	5.0	34
Azoxystrobin	131860-33-8	PE	1	2	43	43	1.2	82
Azoxystrobin acid	1185255-09-7	PE-TP	3	2	43	44	2.4	140
Bentazon	25057-89-0	PE	1	0.1	39	36	1.1	490
Benzotriazole	95-14-7	CI	180	10	23	44	190	2 100
Benzoylecgonine	519-09-5	ID-TP	1	0.5	23	20	2.3	43
Bezafibrate	41859-67-0	PH	1	0.6	17	20	3.5	24
Bicalutamide	90357-06-5	PH	1	0.5	16	22	0.5	6 8
Boscalid	188425-85-6	PE	2	2	16	36	0.9	55
Candesartan	139481-59-7	PH	10	0.5	28	42	15	140
Carbamazepine	298-46-4	PH	2	1	35	41	6.0	110
Carbamazepine epoxide	36507-30-9	PH-TP	1	1	33	32	1.1	31
Carbamazepine-10,11-dihydro-10,11-dihydroxy	58955-93-4	PH-TP	5	5	35	33	9.7	200
Carbendazime	10605-21-7	PE	5	1	36	44	2.9	65
Cetirizine	83881-52-1	PH	25	6	18	19	24	320
Chloridazon	1698-60-8	PE	2	2	36	40	2.2	670
Chloridazone-desphenyl	6339-19-1	PE-TP	120	2	43	14	120	2 200
Chloridazone-methyl-desphenyl	17254-80-7	PE-TP	7	0.5	44	44	50	180
Chlortoluron	15545-48-9	PE	2	0.2	14	31	1.8	20
Clarithromycine	81103-11-9	PH	1	2	35	25	1.1	120
Clindamycine	18323-44-9	PH	1	0.5	19	18	1.4	27
Clopidogrel Carboxylic Acid	144457-28-3	PH	1	0.5	35	34	1.5	56
Cyproconazole	94361-06-5	PE	0.5	1	36	42	0.7	98
Cyprodinil	121552-61-2	PE	5	2	17	30	6.4	330
D617 (2-(3,4-dimethoxyphenyl)-5-methylamino-2-isopropylvaleronitrile)	34245-14-2	PH-TP	2	0.5	28	27	1.1	56
Diazinon	333-41-5	PE	3	0.6	27	44	1.3	43
Diclofenac	15307-86-5	PH	2	2	38	39	1.4	320
DEET (Diethyltoluamide)	134-62-3	PE	7	25	39	20	4.3	520
Dimethachlor	50563-36-5	PE	1	0.5	14	34	1.1	5.6
Dimethenamid	87674-68-8	PE	1	0.3	22	38	1.1	14
Dimethoat	60-51-5	PE	3	2	11	29	3.5	21
Dimethomorph	110488-70-5	PE	2	2	33	33	2.1	61
Diuron	330-54-1	PE	2	4	39	33	1.1	52
EDDP (2-Ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidin)	30223-73-5	ID-TP	1	0.1	16	28	1.7	33
Epoxiconazole	133855-98-8	PE	4	0.6	15	41	4.4	64
Ethofumesate	26225-79-6	PE	3	2	38	41	3.6	290
Fenamidone	161326-34-7	PE	1	1	20	21	0.5	18
Fenhexamid	126833-17-8	PE	3	3	12	15	1.1	22
Fenofibric acid	42017-89-0	PH-TP	1	0.5	22	21	0.7	3.4
Fipronil	120068-37-3	PE	0.5	0.6	29	36	0.5	14
Fluazifop free acid	69335-91-7	PE-TP	1	0.5	23	30	1.1	48
Fluconazole	86386-73-4	PH	1	0.5	29	34	1.4	33
Flufenacet	142459-58-3	PE	3	0.5	23	36	3.6	290
Flufenacet ESA	201668-32-8	PE-TP	3	0.5	27	32	1.6	38
Gabapentin	60142-96-3	PH	90	3	17	35	60	390
Hydrochlorothiazide	58-93-5	PH	2	0.5	38	42	2.4	380
Indomethacine	53-86-1	PH	1	0.5	33	29	1.1	19
Ioxynil	1689-83-4	PE	1	0.2	31	38	1.0	41
Isoproturon	34123-59-6	PE	1	1	44	44	1.1	350
Lamotrigine	84057-84-1	PH	2	0.5	35	36	6.1	220
Lenacil	2164-08-1	PE	9	0.5	15	32	5.5	140

compound name	CAS No.	substance class[b]	LOQw (ng/L)	LOQ SDB (ng/SDB)[c]	no. of detections in water	no. of detections in SDB	minimal concentration (ng/L)[d]	maximal concentration (ng/L)[d]
Levamisole	14769-73-4	PH	1	0.5	15	13	0.6	8.7
Levetiracetam	102767-28-2	PH	15	2	31	32	9.0	95
Lidocaine	137-58-6	PH	1	2	35	27	2.4	55
MCPA	94-74-6	PE	7	0.5	35	41	4.9	270
Mecoprop	16484-77-8	PE	1	0.5	44	43	4.9	470
Mefenamic acid	61-68-7	PH	4	1	31	37	2.2	95
Metalaxyl	70630-17-0	PE	1	1	31	38	4.1	380
Metamitron	41394-05-2	PE	10	2	28	44	48	1 500
Metamitron-desamino	36993-94-9	PE-TP	8	0.5	38	44	8.4	680
Metazachlor	67129-08-2	PE	2	0.5	23	30	1.4	180
Metazachlor ESA	172960-62-2	PE-TP	7	0.5	44	43	11	520
Metformin	657-24-9	PH	50	1	38	42	49	2 600
Methyl-benzotriazole	136-85-6	CI	50	1	37	44	27	(17 000)[e]
Metolachlor	87392-12-9	PE	1	1	44	44	2.6	960
Metolachlor ESA	171118-09-5	PE-TP	2	0.5	44	43	36	310
Metolachlor OXA	152019-73-3	PE-TP	9	1	36	43	9.0	130
Metolachlor-Morpholinon	120375-14-6	PE-TP	1	0.5	15	32	2.2	10
Metoprolol	37350-58-6	PH	4	0.8	35	19	2.3	130
Metribuzin	21087-64-9	PE	1	0.5	30	35	0.9	120
Metribuzin-deamino (DA)	35045-02-4	PE-TP	1	0.1	20	38	1.1	26
N4-Acetylsulfamethoxazole	21312-10-7	PH-TP	3	2	22	21	3.0	26
Napropamide	15299-99-7	PE	6	0.5	17	38	7.0	78
Naproxen	22204-53-1	PH	10	3	21	26	26	87
O-Desvenlafaxine + Tramadol[a]	93413-62-8/ 220-831-4	PH	4	0.5	35	35	11	340
Nicosulfuron	111991-09-4	PE	1	0.2	23	16	1.2	44
Oxazepam	604-75-1	ID	1	0.2	34	35	1.1	58
Pencycuron	66063-05-6	PE	3	3	20	23	1.8	160
Pethoxamid	106700-29-2	PE	1	0.5	19	24	1.1	80
Phenazone (Antipyrene)	60-80-0	PH	2	2	14	16	2.0	8 0
Pirimicarb	23103-98-2	PE	0.4	1	37	35	0.2	48
Prometryn + Terbutryn	7287-19-6 886-50-0	PE	2	2	17	19	1.4	34
Propachlor	1918-16-7	PE	1	3	13	13	1.4	220
Propazin-2-hydroxy + Terbutylazin-2-hydroxy[a]	7374-53-0/ 66753 07-9	PE-TP	4	0.7	35	43	2.0	45
Propamocarb	24579-73-5	PE	0.3	1	32	23	0.2	160
Propiconazole	60207-90-1	PE	3	0.6	28	44	1.9	65
Prosulfocarb	52888-80-9	PE	10	0.5	20	24	13	690
Pyrimethanil	53112-28-0	PE	1	0.8	14	20	0.9	89
Simeton	673-04-1	PE	1	0.2	33	44	1.0	14
Sitagliptin	486460-32-6	PH	10	0.5	20	35	11	160
Sotalol	3930-20-9	PH	7	0.5	27	34	4.1	78
Sucralose	56038-13-2	AS	20	5	35	34	49	2 100
Sulfamethazine	57-68-1	PH	2	0.5	29	42	1.2	11
Sulfamethoxazole	723-46-6	PH	6	2	28	35	5.5	82
Sulfapyridine	144-83-2	PH	2	0.1	23	40	2.1	43
Tebuconazole	107534-96-3	PE	2	1	33	43	1.9	86
Tebufenozide	112410-23-8	PE	2	2	12	15	2.6	29
Terbutylazine	5915-41-3	PE	9	2	28	44	5.0	630
Terbutylazine-desethyl	30125-63-4	PE-TP	8	0.5	21	43	5.0	54
Thiacloprid	111988-49-9	PE	4	2	16	26	3.4	65
Thiacloprid-amide	676228-91-4	PE-TP	2	2	12	30	1.7	7 5
Thiamethoxam	153719-23-4	PE	3	2	26	40	2.2	47
Trimethoprim	738-70-5	PH	2	0.2	24	19	1.5	33
Venlafaxine	93413-69-5	PH	2	0.5	35	24	2.4	94

[a] due to the same parent mass and retention time, substances were quantified as the sum, [b] substance class: PE: pesticide, PH: pharmaceutical, PE-TP: pesticide transformation product, PH-TP: pharmaceutical transformation product, ID: illicit drug, ID-TP: illicit drug transformation product, CI: corrosion inhibitor, AS: artificial sweetener, [c] only substances that were detected in at least 10 water samples were quantiatively evaluated in the passive samples, [d] from the measurement of composite water samples, [e] exact quantification not possile because above limit of linearity

Substances with Qualitative Comparison

Table B.3. Substances with qualitative comparison

compound name	CAS No.	substance class[b]	LOQw (ng/L)	LOQ SDB (ng/SDB)[c]	no. of detections in water	no. of detections in SDB	minimal concentration (ng/L)[d]	maximal concentration (ng/L)[d]
1-(3-Chlorophenyl)piperazine	6640-24-0	ID	4		0	0		
1-(3-Trifluoromethylphenyl)-piperazine	15532-75-9	ID	4		0	0		
1-Benzylpiperazine	2759-28-6	ID	180		0	0		
2',2'-Difluoro-2'-deoxyuridine	114248-23-6	PH-TP	10		0	0		
2',3'-di-O-acetyl-5'-deoxy-5-fluorocytidine	161599-46-8	PH-TP	10		0	0		
2,7-Naphthalenedisulfonic acid	92-41-1	IC	100		0	0		
2-Aminobenzimidazole	934-32-7	PE-TP	10		0	0		
2-Methyl-4-amino-6-methoxy-s-triazine	1668-54-8	PE-TP	2		0	0		
2-Naphthalenesulfonic acid	120-18-3	IC	90	25	15	0	110	2 900
2-n-Octyl-4-isothiazolin-3-one (OI)	26530-20-1	PE	1		0	0		
3-Phenoxybenzoic acid	3739-38-6	PE-TP	1		7	0	1.5	6 9
4,5-Dichloro-2-n-octyl-3(2H)-isothiazolone (DCOIT)	64359-81-5	PE	35		0	0		
4-Trifluoromethylphenol	402-45-9	PH-TP	50		0	0		
5-Chloro-2-methyl-4-isothiazolin-3-one (CMI)	26172-55-4	PE	8		4	0	22	510
Acetamiprid	135410-20-7	PE	4		0	5		
Acetochlor	34256-82-1	PE	70		0	0		
Acetochlor-, Alachlor-ESA[a]	187022-11-3/ 142363-53-9	PE-TP	1	0.3	10	21	1.1	4 2
Alachlor	15972-60-8	PE	70		0	0		
Albuterol	18559-94-9	PH	5		0	0		
Aldicarb	116-06-3	PE	200		0	0		
Aminopyrine	58-15-1	PH	3		0	0		
Amitriptyline	50-48-6	PH	5		0	0		
Amphetamine	300-62-9	ID	10		0	0		
Aspartam	22839-47-0	AS	50		0	0		
Asulam	3337-71-1	PE	140		1	0	140	140
Atenolol-desisopropyl	81346-71-6	PH-TP	50		0	0		
Atomoxetine	83015-26-3	PH	9		0	0		
Atorvastatin	134523-03-8	PH	5		0	0		
Atraton	1610-17-9	PE	2		0	0		
Atrazine-6-desisopropyl	1007-28-9	PE-TP	30		0	19		
Atrazine-desethyl-2-hydroxy	19988-24-0	PE-TP	3	0 25	40	4	2.1	27
Azamethiphos	35575-96-3	PE	20		0	0		
Azithromycin	83905-01-5	PH	20		0	0		
Benthiavalicarb-isoprop	177406-68-7	PE	2		7	7	3.3	22
Bromazil	314-40-9	PE	30		0	0		
Bromoxynil	1689-84-5	PE	1		6	7	1.2	23
Bronopol	52-51-7	PE	125		0	0		
Bupropion	34911-55-2	PH	2		1	8	6.4	6.4
Caffeine	58-08-2	AS	20		42	0	28	300
Carbetamide	16118-49-3	PE	50		2	2	41	230
Carbofuran	1563-66-2	PE	10	10	10	11	5.5	45
Chlorfenvinphos	470-90-6	PE	3		1	2	4.6	4.6
Chlorpyrifos	2921-88-2	PE	200		0	1		
Chlorpyrifos-methyl	5598-13-0	PE	200		0	1		
Cilastatin	82009-34-5	PH	5		0	0		
Citalopram	59729-33-8	PH	8		9	16	9.8	34
Climbazol	38083-17-9	PCP	85		0	23		
Clofibric acid	882-09-7	PH-TP	3		0	0		
Clomazone	81777-89-1	PE	2		5	26	2.1	3 5
Clothianidin	210880-92-5	PE	4		0	42		
Clozapine	5786-21-0	PH	160		0	1		
Cocaine	50-36-2	ID	1		0	17		
Codeine	76-57-3	ID	5		0	0		
Cyclamate (Cyclamic acid)	139-05-9	AS	9	1	44	2	11	740
Cyclophosphamide	50-18-0	PH	4		0	0		
Cymoxanil	57966-95-7	PE	10		0	0		
Cytarabine	147-94-4	PH	85		0	0		
Deferasirox	201530-41-8	PH	10		1	0	13	13
Dexamethasone	50-02-2	PH	2		0	0		
Dextromethorphan	125-71-3	PH	7		3	0	3.5	10
Diatrizoate	50978-11-5	PH	250		0	0		
Diazepam	439-14-5	ID	2		2	5	2.4	3 0
Dicamba	1918-00-9	PE	25		9	0	110	1 400
Dichlorprop	15165-67-0	PE	2		1	1	16	16
Difenoconazole	119446-68-3	PE	10		2	23	11	30
Diflufenican	83164-33-4	PE	20		0	24		
Dimethachlor ESA	-	PE-TP	15		5	33	15	24

compound name	CAS No.	substance class[b]	LOQw (ng/L)	LOQ SDB (ng/SDB)[c]	no. of detections in water	no. of detections in SDB	minimal concentration (ng/L)[d]	maximal concentration (ng/L)[d]
Dimethachlor OXA	1086384-49-7	PE-TP	15		0	0		
Dimethenamid ESA	205939-58-8	PE-TP	5		8	20	5.6	13
Dimethenamid OXA	380412-59-9	PE-TP	6		1	0	8.9	8 9
Dinoseb	88-85-7	PE	5		7	0	4.0	54
Dioxoaminopyrine	519-65-3	PH-TP	1		0	0		
Diuron-desdimethyl	2327-02-8	PE-TP	7		0	13		
Diuron-monomethyl (DCPMU)	3567-62-2	PE-TP	10		6	28	6.0	22
Ephedrine	299-42-3	PH	5		0	0		
Eprosartan	133040-01-4	PH	4	2	10	1	5.2	47
Ethofumesate-2-keto	26244-33-7	PE-TP	20		0	0		
Exemestane	107868-30-4	PH	4		0	0		
Fenofibrate	49562-28-9	PH	20		0	0		
Fenoxycarb	79127-80-3	PE	15		0	0		
Fenpropidin	67306-00-7	PE	0.8	0.8	10	1	0.4	18
Fenpropimorph	67564-91-4	PE	4		4	17	2.6	15
Fipronil-sulfone	120068-36-2	PE-TP	6		0	25		
Flonicamid	158062-67-0	PE	3		0	0		
Fludioxonil	131341-86-1	PE	7		6	28	8.0	25
Flufenacet OXA	201668-31-7	PE-TP	7		0	0		
Fluoxastrobin	361377-29-9	PE	3		5	6	1.3	11
Fluoxetine	54910-89-3	PH	7		0	0		
Fluroxypyr	69377-81-7	PE	8		4	0	15	49
Flusilazole	85509-19-9	PE	3		3	42	3.4	32
Foramsulfuron	173159-57-4	PE	2	0.2	10	7	2.9	61
Formamide, N-(2,4-dimethylphenyl)	60397-77-5	PE-TP	75		1	0	80	80
Furosemide	54-31-9	PH	50		0	0		
Galaxolidon	256393-37-0	PCP	10		0	8		
Gemcitabine	95058-81-4	PH	25		0	0		
Hexazinone	51235-04-2	PE	2		0	0		
Ibuprofen	15687-27-1	PH	10		0	0		
Ifosfamide	3778-73-2	PH	5		0	0		
Imazamox	114311-32-9	PE	4		7	0	4.3	36
Imidacloprid	138261-41-3	PE	5	3	13	30	3.2	9 2
Imidacloprid-desitro	115970-17-7	PE-TP	2		6	0	4.6	19
Imidacloprid-urea	120868-66-8	PE-TP	1		0	0		
Iminostilbene	256-96-2	PH-TP	120		0	0		
Iodopropynyl butylcarbamate (IPBC)	55406-53-6	PE	2 500		0	0		
Iprovalicarb	140923-17-7	PE	2		3	13	1.5	14
Irbesartan	138402-11-6	PH	600		0	35		
Irgarol 1051	28159-98-0	PE	5		0	1		
Irgarol-descyclopropyl	-	PE-TP	5		2	29	5.3	5 5
Isoproturon-desmethyl	56046-17-4	PE-TP	5		0	0		
Isoproturon-N-monodemethyl	34123-57-4	PE-TP	4		3	24	4.7	14
Ketamine	6740-88-1	PH	1		1	9	1.5	1 5
Ketoprofen	22071-15-4	PH	10		2	11	24	45
Kresoxim-methyl	143390-89-0	PE	4		1	3	15	15
Linuron	330-55-2	PE	9	0.5	16	38	9.7	270
Mandipropamid	374726-62-2	PE	3	3	13	10	1.5	24
MCPB	94-81-5	PE	7		7	9	7.3	290
Mefenpyr-diethyl	135590-91-9	PE	0.5		4	0	0.5	12
Mepanipyrim	110235-47-7	PE	6		2	6	1.4	7 8
Mephedrone (4-Methylmethcathinone)	1189805-46-6	ID	25		0	0		
Mesotrione	104206-82-8	PE	10		8	9	19	61
Mesotrione MNBA	110964-79-9	PE-TP	50		0	0		
Metazachlor OXA	-	PE-TP	10		8	10	49	170
Methadone	1095-90-5	ID	1		9	8	1.2	7.7
Methamphetamine	537-46-2	ID	8		0	0		
Methiocarb	2032-65-7	PE	1		2	16	0.6	1.4
Methiocarb-sulfoxide	2635-10-1	PE-TP	10		0	11		
Methomyl	16752-77-5	PE	10		1	6	11	11
Methoxyfenozide	161050-58-4	PE	3		8	11	3.3	7 0
Metoclopramid	7232-21-5	PH	4		0	0		
Metosulam	139528-85-1	PE	2		2	3	15	20
Metrafenone	220899-03-6	PE	8		2	13	11	29
Metronidazole	73334-05-1	PH	3	0.5	12	10	3.0	18
Metsulfuron-methyl	74223-64-6	PE	35		0	0		
Moclobemide	71320-77-9	PH	5		0	11		
Monuron	150-68-5	PE	2		0	0		
Morphine	57-27-2	ID	10		0	0		
Myclobutanil	88671-89-0	PE	1		9	16	1.7	15
Mycophenolic acid	24280-93-1	PH	5		9	26	11	64
N,N-Didesmethylvenlafaxine	93413-77-5	PH-TP	15		0	6		
N,N-Dimethyl-N'-phenylsulphamide (DMSA)	4710-17-2	PE-TP	7	5	21	3	7.3	140

compound name	CAS No.	substance class[b]	LOQw (ng/L)	LOQ SDB (ng/SDB)[c]	no. of detections in water	no. of detections in SDB	minimal concentration (ng/L)[d]	maximal concentration (ng/L)[d]
N,N-Dimethyl-N'-p-tolylsulphamide	66840-71-9	PE-TP	3		0	3		
N,O-Didesmethylvenlafaxine	135308-74-6	PH-TP	8		5	32	46	67
N4-Acetylsulfadiazine	127-74-2	PH-TP	1		0	0		
N4-Acetylsulfadimethoxine	24341-30-8	PH-TP	2		0	0		
N4-Acetylsulfamethazine	100-90-3	PH-TP	1		2	3	3.9	6.7
N4-Acetylsulfathiazole	127-76-4	PH-TP	1		0	0		
Naltrexone	16590-41-3	PH	1		0	0		
N-Cyclopropyl-1,3,5-triazin-2,4,6-triamine	66215-27-8	PE	8		1	0	10	10
N-Desmethylvenlafaxine	149289-30-5	PH-TP	4	0.5	10	8	2.0	25
Neotame	165450-17-9	AS	6		0	0		
N-Methylacetanilide	579-10-2	IC	8		0	0		
NN-Dimethyldicylamin N-oxid	2605-79-0	IC	7		0	0		
Orbencarb	34622-58-7	PE	10		0	16		
Oseltamivir	196618-13-0	PH	2		0	0		
Oseltamivir carboxylate	187227-45-8	PH-TP	5		0	0		
Paracetamol	103-90-2	PH	40		4	0	44	160
Penconazol	66246-88-6	PE	5		0	4		
Picaridin	119515-38-7	PE	2		0	0		
Piperonyl butoxide	51-03-6	PE	20		8	0	11	220
Pravastatin	81093-37-0	PH	25		0	0		
Prednisolon	50-24-8	PH	2		0	0		
Primidone	125-33-7	PH	5		0	0		
Prochloraz	67747-09-5	PE	200		0	4		
Prometon	1610-18-0	PE	2		9	43	1.5	7.1
Propachlor ESA	123732-85-4	PE-TP	2	1	11	9	4.3	270
Propachlor OXA	70628-36-3	PE-TP	150		1	0	170	170
Propanolol	525-66-6	PH	8		7	0	7.0	24
Propaquizafop	111479-05-1	PE	15		0	0		
Pymetrozine	123312-89-0	PE	5	3	11	15	5.1	54
Pyraclostrobin	175013-18-0	PE	5		5	3	5.3	61
Ranitidine	66357-35-5	PH	9		2	0	10	14
Ranitidin-N-oxid	738557-20-2	PH-TP	200		0	0		
Ranitidin-S-oxid	73851-70-4	PH-TP	20		0	0		
Rimsulfuron	122931-48-0	PE	1		0	0		
Ritalinic acid	19395-41-6	PH-TP	1		9	18	12	34
Ritonavir	155213-67-5	PH	10		1	0	10	10
Rosuvastatin	147098-20-2	PH	3		2	2	3.1	4 0
Roxithromycin	80214-83-1	PH	4		0	0		
Saccharin	6381-61-9	AS	9	10	41	0	4.8	410
Simazine	122-34-9	PE	10		9	44	5.5	29
Simazine-2-hydroxy	2599-11-3	PE-TP	2	0.4	12	12	1.9	5 9
Spironolactone	52-01-7	PH	100		0	0		
Spiroxamine	118134-30-8	PE	2	1	13	5	1.5	16
Sulcotrione	99105-77-8	PE	3	6	13	5	4.2	91
Sulcotrione CMBA	53250-83-2	PE-TP	375		0	0		
Sulfadiazine	68-35-9	PH	3		6	9	1.7	5 2
Sulfadimethoxine	122-11-2	PH	2		0	1		
Sulfathiazole	72-14-0	PH	5		0	0		
Tacrolimus	104987-11-3	PH	125		0	0		
Valganciclovir	175865-59-5	PH	150		0	0		
Rivastigmin	123441-03-2	PH	5		1	17	6.5	6 5
Capecitabin	154361-50-9	PH	2		0	0		
Tebutam	35256-85-0	PE	1		7	2	1.0	38
Teflubenzuron	83121-18-0	PE	50		0	0		
Telmisartan	144701-48-4	PH	75	10	14	0	45	990
Terbumeton	33693-04-8	PE	2		9	43	1.5	7.1
Terbutylazine-desethyl-2-hydroxy	66753-06-8	PE-TP	3	25	36	0	3.5	21
Thifensulfuron-methyl	79277-27-3	PE	5		1	3	4.2	4 2
Thiopental	76-75-5	PH	600		0	0		
Triclopyr	55335-06-3	PE	130		0	0		
Triclosan	3380-34-5	PE	250		0	0		
Trimipramine	739-71-9	PH	4		0	0		
Trinexapac acid	104273-73-6	PE-TP	200		2	0	160	270
Trinexapac-ethyl	95266-40-3	PE	9		6	7	12	34
Tritosulfuron	142469-14-5	PE	2		0	0		
Tylosin	1401-69-0	PH	6		0	0		
Valsartan	137862-53-4	PH	1 000		0	41		
Verapamil	52-53-9	PH	5		0	0		

[a] due to the same parent mass and retention time, substances were quantified as the sum, [b] substance class: PE: pesticide, PH: pharmaceutical, PE-TP: pesticide transformation product, PH-TP: pharmaceutical transformation product, ID: illicit drug, ID-TP: illicit drug transformation product, CI: corrosion inhibitor, AS: artificial sweetener, [c] only substances that were detected in at least 10 water samples were quantiatively evaluated in the passive samples, [d] from the measurement of composite water samples

B.3. Correlation between Water Concentration and Sampled Mass on SDB

Legend to the plots:

cw: water concentration (ng/L)
m SDB: sampled mass on SDB (ng/SDB/d)
Rs: determined field sampling rate (L/d)
R2: R-squared from regression

