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***Pesticides in a tropical Costa Rican stream catchment: from
monitoring and risk assessment to the identification of possible
mitigation options***

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presented by

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This thesis is dedicated to my father

Dr. med. Heinrich Maria Weiss

(1951 – 2016)

-He will never be forgotten-

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Summary

Pesticides are applied at high rates around the globe to protect crops from pest infestation. As a consequence, a broad spectrum of pesticides is found in surface waters. Together with their transformation products (TP), they can elicit adverse effects on aquatic organisms. Threats due to pesticide contamination to aquatic organisms is an especially concerning issue in tropical regions in Low- and Middle-Income Countries. These countries represent the most intensively used agricultural areas of the world and heavy rainfalls are expected to favor the transport of pesticides from the fields into surface water. Additionally, owing to the low level of economic development, environmental monitoring, risk assessment and implementation of risk mitigation strategies receive little attention. One country illustrating this situation is Costa Rica. This thesis set out to 1) monitor agricultural-driven pesticide pollution in tropical Costa Rican streams in order to describe the occurrence, concentrations and distribution of pesticides and pesticide transformation products (PPTP); 2) assess the risks by these PPTP to aquatic biota; and 3) identify relevant pathways of PPTP-transport from the field into the streams as a basis to propose mitigation options to reduce pesticide inputs.

1) The Tapezco river catchment was selected as study site. It is an area with intensive agriculture, characterized by horticultural fields cultivated partially on steep slopes, to grow a variety of different crops. This catchment is located in the central highland plateau in the province of Alajuela and an essential production area for vegetables. Five sites were sampled over a period of two and a half months in 2015 and eight were sampled over a period of four and a half months in 2016. For obtaining PPTP concentration data, three passive samplers were employed. Two were well-known sorbent-based passive samplers, namely styrene-divinylbenzene reverse phase sulfonated (SDB) disks and polydimethylsiloxane (PDMS) sheets, yielding biweekly time-integrated averaged concentrations. The third passive sampler was a water level proportional sampling system (WLPSS), yielding biweekly water level-weighted concentrations. After collecting the samplers in the fields, they were extracted in the laboratory. The SDB disk and the WLPSS water sample extracts were analyzed via high-resolution liquid chromatography tandem mass spectrometry and screened for 258 polar and semi-polar PPTP, including herbicides, insecticides, fungicides and some of their TP. The PDMS sheet extracts were analyzed for 18 non-polar insecticides via atmospheric pressure chemical ionization gas chromatography tandem mass spectrometry. With the SDB disks and the WLPSS, a broad PPTP spectrum was detected throughout the catchment. Despite the different sampling principles, the majority of the PPTP were detected with both sampler types, chemicals that had the highest median water concentrations were identified as such with both the SDB disks and the WLPSS. However, for seven of the pesticides, the concentrations determined with the WLPSS exceeded those of the SDB disks. This finding points to the WLPSS to collect pesticide peaks during heavy rainfall events, linked with water level rises, in a more pronounced fashion than the SDB disks. However, the majority of the WLPSS samplers employed did not sample in the optimal range, i.e. they were completely filled prior to sample collection, calling for a need to further optimize sampler operation. The PDMS approach allowed detection of additional, non-polar pesticides. Based on the reliability and the high share of retrieved samples, chemical concentrations determined from extracts of the SDB disks and PDMS sheets were further processed as measured environmental concentrations (MEC) for a risk assessment.

2) Two MEC-based approaches were used for risk assessment, allowing for identification of risks for both single PPTP as well as PPTP mixtures. The first approach compares the MEC to chemical-specific Environmental Quality Standards (EQS) for primary producers, invertebrates and vertebrates while the second uses the MEC to calculate so-called Toxic Units (TU), focusing on the chemicals' toxicity to invertebrates. Three indices that rely on macroinvertebrate diversity and abundance in the streams were additionally applied to

Summary

investigate the state of water quality: the Species at Risk (SPEAR_{pesticide}), the Costa Rican Biological Monitoring Working Party (BMWP-CR) and the Ephemeroptera, Plecoptera and Tricoptera (EPT)-taxa richness indices. With the EQS and the TU approaches, the quality of the water was indicated as poor at all sites and sampling periods and only few of the PPTP explained the overall risk. Invertebrates were the most affected, without any time window to recover from pesticide stress. The SPEAR_{pesticide}, BMWP-CR and the EPT indices indicated that, despite the continuous pesticide pollution stress, the water quality appeared to improve at the most downstream sites, which maybe due to a large river stretch upstream with a high share of natural forest.

3) To identify potential risk mitigation measures, an analysis of the most important pathways for PPTP transport from the fields into the streams was performed within the Tapezco river catchment. Analysis focused on the pesticides that dominated the aquatic biota health risks in addition to three of their TP and three pesticides with high application rates. The first pathway encompassed direct inputs via handling at four headwater sub-catchments, identified by concentration peaks unrelated to water level increases. Such direct inputs were indicated for several pesticides. The second type of pesticide transport was related to surface run-off, leading to concentrations being positively correlated with water level increases and potentially influenced by hydrological and topographical variables. Linear regression modelling with data from all eight sampling sites revealed that for a selection of insecticides (particularly for acephate, cyhalothrin, and thiamethoxam) the flux increased at sites with fields with high average slopes while for other PPTP (2,6 dichlorbenzamide, boscalid, carbofuran, diazinon, diuron TP, linuron and prometryn + terbutryn) flux decreased in areas with a high share of forested buffer zones. These trends, however, did not hold true for all pesticides. Different input patterns were, e.g. observed for the fungicide carbendazim. The third pathway of PPTP transport considered was via exfiltration of contaminated groundwater through the river bank, which was likely to lead to constant inputs, showing an inverse relationship with water levels due to dilution. Such inputs were principally possible for several PPTP based on their detection in groundwater samples, even though their contribution would be expected to be much lower, compared to the other pathways. Though the data set was limited and more research would be needed to more precisely delineate the input pathways, several mitigation strategies could be proposed: offering workshops about improved pesticide handling; avoid cultivation of those crops that demand high use of herbicides and insecticides on fields with steep slopes; and installation of stream buffer zones with natural forest.

Zusammenfassung

Pestizide werden weltweit in hohen Mengen ausgebracht, um Nutzpflanzen vor Schädlingsbefall zu schützen. Infolgedessen gelangt ein breites Spektrum an Pestiziden in Oberflächengewässer, wo sie zusammen mit ihren Transformationsprodukten (TP) schädliche Auswirkungen auf Wasserorganismen ausüben können. Die Bedrohung aquatischer Organismen durch Pestizide ist besonders in tropischen Gebieten in Schwellen- und Entwicklungsländern ein besorgniserregendes Thema. Diese Länder stellen die am intensivsten genutzten landwirtschaftlichen Gebiete der Welt dar und