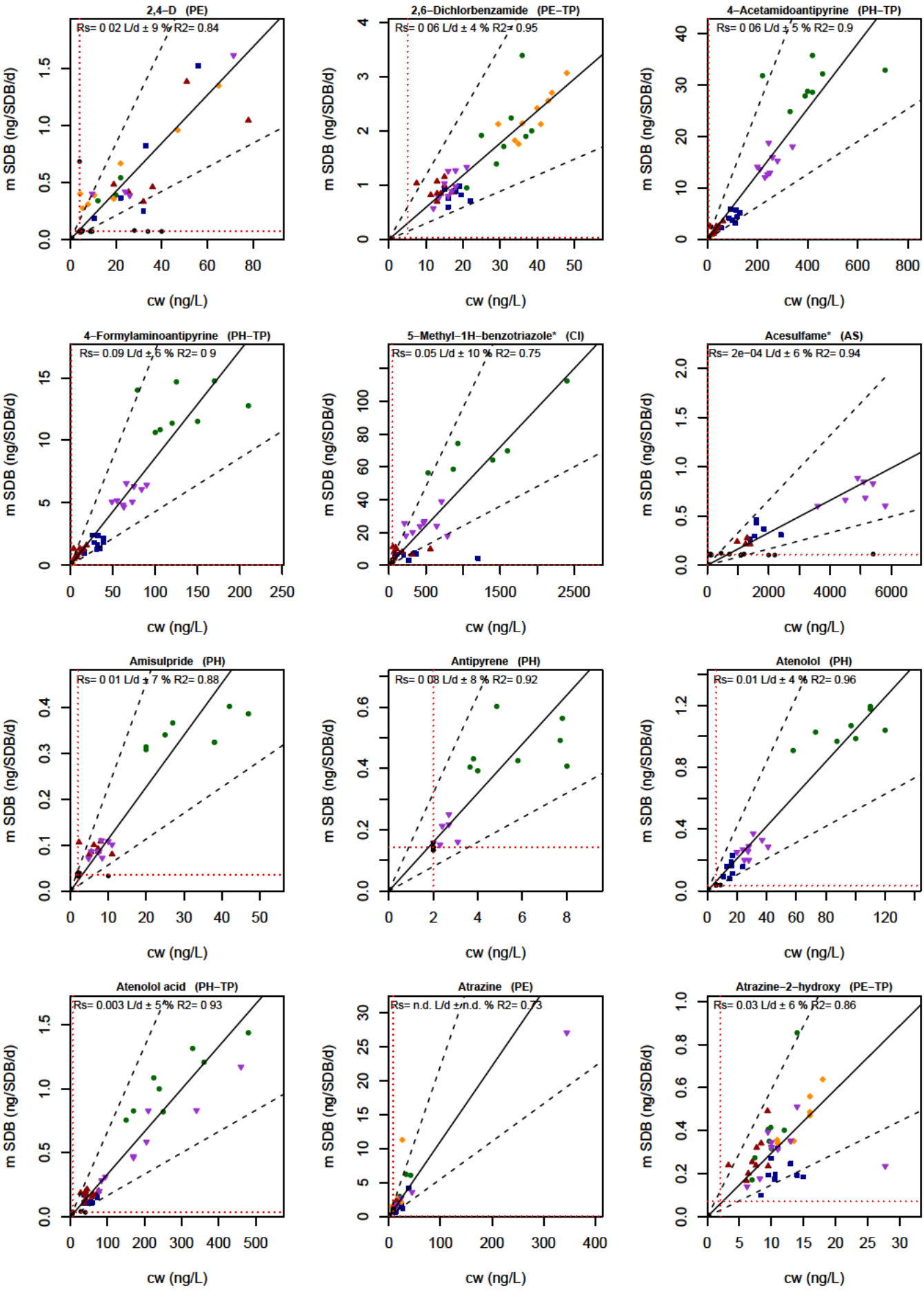
PE: pesticide,
PE-TP: pesticide transformation product,
PH: pharmaceutical,
PH-TP: pharmaceutical transformation product,
ID: illicit drug,
ID-TP: illicit drug transformation product,
CI: corrosion inhibitor,
AS: artificial sweetener

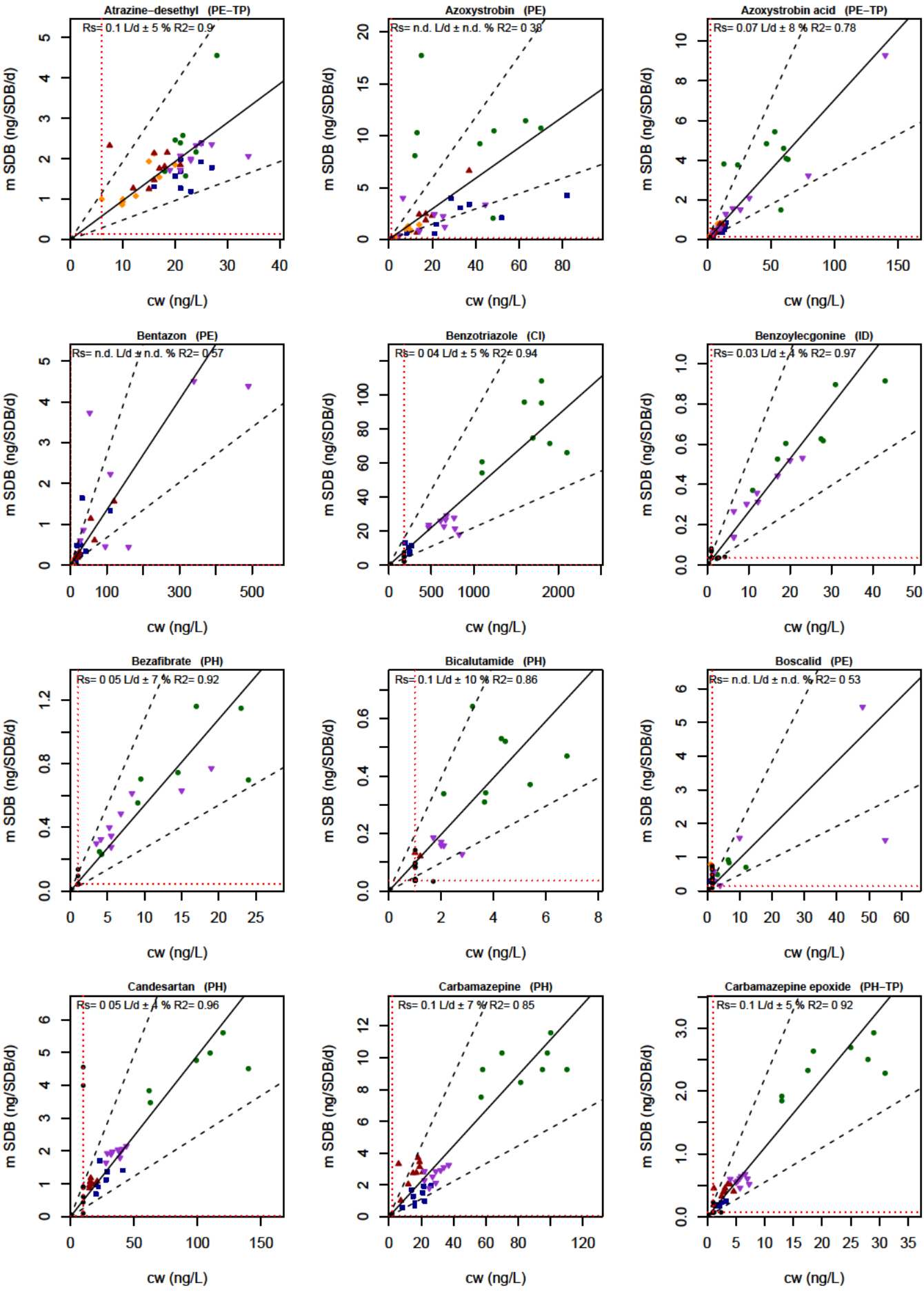
linear regression
deviation factor 2
LOQ (vertical: composite water sample, horizontal: SDB passive sample)

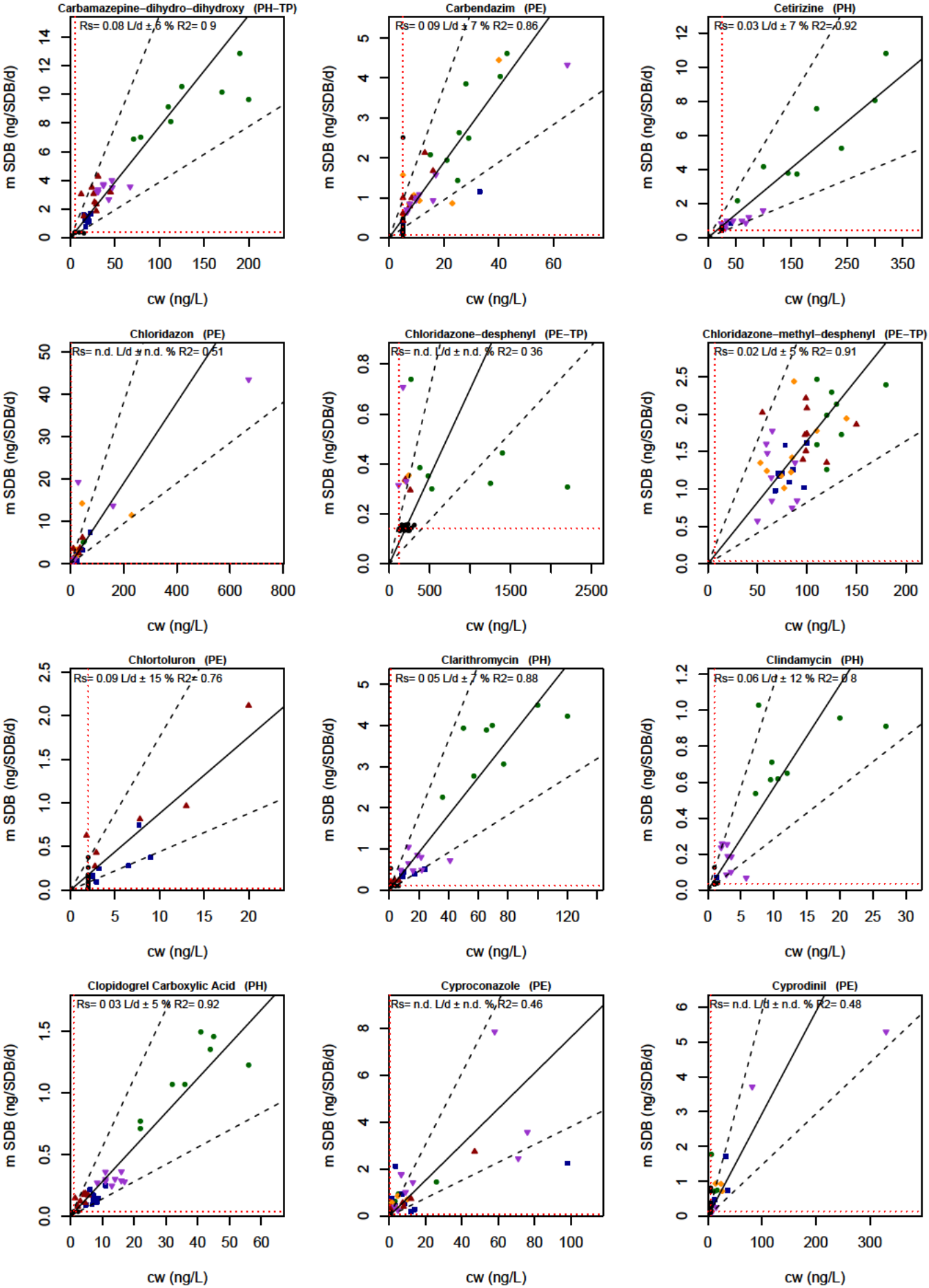
river Limpach
river Furtbach
river Salmsacher Aach
river Surb
river Mentue
below LOQ in either composite water sample or SDB passive sample (value <LOQ is shown as LOQ)

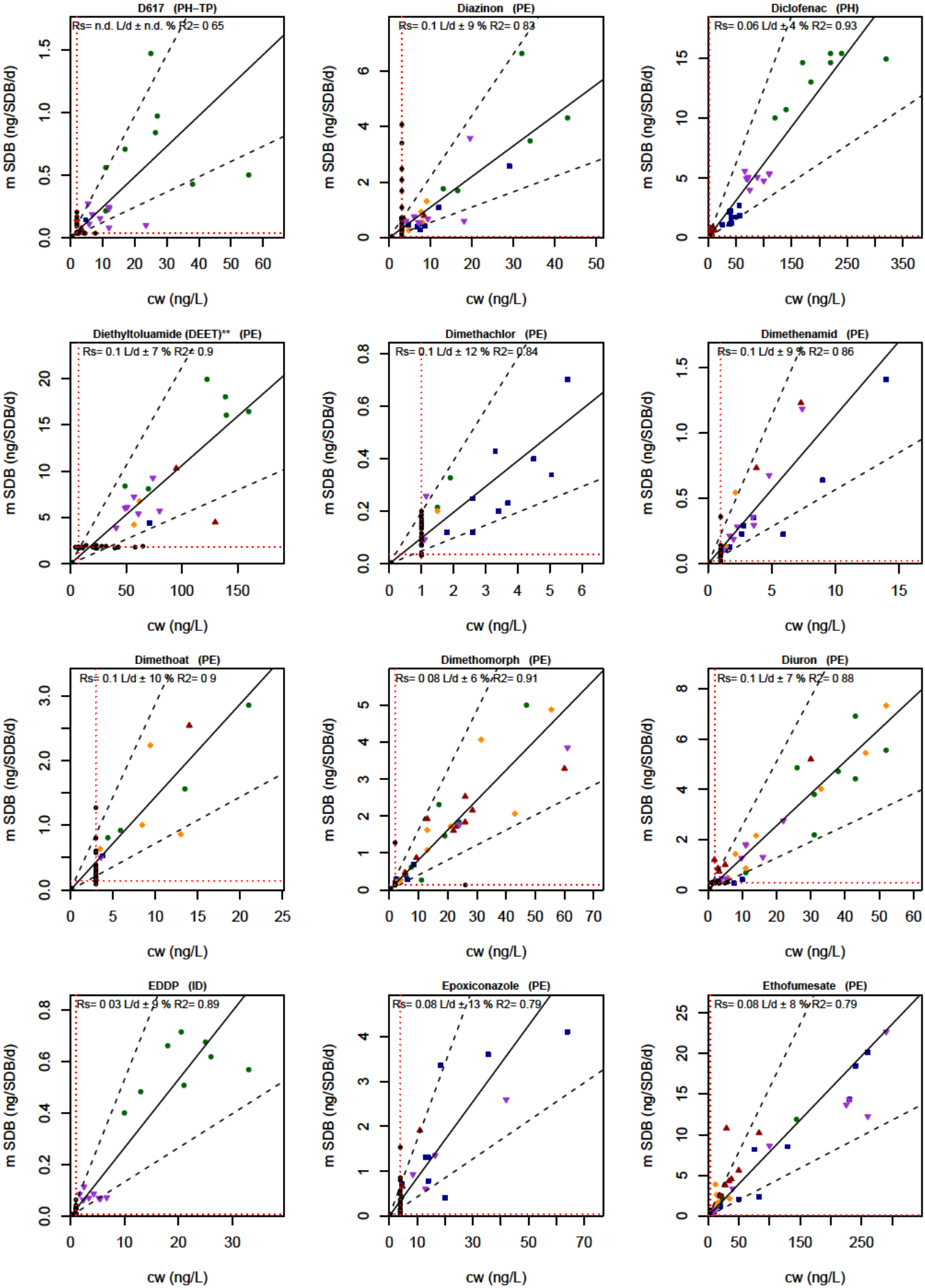
* values above 5000 ng/L (5-methyl-1-benzotriazole, acesulfame) were excluded from the analysis because they were above the limit of linearity (exact quantification not possible)

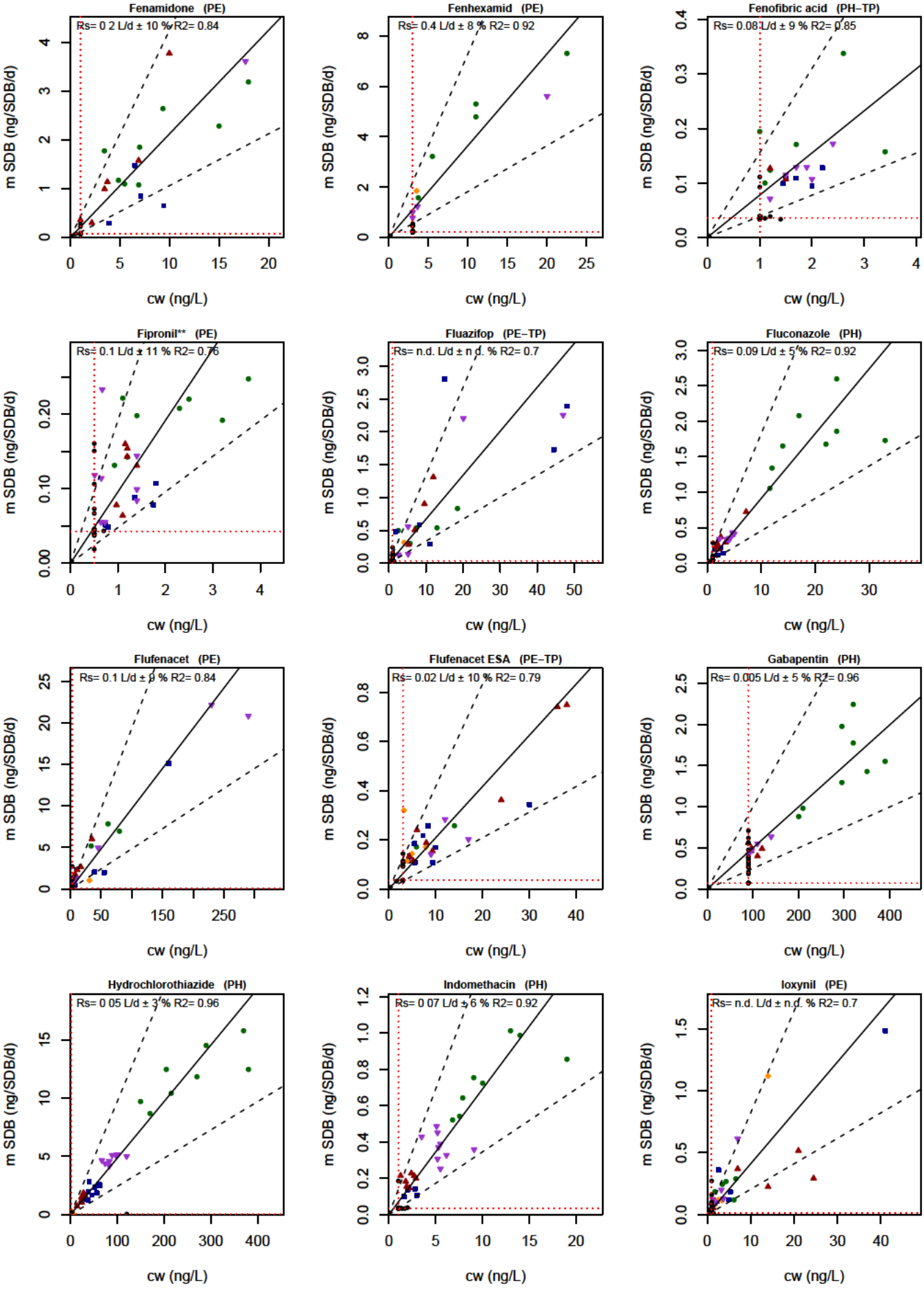
** clear outliner were excluded:
fipronil: cw = 14 ng/L, mSDB = 0.06 ng/SDB/d
DEET: cw = 520 ng/L, mSDB = 6 ng/SDB/d

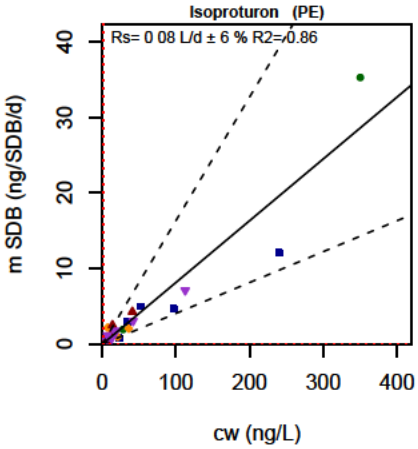

2,4–D (PE)
Rs= 0 02 L/d ± 9 % R2= 0.84
2,6–Dichlorbenzamide (PE–TP)
Rs= 0 06 L/d ± 4 % R2= 0.95
4–Acetamidoantipyrine (PH–TP)
Rs= 0 06 L/d ± 5 % R2= 0.9
4–Formylaminoantipyrine (PH–TP)
Rs= 0.09 L/d ± 6 % R2= 0 9
5–Methyl–1H–benzotriazole* (CI)
Rs= 0.05 L/d ± 10 % R2= 0.75
Acesulfame* (AS)
Rs= 2e–04 L/d ± 6 % R2= 0.94
Amisulpride (PH)
Rs= 0 01 L/d ± 7 % R2= 0.88
Antipyrene (PH)
Rs= 0 08 L/d ± 8 % R2= 0.92
Atenolol (PH)
Rs= 0.01 L/d ± 4 % R2= 0.96
Atenolol acid (PH–TP)
Rs= 0.003 L/d ± 5 % R2= 0 93
Atrazine (PE)
Rs= n.d. L/d ±n.d. % R2= 0.73
Atrazine–2–hydroxy (PE–TP)
Rs= 0.03 L/d ± 6 % R2= 0.86
m SDB (ng/SDB/d)
cw (ng/L)

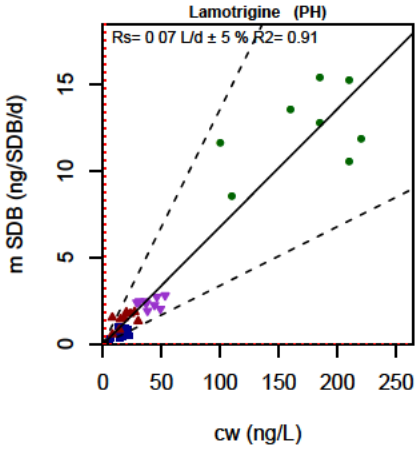

Atrazine−desethyl (PE−TP)
Rs= 0.1 L/d ± 5 % R2= 0.9
Azoxystrobin (PE)
Rs= n.d. L/d ± n.d. % R2= 0.38
Azoxystrobin acid (PE−TP)
Rs= 0.07 L/d ± 8 % R2= 0.78
Bentazon (PE)
Rs= n.d. L/d ± n.d. % R2= 0.57
Benzotriazole (CI)
Rs= 0.04 L/d ± 5 % R2= 0.94
Benzoylecgonine (ID)
Rs= 0.03 L/d ± 4 % R2= 0.97
Bezafibrate (PH)
Rs= 0.05 L/d ± 7 % R2= 0.92
Bicalutamide (PH)
Rs= 0.1 L/d ± 10 % R2= 0.86
Boscalid (PE)
Rs= n.d. L/d ± n.d. % R2= 0.53
Candesartan (PH)
Rs= 0.05 L/d ± 4 % R2= 0.96
Carbamazepine (PH)
Rs= 0.1 L/d ± 7 % R2= 0.85
Carbamazepine epoxide (PH−TP)
Rs= 0.1 L/d ± 5 % R2= 0.92
m SDB (ng/SDB/d)
cw (ng/L)

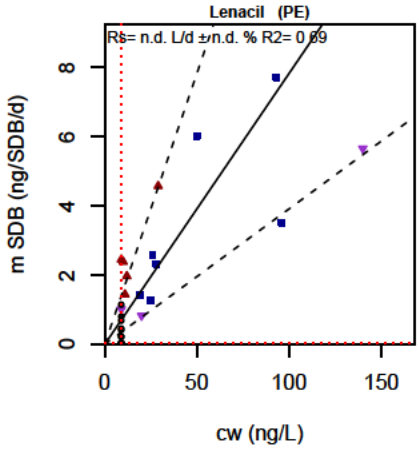

Carbamazepine−dihydro−dihydroxy (PH−TP)
Rs= 0.08 L/d ± 6 % R2= 0 9
Carbendazim (PE)
Rs= 0 09 L/d ± 7 % R2= 0.86
Cetirizine (PH)
Rs= 0.03 L/d ± 7 % R2= 0.92
Chloridazon (PE)
Rs= n.d. L/d ± n.d. % R2= 0.51
Chloridazone−desphenyl (PE−TP)
Rs= n.d. L/d ± n.d. % R2= 0 36
Chloridazone−methyl−desphenyl (PE−TP)
Rs= 0.02 L/d ± 5 % R2= 0.91
Chlortoluron (PE)
Rs= 0.09 L/d ± 15 % R2= 0.76
Clarithromycin (PH)
Rs= 0 05 L/d ± 7 % R2= 0.88
Clindamycin (PH)
Rs= 0.06 L/d ± 12 % R2= 0 8
Clopidogrel Carboxylic Acid (PH)
Rs= 0 03 L/d ± 5 % R2= 0.92
Cyproconazole (PE)
Rs= n.d. L/d ± n.d. % R2= 0.46
Cyprodinil (PE)
Rs= n.d. L/d ± n.d. % R2= 0.48
m SDB (ng/SDB/d)
cw (ng/L)

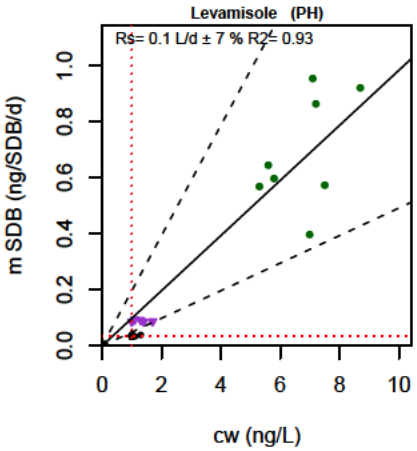

D617 (PH−TP)
Rs= n.d. L/d ± n.d. % R2= 0 65
Diazinon (PE)
Rs= 0.1 L/d ± 9 % R2= 0 83
Diclofenac (PH)
Rs= 0.06 L/d ± 4 % R2= 0.93
Diethyltoluamide (DEET)** (PE)
Rs= 0.1 L/d ± 7 % R2± 0.9
Dimethachlor (PE)
Rs= 0.1 L/d ± 12 % R2= 0.84
Dimethenamid (PE)
Rs= 0.1 L/d ± 9 % R2= 0 86
Dimethoat (PE)
Rs= 0.1 L/d ± 10 % R2= 0 9
Dimethomorph (PE)
Rs= 0 08 L/d ± 6 % R2= 0.91
Diuron (PE)
Rs= 0.1 L/d ± 7 % R2= 0 88
EDDP (ID)
Rs= 0 03 L/d ± 9 % R2= 0.89
Epoxiconazole (PE)
Rs= 0.08 L/d ± 13 % R2= 0.79
Ethofumesate (PE)
Rs= 0.08 L/d ± 8 % R2= 0.79
m SDB (ng/SDB/d)
cw (ng/L)

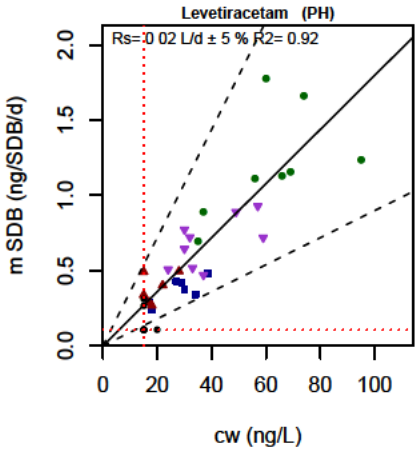

Fenamidone (PE)
Rs= 0 2 L/d ± 10 % R2= 0.84
Fenhexamid (PE)
Rs= 0.4 L/d ± 8 % R2= 0 92
Fenofibric acid (PH–TP)
Rs= 0.08 L/d ± 9 % R2= 0.85
Fipronil** (PE)
Rs= 0.1 L/d ± 11 % R2= 0.76
Fluazifop (PE–TP)
Rs= n.d. L/d ± n.d. % R2= 0.7
Fluconazole (PH)
Rs= 0.09 L/d ± 5 % R2= 0.92
Flufenacet (PE)
Rs= 0.1 L/d ± 9 % R2= 0.84
Flufenacet ESA (PE–TP)
Rs= 0.02 L/d ± 10 % R2= 0.79
Gabapentin (PH)
Rs= 0.005 L/d ± 5 % R2= 0.96
Hydrochlorothiazide (PH)
Rs= 0 05 L/d ± 3 % R2= 0.96
Indomethacin (PH)
Rs= 0 07 L/d ± 6 % R2= 0.92
Ioxynil (PE)
Rs= n.d. L/d ± n.d. % R2= 0.7
m SDB (ng/SDB/d)
cw (ng/L)

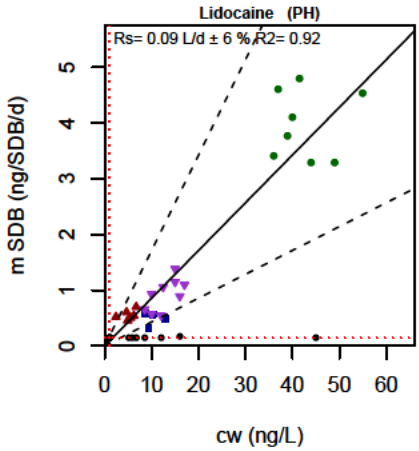

Isoproturon (PE)
Rs= 0 08 L/d ± 6 % R2= 0.86
m SDB (ng/SDB/d)
cw (ng/L)

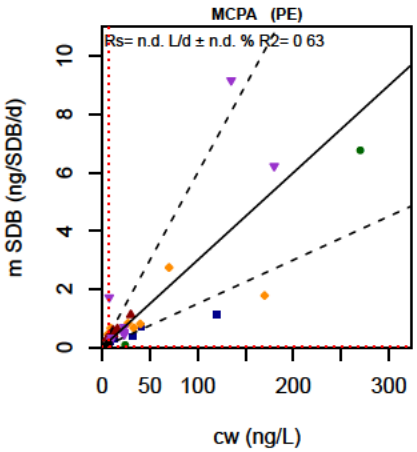

Lamotrigine (PH)
Rs= 0 07 L/d ± 5 % R2= 0.91
m SDB (ng/SDB/d)
cw (ng/L)

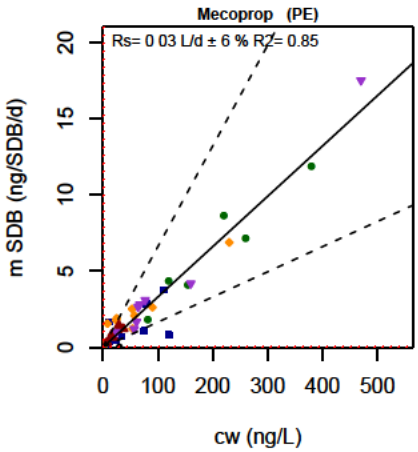

Lenacil (PE)
Rs= n.d. L/d ± n.d. % R2= 0.89
m SDB (ng/SDB/d)
cw (ng/L)

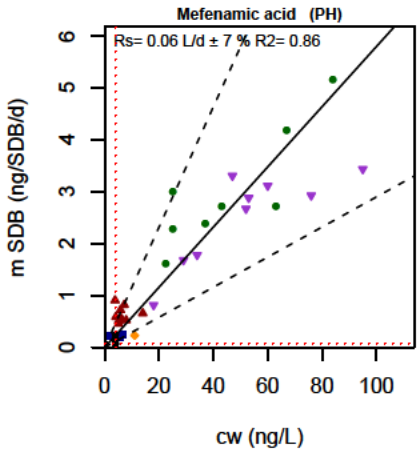

Levamisole (PH)
Rs= 0.1 L/d ± 7 % R2= 0.93
m SDB (ng/SDB/d)
cw (ng/L)

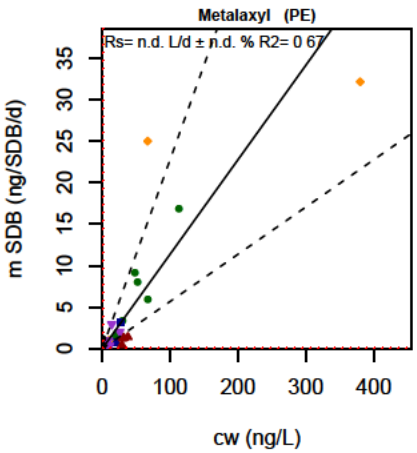

Levetiracetam (PH)
Rs= 0 02 L/d ± 5 % R2= 0.92
m SDB (ng/SDB/d)
cw (ng/L)

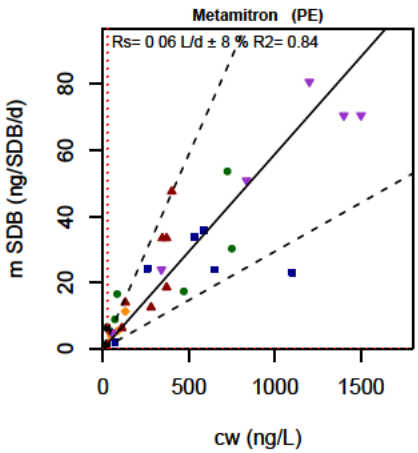

Lidocaine (PH)
Rs= 0.09 L/d ± 6 % R2= 0.92
m SDB (ng/SDB/d)
cw (ng/L)

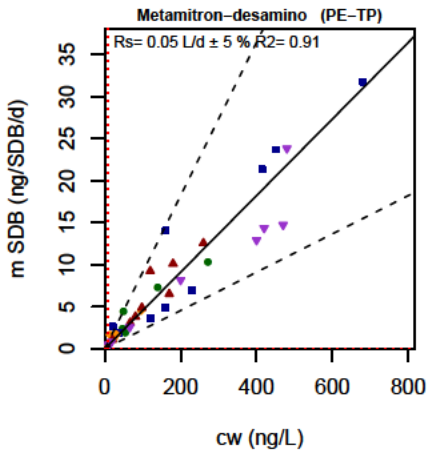

MCPA (PE)
Rs= n.d. L/d ± n.d. % R2= 0 63
m SDB (ng/SDB/d)
cw (ng/L)

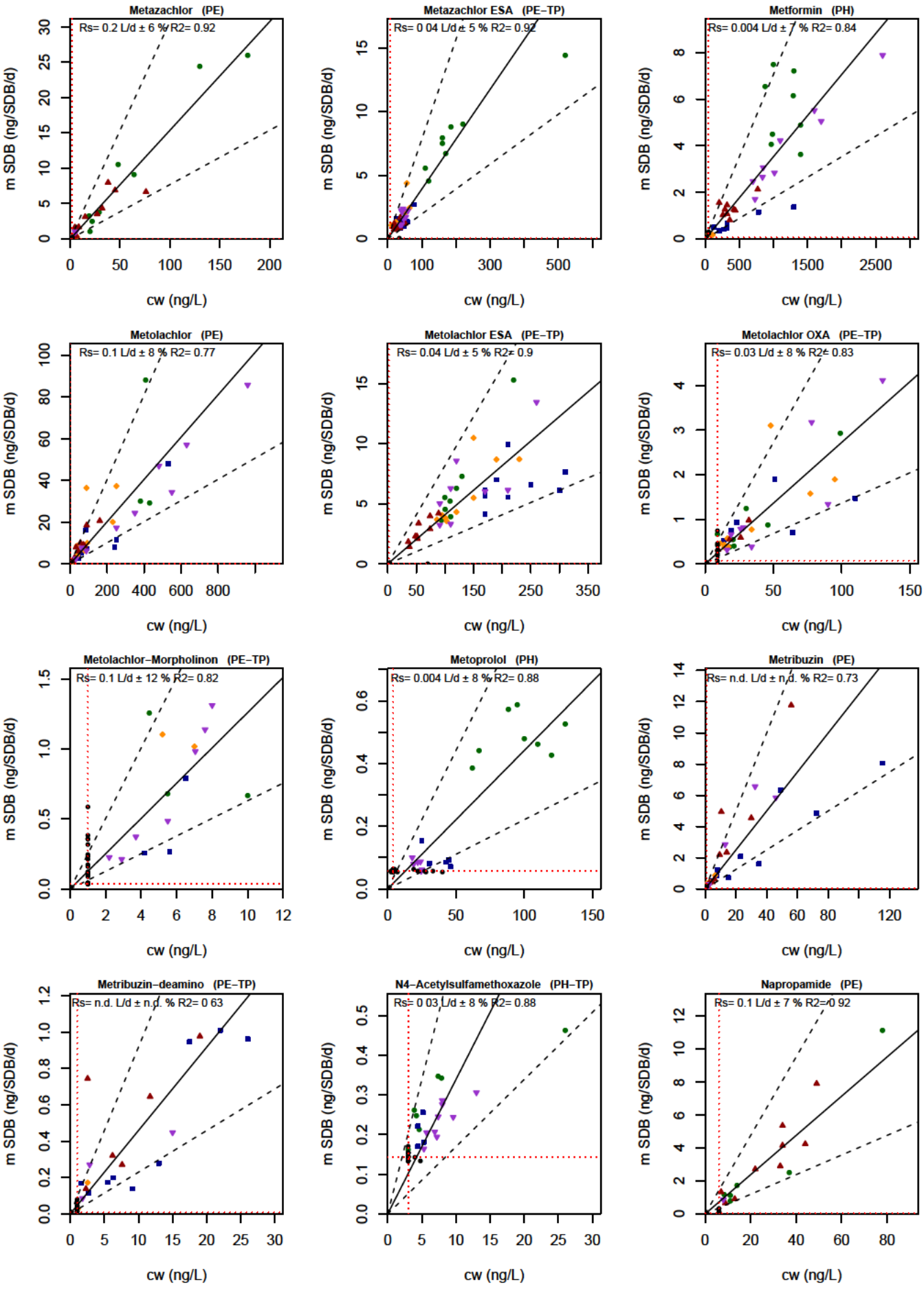

Mecoprop (PE)
Rs= 0 03 L/d ± 6 % R2= 0.85
m SDB (ng/SDB/d)
cw (ng/L)

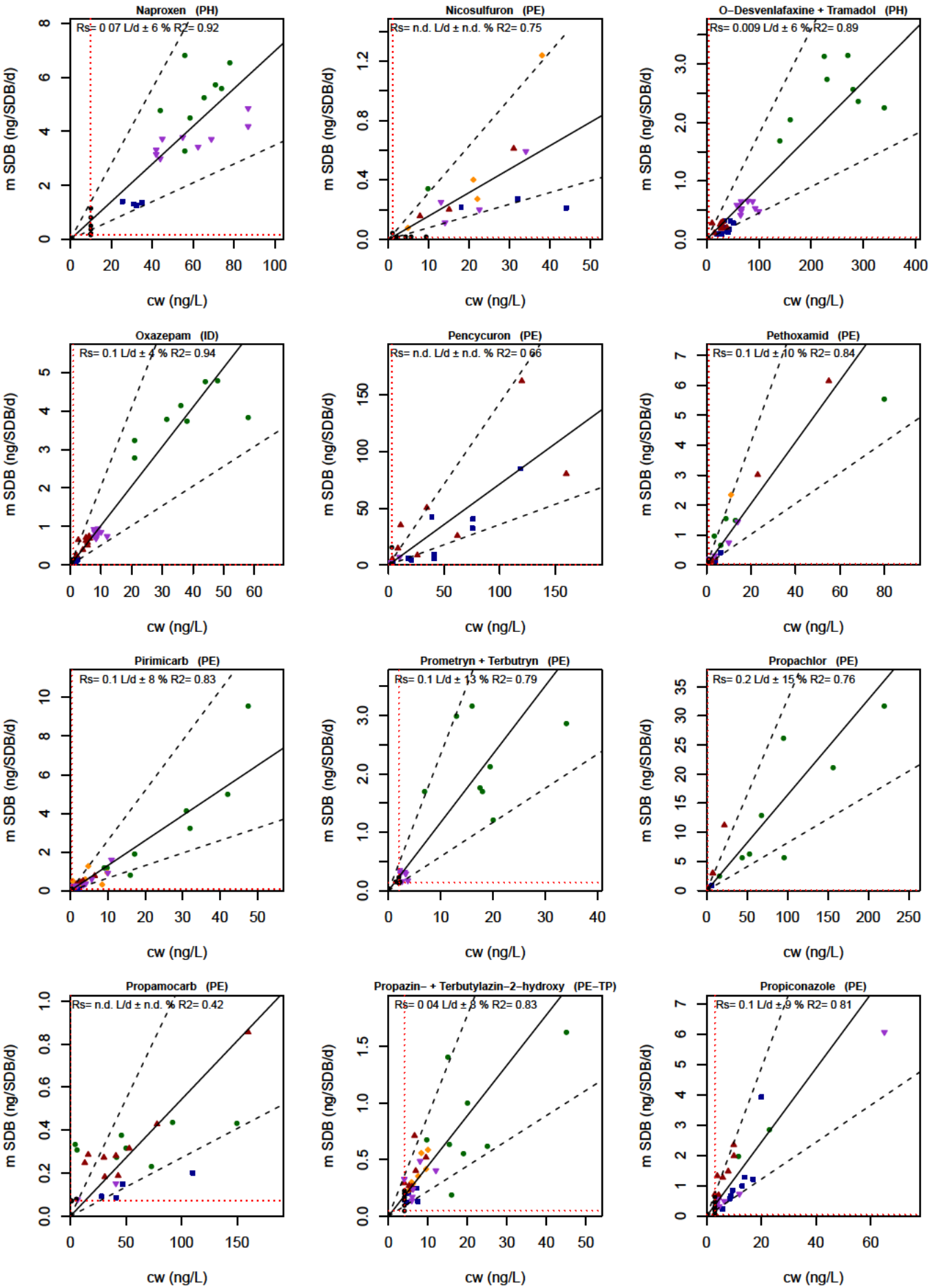

Mefenamic acid (PH)
Rs= 0.06 L/d ± 7 % R2= 0.86
m SDB (ng/SDB/d)
cw (ng/L)

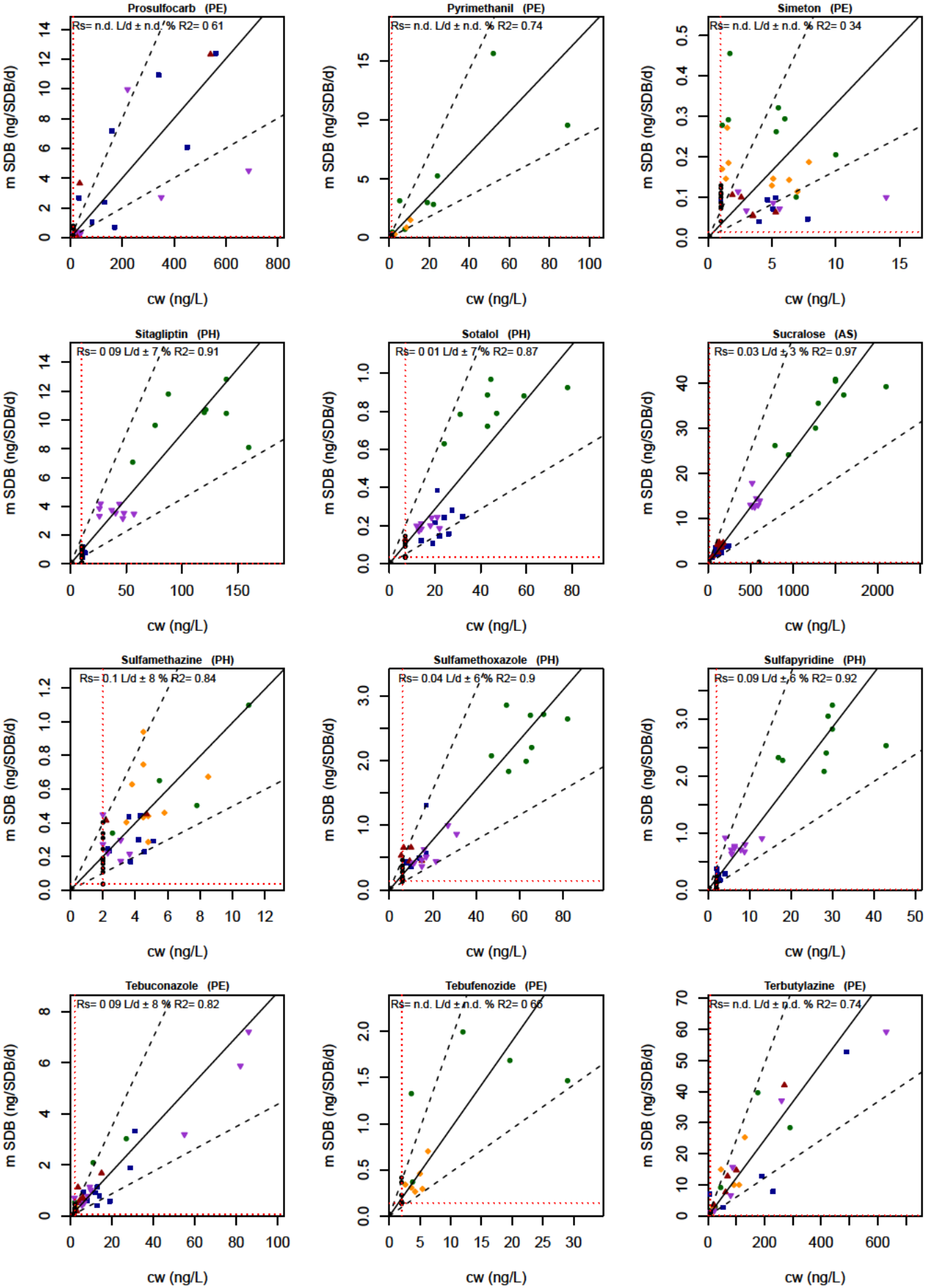

Metalaxyl (PE)
Rs= n.d. L/d ± n.d. % R2= 0 67
m SDB (ng/SDB/d)
cw (ng/L)

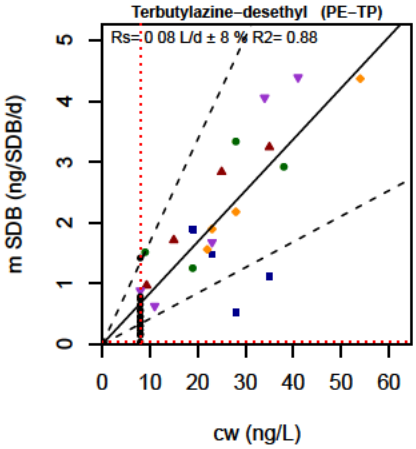

Metamitron (PE)
Rs= 0 06 L/d ± 8 % R2= 0.84
m SDB (ng/SDB/d)
cw (ng/L)

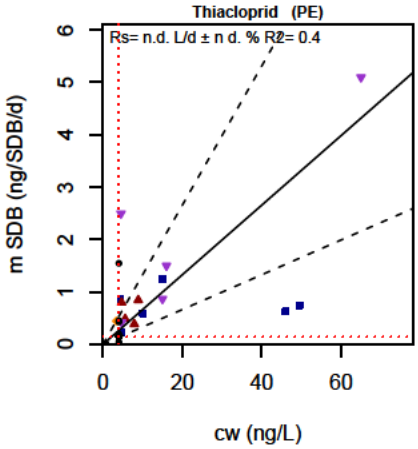

Metamitron–desamino (PE–TP)
Rs= 0.05 L/d ± 5 % R2= 0.91
m SDB (ng/SDB/d)
cw (ng/L)

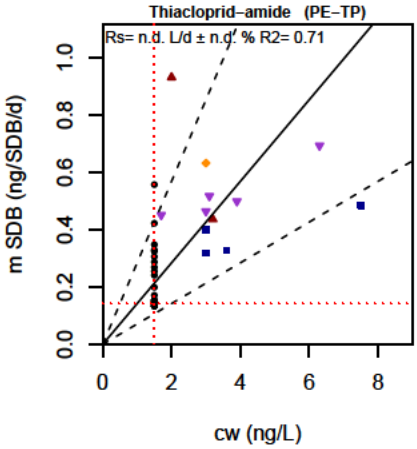

Metazachlor (PE)
Rs= 0.2 L/d ± 6 % R2= 0.92
Metazachlor ESA (PE−TP)
Rs= 0 04 L/d ± 5 % R2= 0.92
Metformin (PH)
Rs= 0.004 L/d ± 7 % R2= 0.84
Metolachlor (PE)
Rs= 0.1 L/d ± 8 % R2= 0.77
Metolachlor ESA (PE−TP)
Rs= 0.04 L/d ± 5 % R2= 0.9
Metolachlor OXA (PE−TP)
Rs= 0.03 L/d ± 8 % R2= 0.83
Metolachlor−Morpholinon (PE−TP)
Rs= 0.1 L/d ± 12 % R2= 0.82
Metoprolol (PH)
Rs= 0.004 L/d ± 8 % R2= 0.88
Metribuzin (PE)
Rs= n.d. L/d ± n.d. % R2= 0.73
Metribuzin−deamino (PE−TP)
Rs= n.d. L/d ± n.d. % R2= 0 63
N4−Acetylsulfamethoxazole (PH−TP)
Rs= 0 03 L/d ± 8 % R2= 0.88
Napropamide (PE)
Rs= 0.1 L/d ± 7 % R2= 0 92
m SDB (ng/SDB/d)
cw (ng/L)

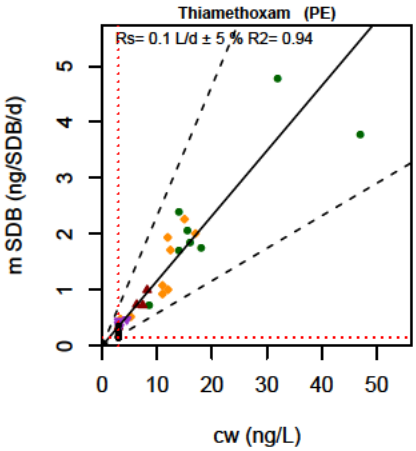

Naproxen (PH)
Rs= 0 07 L/d ± 6 % R2= 0.92
Nicosulfuron (PE)
Rs= n.d. L/d ± n.d. % R2= 0.75
O–Desvenlafaxine + Tramadol (PH)
Rs= 0.009 L/d ± 6 % R2= 0.89
Oxazepam (ID)
Rs= 0.1 L/d ± 4 % R2= 0.94
Pencycuron (PE)
Rs= n.d. L/d ± n.d. % R2= 0 66
Pethoxamid (PE)
Rs= 0.1 L/d ± 10 % R2= 0.84
Pirimicarb (PE)
Rs= 0.1 L/d ± 8 % R2= 0.83
Prometryn + Terbutryn (PE)
Rs= 0.1 L/d ± 13 % R2= 0.79
Propachlor (PE)
Rs= 0.2 L/d ± 15 % R2= 0.76
Propamocarb (PE)
Rs= n.d. L/d ± n.d. % R2= 0.42
Propazin– + Terbutylazin–2–hydroxy (PE–TP)
Rs= 0 04 L/d ± 8 % R2= 0.83
Propiconazole (PE)
Rs= 0.1 L/d ± 9 % R2= 0 81
m SDB (ng/SDB/d)
cw (ng/L)

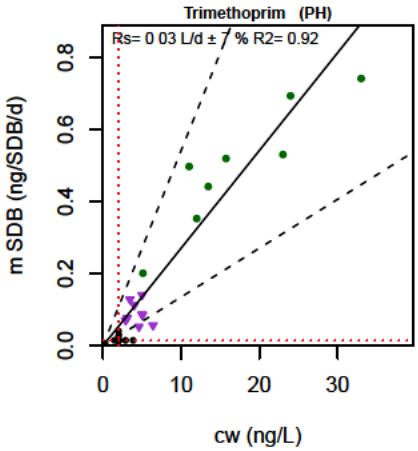

Prosulfocarb (PE)
Rs= n.d. L/d ± n.d. % R2= 0 61
Pyrimethanil (PE)
Rs= n.d. L/d ± n.d. % R2= 0.74
Simeton (PE)
Rs= n.d. L/d ± n.d. % R2= 0 34
Sitagliptin (PH)
Rs= 0 09 L/d ± 7 % R2= 0.91
Sotalol (PH)
Rs= 0 01 L/d ± 7 % R2= 0.87
Sucralose (AS)
Rs= 0.03 L/d ± 3 % R2= 0.97
Sulfamethazine (PH)
Rs= 0.1 L/d ± 8 % R2= 0.84
Sulfamethoxazole (PH)
Rs= 0.04 L/d ± 6 % R2= 0.9
Sulfapyridine (PH)
Rs= 0.09 L/d ± 6 % R2= 0.92
Tebuconazole (PE)
Rs= 0 09 L/d ± 8 % R2= 0.82
Tebufenozide (PE)
Rs= n.d. L/d ± n.d. % R2= 0 65
Terbutylazine (PE)
Rs= n.d. L/d ± n.d. % R2= 0.74
m SDB (ng/SDB/d)
cw (ng/L)

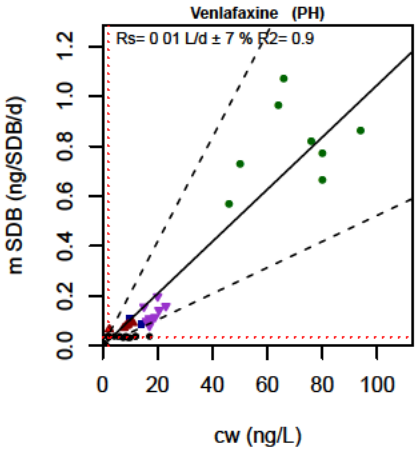

Terbutylazine−desethyl (PE−TP)
Rs= 0 08 L/d ± 8 % R2= 0.88
m SDB (ng/SDB/d)
cw (ng/L)


Thiacloprid (PE)
Rs= n.d. L/d ± n d. % R2= 0.4
m SDB (ng/SDB/d)
cw (ng/L)


Thiacloprid−amide (PE−TP)
Rs= n.d. L/d ± n.d. % R2= 0.71
m SDB (ng/SDB/d)
cw (ng/L)


Thiamethoxam (PE)
Rs= 0.1 L/d ± 5 % R2= 0.94
m SDB (ng/SDB/d)
cw (ng/L)


Trimethoprim (PH)
Rs= 0 03 L/d ± 7 % R2= 0.92
m SDB (ng/SDB/d)
cw (ng/L)


Venlafaxine (PH)
Rs= 0 01 L/d ± 7 % R2= 0.9
m SDB (ng/SDB/d)
cw (ng/L)

B.4. Additional Information to the Results

Comparison of Sampling Rates with Literature Data

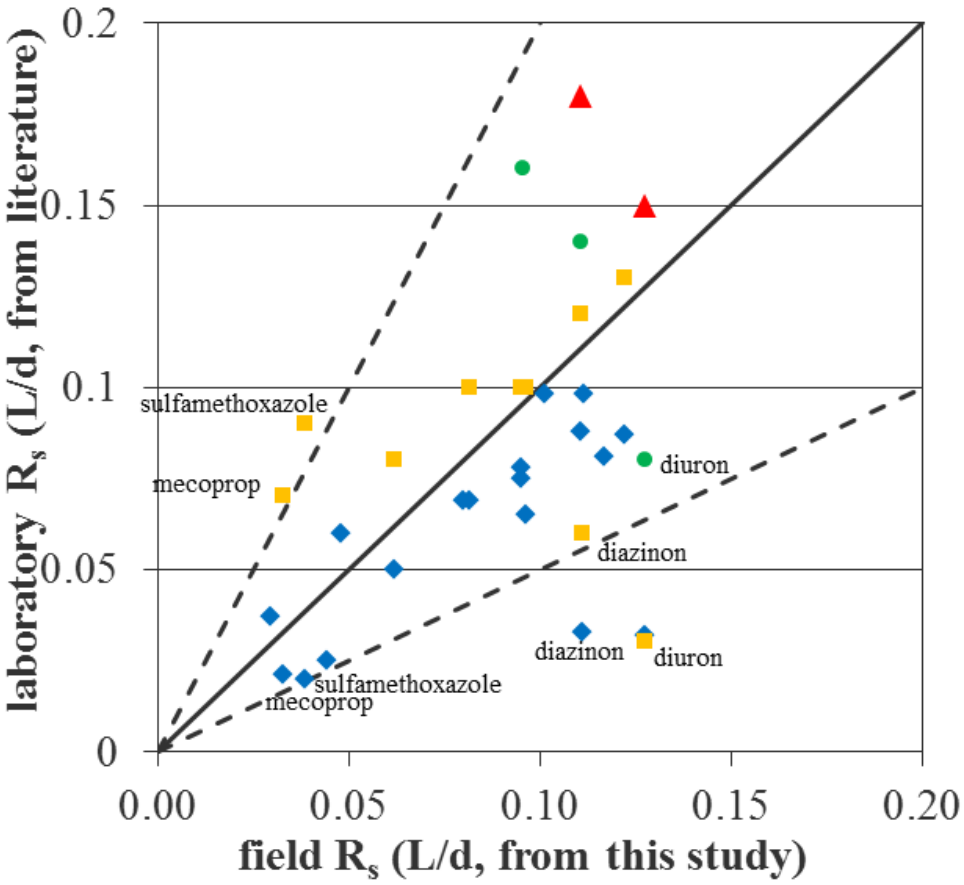


Figure B.4. Comparison of sampling rates (R_s) determined in this study (x-axis) and previous studies (y-axis) using SDB-RPS disks covered by a PES membrane (blue: Vermeirssen et al. 2012, orange: Vermeirssen et al. 2009, green: Shaw et al. 2009, red: Stephens et al. 2009. Black, solid line: equal sampling rate, dashed line: deviation of factor two in the sampling rates.

Influence of Environmental Parameters on Field Sampling Rate

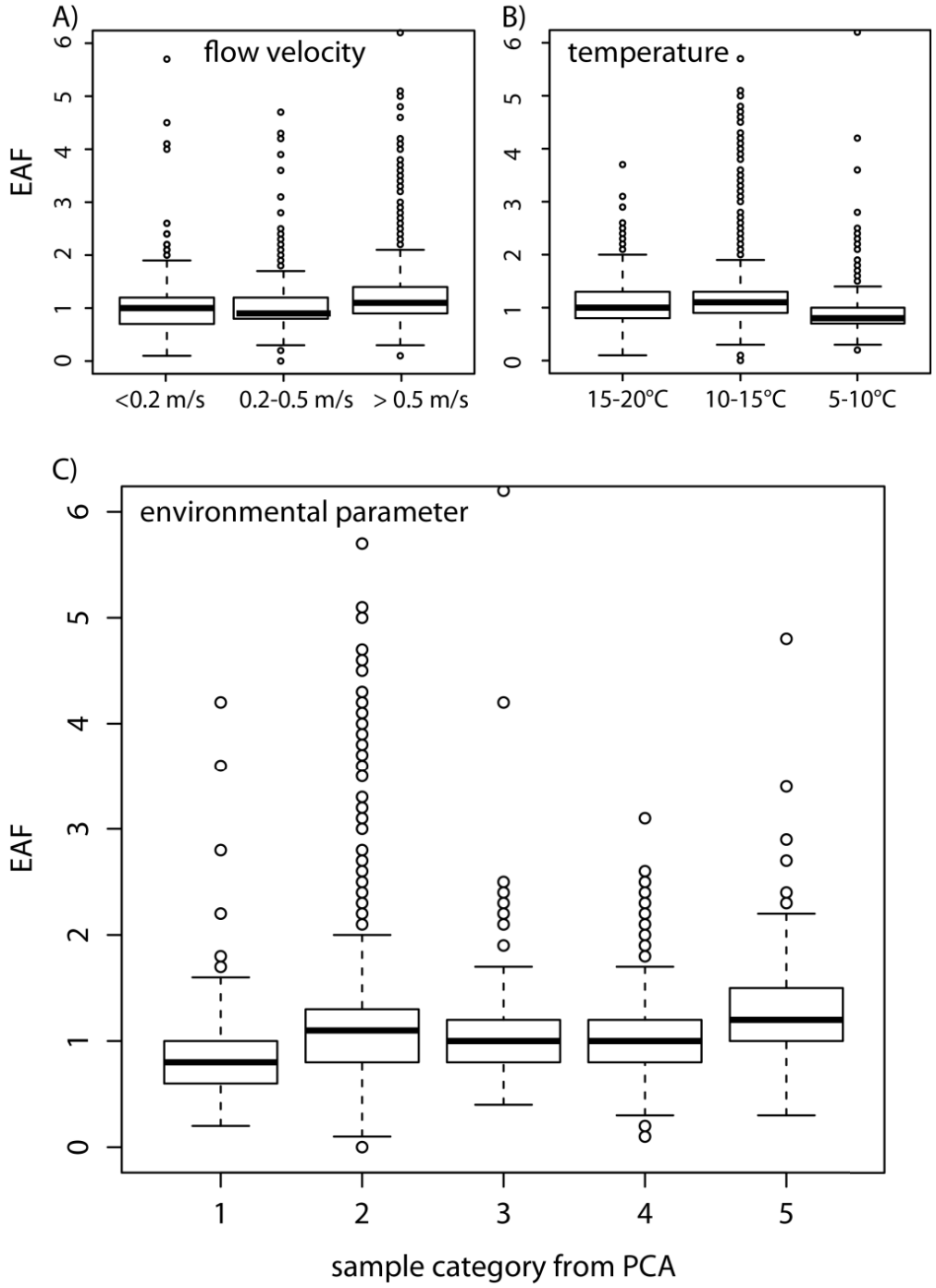


Figure B.5. Influence of environmental parameters on the sampling rate. A) flow velocity, B) temperature, C) samples divided into different categories using a PCA (see **Table B.1**, **Figure B.3**). EAF: environmental adjustment factor, i.e. the division of the ~~l~~ocal" sampling rate calculated for each sample divided by the determined average field sampling rate (**Table 3.1**).

Correlation between $LogK_{ow}$ and Field Sampling Rate

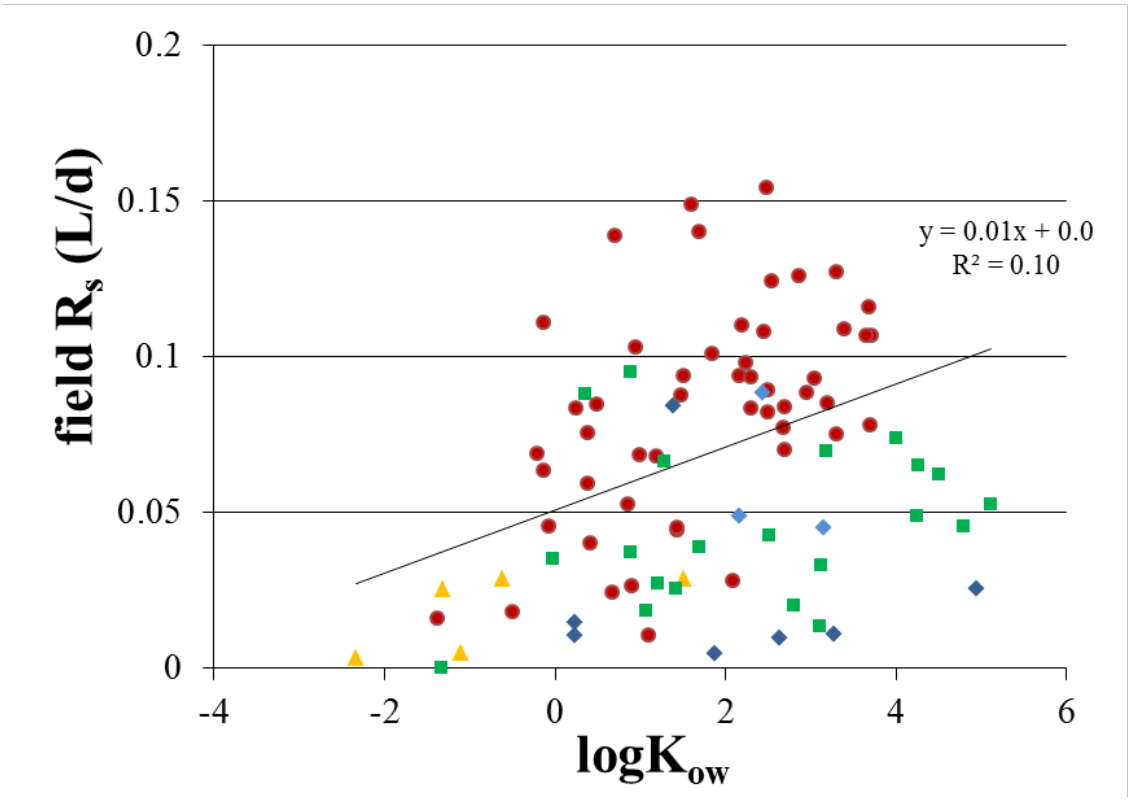


Figure B.6. Correlation between $logK_{ow}$ and the determined field sampling rate (field R_s, L/d). Red dots: neutral species, green squares: anionic, dark blue diamonds: cationic, light blue diamonds: cationic/neutral, orange triangles: zwitterionic (at pH=8)

Distribution of Field Sampling Rates

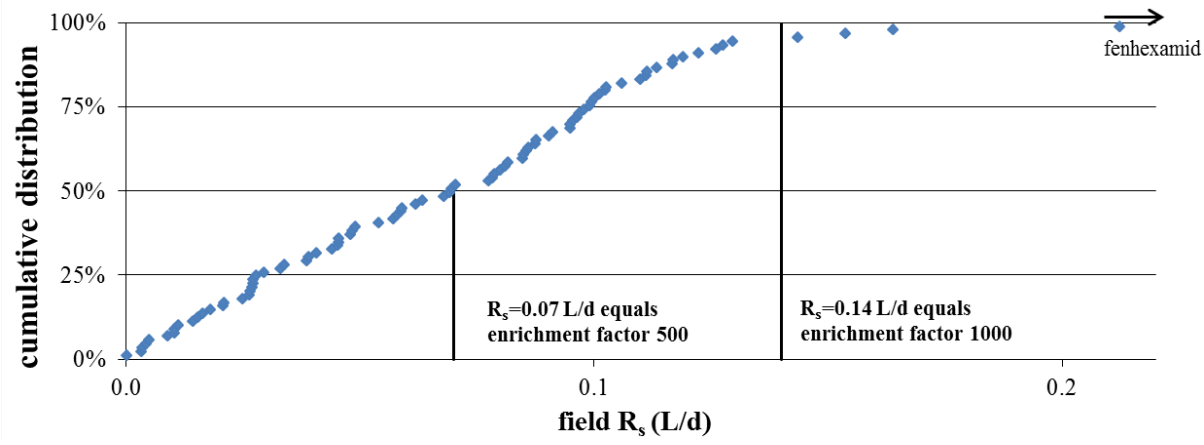


Figure B.7. Cumulative distribution of the field sampling rates (field R_s, see **Table 3.1**) determined in this study**.**

Comparison of Matrix Effects in Water Samples and Passive Samples

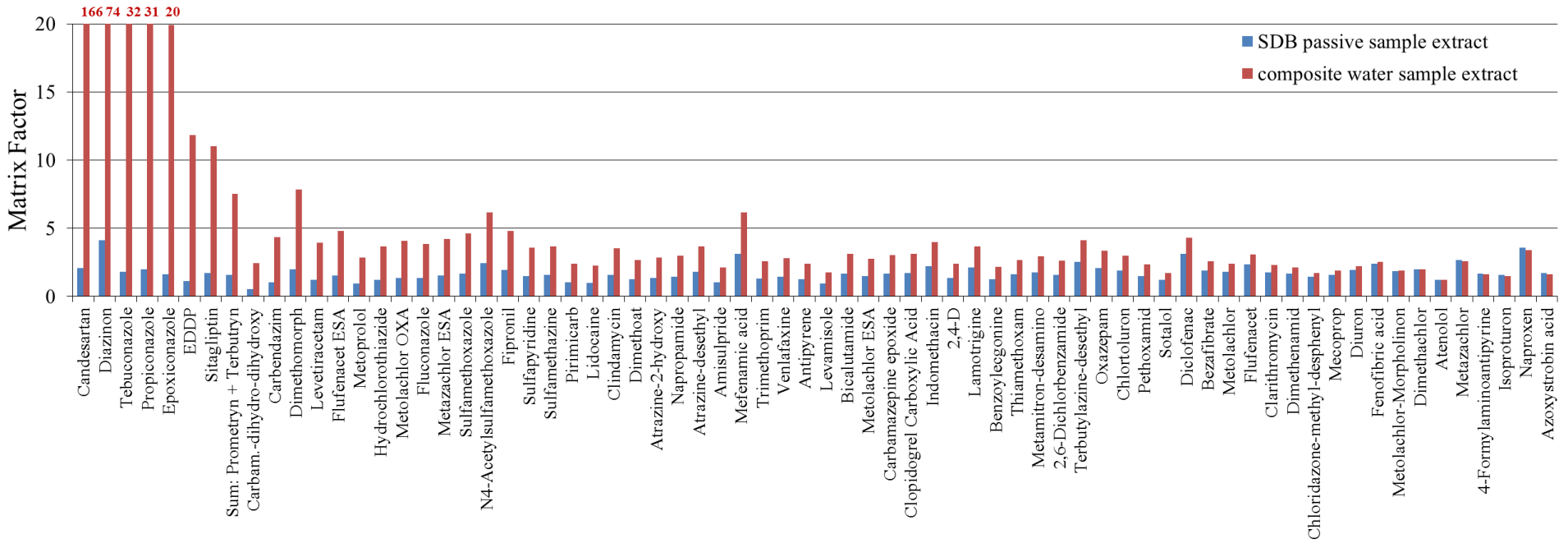


Figure B.8. Comparison between matrix factor in the SDB passive sample extracts (blue) and in composite water sample extracts (red). Matrix factors were calculated by comparing the peak area of each substance in a calibration standard (in nanopure water) with the peak area in a spiked environmental sample (see section 3.2.6). The list is sorted by the difference in the matrix factor in the SDB and the matrix factor in the water sample.

APPENDIX C SUPPORTING INFORMATION TO CHAPTER 4

C.1. Substance Information and Analytical Parameter

Table C.1. Substance properties of all investigated analytes[a]

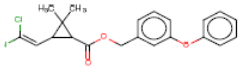
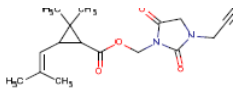
Substance Name	Cas-No.	Chemical Formula	Molecular Mass (g/mol)	Structure	Photolyisis half-life in water (d)	Hydrolysis half-life in water (d)
Target Analytes						
Bifenthrin	82657-04-3	C23H22ClF3O2	422.88		12	Stable
Chlorpyrifos	2921-88-2	C9H11Cl3NO3PS	350.89		29.6	25.5
Chlorpyrifos-me hyl	5598-13-0	C7H7Cl3NO3PS	322.53		5.5	21
Cypermethrin (alpha)	52315-07-8	C22H19Cl2NO3	416.3		13	179
Deltamethrin	52918-63-5	C22H19Br2NO3	505.2		48	Stable
Esfenvalerat	66230-04-4	C25H22ClNO3	419.9		10	-
Etofenprox	80844-07-1	C25H28O3	376.49		6.3	Stable
lambda-Cyhalo hrin	91465-08-6	C23H19ClF3NO3	449.85		40	Stable
Permethrin	52645-53-1	C21H20Cl2O3	391.3		1	31

Table C.1. continuation.

Substance Name	Cas-No.	Chemical Formula	Molecular Mass (g/mol)	Structure	Photolyisis half-life in water (d)	Hydrolysis half-life in water (d)
Target Analytes						
Phenothrin	26002-80-2	C23H26O3	350.46		-	-
Tefluthrin	79538-32-2	C17H14ClF7O2	418.73		11.2	Stable
Tetramethrin	7696-12-0	C19H25NO4	331.41		-	-
Performance Reference Compounds						
Acrinathrin	101007-06-1	C26H21F6NO5	541.44		2.3	Stable
Allethrin	584-79-2	C19H26O3	302.41		-	-
Fenpropathrin	39515-41-8	C22H23NO3	349.42		14	1130
Fluvalinat (tau)	102851-06-9	C26H22ClF3N2O3	502 9		4	22 5
Imiprothrin	72963-72-5	C17H22N2O4	318.37		-	58.6

[a] all information taken from the Footprint database (University of Hertfordshire 2013). Chemical structures were drawn from smiles codes with the program Jchem for Excel (ChemAxon). – no data for half-lives available.

Detailed Information of the Used Instruments

Table C.2. Detailed information of the used instruments

	GC-MS/MS (all environmal samples, final validation and elimination experiments)	**GC-MS (all experiments for optimization of the method)**
Gas chromatograph	Trace GC UltraTM Gas Chromatograph	Thermo Quest CE Instruments Trace GC Ultra Series Gas Chromatograph
Injector temperature	55°C	250°C
Injection volume	3 µL	3 µL
Injection mode	PTV with baffle liner	splitless (time 1 min)
Split flow	20 mL/min	50 mL/min
Carrier gas flow (He)	1.2 mL/min, constant flow	1 mL/min, constant flow
Oven Program		
run time	59.8 min	28 min
start	55°C for 1 min	100°C for 1 min
ramp	+30°C/min to 140°C (2.8 min); +2°C/min to 252°C (56 min)	+15°C/min to 280°C (12 min)
hold	-	280°C for 15 min
Column type	Zebron ZB-5MS (15m, 0.25 mm inner diameter, film thickness 0.25 µm)	RTX-5MS (15m, 0.25 mm inner diameter, film thickness 0.1 µm)
Mass spectrometer	Thermo Scientific TSQ Quantum GC, Triplequadropol	Thermo Scientific DSQ II Mass Spectrometer
Transfer line temperature	240°C	220°C
source temperature	230°C	250°C
ionization mode	positive electron ionization (EI)	positive electron ionization (EI)
Detection mode	selected reaction monitoring (SRM)	fullscan
Isolation window (m/z)	transitions see Table 1 in main text	50-350

C.2. Experiments for the Estimation of Specific Sampling Rates

Kinetic Experiments for Estimating the Elimination of Pyrethroids/Organophosphates from Silicone Rubber (SR)

Kinetic parameters for the exchange of pyrethroids and organophosphates between silicone rubber (SR) and water were tested by two approaches. In the first approach, a kinetic experiment in a flow channel system as described in Vermeirssen et al. (2008) was set up for testing the elimination of all analytes (targets and performance reference compounds (PRCs)) from SR sheets (**Figure C.1**). Two flow channels were run with a flow velocity of 0.23±0.02 m/s. Water from the nearby Chriesbach river was pumped into a storage tank. The water was run through the channels and pumped back at a rate of 20 m^3/h. Freshwater was added at 0.24 m^3/h in order to exchange the water in the system (0.48 m^3) within 2 h.

Thirty-four SR sheets with a size of 3 x 10 cm^2 were loaded with a mix of all substances analogue to the method described in Smedes and Booij (2012) to achieve a concentration of approximately 1 mg/L in the final extract. For this, 15 µg of each substance was spiked into a glass bottle filled with 70 mL methanol and the 34 sheets were added. The bottle was shaken for seven days with daily addition of nanopure water up to a water content of 60%. The loaded sheets were placed into the two flow channels for different time periods. During the whole experiment, temperature was measured, flow velocities were checked and the whole system was shaded with a black cover to prevent biofouling and photolysis. At the following 17 time points, one passive sample was taken from each channel: 0, 0.5, 1, 1.5, 2, 3, 4, 7, 10, 14, 23, 30, 35, 42, 49, 56, 60 days. In addition, non-spiked samples (blank) were taken at five time points (10, 14, 35, 49, 60 days). All samples were extracted and measured with the optimized method described in the main text.

In the second approach, 28 of the 40 environmental samples from the medium sized rivers (see **Figure C.6**) were spiked with five pyrethroids that were possible candidates for PRCs (allethrin, imiprothrin, acrinathrin, fluvalinate, fenpropathrin, **Table C.3**). The five pyrethroids were the only substances that are not allowed to be used in Switzerland, neither in plant protection products nor as biocide. Two concentrations were selected: 1 mg/SR sheet (30 x 10 cm^2) and 0.5 mg/SR sheet (**Table C.3**). The addition of the substances was done by spiking the exact volume of the PRC mix with 30 droplets onto the SR sheet. The sheets were dried under the hood (overnight) and were deployed for two weeks in the six medium-sized rivers. Six reference SR sheets were also spiked with the same concentration of PRC mix (**Table C.3**). These sheets were not deployed in water, but stored in the dark at room temperature. After deployment, environmental sheets and the corresponding reference sheets were stored at -20°C and analyzed as described in the main text.

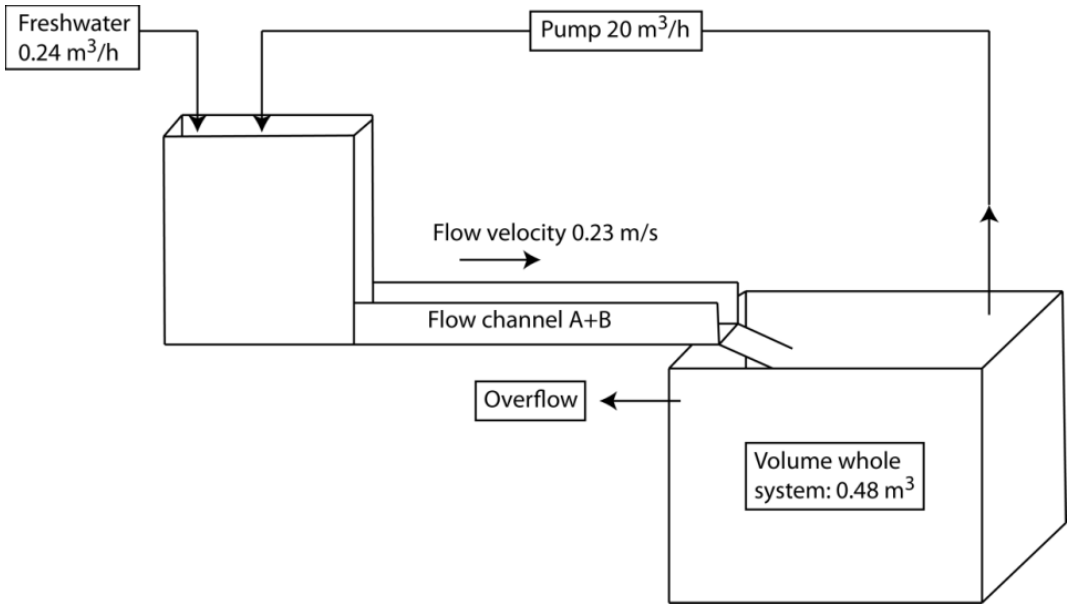


Figure C.1. Set-up of the flow channel system.

Estimation of the Elimination Constant in the Flow Channel Experiment

Because the exchange of non-polar substances between SR and water is isotropic (Rusina et al. 2010b), the determination of an elimination constant is a possible approach to calculate sampling rates. A clear elimination of the two substances with the lowest $\log K_{ow}$ values (imiprothrin 2.9 and chlorpyrifos-methyl 4.3, respectively) from the SR over the whole 60 days was found in the flow channel experiment (see **Figure C.2A** for the example of chlorpyrifos-methyl). Substances with $\log K_{ow}$ values above five (except tefluthrin) were not eliminated at all during the 60 days of the experiment (see **Figure C.2C** for the example of etofenprox). Questions arise for substances with medium $\log K_{ow}$ values such as chlorpyrifos and allethrin (5.0 and 4.8, respectively). A clear elimination was visible over the first 7-14 days (see **Figure C.2B** for chlorpyrifos). After this period, however, no further elimination occurred. For chlorpyrifos, natural occurrence of the substance in the river water could be the reason for this observation (peaks in blank samples after 14 days were present), for allethrin, there must be another reason. A non-homogenous distribution in the sheet can be excluded as the substances were loaded onto the sheet by using a water/methanol mixture and not by spiking the sheets with droplets. A reduction of the diffusion due to a biofilm or chalk deposition could be another reason.

For five substances (chlorpyrifos, chlorpyrifos-methyl, imiprothrin, allethrin, tefluthrin), an elimination constant (k_e) could be calculated for the first 14 days of deployment (see **Figure C.3**) by equation 1:

$$Retained\ fraction\ (f) = \frac{N(t)}{N(0)} = \ exp(-k_e \times t), \qquad (1)$$

where *N(t)* is the amount in the SR at time point *t* and *N(0)* is the initial amount of substance in the SR. A slight correlation between $\log K_{ow}$ and $\log k_e$ was found (**Figure C.3**), but much less pronounced than found for PAHs by Rusina et al. (2010b).

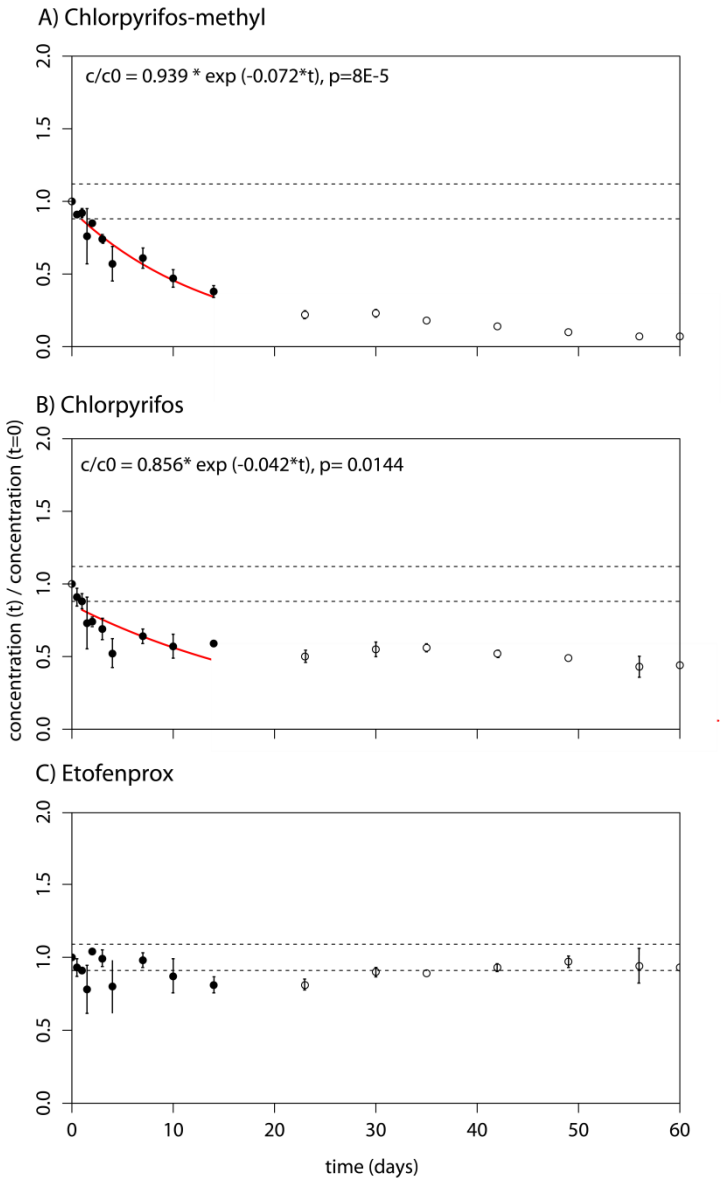


Figure C.2. Elimination of three substances with different $logK_{ow}$ values from the SR in the flow channel experiment. A) chlorpyrifos-methyl ($logK_{ow}$ 4.3), B) chlorpyrifos ($logK_{ow}$ 5.0), C) etofenprox ($logK_{ow}$ 7.1). A regression could be fitted for the first 14 days (black dots) for chlorpyifos-methyl and chlorpyrifos (red line, p equals the statistical p-value of the regression). Uncertainty bars show the standard deviation from the two flow channels.

Estimation of Distribution Coefficients Between SR and Water (K_{pw})

When k_e values are measured properly, laboratory sampling rates (R_s) can be calculated from k_e values with the following equation (Rusina et al. 2010b):

$$R_s = k_e \times m_{SR} \times K_{pw}, \qquad (2)$$

where m_{SR} is the mass of the sampler and K_{pw} is the distribution coefficient between SR and water. As R_s is directly proportional to the K_{pw} value, it is important to have accurately measured K_{pw} values (Rusina et al. 2010b). For an in-situ measurement of sampling rates, this

is especially true for the substances used as PRCs. For the target substances which do not reach equilibrium within the sampling period, an estimation of K_{pw} from an empirical correlation is sufficient because the extrapolation of the sampling rate from PRCs to targets compounds only shows a weak correlation with K_{pw} (Smedes and Booij 2012, Rusina et al. 2010b). In comparison to PCBs and PAHs (Smedes et al. 2009), for pyrethroids and organophosphates, no measured K_{pw} values exist for the material we used (Altesil^{TM}). K_{pw} values for some pyrethroids (Hunter et al. 2009, Lao et al. 2012, Bondarenko et al. 2007) and organophosphates (Magdic et al. 1996) for SR from different manufacturers are available in the literature, but the values for the pyrethroids only cover a narrow $logK_{ow}$ range between 6 and 6.5. Difilippo and Eganhouse (2010) found that differences in K_{pw} values derived for SR from different manufacturers and between SR with different thickness are insignificant. Nevertheless, values for pyrethroids between the three studies differed up to a factor of six. Reasons for this could be different approaches used to determine K_{pw} values. In such experiments, it is important that there is negligible depletion of the substances in the water phase, that there is no sorption to equipment and that equilibrium is reached (Difilippo and Eganhouse 2010). No correlation between $logK_{ow}$ and $logK_{pw}$ values were found for pyrethroids. Due to different functional groups that determine the polarity of the pyrethroids, an empirical correlation can *per se* not be expected for this substance class (compared to PCBs or PAHs).

Thus, it is essential that in further studies, K_{pw} values for pyrethroids and organophosphates are measured exactly and are determined for the used material. With this information available, sampling rates under defined conditions (e.g. flow channel) can be calculated for all substances. If an empirical correlation between $logK_{ow}$ and $logK_{pw}$ exists, the extrapolated K_{pw} values can be used to determine in-situ sampling rates by using PRCs. In addition, experiments that determine the duration of linear uptake of pyrethroids/organophosphates would help for the understanding of the kinetic behavior of the investigated substances. It is possible that smaller substances are already in equilibrium after a two week deployment in the river (personal communication Kees Booij, NIOZ, The Netherlands).

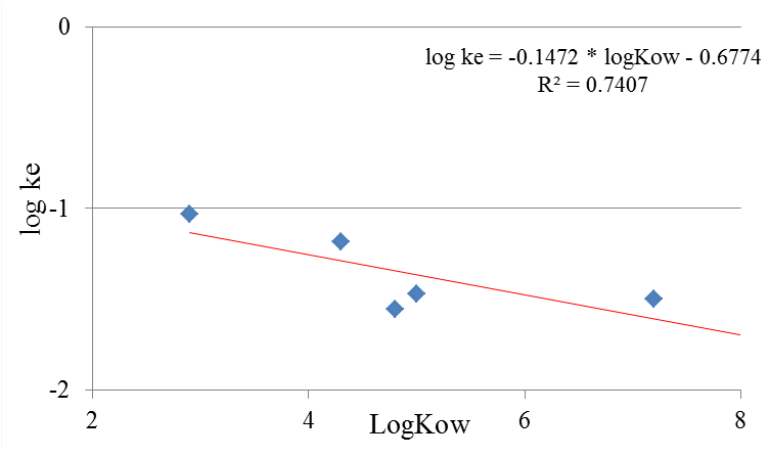


Figure C.3. Correlation between $logK_{ow}$ and $logk_e$ values for the five substances (imiprothrin, chlorpyrifos-methyl, chlorpyrifos, allethrin, tefluthrin) that showed an elimination within 14 days of the experiment. Red line shows the linear regression.

Suitable Performance Reference Compounds (PRCs)

Original PRC methods focused on PRCs for which between 20-80% are retained in the sheet after the deployment time (Booij and Smedes 2010). Often, only one substance was used as PRC in a sample. A new method, the nonlinear least squares (NLS) method, developed by Booij and Smedes (2010), makes use of multiple PRCs with different environmental properties, e.g. at least six substances covering a $\log K_{ow}$ range of 3.5-5.5 with a distance of 0.3 log units (Smedes and Booij 2012). The PRC must not be present in the environment, that is, either isotope labeled substances or substances that are not allowed/used in the study area have to be selected. For substances such as PCBs and PAHs, there are enough substances from the same substance class available, either deuterated ones or substances that have not been produced in Europe. For pyrethroids and organophosphates, however, only a limited set of substances are possible candidates for PRCs. Only few isotope labeled substances are commercially available. Most of them were already used as internal standards in the analytics of this study (see main text). Five pyrethroids were selected that are not permitted in Switzerland: acrinathrin, allethrin, imiprothrin, fenpropathrin, and fluvalinate. From them, only allethrin fulfills the above mentioned $\log K_{ow}$ criterion. The $\log K_{ow}$ value of imiprothrin (2.9) is too low, while for the other substances it is too high (>5.5). It is therefore very important that more suitable PRCs for pyrethroids are made available, e.g. by synthesizing more isotope labeled pyrethroids. It may also be possible that other chemical classes (e.g. PCBs) are suitable as PRCs for the determination of in-situ sampling rates of pyrethroids and organophosphates. For this, it has to be confirmed if the diffusion of pyrethroids and organophosphates are also water boundary layer controlled, as it is the case for PCBs and PAHs (Kees Booij, NIOZ, The Netherlands, personal communication).

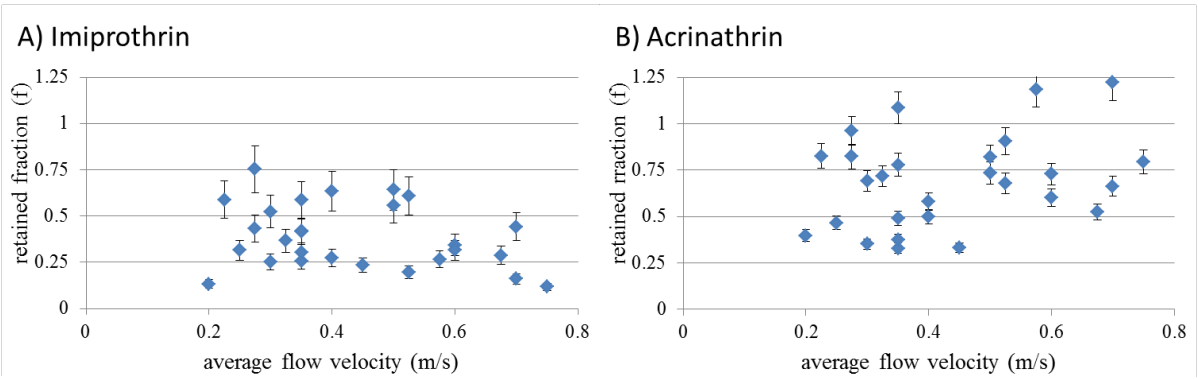


Figure C.4. Retained fraction (f) of (A) imiprothrin and (B) acrinathrin at different flow velocities (average measurement at beginning and end of deployment) in the 28 spiked environmental samples. Error bars show the uncertainties of the analysis (see **Table 4.1**).

Elimination of PRCs from Environmental Samples

In the second approach, the elimination of the five PRCs from SR sheets deployed in the environment was checked. An elimination of four of the five PRCs could be observed in most of the deployed SR sheets. For imiprothrin and allethrin, this was expected from their $\log K_{ow}$ values, but for acrinathrin and fenpropathrin, this was not expected. No correlation between flow velocities and retained fraction was observed (**Figure C.4** for the examples of imiprothrin and acrinathrin). A correlation was expected as the increase in flow velocity strongly increases the sampling rate (Vermeirssen et al. 2009). It is, however, not clear up to which flow velocity an increase in the sampling rate occurs. For this, kinetic experiments should be carried out at different flow velocities. Other factors than the flow velocity were expected to be less significant. Biofouling was expected to be of less relevance because the investigated samples did not show significant biofouling. The temperature increased by maximal 15°C within the five month of investigation. This should have less effect than a factor of two (Booij et al. 2002).

There are two hypothesis why no correlation was observed and why also very non-polar substances showed an elimination in the environmental samples. First, spiking of the sheets with PRCs (dripping droplets onto sheet and let it dry overnight) could lead to an inhomogeneous distribution of the substances in the sheet. This could lead to a faster and less homogenous elimination from the sheets. It is therefore important to determine the diffusion of pyrethroids and organophosphate in the SR sheets. Previous investigations showed that the spike method is less reliable than the loading method (personal communication Kees Booij, NIOZ, The Netherlands and Markus Zennegg, Empa, Switzerland).

Second, the PRCs could have undergone photolysis in the SR sheets. An elimination of PRC due to photolysis was already described for PAHs in semi-permeable membrane devices (SPMD) by Komarova et al. (2009). As the investigated PRCs have low photolysis half-lives in water (< 14 d, see **Table C.1**, University of Hertfordshire 2013), the photolysis in the SR could also be of relevance. Interestingly, a correlation between the elimination of imiprothrin and allethrin was found (**Figure C.5A**); these are the two substances for which a *real* desorption can be expected. It is reasonable that substance behave similar when the elimination is due to the same process. It is, however, not sure that the flow velocity was the driving factor. On the other hand, no correlation between imiprothrin and acrinathrin elimination was found (**Figure C.5B**). When the acrinathrin elimination was due to photolysis and imiprothrin elimination due to desorption, it is reasonable that there is no correlation between the two substances.

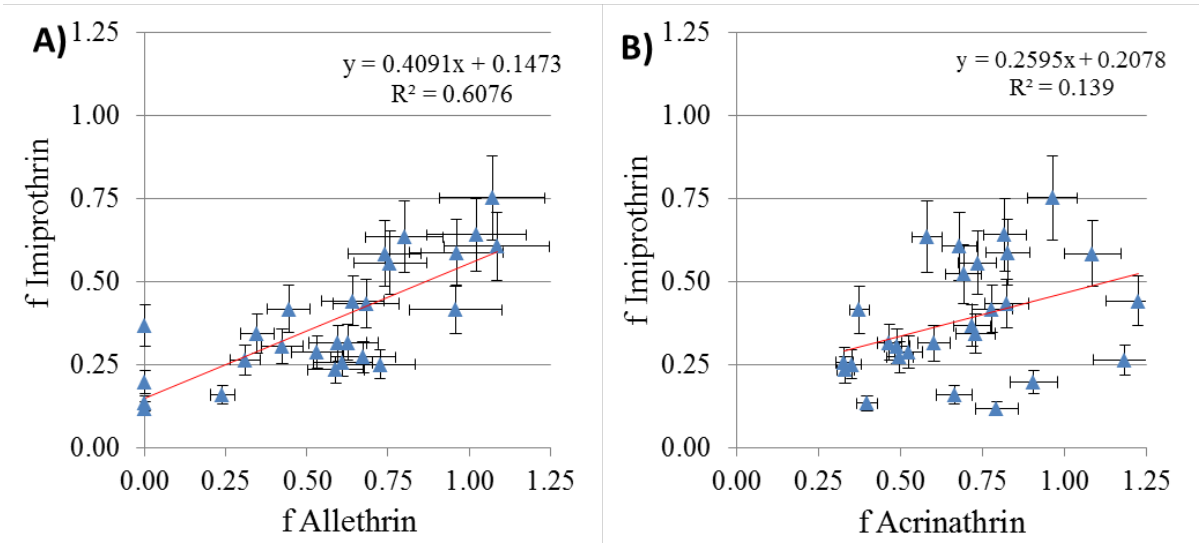


Figure C.5. Comparison of the retained fraction (f) between (A) allethrin and imiprothrin and (B) acrinathrin and imiprithrin in the 28 spiked environmental samples. Error bars show the uncertainties of the analysis (see **Table 4.1**).

C.3. Field Study Information

Map of the study site

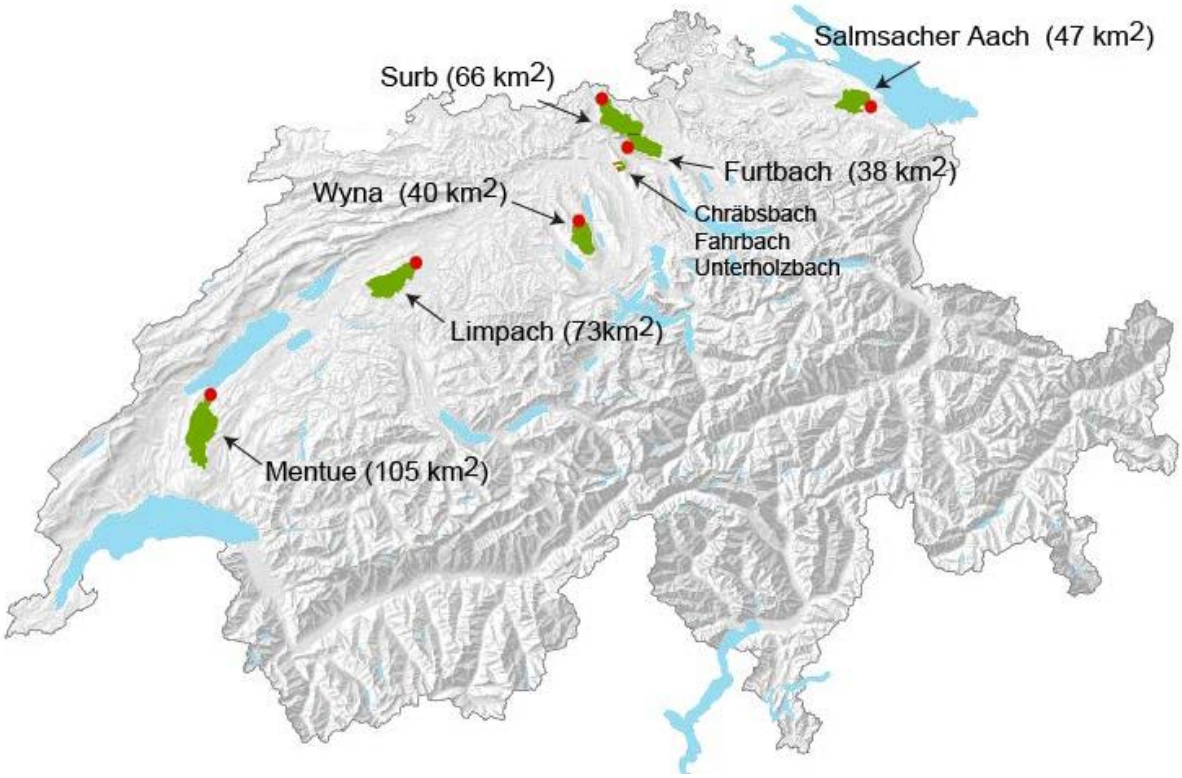


Figure C.6. Map of Switzerland with the field study sites (catchments: green, sampling locations: red dots) of the 6 medium-sized rivers and the three small streams. Catchment sizes are indicated in brackets, if available.

Sampling Times and Flow Velocities

Table C.3. Sampling times and flow velocities

River Name / Sample Number	Date of deployment	Date of recovery	Deployment time (d)	Flow velocity at deployment (m/s)	Flow velocity at recovery (m/s)	Spike amount of PRC mix (mg/L)
Furtbach 1	09.03.2012	20.03.2012	11	0.65	0.65	
Furtbach 2	20.03.2012	03.04.2012	14	0.65	0.5	1.0
Furtbach 3	03.04.2012	17.04.2012	14	-	0.7	1.0
Furtbach 4	17.04.2012	30.04.2012	13	0.80	0.6	1.0
Furtbach 5	30.04.2012	15.05.2012	15	0.10	0.3	0.5
Furtbach 6	15.05.2012	29.05.2012	14	0.30	0.75	0.5
Furtbach 8	11.06.2012	26.06.2012	15	0.75	0.75	0.5
Furtbach 9	26.06.2012	10.07.2012	14	0.75	0.7	
Furtbach 10	10.07.2012	23.07.2012	13	0.40	0.25	
Surb 1	09.03.2012	20.03.2012	11	0.25	0.4	
Surb 2	20.03.2012	04.04.2012	15	0.35	-	1.0
Surb 3	04.04.2012	18.04.2012	14	-	0.6	1.0
Surb 5	02.05.2012	16.05.2012	14	0.40	0.5	0.5
Surb 6	16.05.2012	30.05.2012	14	0.50	0.15	0.5
Surb 8	13.06.2012	27.06.2012	14	0.40	0.4	0.5
Surb 9	27.06.2012	10.07.2012	13	0.30	0.35	
Surb 10	10.07.2012	23.07.2012	13	0.35	0.35	
Limpach 2	19.03.2012	03.04.2012	15	0.25	0.2	1.0
Limpach 3	03.04.2012	17.04.2012	14	0.15	0.4	1.0
Limpach 4	17.04.2012	30.04.2012	13	0.60	-	1.0
Limpach 5	30.04.2012	15.05.2012	15	0.35	0.15	0.5
Mentue 2	19.03.2012	03.04.2012	15	0.25	0.3	1.0
Mentue 3	03.04.2012	17.04.2012	14	0.35	0.7	1.0
Mentue 4	17.04.2012	30.04.2012	13	0.65	0.7	1.0
Mentue 5	30.04.2012	15.05.2012	15	0.65	0.05	0.5
Salmsacher Aach 2	20.03.2012	04.04.2012	15	0.50	-	1.0
Salmsacher Aach 3	04.04.2012	18.04.2012	14	-	0.4	1.0
Salmsacher Aach 4	18.04.2012	02.05.2012	14	0.40	0.3	1.0
Salmsacher Aach 6	16.05.2012	30.05.2012	14	0.30	0.3	0.5
Salmsacher Aach 7	30.05.2012	14.06.2012	15	0.20	0.4	0.5
Salmsacher Aach 8	14.06.2012	27.06.2012	13	0.40	0.3	0.5
Wyna 2	19.03.2012	03.04.2012	15	0.60	0.1	1.0
Wyna 3	03.04.2012	17.04.2012	14	0.20	0.8	1.0
Wyna 4	17.04.2012	30.04.2012	13	-	0.3	1.0
Chräbsbach 1	03.04.2013	15.04.2013	14	0.05	-	
Chräbsbach 2	15.04.2013	30.04.2013	14	0.05	-	
Fahrbach 3	30.04.2013	14.05.2013	14	-	0.4	
Fahrbach 4	14.05.2013	28.05.2013	14	-	0.3	
Unterholzbach 1	03.04.2013	15.04.2013	14	0.05	-	
Unterholzbach 2	15.04.2013	30.04.2013	14	0.4	-	
Reference Blank 2						1.0
Reference Blank 3						1.0
Reference Blank 4						1.0
Reference Blank 5						0.5
Reference Blank 6						0.5
Reference Blank 8						0.5

- Flow velocity could not be determined

Estimated Concentrations from the Measurements in the Field (ng/L)

Table C.4. Estimated concentrations from the measurements in the field (ng/L)[1]

River Name / Sample Number	Chlorpyri-fos	Chlorpyri-fos-methyl	Bifenthrin	Cyper-methrin	Delta-methrin	Etofenprox	Lambda-Cyhalothrin	Permethrin
LOD (environment)	-	0.06	0.006	0.008	-	-	0.10	-
LOQ (environment)	0.02	0.20	0.02	0.02	0.10	0.03	0.30	0.06
Furtbach 1	0.9	0.3		0.03	0.5			
Furtbach 2	0.7	<LOQ		<LOQ	0.3			
Furtbach 3	0.9	1		0.1	1		<LOQ	
Furtbach 4	0.8	0.3		0.1	2		<LOQ	
Furtbach 5	0.6	8		0.08	0.3		<LOQ	
Furtbach 6	0.9	1		0.07	0.7		0.5	
Furtbach 8	1	6		0.1	0.5		0.4	0.4
Furtbach 9	2	1		0.06	0.3		<LOQ	0.8
Furtbach 10	0.9	3		0.1	0.8		0.4	0.4
Surb 1	0.3							
Surb 2	0.4			0.03				
Surb 3	0.5			0.03				0.07
Surb 5	0.3			0.06				0.1
Surb 6	0.3			0.09				
Surb 8	10			0.03				0.08
Surb 9	2			0.04				0.2
Surb 10	0.5			0.05				0.2
Limpach 2	0.3			0.04				
Limpach 3	0.4		<LOQ	0.05				
Limpach 4	0.3		<LOQ	0.04				
Limpach 5	0.2			0.03				
Mentue 2	0.06			0.1	0.1			
Mentue 3	0.1			0.04				
Mentue 4	0.1			0.2				
Mentue 5	0.08			0.06				
Salmsacher Aach 2	0.1	0.6						
Salmsacher Aach 3	0.4	3						
Salmsacher Aach 4	0.3	2						
Salmsacher Aach 6	0.6	1						
Salmsacher Aach 7	0.5	0.2						
Salmsacher Aach 8	0.4	3						
Wyna 2								
Wyna 3	0.1					0.2		
Wyna 4	0.04							
Chräbsbach 1								
Chräbsbach 2	0.08	<LOQ						
Fahrbach 3	1							
Fahrbach 4	0.5							
Unterholzbach 1								
Unterholzbach 2	0.5	2						

[1] uncertainties of the quantification: factor 3 in both directions (see main text). LOD: limit of detection, LOQ: limit of quantification. - if a signal was present in the blank samples, only LOQ was determined by ten times the intensity of the blank value.

APPENDIX D SUPPORTING INFOMRATION TO CHAPTER 5

D.1. Additional Study Site Information

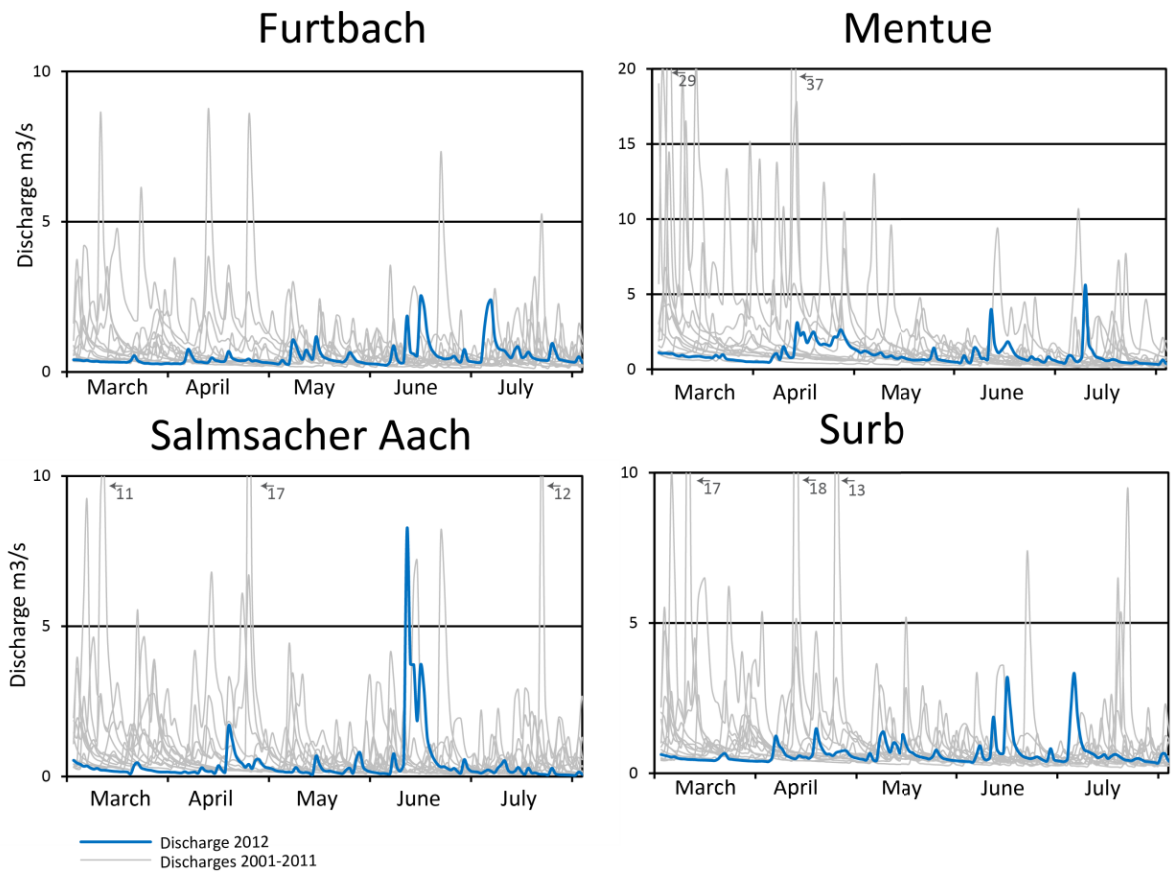


Figure D.1. Comparison of daily discharge from 2001-2012 at four sampling locations. For the river Limpach, no discharge data were available between 2000 and 2011.

D.2 Additional substance information

Table D.1. Screening Type, LOQ, Scenario-Selection

Substance Name	CAS Number[1]	Pesticide Type[2]	Measurement Method	LOQ (ng/L)[3]	Included in Scenario "Swiss Monitoring"	Included in Scenario "Internat. Studies"	Included in Scenario "WFD Pesticides"
2,4-D	94-75-7	H	Target Method	4		1	
Aclonifen	74070-46-5	H	Suspect Method				1
Alachlor	15972-60-8	H	Target Method	70	1	1	1
Amidosulfuron[4]	120923-37-7	H	Target Method	0 2			
Asulam	3337-71-1	H	Target Method	140			
Atrazine	1912-24-9	H	Target Method	8	1	1	1
Beflubutamid	113614-08-7	H	Suspect Method				
Bentazon	25057-89-0	H	Target Method	1			
Bifenox	42576-02-3	H	Suspect Method				1
Bromacil	314-40-9	H	Target Method	30			
Bromoxynil	1689-84-5	H	Target Method	1			
Butafenacil	134605-64-4	H	Suspect Method				
Butralin	33629-47-9	H	Suspect Method				
Carbetamide	16118-49-3	H	Target Method	50			
Carfentrazone-ethyl	128639-02-1	H	Suspect Method				
Chlorbufam	1967-16-4	H	Suspect Method				
Chloridazon	1698-60-8	H	Target Method	2	1	1	
Chlorotoluron	15545-48-9	H/B	Target Method	2	1	1	
Chlorpropham (CIPC)	101-21-3	H	Suspect Method				
Clethodim	99129-21-2	H	Suspect Method				
Clodinafop-propargyl	105512-06-9	H	Suspect Method				
Clomazone	81777-89-1	H	Target Method	2			
Clopyralid	1702-17-6	H	Suspect Method				
Cyanazine	21725-46-2	H	Suspect Method		1		
Cycloxydim[4]	101205-02-1	H	Target Method	2			
Cycluron	2163-69-1	H	Suspect Method				
Desmedipham	13684-56-5	H	Target Method	30			
Dicamba	1918-00-9	H	Target Method	25			
Dichlobenil	1194-65-6	H	not covered				
Dichlorprop	15165-67-0	H	Target Method	2		1	
Diflufenican	83164-33-4	H	LOQ above AA-EQS[5]	20			
Dimefuron[4]	34205-21-5	H	Target Method	0 9			
Dimethachlor	50563-36-5	H	Target Method	1			
Dimethenamid	87674-68-8	H	Target Method	1	1		
Diquat	2764-72-9	H	not covered				
Diuron	330-54-1	H/B	Target Method	2	1	1	1
Ethofumesate	26225-79-6	H	Target Method	3	1	1	
Fenoxapropethyl	71283-80-2	H	Suspect Method				
Flazasulfuron	104040-78-0	H	Suspect Method				
Florasulam	145701-23-1	H	Suspect Method				
Fluazifop-P-butyl	79241-46-6	H	Suspect Method				
Flufenacet	142459-58-3	H	Target Method	3			
Flumioxazin	103361-09-7	H	Suspect Method				
Fluorochloridone	61213-25-0	H	Suspect Method				
Flupyrsulfuron-methyl-sodium	144740-54-5	H	Suspect Method				
Fluroxypyr	69377-81-7	H	Target Method	8			
Foramsulfuron	173159-57-4	H	Target Method	2			
Glufosinate	51276-47-2	H	not covered				
Glyphosat	1071-83-6	H	not covered				
Haloxyfop-(R)-Methylester	72619-32-0	H	Suspect Method				
Iodosulfuron	185119-76-0	H	Suspect Method				
Iodosulfuron-methyl-Natrium	144550-36-7	H	Suspect Method				
Ioxynil	1689-83-4	H	Target Method	1			
Isoproturon	34123-59-6	H/B	Target Method	1	1	1	1
Isoxadifen-ethyl	163520-33-0	H	Suspect Method				
Lenacil	2164-08-1	H	Target Method	9			
Linuron	330-55-2	H	Target Method	9	1	1	
MCPA	94-74-6	H	Target Method	7		1	
MCPB	94-81-5	H	Target Method	7			
Mecoprop-P	16484-77-8	H	Target Method	1		1	
Mefenpyr-Diethyl[4]	135590-91-9	H	Target Method	0 5			
Mepiquatchlorid	15302-91-7	H	not covered				
Mesosulfuron	208465-21-8	H	Suspect Method				
Mesosulfuron-methyl[4]	208465-21-8	H	Target Method	1			
Mesotrione	104206-82-8	H	Target Method	10			
Metamitron	41394-05-2	H	Target Method	25	1	1	
Metazachlor	67129-08-2	H	Target Method	2	1	1	
Metosulam[4]	139528-85-1	H	Target Method	2			
Metoxuron	19937-59-8	H	Suspect Method		1	1	
Metribuzin	21087-64-9	H	Target Method	1		1	

Substance Name	CAS Number[1]	Pesticide Type[2]	Measurement Method	LOQ (ng/L)[3]	Included in Scenario "Swiss Monitoring"	Included in Scenario "Internat. Studies"	Included in Scenario "WFD Pesticides"
Metsulfuron-methyl	74223-64-6	H	Target Method	35			
Monolinuron [4]	1746-81-2	H/B	Target Method	0 4	1		
Napropamide	15299-99-7	H	Target Method	6			
Nicosulfuron	111991-09-4	H	Target Method	1			
Orbencarb	34622-58-7	H	Target Method	10	1		
Oryzalin[4]	19044-88-3	H	Target Method	0 2			
Oxadiargyl	39807-15-3	H	Suspect Method				
Oxyfluorfen	42874-03-3	H	Suspect Method				
Pethoxamid	106700-29-2	H	Target Method	1			
Phenmedipham	13684-63-4	H	Target Method	30			
Pinoxaden	243973-20-8	H	Suspect Method				
Propachlor	1918-16-7	H	Target Method	1	1		
Propaquizafop	111479-05-1	H	Target Method	15			
Propyzamide[4]	23950-58-5	H	Target Method	1	1		
Prosulfocarb	52888-80-9	H	Target Method	10			
Pyraflufen-ethyl	129630-19-9	H	Suspect Method				
Pyridate	55512-33-9	H	Suspect Method				
Quinoclamine	2797-51-5	H	Suspect Method				
Quizalofop-P-ethyl	100646-51-3	H	Suspect Method				
Rimsulfuron	122931-48-0	H	Target Method	1			
Simazine	122-34-9	H	Target Method	10	1	1	1
S-Metolachlor	87392-12-9	H	Target Method	1	1	1	
Sulcotrione	99105-77-8	H	Target Method	3			
Sulfosulfuron	141776-32-1	H	Suspect Method				
Tembotrione[4]	335104-84-2	H	Target Method	0 5			
Tepraloxydim[4]	149979-41-9	H	Target Method	1			
Terbacil[4]	5902-51-2	H	Target Method	0 2			
Terbuthylazine	5915-41-3	H/B	Target Method	9	1	1	
Terbutryn	886-50-0	H/B	Target Method	2	1		1
Thifensulfuron	79277-27-3	H	Suspect Method				
Thifensulfuron-methyl	79277-27-3	H	Target Method	5			
Tribenuron-methyl	101200-48-0	H	Suspect Method				
Triclopyr	55335-06-3	H	Target Method	130			
Trifluralin	1582-09-8	H	Suspect Method				1
Triflusulfuron-methyl[4]	126535-15-7	H	Target Method	0 4			
Tritosulfuron	142469-14-5	H	Target Method	2			
Azaconazole	60207-31-0	F	Suspect Method				
Azoxystrobin	131860-33-8	F	Target Method	1		1	
Benalaxyl-M	98243-83-5	F	Suspect Method				
Benthiavalicarb-isopropyl[4]	177406-68-7	F	Target Method	2			
Biphenyl-2-ol	90-43-7	F/B	Suspect Method				
Boscalid	188425-85-6	F	Target Method	2			
Bupirimate	41483-43-6	F	Suspect Method				
Captan	133-06-2	F/B	Suspect Method				
Carbendazim	10605-21-7	F/B	Target Method	5		1	
Chlorothalonil (TCPN)	1897-45-6	F/B	not covered				
Cyazofamid	120116-88-3	F	Suspect Method				
Cyflufenamid	180409-60-3	F	Suspect Method				
Cymoxanil	57966-95-7	F	Target Method	10		1	
Cyproconazole	94361-06-5	F/B	Target Method	0 5		1	
Cyprodinil	121552-61-2	F	Target Method	5		1	
Dazomet (DMTT)	533-74-4	F/B	Suspect Method				
Dichlofluanid	1085-98-9	F/B	Suspect Method				
Diethofencarb	87130-20-9	F	Suspect Method				
Difenoconazole	119446-68-3	F	Target Method	10			
Dimethomorph	110488-70-5	F	Target Method	2			
Dithianon	3347-22-6	F	not covered				
Dodine	2439-10-3	F	Suspect Method				
Epoxiconazole	133855-98-8	F	Target Method	4			
Famoxadone	131807-57-3	F	Suspect Method				
Fenamidone[4]	161326-34-7	F	Target Method	1			
Fenbuconazole	114369-43-6	F	Suspect Method				
Fenhexamid[4]	126833-17-8	F	Target Method	3			
Fenpropidin	67306-00-7	F	Target Method	0 8			
Fenpropimorph	67564-91-4	F/B	Target Method	4	1		
Fluazinam	79622-59-6	F	Suspect Method				
Fludioxonil	131341-86-1	F	Target Method	7			
Fluoxastrobin[4]	361377-29-9	F	Target Method	3			
Fluquinconazole	136426-54-5	F	Suspect Method				
Flusilazole	85509-19-9	F	Target Method	3			
Folpet	133-07-3	F/B	Suspect Method				

Substance Name	CAS Number[1]	Pesticide Type[2]	Measurement Method	LOQ (ng/L)[3]	Included in Scenario "Swiss Monitoring"	Included in Scenario "Internat. Studies"	Included in Scenario "WFD Pesticides"
Fosetyl	15845-66-6	F	Suspect Method				
Imazalil	35554-44-0	F/B	Suspect Method				
Iprodione	36734-19-7	F	Suspect Method				
Iprovalicarb	140923-17-7	F	Target Method	2			
Kresoxim-methyl	143390-89-0	F	Target Method	4			
Mandipropamid[4]	374726-62-2	F	Target Method	3			
Mepanipyrim[4]	110235-47-7	F	Target Method	6			
Mepronil	55814-41-0	F	Suspect Method				
Metalaxyl-M	70630-17-0	F	Target Method	1	1	1	
Metconazole	125116-23-6	F	Suspect Method				
Metrafenone[4]	220899-03-6	F	Target Method	8			
Myclobutanil	88671-89-0	F	Target Method	1		1	
Oxychinolin	148-24-3	F	Suspect Method				
Penconazole	66246-88-6	F	Target Method	5	1		
Pencycuron[4]	66063-05-6	F	Target Method	3			
Picoxystrobin	117428-22-5	F	Suspect Method				
Prochloraz	67747-09-5	F	LOQ above AA-EQS[5]	200			
Propamocarb	24579-73-5	F	Target Method	0 3			
Propiconazole	60207-90-1	F/B	Target Method	3	1	1	
Prothioconazole	178928-70-6	F	Suspect Method				
Pyraclostrobin	175013-18-0	F	Target Method	5			
Pyrifenox	88283-41-4	F	Suspect Method				
Pyrimethanil	53112-28-0	F	Target Method	1			
Quinoxyfen	124495-18-7	F	Suspect Method				1
Spiroxamine	118134-30-8	F	Target Method	2			
Tebuconazole	107534-96-3	F/B	Target Method	2	1	1	
Thiabendazole	148-79-8	F/B	Suspect Method				
Thiophanate-methyl	23564-05-8	F	Suspect Method				
Thiram (TMTD)	137-26-8	F/B	Suspect Method				
Tolylfluanid	731-27-1	F/B	Suspect Method				
Triadimenol	55219-65-3	F	Suspect Method				
Triazoxide	72459-58-6	F	Suspect Method				
Trifloxystrobin[4]	141517-21-7	F	Target Method	2			
Triflumizole	99387-89-0	F	Suspect Method				
Triforine	26644-46-2	F	Suspect Method				
Vinclozolin	50471-44-8	F	Suspect Method				
Zineb	12122-67-7	F/B	Suspect Method				
Ziram	137-30-4	F/B	Suspect Method				
Zoxamid	156052-68-5	F	Suspect Method				
Abamectin	71751-41-2	I/B	not covered				
Acephate	30560-19-1	I	Suspect Method				
Acetamiprid	135410-20-7	I	Target Method	4			
Aldicarb	116-06-3	I	LOQ above AA-EQS5	200			
Bifenazat	149877-41-8	I	Suspect Method				
Buprofezin	69327-76-0	I	Suspect Method				
Carbofuran[4]	1563-66-2	I	Target Method	10		1	
Chlorfenvinphos[4]	470-90-6	I	Target Method	3		1	1
Chlorpyrifos	2921-88-2	I/B	LOQ above AA-EQS[5]	200	1	1	1
Chlorpyrifos-methyl	5598-13-0	I/B	LOQ above AA-EQS[5]	200			
Clothianidin	210880-92-5	I/B	Target Method	4			
Cyfluthrin	68359-37-5	I/B	not covered				
Cyhexatin	13121-70-5	I	not covered				
Cyromazine	66215-27-8	I/B	Target Method	8			
Diazinon	333-41-5	I/B	Target Method	3	1	1	
Dichlorvos (DDVP)	62-73-7	I/B	Suspect Method			1	1
Diflubenzuron	35367-38-5	I/B	Suspect Method				
Dimethoate	60-51-5	I	Target Method	3	1	1	
Endosulfan	115-29-7	I	not covered				1
Fenitrothion	122-14-5	I/B	Suspect Method				
Fenoxycarb	79127-80-3	I	LOQ above AA-EQS[5]	15			
Fipronil	120068-37-3	I/B	Target Method	0 5			
Flonicamid	158062-67-0	I	Target Method	3			
Imidacloprid	138261-41-3	I/B	Target Method	5		1	
Indoxacarb	173584-44-6	I/B	Suspect Method				
Methidathion	950-37-8	I	Suspect Method				
Methiocarb	2032-65-7	I	Target Method	1			
Methomyl	16752-77-5	I/B	Target Method	10			
Methoxyfenozid	161050-58-4	I	Target Method	3			

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Mevinphos	7786-34-7	I	Suspect Method				
Novaluron	116714-46-6	I	Suspect Method				
Phosalone	2310-17-0	I	Suspect Method				
Piperonyl butoxide	51-03-6	I/B	Target Method	20			
Pirimicarb	23103-98-2	I	Target Method	0 4	1	1	
Pymetrozine	123312-89-0	I	Target Method	5			
Tebufenozide	112410-23-8	I	Target Method	2			
Teflubenzuron	83121-18-0	I	LOQ above AA-EQS[5]	50			
Terbufos	13071-79-9	I	Suspect Method				
Thiacloprid	111988-49-9	I/B	Target Method	4			
Thiamethoxam	153719-23-4	I/B	Target Method	3			
Thiocyclam hydrogen oxalat	31895-21-3	I	Suspect Method				
Triazamat	112143-82-5	I	Suspect Method				
(d)-Limonene	5989-27-5	B	Suspect Method				
(Z,E)-Tetradeca-9,12-dienylacetat	30507-70-1	B	Suspect Method				
alpha , alpha ′, alpha ″-Trimethyl-1,3,5-triazin-1,3,5(2H,4H,6H)-triethanol	25254-50-6	B	Suspect Method				
1,3-Bis(hydroxymethyl)-5,5-dimethylimidazolidin-2,4-dion	6440-58-0	B	Suspect Method				
1,3-Dichlor-5-ethyl-5-methylimidazolidin-2,4-dion	89415-87-2	B	Suspect Method				
1,4-Dichlorbenzol	106-46-7	B	not covered				
2,2'-Dithiobis[N-methylbenzamid]	2527-58-4	B	Suspect Method				
2-Butyl-benzo[d]isothiazol-3-on	4299-07-4	B	Suspect Method				
4-(2-Nitrobutyl)morpholin	2224-44-4	B	Suspect Method				
4,4-Dimethyloxazolidin	51200-87-4	B	Suspect Method				
6-(Phthalimid)peroxyhexansäure	128275-31-0	B	Suspect Method				
Allethrin	584-79-2	B	not covered				
Azamethiphos	35575-96-3	B	Target Method	20			
Benzothiazol-2-thiol	149-30-4	B	Suspect Method				
Benzylbenzoat	120-51-4	B	Suspect Method				
Bethoxazin	163269-30-5	B	not covered				
Bioresmethrin	28434-01-7	B	not covered				
BIT	2634-33-5	B	Suspect Method				
Bromadiolone	28772-56-7	B	Suspect Method				
Bromothalonil	35691-65-7	B	Suspect Method				
Bronopol	52-51-7	B	Target Method	125			
Chloralose	15879-93-3	B	Suspect Method				
Chlorfenapyr	122453-73-0	B	Suspect Method				
Chlorkresol	59-50-7	B	not covered				
Chlorophacinon	3691-35-8	B	Suspect Method				
Chlorophen	120-32-1	B	Suspect Method				
CMI	26172-55-4	B	Target Method	8			
Coumatetralyl	5836-29-3	B	Suspect Method				
DCOIT / Sea-Nine	64359-81-5	B	LOQ above AA-EQS[5]				
DEET	134-62-3	B	Target Method	7	1		
Diazolidinylurea	78491-02-8	B	Suspect Method				
Didecylpolyoxethylammoniumborat	214710-34-6	B	Suspect Method				
Dipyrithion	3696-28-4	B	not covered				
Dodecylguanidin Monohydrochlorid	13590-97-1	B	Suspect Method				
d-Phenothrin	188023-86-1	B	not covered				
d-trans-Tetramethrin	1166-46-7	B	not covered				
Ethyl N-acetyl-N-butyl- beta -alaninat	52304-36-6	B	Suspect Method				
Flocoumafen	90035-08-8	B	Suspect Method				
Hydramethylnon	67485-29-4	B	Suspect Method				
Icaridin	119515-38-7	B	Target Method	2			
Imiprothrin	72963-72-5	B	not covered				
IPBC	55406-53-6	B	LOQ above AA-EQS[5]				
Irgarol / Cybutryne	28159-98-0	B	LOQ above AA-EQS[5]		1		1
Laurylamine dipropylenediamine	2372-82-9	B	Suspect Method				
Malathion	121-75-5	B	Suspect Method				
Methylanthranilat	134-20-3	B	Suspect Method				
Methylendithiocyanat	6317-18-6	B	Suspect Method				
MI	2682-20-4	B	Suspect Method				
N,N′-Methylenbismorpholin	5625-90-1	B	Suspect Method				
Naphthalin	91-20-3	B	not covered				
Natrium 2-biphenylat	132-27-4	B	Suspect Method				
Natriumdimethyldithiocarbamat	128-04-1	B	Suspect Method				

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OIT	26530-20-1	B	Target Method	1			
Oxazolidin	66204-44-2	B	Suspect Method				
Oxazolidine-E	7747-35-5	B	Suspect Method				
p-[(Diiodmethyl)sulfonyl]toluol	20018-09-1	B	Suspect Method				
Phoxim	14816-18-3	B	Suspect Method				
Prallethrin	23031-36-9	B	not covered				
Prometryn	7287-19-6	B	Target Method	2			
Propetamphos	31218-83-4	B	Suspect Method				
Propoxur	114-26-1	B	Suspect Method				
Pyridin-2-thiol-1-oxid, Natriumsalz	3811-73-2	B	Suspect Method				
Soneclosan	3380-30-1	B	Suspect Method				
Sulfochloranthine	118-52-5	B	Suspect Method				
Tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazol-2,5(1H,3H)-dion	5395-50-6	B	Suspect Method				
Triazinetriethanol	4719-04-4	B	Suspect Method				
Triclocarban	101-20-2	B	Suspect Method				
Triclosan	3380-34-5	B	LOQ above AA-EQS[5]				
(S)-5-methyl-5-phenylimidazolidine-2,4-dione	6843-49-8	TP F	Suspect Method				
1-(3,5-dichlorophenyl)-5-isopropyl biuret	63637-88-7	TP F	Suspect Method				
1-(6-fluoro-2-benzothiazol-2-yl)ethanol	782480-72-2	TP F	Suspect Method				
1-(6-fluoro-2-benzothiazolyl)ethylamine	177407-12-4	TP F	Suspect Method				
1-[(6-chloro-3-pyridinyl)methyl]N-nitro-1H-imidazol-2-amine	115086-54-9	TP I	Suspect Method				
1-[2-[2-chloro-4-(4-chloro-phenoxy)-phenyl]-2-1H-[1,2,4]triazol-yl]-ethanol	-	TP F	Suspect Method				
1H-1,2,4-triazol-1-ylacetic acid	4314-22-1	TP F	Suspect Method				
2-(4-chlorophenyl)-2-hydroxy-N-[2-(3-methoxy-4-prop-2-ynyloxy-phenyl)-ethyl]-acetamide	282720-26-7	TP F	Suspect Method				
2,3 dihydro-2,2-diemethyl-7-benzofuranol	1563-38-8	TP I	Suspect Method				
2,4-dimethylphenylformamid	60397-77-5	TP I	Target Method	75			
2,6-Dichlorbenzamid	2008-58-4	TP H	Target Method	5			
2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]benzoic acid	951009-69-1	TP F	Suspect Method				
2_Isopropyl_6_methyl_4_pyrimidinol	2814-20-2	TP I	not covered				
2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid	1418095-02-9	TP F	Suspect Method				
2-amino-4,6-dimethylpyrimidine	767-15-7	TP F	Suspect Method				
2-Amino-4-methoxy-6-methyl-1,3,5 triazin	1668-54-8	TP H	Target Method	2			
2-Aminobenzimidazol	934-32-7	TP F	Target Method	10			
2-aminobenzimidazole	934-32-7	TP F	Suspect Method				
2-dimethylamino-5,6-dimethylpyrimidin-4-ol	40778-16-3	TP I	Suspect Method				
2-isopropyl-6-methyl-4-pyrimidinol	2814-20-2	TP I	Suspect Method				
2-methyl-2-(4-(2-methyl-3-piperidin-1-yl-propyl)-phenyl)-propionic acid	29091-21-2	TP F	Suspect Method				
2-methyl-2-(methylsulfinyl)propanal O-((methylamino)carbonyl)oxime	1646-87-3	TP I	Suspect Method				
3-(2-((1H-1,2,4-triazol-1-yl)methyl)-2-(2,4-dichlorophenyl)-1,3-dioxolan-4-yl)propan-1-ol	104390-58-1	TP F	Suspect Method				
3-(4-cyclopropyl-6-methylpyrimidin-2-ylamino)phenol	694520-26-8	TP F	Suspect Method				
3,5,6-trichloro-2-pyridinol	6515-38-4	TP I	Suspect Method				
3,5-dibromo-4-hydroxybenzoesäure	3337-62-0	TP H	Target Method	2			
3,5-dichloro-2,4-difluoroaniline	83121-15-7	TP I	Suspect Method				
3_5_6_Trichloro_2_pyridinol	6515-38-4	TP I	not covered				
3-hydroxycarbofuran	16655-82-6	TP I	Suspect Method				

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3-Ketocarbofuran	16709-30-1	TP I	Suspect Method				
3-Phenoxybenzoesäure	3739-38-6	TP I	Target Method	1			
3-phenoxybenzoic acid	3739-38-6	TP I	Suspect Method				
4-(2-cyanophenoxy)-6-hydroxypyrimidine	240802-59-9	TP F	Suspect Method				
4-(N'-(3,5-dimethylbenzoyl-N-(1,1-dimethylethyl)hydrazinocarbonyl)phenyl acetic acid	163860-35-3	TP I	Suspect Method				
4-cyclopropyl-6-methyl-pyrimidine-2-ylamine	92238-61-4	TP F	Suspect Method				
4-hydroxy-2,5,6-trichloroisophtalonitrile	28343-61-5	TP F	Suspect Method				
5,6-dimethyl-2-(methylamino)pyrimidin-4-ol	1300-71-6	TP I	Suspect Method				
6-chloronicotinic acid	5326-23-8	TP I	Suspect Method				
aldoxycarb	1646-88-4	TP I	Suspect Method				
AMPA	1066-51-9	TP H	not covered				
Atrazin-2-Hydroxy	2163-68-0	TP H	Target Method	2			
Atrazin-Desethyl	6190-65-4	TP H	Target Method	6			
Atrazin-desethyl-2-hydroxy (=Prometon-Hydroxy-Desi	19988-24-0	TP H	Target Method	3			
Atrazin-Desisopropyl	1007-28-9	TP H	Target Method	30			
azoxystrobin free acid	1185255-09-	TP F	Suspect Method				
Azoxystrobin_free_acid	1185255-09-7	TP F	Target Method	3			
Bifenox Acid	53774-07-5	TP H	Target Method	5			
CGA 353042	915125-06-3	TP I	Suspect Method				
CGA 355190	902493-06-5	TP I	Suspect Method				
Chloridazon-desphenyl	6339-19-1	TP H	Target Method	120			
Chloridazon-methyl-desphenyl	17254-80-7	TP H	Target Method	7			
dimer imidacloprid	-	TP I	Suspect Method				
Dimethachlor-ESA	-	TP H	Target Method	15			
Dimethachlor-OXA	1086384-49-7	TP H	Target Method	15			
Dimethenamid-ESA	205939-58-8	TP H	Target Method	5			
Dimethenamid-OXA	380412-59-9	TP H	Target Method	6			
Diuron-desdimethyl = 1-(3,4-Dichlorophenyl)urea	2327-02-8	TP H	Target Method	7			
Diuron-desmonomethyl (DCPMU) = 1-(3,4-Dichlorophen	3567-62-2	TP H	Target Method	10			
DMSA (=N,N-Dimethylaminosulfanilid)	4710-17-2	TP F	Target Method	7			
DPB	-	TP I	Suspect Method				
DPC (ring-open-guanidin)	-	TP I	Suspect Method				
Ethofumesat-2-keto	26244-33-7	TP H	Target Method	20			
ethylene bisisothiocyanate sulphide	33813-20-6	TP F	Suspect Method				
ethylenethiourea	96-45-7	TP F	Suspect Method				
fenpropimorph carboxylic acid	121098-45-1	TP F	Suspect Method				
fipronil amide	205650-69-7	TP I	Suspect Method				
fipronil sulfide	120067-83-6	TP I	Suspect Method				
fipronil sulfone	120068-36-2	TP I	Suspect Method				
Fipronil_sulfide	120067-83-6	TP I	Target Method	10			
Fipronil_sulfon	120068-36-2	TP I	Target Method	6			
Fluazifop free adid	69335-91-7	TP H	Target Method	1			
Flufenacet-ESA	201668-32-8	TP H	Target Method	3			
Flufenacet-OXA	201668-31-7	TP H	Target Method	7			
HEC-5725-carboxylic acid	-	TP F	Suspect Method				
HEC-5725-des-chlorophenyl	-	TP F	Suspect Method				
Imidacloprid_desnitro	115970-17-7	TP I	Target Method	2			
Imidacloprid_urea	120868-66-8	TP I	Target Method	1			
Imidacloprid-5-hydroxy	-	TP I	Suspect Method				
Imidacloprid-AMCP	-	TP I	Suspect Method				
Imidacloprid-desnitro	115970-17-7	TP I	Suspect Method				

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Imidacloprid-desnitro-olefin	-	TP I	Suspect Method				
Imidacloprid-dihydroxy-guanidin	-	TP I	Suspect Method				
Imidacloprid-formyl-AMCP	-	TP I	Suspect Method				
Imidacloprid-nitrosimine	-	TP I	Suspect Method				
Imidacloprid-nitroso	-	TP I	Suspect Method				
Imidacloprid-urea	120868-66-8	TP I	Suspect Method				
Irgarol-descyclopropyl		TP B	Target Method	5			
Isoproturon-didemethyl = 1-(4-Isoprophenyl)urea	56046-17-4	TP H	Target Method	5			
Isoproturon-monodemethyl = 1-(4-Isoprophenyl)-3-me	34123-57-4	TP H	Target Method	4			
Mesotrion-MNBA	110964-79-9	TP H	Target Method	50			
Met 3 (imidacloprid)	-	TP I	Suspect Method				
Met 4 (imidacloprid) / DPD	-	TP I	Suspect Method				
Metamitron-Desamino	36993-94-9	TP H	Target Method	8			
Metazachlor-ESA	172960-62-2	TP H	Target Method	7			
Metazachlor-OXA		TP H	Target Method	10			
Methiocarb sulfone	2179-25-1	TP I	Suspect Method				
methiocarb sulfoxide	2635-10-1	TP I	Suspect Method				
Methiocarb_sulfoxide	2635-10-1	TP I	Target Method	10			
methomyl oxime	13749-94-5	TP I	Suspect Method				
methyl N-(2{[1-(4-chlorophenyl)-1H-pyrazol-3-yl] oxymethyl} phenyl)carbamate	512165-96-7	TP F	Suspect Method				
Metolachlor-ESA	171118-09-5	TP H	Target Method	2			
Metolachlor-Morpholinon	120375-14-6	TP H	Target Method	1			
Metolachlor-OXA	152019-73-3	TP H	Target Method	9			
Metribuzin-Desamino (DA)	35045-02-4	TP H	Target Method	1			
N-((4-chlorophenyl)-methyl)-N-cyclopentylamide	66063-15-8	TP F	Suspect Method				
N-(1,1-dimethyethyl)-N-(4-acetylebenzoyl)-3,5-dimethylbenzohydrazine	166547-60-0	TP I	Suspect Method				
N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine	8764-37-2	TP F	Suspect Method				
N-(2-chlorothiazol-5-ylmethyl)-N'-nitroguanidine	1155875-72-1	TP I	Suspect Method				
N,N-dimethyl-N'-(4-methylphenyl)-sulfamid	66840-71-9	TP F	Target Method	3			
N-formyl-N'-propyl-N'-2(2,4,6-trichlorophenoxy)ethylurea	-	TP F	Suspect Method				
Nitroguanidin	556-88-7	TP I	Suspect Method				
N-methyl-N-nitroguanidine	4245-76-5	TP I	Suspect Method				
NOA 407475	868542-26-1	TP I	Suspect Method				
omethoate	1113-02-6	TP I	Suspect Method				
phthalic acid	88-99-3	TP F	Suspect Method				
phthalimide	85-41-6	TP F	Suspect Method				
p-methyl-phenethylamine	3261-62-9	TP F	Suspect Method				
Propachlor-ESA	123732-85-4	TP H	Target Method	2			
Propachlor-OXA	70628-36-3	TP H	Target Method	150			
Prothioconazole-desethio	120983-64-4	TP F	Target Method	0 8			
Simazin-2-hydroxy	2599-11-3	TP H	Target Method	2			
Sulcotrion-CMBA	53250-83-2	TP H	Target Method	375			
Acetochlor-, Alachlor-ESA	947601-84-5	TP H	Target Method	1			
Acetochlor-, Alachlor-OXA	184992-44-4	TP H	Target Method	2			
Propazin-, Terbutylazin-2-hydroxy	66753-07-9	TP H	Target Method	4			
Terbutylazin-desethyl	30125-63-4	TP H	Target Method	8			
Terbutylazin-desethyl-2-hydroxy	66753-06-8	TP H	Target Method	3			
tetrahydrophthalamic acid	2028-12-8	TP F	Suspect Method				
tetrahydrophthalimide	85-40-5	TP F	Suspect Method				
thiacloprid sulfonic acid	-	TP I	Suspect Method				
Thiacloprid_amide	676228-91-4	TP I	Target Method	3			
thiacloprid-amide	676228-91-4	TP I	Suspect Method				
Trinexapac-Säure	104273-73-6	TP H	Target Method	200			
TZMU	634192-72-6	TP I	Suspect Method				

[1] - Transformation products that do not have a CAS Number

[2] H: Herbicide, F: Fungicide, I: Insecticide, B: Biocide, X/B: Registered as Plant protection product and biocide

[3] Limit of quantification in surface water matrix

[4] Substance that was confirmed in the suspect screening and later quantified with a reference standard

[5] Limit of Quantification (LOQ) in the target method is higher than the annual average envrionmental quality standard (AA-EQS)

Table D.2. Annual average environmental quality standards (AA-EQS) for all detected substances in the screening

substance name	AA-EQS (µg/L)	reference
2,4-D	0.2	[1]
5-Chloro-2-methyl-4-isothiazolin-3-on CMI)	0.28	[2]
Amidosulfuron	0.87	[3]
Asulam	1.4	[4]
Atrazine	0.6	[5]
Azoxystrobin	0.95	[3]
Bentazone	73	[6]
Benthiavalicarb-isopropyl	20	-
Boscalid	11.6	[1]
Bromoxynil	0.5	[7]
Carbendazime	0.34	[1]
Carbetamide	39.1	[8]
Carbofuran	0.02	[9]
Chlorfenvinphos	0.1	[5]
Chloridazon	10	[10]
Chlortoluron	0.6	[1]
Clomazon	2	[11]
Clothianidin	0.13	[12]
Cycloxydim	464	-
Cyproconazole	18.9	[13]
Cyprodinil	0.16	[8]
Cyromazine	1.9	[4]
Diazinon	0.015	[1]
Dicamba	1.1	[3]
Dichlorprop-p	1	[6]
Diethyltoluamide (DEET)	41	[1]
Difenoconazole	0.76	[14]
Dimefuron	0.008	-
Dimethachlor	0.046	-
Dimethenamide	0.13	[15]
Dimethoate	0.07	[1]
Dimethomorph	5.6	[16]
Diuron	0.02	[1]
Epoxiconazole	0.19	[8]
Ethofumesate	22	[1]
Fenamidone	1.25	[8]
Fenhexamid	10	[3]
Fenpropidin	0.078	[3]
Fenpropimorph	0.016	[3]
Fipronil	0.012	[17]
Fludioxonil	0.1	[3]

substance name	AA-EQS (µg/L)	reference
Flufenacet	0.137	[8]
Fluoxastrobin	0.572	-
Fluroxypyr (free acid)	20	[18]
Flusilazole	1	[13]
Foramsulfuron	0.007	[19]
Imazamox	1.1	[20]
Imidacloprid	0.013	[1]
Ioxynil	0.13	[3]
Iprovalicarb	19	[4]
Isoproturon	0.32	[1]
Kresoxim-methyl	0.63	[21]
Lenacil	0.77	[22]
Linuron	0.26	[1]
Mandipropamid	28	[3]
MCPA	1.34	[1]
MCPB	0.42	[13]
Mecoprop	3.6	[1]
Mefenpyr-diethyl	1.65	-
Mepanipyrim	2.5	[3]
Mesosulfuron-methyl	4	[13]
Mesotrion	0.08	[19]
Metalaxyl-M	120	[3]
Metamitron	4	[1]
Metazachlor	0.02	[23]
Methiocarb	0.01	[24]
Methomyl	0.08	[25]
Methoxyfenozid	0.18	[8]
Metosulam	0.015	-
Metrafenone	2.25	-
Metribuzin	0.12	[8]
Monolinuron	0.15	[8]
Myclobutanil	55	[8]
Napropamid	5.12	[22]
Nicosulfuron	0.035	[26]
Oryzalin	1.54	[27]
Pencycuron	1.34	[28]
Pethoxamide	0.079	-
Piperonyl butoxide	0.24	-
Pirimicarb	0.09	[1]
Propachlor	1.3	[25]
Propamocarb	1030	[1]
Propiconazole	1.8	[3]
Propyzamide	6	-

substance name	AA-EQS (µg/L)	reference
Prosulfocarb	0.6	[3]
Pymetrozin	0.5	[13]
Pyraclostrobin	0.2	[3]
Pyrimethanil	7	[29]
Simazin	1	[5]
S-Metolachlor	0.27	[30]
Spiroxamin	0.06	[13]
Sulcotrion	5	[31]
Tebuconazole	1.2	[1]
Tebufenozid	0.23	[13]
Tembotrione	0.32	-
Tepraloxydim (E-Isomer)	110	[3]
Terbacil	0.011	-
Terbutryn	0.065	[1]
Terbuthylazine	0.22	[1]
Thiacloprid	0.01	[8]
Thiamethoxam	0.14	[8]
Thifensulfuron	0.05	[3]
Trifloxystrobin	0.03	[19]
Triflusulfuron-methyl	0.15	[3]

[1] Swiss Center for Applied Ecotoxicology Eawag/EPFL 2013, [2] Beek et al. 2008, [3] Kontiokari and Mattsoff 2011, [4] RIVM 2014b, [5] EC 2013, [6] IKSR 2009, [7] INERIS 2013a, [8] RIVM 2014c, [9] INERIS 2013b, [10] INERIS 2009b, [11] INERIS 2013c, [12] EC 2007, [13] Steurbaut 2006, [14] Mensink 2008, [15] Scheepmaker 2008, [16] INERIS 2011a, [17] EC 2011b, [18] INERIS 2013d, [19] AGRITOX 2009a, [20] AGRITOX 2009a, [21] Van Leeuwen and Vonk 2008b, [22] INERIS 2009a, [23] INERIS 2011b, [24] Johnson et al. 2009, [25] Crommentuijn et al. 1997, [26] INERIS 2011d, [27] AGRITOX 2009b, [28] Jahnel et al. 2004, [29] Van Leeuwen and Vonk 2008a, ZZV Maribor 2009, INERIS 2011c, - ad hoc values with limited data set, underlying data see **Table D.3**.

Table D.3. Underlying ecotoxicological data for substances with *ad hoc* estimations of EQS (see **Table D.2**).

Substance	CAS- Nr	Ad hoc AA-EQS (µg/l)	Ad hoc MAC-EQS (µg/l)	acute or chronic	Expo-sure time	EC50 (µg/l)	NOEC (µg/l)	Organism class	*Organism name*	Source	Source document
Benthiavalicarb-isopropyl	177406-68-7			acute	96 h	>10000		fish	Oncorhynchus mykiss	Footprint	http://sitem.herts.ac.uk/aeru/footprint/en/index.htm
Benthiavalicarb-isopropyl	177406-68-7			acute	48 h	>10000		crustacean	Daphnia magna	Footprint	http://sitem.herts.ac.uk/aeru/footprint/en/index.htm
Benthiavalicarb-isopropyl	177406-68-7			acute	72 h	>10000		algae	Pseudokirchneriella subcapitata	Footprint	http://sitem.herts.ac.uk/aeru/footprint/en/index.htm
Benthiavalicarb-isopropyl	177406-68-7			chronic	28 d		1000	fish	*Oncorhynchus mykiss*	Footprint	http://sitem.herts.ac.uk/aeru/footprint/en/index.htm
Benthiavalicarb-isopropyl	177406-68-7			chronic	21 d		3000	crustacean	*Daphnia magna*	Footprint	http://sitem.herts.ac.uk/aeru/footprint/en/index.htm
Benthiavalicarb-isopropyl	**177406-68-7**	**20**	**>100**								
Cycloxydim	101205-02-1			acute	96 h	220000		fish	*Oncorhynchus mykiss*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			acute	48 h	>70800		crustacean	*Daphnia magna*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			acute	72 h	38200		cyano bacteria	*Anabaena flos-aquae*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			acute	7 d	81700		plants	*Lemna gibba*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			chronic	28 d		21500	fish	*Oncorhynchus mykiss*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			chronic	21 d		62500	crustacean	*Daphnia magna*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			chronic	96 h		7800	cyano bacteria	*Anabaena flos-aquae*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			acute	96 h	>100000		fish	*Lepomis macrochirus*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			chronic	7 d		4640	plants	*Lemna gibba*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			acute	96 h	44900		algae	*Pseudokirchneriella subcapitata*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			chronic	96 h		12400	algae	*Pseudokirchneriella subcapitata*	DAR Cycloxydim	http://dar efsa.europa.eu/dar-web/provision
Cycloxydim	101205-02-1			acute	24 h	90478		algae	*Scenedesmus vacuolatus*	Junghans et al. 2006	Junghans et al. 2006
Cycloxydim	101205-02-1			chronic	24 h		4752	algae	*Scenedesmus vacuolatus*	Junghans et al. 2006	Junghans et al. 2006
Cycloxydim	**101205-02-1**	**464**	**3820**								
Dimefuron	34205-21-5			acute	96 h	1000000		fish	*Lepomis macrochirus*	Footprint data base	http://sitem.herts.ac.uk/aeru/footprint/en/
Dimefuron	34205-21-5			acute	48 h	575000		invertebrates	*Unbekannte Art*	Footprint data base	http://sitem.herts.ac.uk/aeru/footprint/en/
Dimefuron	34205-21-5			acute	72 h	8		algae	*Unbekannte Art*	Footprint data base	http://sitem.herts.ac.uk/aeru/footprint/en/
Dimefuron	**34205-21-5**	**0.008**	**0.8**								
Dimethachlor	50563-36-5			acute	96 h	5900		fish	*Oncorhynchus mykiss*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	96 h	7600		fish	*Cyprinus carpio*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	96 h	3900		fish	*Oncorhynchus mykiss*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	96 h	8000		fish	*Carassius carassius (Crucian carp)*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	96 h	7400		fish	*Poecilica reticulata (Guppy)*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	96 h	10000		fish	*Ictalurus melas (Black bullhead catfish)*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	96 h	15000		fish	*Lepomis macrochirus (Bluegill sunfish)*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			chronic	28 d		4000	insects	*Chironomus riparius*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			chronic	7 d	66	2.4	plants	*Lemna gibba*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			prolonged	21 d		>850	fish	*Oncorhynchus mykiss*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	48 h	24000		crustacean	*Daphnia magna*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			chronic	22 d		2300	crustacean	*Daphnia magna*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			chronic	21 d		810	crustacean	*Daphnia magna*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	72 h	91		algae	*Desmodesmus subspicatus*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			acute	72 h	12300		cyano bacteria	*Anabaena flos-aquae*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	50563-36-5			chronic	14 d	2.17	0.46	plants	*Lemna gibba*	DAR Dimethachlor	http://dar efsa.europa.eu/dar-web/provision
Dimethachlor	**50563-36-5**	**0.046**	**6.6**								

Table D.3. Continuation.

Substance	CAS- Nr	Ad hoc AA-EQS (µg/l)	Ad hoc MAC-EQS (µg/l)	acute or chronic	Expo-sure time	EC50 (µg/l)	NOEC (µg/l)	Organism class	*Organism name*	Source	Source document
Fluoxastrobin	361377-29-9			acute	72 h	350		algae	*Pseudokirchneriella subcapitata*	Footprint data base	
Fluoxastrobin	361377-29-9			acute	48 h	480		crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Fluoxastrobin	361377-29-9			acute	96 h	60.4		crustacean	*Americamysis bahia*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Fluoxastrobin	361377-29-9			acute	96 h	435		fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Fluoxastrobin	361377-29-9			acute	7 d	>6000		water plants	*Leman gibba*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Fluoxastrobin	361377-29-9			chronic	21 d		180	crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Fluoxastrobin	361377-29-9			chronic	28 d		1200	insects	*Chironomus riparius*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Fluoxastrobin	361377-29-9			chronic	21 d		28.6	fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Fluoxastrobin	**361377-29-9**	**0.572**	**0.604**								
Mefenpyr-diethyl	135590-91-9			acute	96 h	2400		fish	*unbekannte Art der Cyprinidae*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Mefenpyr-diethyl	135590-91-9			acute	48 h	53000		crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Mefenpyr-diethyl	135590-91-9			acute	72 h	1650		algae	*Navicula pelliculosa*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Mefenpyr-diethyl	135590-91-9			acute	7 d	12000		plants	*Lemna gibba*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Mefenpyr-diethyl	**135590-91-9**	**1.65**	**16.5**								
Metosulam	139528-85-1			acute	96 h	>29300		fish	*Oncorhynchus mykiss*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			acute	48 h	>100000		crustacean	*Daphnia magna*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			acute	7 d	0.789	0.15	plants	*Lemna gibba*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			chronic	72 h	75	20	algae	*Scenedemus subspicatus*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			chronic	21 d		24400	fish	*Oncorhynchus mykiss*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			chronic	21 d		2500	crustacean	*Daphnia magna*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			acute	96 h	>53200		fish	*Pimephales promelas*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			acute	96 h	>93200		fish	*M. beryllina*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			acute	48 h	>100200		crustacean	*Paleomonetes pugio*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			acute	48 h	87700		mollusca	*Crassostrea virginica*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	139528-85-1			chronic	72 h	>53600	53600	algae	*Navicula pelliculosa*	DAR Metosulam	http://dar.efsa.europa eu/dar-web/provision
Metosulam	**139528-85-1**	**0.015**	**0.0789**							**DAR Metosulam**	**http://dar.efsa.europa.eu/dar-web/provision**
Metrafenone	220899-03-6			acute	96 h	>820		fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Metrafenone	220899-03-6			acute	48 h	>920		crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Metrafenone	220899-03-6			acute	72 h	710		algae	*Raphidocelis subcapitata*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Metrafenone	220899-03-6			chronic	40 d		1000	insects	*Chironomus riparius*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Metrafenone	220899-03-6			chronic	21 d		225	crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Metrafenone	**220899-03-6**	**2.25**	**7.1**								
Pethoxamid	106700-29-2			acute	96 h	2200		fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Pethoxamid	106700-29-2			chronic	28 d		1100	fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Pethoxamid	106700-29-2			acute	48 h	23000		crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Pethoxamid	106700-29-2			chronic	21 d		2800	crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Pethoxamid	106700-29-2			acute	72 h	9400		cyano bacteria	*Anabaena flos-aquae*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Pethoxamid	106700-29-2			acute	7 d	7.9		plants	*Lemna minor*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Pethoxamid	**106700-29-2**	**0.079**	**0.79**								
Piperonyl-butoxide	51-03-6			acute	96 h	5300		fish	*Cyprinidae*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Piperonyl-butoxide	51-03-6			acute	48 h	510		crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Piperonyl-butoxide	51-03-6			acute	72 h	240		algae	*Unbekannt*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Piperonyl-butoxide	**51-03-6**	**0.24**	**2.4**								

Table D.3. Continuation.

Substance	CAS- Nr	Ad hoc AA-EQS (µg/l)	Ad hoc MAC-EQS (µg/l)	acute or chronic	Expo-sure time	EC50 (µg/l)	NOEC (µg/l)	Organism class	*Organism name*	Source	Source document
Propyzamide	23950-58-5			acute	96 h	>4700		fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Propyzamide	23950-58-5			acute	48 h	>5600		crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Propyzamide	23950-58-5			acute	96 h	3900		crustacean	*Americamysis bahia*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Propyzamide	23950-58-5			chronic	7 d	1400		plants	*Lemna spp.*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Propyzamide	23950-58-5			chronic	72 h	2800		algae	*Raphidocelis subcapitata*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Propyzamide	23950-58-5			chronic	21 d		940	fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Propyzamide	23950-58-5			chronic	21 d		600	crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/
Propyzamide	**23950-58-5**	**6**	**140**								
Tembotrione	335104-84-2			acute	96 h	>100000		fish	*Oncorhynchus mykiss*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			acute	96 h	>100000		fish	*Lepomis macrochirus*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			acute	96 h	>100000		fish	*Cyprinodon variegatus*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	34 d		604	fish	*Pimephales promelas*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			acute	48 h	49800		crustacean	*Daphnia magna*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			acute	96 h	100		crustacean	*Americamysis bahia*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			acute	96 h	14000		mollusca	*Crassostrea virginica*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	21 d		5000	crustacean	*Daphnia magna*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	28 d		2000	insects	*Chironomus riparius*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	96 h	750	200	algae	*Pseudokirchneriella subcapitata*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	72 h	71000	39000	cyano bacteria	*Anabaena flos-aquae*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	72 h	47900	5600	algae	*Navicula pelliculosa*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	72 h	4500	2600	algae	*Skeletonema costatum*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	7 d	8.48	3.2	plants	*Lemna gibba*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	335104-84-2			chronic	7 d	11.4	3.2	plants	*Lemna gibba*	DAR Tembotrione	http://dar.efsa.europa.eu/dar-web/provision
Tembotrione	**335104-84-2**	**0.32**	**0.848**								
Terbacil	5902-51-2			acute	96 h	46200		fish	*Oncorhynchus mykiss*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Terbacil	5902-51-2			acute	48 h	65000		crustacean	*Daphnia magna*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Terbacil	5902-51-2			acute	7 d	140		water plants	*Lemna gibba*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Terbacil	5902-51-2			acute	72 h	42		algae	*Unbekannte Spezies*	Footprint data base	http://sitem.herts ac.uk/aeru/footprint/en/index.htm
Terbacil	5902-51-2			chronic	14 d	140		water plants	*Lemna gibba*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	1000000		crustacean	*Uca pugilator*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	180000		fish	*Cyprinodon variegatus*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	102900		fish	*Lepomis macrochirus*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	112000		fish	*Lepomis macrochirus*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	46200		fish	*Oncorhynchus mykiss*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	79000		fish	*Oncorhynchus mykiss*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	54000		fish	*Oncorhynchus mykiss*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	48 h	4900		mollusca	*Crassostrea virginica*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	120 h	120		cyano bacteria	*Anabaena flosaquae*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	120 h	11		algae	*Navicula pelliculosa*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	120 h	140		algae	*Skeletonema costatum*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	k A.	1000		algae	*Chlorella pyrenoidosa*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	48 h	65000		crustacean	*Daphnia magna*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	5902-51-2			acute	96 h	56400		crustacean	*Palaemonetes vulgaris*	PAN data base	http://www.pesticideinfo org/Search_Ecotoxicity jsp
Terbacil	**5902-51-2**	**0.011**	**1.1**								

D.3. Measured Concentrations

Table D.4. Detection frequency (DF) and maximum concentrations (Max. conc.) of all detected herbicides in the five rivers. Additional information to **Table 5.2**.

Substance Name	LOQ (ng/L)	AA-EQS[2] (ng/L)	Furtbach DF (Max. conc)	Limpach DF (Max. conc)	Mentue DF (Max. conc)	Salms. Aach DF (Max. conc)	Surb DF (Max. conc)	All DF (Max. conc)	No. of rivers with detec-tions	Pesticide Class
S-Metolachlor	1	270	100% (430 ng/L)	100% (530 ng/L)	100% (160 ng/L)	100% (250 ng/L)	100% (960 ng/L)	100% (960 ng/L)		
Mecoprop-P	1	3'600	100% (380 ng/L)	100% (120 ng/L)	100% (38 ng/L)	100% (230 ng/L)	100% (470 ng/L)	100% (470 ng/L)		
Isoproturon[1]	1	320	100% (350 ng/L)	100% (240 ng/L)	100% (41 ng/L)	100% (36 ng/L)	100% (110 ng/L)	100% (350 ng/L)		
Bentazon	1	73'000	100% (30 ng/L)	100% (110 ng/L)	100% (120 ng/L)	44% (5 ng/L)	100% (490 ng/L)	89% (490 ng/L)		
Diuron[1]	2	20	100% (52 ng/L)	78% (10 ng/L)	67% (30 ng/L)	100% (52 ng/L)	100% (22 ng/L)	89% (52 ng/L)		
Ethofumesate	3	22'000	67% (140 ng/L)	89% (260 ng/L)	100% (83 ng/L)	78% (35 ng/L)	100% (290 ng/L)	87% (290 ng/L)		
Chloridazon	2	10'000	78% (52 ng/L)	89% (74 ng/L)	67% (45 ng/L)	89% (230 ng/L)	89% (670 ng/L)	82% (670 ng/L)		
2,4-D	4	200	56% (22 ng/L)	89% (56 ng/L)	100% (78 ng/L)	89% (65 ng/L)	67% (72 ng/L)	80% (78 ng/L)		
MCPA	7	1'340	78% (270 ng/L)	67% (120 ng/L)	67% (30 ng/L)	89% (170 ng/L)	89% (180 ng/L)	78% (270 ng/L)		
Atrazine	8	600	100% (66 ng/L)	100% (39 ng/L)	33% (16 ng/L)	67% (26 ng/L)	56% (345 ng/L)	71% (345 ng/L)	5	
Ioxynil	1	130	78% (6.6 ng/L)	89% (41 ng/L)	67% (25 ng/L)	44% (14 ng/L)	78% (7 ng/L)	71% (41 ng/L)		
Metribuzin	1	120	44% (2.3 ng/L)	100% (120 ng/L)	89% (56 ng/L)	44% (6.5 ng/L)	67% (46 ng/L)	69% (120 ng/L)		
Terbuthylazine[1]	9	220	67% (290 ng/L)	56% (490 ng/L)	56% (270 ng/L)	78% (130 ng/L)	67% (630 ng/L)	64% (630 ng/L)		
Metamitron	25	4'000	67% (750 ng/L)	67% (1100 ng/L)	78% (400 ng/L)	33% (130 ng/L)	67% (1500 ng/L)	62% (1500 ng/L)		
Flufenacet	3	137	56% (80 ng/L)	78% (160 ng/L)	67% (35 ng/L)	11% (31 ng/L)	56% (290 ng/L)	53% (290 ng/L)		
Nicosulfuron	1	35	56% (18 ng/L)	56% (44 ng/L)	33% (31 ng/L)	67% (38 ng/L)	56% (34 ng/L)	53% (44 ng/L)		
Dimethenamid	1	130	11% (1.1 ng/L)	89% (14 ng/L)	22% (7.3 ng/L)	22% (2.2 ng/L)	100% (7.4 ng/L)	49% (14 ng/L)		
Pethoxamid	1	79	67% (80 ng/L)	22% (6.2 ng/L)	56% (55 ng/L)	33% (11 ng/L)	44% (14 ng/L)	44% (80 ng/L)		
Sulcotrione	3	5'000	11% (19 ng/L)	33% (29 ng/L)	22% (42 ng/L)	33% (43 ng/L)	44% (91 ng/L)	29% (91 ng/L)		
Tepraloxydim	1	110'000	11% (1.7 ng/L)	44% (4.9 ng/L)	33% (3.5 ng/L)	11% (1 ng/L)	11% (1 ng/L)	22% (4.9 ng/L)		
Propyzamide	1	6'000	100% (1400 ng/L)	-	100% (330 ng/L)	67% (34 ng/L)	100% (100 ng/L)	73% (1400 ng/L)		
Cycloxydim	2	464'000	100% (160 ng/L)	100% (13 ng/L)	11% (3.7 ng/L)	-	100% (72 ng/L)	62% (160 ng/L)		
Metazachlor	2	20	100% (178 ng/L)	-	100% (76 ng/L)	33% (6.6 ng/L)	33% (5.8 ng/L)	53% (178 ng/L)		
Prosulfocarb	10	600	11% (13 ng/L)	100% (560 ng/L)	44% (540 ng/L)	-	67% (690 ng/L)	44% (690 ng/L)		
Linuron	9	260	100% (270 ng/L)	-	44% (27 ng/L)	22% (23 ng/L)	22% (67 ng/L)	38% (270 ng/L)		
Tembotrione	0.5	320	-	44% (50 ng/L)	56% (8.8 ng/L)	22% (7.7 ng/L)	33% (29 ng/L)	31% (50 ng/L)	4	
Triflusulfuron-methyl	0.4	150	-	56% (2.6 ng/L)	67% (10 ng/L)	11% (0.5 ng/L)	22% (0.8 ng/L)	31% (10 ng/L)		
Dimethachlor	1	46	22% (1.9 ng/L)	100% (5.6 ng/L)	-	11% (1.5 ng/L)	22% (1.2 ng/L)	31% (5.6 ng/L)		
Foramsulfuron	2	7	-	22% (5 ng/L)	11% (30 ng/L)	56% (31 ng/L)	22% (61 ng/L)	22% (61 ng/L)		
Mesosulfuron-methyl	1	4'000	11% (4.3 ng/L)	22% (5.3 ng/L)	44% (3.8 ng/L)	-	33% (8.7 ng/L)	22% (8.7 ng/L)		
Mesotrione	10	80	22% (61 ng/L)	33% (22 ng/L)	-	11% (21 ng/L)	22% (32 ng/L)	18% (61 ng/L)		
Napropamide	6	5'120	89% (78 ng/L)	-	100% (49 ng/L)	-	11% (8 ng/L)	40% (78 ng/L)		
Terbutryn[1]	2	65	100% (34 ng/L)	-	-	22% (2.2 ng/L)	78% (3.7 ng/L)	40% (34 ng/L)		
Lenacil	9	770	-	78% (96 ng/L)	56% (29 ng/L)	-	33% (140 ng/L)	33% (140 ng/L)		
Propachlor	1	1'300	100% (220 ng/L)	11% (6.5 ng/L)	44% (22 ng/L)	-	-	31% (220 ng/L)		
Monolinuron [1]	0.4	150	-	44% (2.7 ng/L)	22% (7.5 ng/L)	-	78% (2.6 ng/L)	29% (7.5 ng/L)		
Dicamba	25	1'100	-	-	78% (1400 ng/L)	11% (110 ng/L)	11% (150 ng/L)	20% (1400 ng/L)	3	
Oryzalin	0.2	1'540	33% (4.8 ng/L)	-	-	56% (1.7 ng/L)	11% (0.2 ng/L)	20% (4.8 ng/L)		
Amidosulfuron	0.2	870	-	22% (1.7 ng/L)	44% (2.7 ng/L)	-	33% (0.8 ng/L)	20% (2.7 ng/L)		
MCPB	7	420	-	33% (290 ng/L)	-	22% (51 ng/L)	22% (26 ng/L)	16% (290 ng/L)		
Imazamox	4	1'100	-	-	22% (8.9 ng/L)	22% (4.7 ng/L)	33% (36 ng/L)	16% (36 ng/L)		
Bromoxynil	1	500	-	11% (23 ng/L)	33% (4.1 ng/L)	-	22% (4 ng/L)	13% (23 ng/L)		
Clomazone	2	2'000	-	11% (2.7 ng/L)	22% (3.5 ng/L)	-	22% (2.6 ng/L)	11% (3.5 ng/L)		
Chlorotoluron[1]	2	600	-	89% (9 ng/L)	67% (20 ng/L)	-	-	31% (20 ng/L)		
Simazine	10	1'000	-	-	33% (28 ng/L)	67% (29 ng/L)	-	20% (29 ng/L)		
Terbacil	0.2	11	33% (1.8 ng/L)	-	-	56% (2.2 ng/L)	-	18% (2.2 ng/L)	2	
Fluroxypyr (free acid)	8	20'000	-	22% (32 ng/L)	-	-	22% (49 ng/L)	9% (49 ng/L)		
Mefenpyr-diethyl	0.5	1'650	-	33% (7.9 ng/L)	11% (12 ng/L)	-	-	9% (12 ng/L)		
Carbetamide	50	39'100	-	-	11% (41 ng/L)	11% (230 ng/L)	-	4% (230 ng/L)		
Dimefuron	0.9	8	-	-	100% (1.8 ng/L)	-	-	20% (1.8 ng/L)		
Metosulam	2	15	-	-	-	-	22% (21 ng/L)	4% (21 ng/L)		
Asulam	140	1'400	-	-	11% (140 ng/L)	-	-	2% (140 ng/L)	1	
Dichlorprop	2	1'000	-	-	-	11% (16 ng/L)	-	2% (16 ng/L)		
Thifensulfuron	5	50	-	-	11% (4.2 ng/L)	-	-	2% (4.2 ng/L)		

Herbicides

[1] also registered as biocide, [2] annual average environmental quality standard: see **Table D.2**.

Table D.5. Detection frequency (DF) and maximum concentrations (Max. conc.) of all detected fungicides, insecticides and biocides in the five rivers. Additional information to **Table 5.2**.

Substance Name	LOQ (ng/L)	AA-EQS[2] (ng/L)	Furtbach DF (Max. conc)	Limpach DF (Max. conc)	Mentue DF (Max. conc)	Salms. Aach DF (Max. conc)	Surb DF (Max. conc)	All DF (Max. conc)	No. of rivers with detec-tions	Pesticide Class
Azoxystrobin	1	950	100% (120 ng/L)	100% (82 ng/L)	100% (37 ng/L)	89% (14 ng/L)	100% (45 ng/L)	98% (120 ng/L)		
Cyproconazole[1]	0.5	18'900	89% (26 ng/L)	89% (98 ng/L)	67% (47 ng/L)	67% (9.9 ng/L)	100% (76 ng/L)	82% (98 ng/L)		
Carbendazim[1]	5	340	100% (43 ng/L)	33% (33 ng/L)	89% (16 ng/L)	89% (40 ng/L)	100% (65 ng/L)	82% (65 ng/L)		
Tebuconazole[1]	2	1'200	78% (27 ng/L)	100% (31 ng/L)	89% (15 ng/L)	11% (2.6 ng/L)	100% (86 ng/L)	76% (86 ng/L)	5	
Dimethomorph	2	5'600	100% (54 ng/L)	44% (8.5 ng/L)	100% (60 ng/L)	89% (56 ng/L)	44% (61 ng/L)	76% (61 ng/L)		
Propamocarb	0.3	1'030'000	100% (150 ng/L)	56% (110 ng/L)	100% (160 ng/L)	33% (1.1 ng/L)	78% (41 ng/L)	73% (160 ng/L)		
Metalaxyl-M	1	120'000	100% (113 ng/L)	44% (27 ng/L)	44% (38 ng/L)	67% (380 ng/L)	100% (26 ng/L)	71% (380 ng/L)		
Propiconazole[1]	3	1'800	111% (23 ng/L)	178% (20 ng/L)	178% (10 ng/L)	-	178% (65 ng/L)	129% (65 ng/L)		
Fenamidone	1	1'250	100% (18 ng/L)	44% (9.4 ng/L)	67% (10 ng/L)	-	22% (18 ng/L)	47% (18 ng/L)		
Pencycuron	3	1'340	11% (3.6 ng/L)	100% (120 ng/L)	89% (160 ng/L)	-	22% (10 ng/L)	44% (160 ng/L)	4	
Cyprodinil	5	160	56% (17 ng/L)	44% (36 ng/L)	-	44% (27 ng/L)	44% (330 ng/L)	38% (330 ng/L)		
Boscalid	2	11'600	56% (12 ng/L)	11% (0.9 ng/L)	-	11% (1 ng/L)	100% (55 ng/L)	36% (55 ng/L)		
Epoxiconazole	4	190	11% (4.4 ng/L)	89% (64 ng/L)	22% (11 ng/L)	-	44% (42 ng/L)	33% (64 ng/L)		
Pyrimethanil	1	7'000	100% (89 ng/L)	-	-	56% (11 ng/L)	11% (0.9 ng/L)	33% (89 ng/L)		
Mandipropamid	3	28'000	100% (24 ng/L)	44% (8 ng/L)	11% (1.5 ng/L)	-	-	31% (24 ng/L)		
Fenhexamid	3	10'000	78% (23 ng/L)	-	-	22% (3.5 ng/L)	44% (20 ng/L)	29% (23 ng/L)	3	
Spiroxamine	2	60	-	78% (16 ng/L)	22% (3.8 ng/L)	-	44% (4.7 ng/L)	29% (16 ng/L)		
Fenpropidin	0.8	78	22% (2.4 ng/L)	11% (1.3 ng/L)	-	-	78% (18 ng/L)	22% (18 ng/L)		
Trifloxystrobin	2	30	-	-	67% (12 ng/L)	11% (0.8 ng/L)	11% (1.9 ng/L)	18% (12 ng/L)		
Myclobutanil	1.0	55'000	-	11% (2.1 ng/L)	-	89% (15 ng/L)	-	20% (15 ng/L)		
Fludioxonil	7	100	44% (25 ng/L)	-	22% (10 ng/L)	-	-	13% (25 ng/L)		
Pyraclostrobin	5	200	-	44% (61 ng/L)	-	-	11% (5.3 ng/L)	11% (61 ng/L)	2	
Fluoxastrobin	3	572	-	11% (1.3 ng/L)	44% (11 ng/L)	-	-	11% (11 ng/L)		
Fenpropimorph[1]	4	16	-	22% (15 ng/L)	-	-	22% (5.4 ng/L)	9% (15 ng/L)		
Mepanipyrim	6	2'500	11% (7.8 ng/L)	-	-	-	11% (1.4 ng/L)	4% (7.8 ng/L)		
Benthiavalicarb-isopropyl	2	20'000	-	-	78% (22 ng/L)	-	-	16% (22 ng/L)		
Flusilazole	3	1'000	-	-	-	-	33% (32 ng/L)	7% (32 ng/L)		
Iprovalicarb	2	19'000	-	-	-	-	33% (14 ng/L)	7% (14 ng/L)	1	
Difenoconazole	10	760	-	-	-	-	22% (30 ng/L)	4% (30 ng/L)		
Metrafenone	8	2'250	-	22% (29 ng/L)	-	-	-	4% (29 ng/L)		
Kresoxim-methyl	4	630	-	11% (15 ng/L)	-	-	-	2% (15 ng/L)		
Pirimicarb	0.4	90	100% (48 ng/L)	56% (3 ng/L)	78% (6.5 ng/L)	89% (9.9 ng/L)	100% (11 ng/L)	84% (48 ng/L)		
Fipronil[1 2]	0.5	12	100% (3.8 ng/L)	56% (1.8 ng/L)	67% (1.4 ng/L)	11% (0.7 ng/L)	100% (14 ng/L)	67% (14 ng/L)		
Diazinon[1 2]	3	15	67% (43 ng/L)	78% (29 ng/L)	22% (8.4 ng/L)	67% (9 ng/L)	78% (20 ng/L)	62% (43 ng/L)	5	
Thiamethoxam[1]	3	140	100% (47 ng/L)	11% (2.2 ng/L)	44% (8.2 ng/L)	100% (17 ng/L)	44% (4.5 ng/L)	60% (47 ng/L)		
Dimethoate	3	70	56% (21 ng/L)	11% (3.8 ng/L)	11% (14 ng/L)	44% (13 ng/L)	11% (3.6 ng/L)	27% (21 ng/L)		
Thiacloprid	4	10	-	67% (50 ng/L)	44% (8.9 ng/L)	11% (3.4 ng/L)	56% (65 ng/L)	36% (65 ng/L)		
Pymetrozine	5	500	56% (54 ng/L)	22% (15 ng/L)	33% (35 ng/L)	-	22% (25 ng/L)	27% (54 ng/L)	4	
Carbofuran	10	20	33% (29 ng/L)	11% (18 ng/L)	22% (45 ng/L)	44% (32 ng/L)	-	22% (45 ng/L)		
Imidacloprid	5	13	78% (9.2 ng/L)	-	33% (7.8 ng/L)	-	44% (5.9 ng/L)	31% (9.2 ng/L)	3	
Tebufenozide	2	230	78% (29 ng/L)	-	-	67% (6.3 ng/L)	-	29% (29 ng/L)	2	
Piperonyl butoxide	20	240	-	-	11% (11 ng/L)	78% (220 ng/L)	-	18% (220 ng/L)		
Methoxyfenozid	3	180	-	-	-	89% (7 ng/L)	-	18% (7 ng/L)		
Methiocarb	1.0	10	-	22% (1.4 ng/L)	-	-	-	4% (1.4 ng/L)		
Methomyl	10	80	11% (11 ng/L)	-	-	-	-	2% (11 ng/L)	1	
Cyromazine[1]	8	1'900	-	-	-	11% (10 ng/L)	-	2% (10 ng/L)		
Chlorfenvinphos	3	100	11% (4.6 ng/L)	-	-	-	-	2% (4.6 ng/L)		
Clothianidin[1]	4	130	11% (4.4 ng/L)	-	-	-	-	2% (4.4 ng/L)		
Diethyltoluamide (DEET)	7	41'000	100% (160 ng/L)	89% (71 ng/L)	100% (520 ng/L)	56% (62 ng/L)	100% (80 ng/L)	89% (520 ng/L)	5	
5-Chloro-2-methyl-4-isothiazolin -3-on (CMI)	8	280	-	-	22% (510 ng/L)	22% (57 ng/L)	-	9% (510 ng/L)	2	Biocide

Fungicides

Insecticides

[1] also registered as biocide, [2] annual average environmental quality standard: see **Table D.2**.

Table D.6. Detection frequency (DF) and maximum concentrations (Max. conc.) of all detected transformation products (TPs) in the five investigated rivers

Substance Name	LOQ (ng/L)	Furtbach DF (Max. conc)	Limpach DF (Max. conc)	Mentue DF (Max. conc)	Salms.Aach DF (Max. conc)	Surb DF (Max. conc)	All DF (Max. conc)	No. of rivers with detec-tions	TP Class
Metazachlor-ESA	7	100% (520 ng/L)	100% (78 ng/L)	100% (51 ng/L)	100% (64 ng/L)	100% (59 ng/L)	100% (520 ng/L)		
Metolachlor-ESA	2	100% (220 ng/L)	100% (310 ng/L)	100% (89 ng/L)	100% (230 ng/L)	100% (260 ng/L)	100% (310 ng/L)		
Chloridazon-methyl-desphenyl	7	100% (210 ng/L)	100% (100 ng/L)	100% (150 ng/L)	100% (140 ng/L)	100% (90 ng/L)	100% (210 ng/L)		
2,6-Dichlorbenzamid	5	100% (39 ng/L)	100% (22 ng/L)	100% (17 ng/L)	100% (48 ng/L)	100% (21 ng/L)	100% (48 ng/L)		
Atrazin-Desethyl	6	100% (28 ng/L)	100% (27 ng/L)	100% (21 ng/L)	100% (20 ng/L)	100% (34 ng/L)	100% (34 ng/L)		
Atrazin-2-Hydroxy	2	100% (15 ng/L)	100% (15 ng/L)	100% (10 ng/L)	100% (18 ng/L)	100% (28 ng/L)	100% (28 ng/L)		
Chloridazon-desphenyl	120	89% (2200 ng/L)	100% (200 ng/L)	100% (310 ng/L)	100% (240 ng/L)	100% (250 ng/L)	98% (2200 ng/L)		
Atrazin-desethyl-2-hydroxy	3	100% (14 ng/L)	89% (8 ng/L)	78% (27 ng/L)	100% (7.4 ng/L)	89% (10 ng/L)	91% (27 ng/L)		
Metamitron-Desamino	8	67% (273 ng/L)	100% (680 ng/L)	89% (260 ng/L)	67% (96 ng/L)	100% (480 ng/L)	84% (680 ng/L)	**5**	
Metolachlor-OXA	9	100% (99 ng/L)	78% (110 ng/L)	44% (32 ng/L)	100% (95 ng/L)	89% (130 ng/L)	82% (130 ng/L)		
Terbutylazin-desethyl-2-hydroxy	3	100% (20 ng/L)	56% (5.7 ng/L)	67% (6.9 ng/L)	100% (21 ng/L)	89% (12 ng/L)	82% (21 ng/L)		
Propazin-/Terbutylazin-2-hydroxy	4	100% (45 ng/L)	67% (7.4 ng/L)	78% (9.5 ng/L)	89% (10 ng/L)	67% (12 ng/L)	80% (45 ng/L)		
Flufenacet-ESA	3	44% (14 ng/L)	100% (30 ng/L)	89% (38 ng/L)	44% (7.9 ng/L)	33% (17 ng/L)	62% (38 ng/L)		
Fluazifop (free acid)	1	67% (19 ng/L)	67% (48 ng/L)	56% (12 ng/L)	11% (4.1 ng/L)	67% (47 ng/L)	53% (48 ng/L)		
Terbutylazin-desethyl	8	56% (38 ng/L)	44% (35 ng/L)	44% (35 ng/L)	44% (54 ng/L)	56% (41 ng/L)	49% (54 ng/L)		
Acetochlor-/Alachlor-OXA	2	33% (42 ng/L)	33% (47 ng/L)	11% (12 ng/L)	44% (54 ng/L)	44% (39 ng/L)	33% (54 ng/L)		
Bifenox-acid	5	67% (11 ng/L)	11% (3 ng/L)	11% (7.4 ng/L)	22% (13 ng/L)	11% (5.7 ng/L)	24% (13 ng/L)		
Metribuzin-Desamino	1	-	100% (26 ng/L)	67% (19 ng/L)	22% (2.6 ng/L)	33% (15 ng/L)	44% (26 ng/L)		
3,5-dibromo-4-hydroxybenzoe acid	2	11% (10 ng/L)	-	78% (15 ng/L)	11% (2.1 ng/L)	67% (5.6 ng/L)	33% (15 ng/L)	**4**	
Metolachlor-Morpholinon	1	33% (10 ng/L)	33% (6.5 ng/L)	-	22% (7 ng/L)	78% (8 ng/L)	33% (10 ng/L)		
Acetochlor-/Alachlor-ESA	1	22% (2.5 ng/L)	78% (4.2 ng/L)	-	-	11% (2.3 ng/L)	22% (4.2 ng/L)	**3**	
Isoproturon-monodemethyl	4	11% (14 ng/L)	11% (4.7 ng/L)	-	-	11% (6 ng/L)	7% (14 ng/L)		
Propachlor-ESA	2	100% (270 ng/L)	-	33% (20 ng/L)	-	-	27% (270 ng/L)		
Simazin-2-hydroxy	2	33% (2.2 ng/L)	-	-	100% (5.9 ng/L)	-	27% (5.9 ng/L)		
Dimethenamid-ESA	5	-	56% (13 ng/L)	-	-	33% (10 ng/L)	18% (13 ng/L)	**2**	
Diuron-desmonomethyl (DCPMU)	10	-	-	11% (11 ng/L)	56% (22 ng/L)	-	13% (22 ng/L)		
Dimethachlor-ESA	15	-	22% (19 ng/L)	33% (24 ng/L)	-	-	11% (24 ng/L)		
Metazachlor-OXA	10	100% (170 ng/L)	-	-	-	-	20% (170 ng/L)		
Trinexapac acid	200	-	-	-	-	22% (270 ng/L)	4% (270 ng/L)	**1**	
Propachlor-OXA	150	11% (170 ng/L)	-	-	-	-	2% (170 ng/L)		
Dimethenamid-OXA	6	-	11% (8.9 ng/L)	-	-	-	2% (8.9 ng/L)		
Azoxystrobin free_acid	3	100% (64 ng/L)	100% (15 ng/L)	100% (12 ng/L)	89% (12 ng/L)	100% (140 ng/L)	98% (140 ng/L)		
Prothioconazole-desethio	0.8	11% (1 ng/L)	100% (32 ng/L)	67% (13 ng/L)	56% (1.7 ng/L)	89% (4.4 ng/L)	64% (32 ng/L)	**5**	
DMSA (=N,N-Dimethylaminosulfanilid)	7	78% (19 ng/L)	11% (8.6 ng/L)	100% (140 ng/L)	22% (43 ng/L)	33% (28 ng/L)	49% (140 ng/L)		
Thiacloprid_amide	3	-	44% (7.5 ng/L)	22% (3.2 ng/L)	11% (3 ng/L)	56% (6.3 ng/L)	27% (7.5 ng/L)	**4**	
3-Phenoxybenzoesäure	1	44% (6.9 ng/L)	-	-	-	44% (2.9 ng/L)	18% (6.9 ng/L)	**2**	
Imidacloprid_desnitro	2	78% (19 ng/L)	-	-	-	-	16% (19 ng/L)	**1**	
2,4-dimethylphenylformamid	75	-	-	-	11% (80 ng/L)	-	2% (80 ng/L)		
Irgarol-descyclopropyl	5	22% (5.5 ng/L)	-	-	-	-	4% (5.5 ng/L)	**1**	

D.4. Risk Assessment and Scenario Analysis

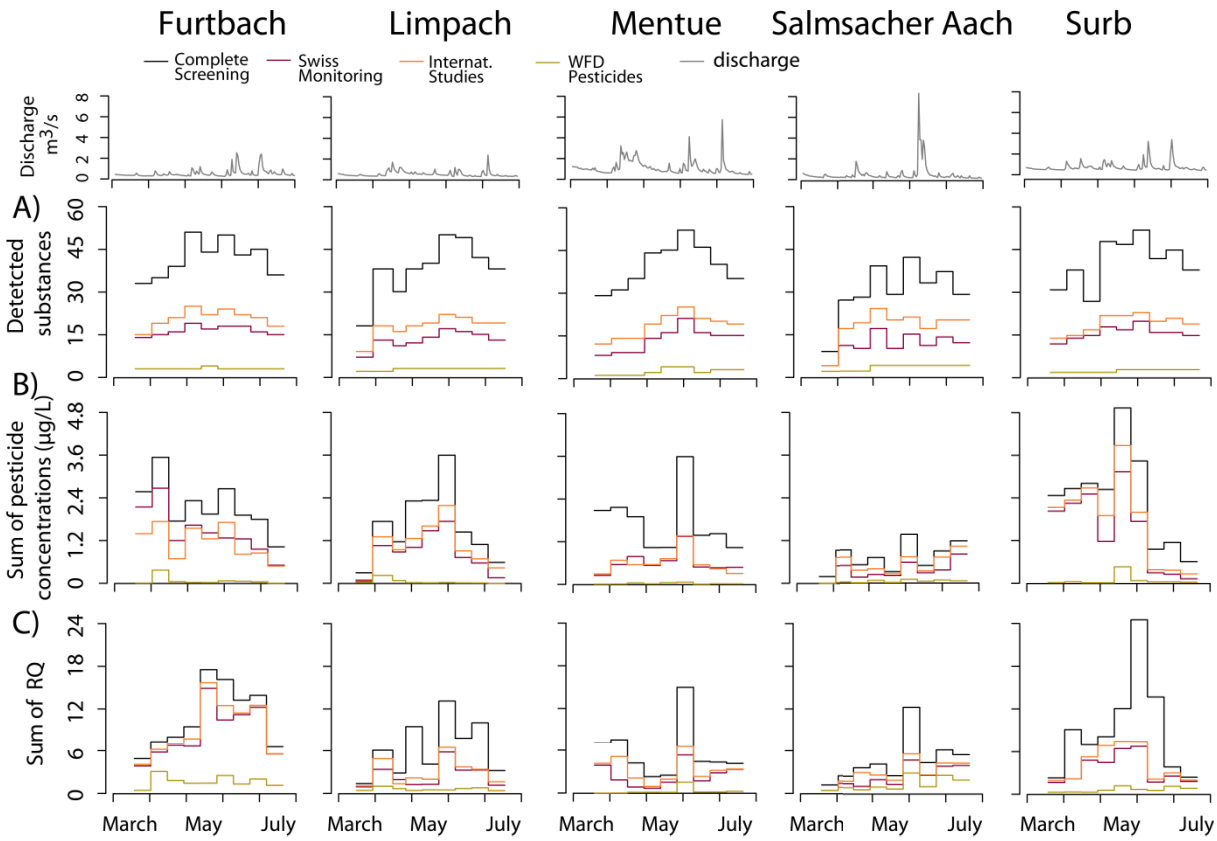

Figure D.2. Number of detected substances (A), sum of pesticide concentrations (µg/L) (B) and sum of risk quotients (RQ, worst case estimation) (C) in the five rivers when considering a complete screening compared to a subset of substances (three scenarios).

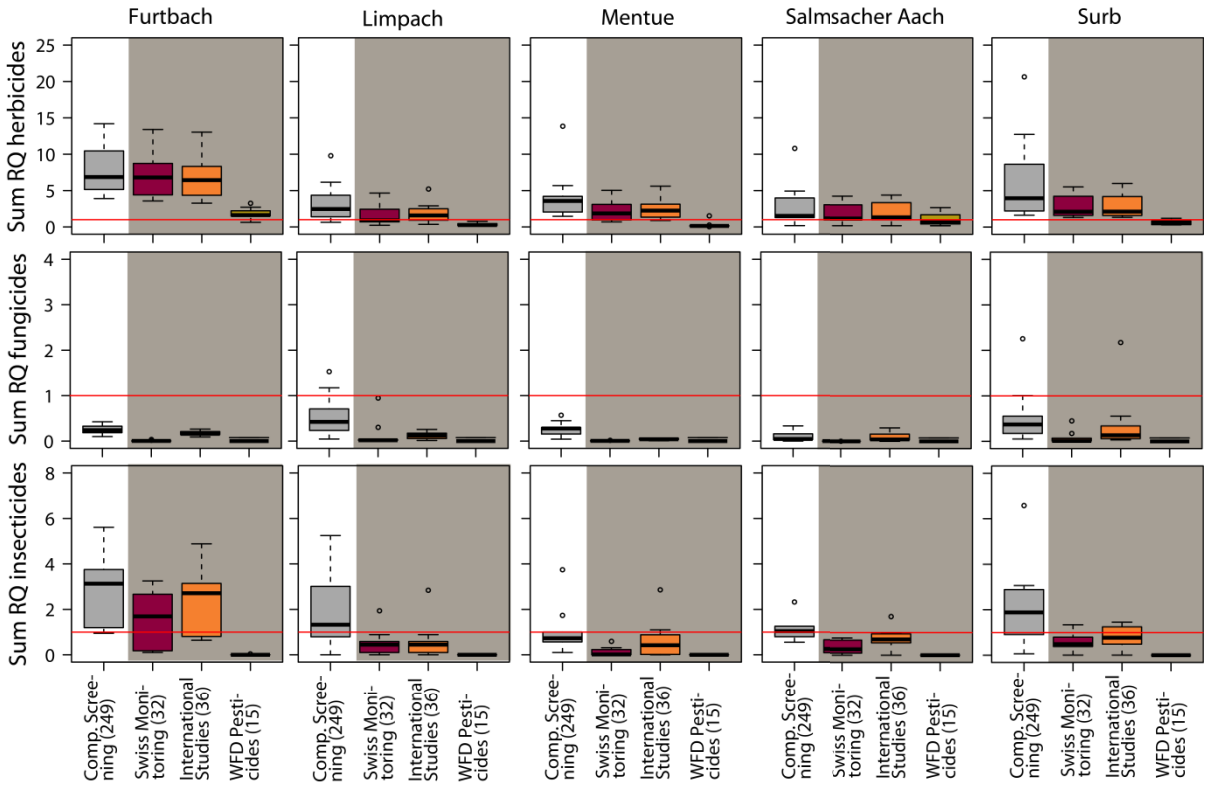

Figure D.3. Sum of risk quotients (RQ) for herbicides, fungicides and insecticides measured in the five rivers with the complete screening (left plot) and calculated using three scenarios for which only a subset of substances were selected (gray shaded scenarios). Number in brackets correspond to the number of investigated substances in the scenarios

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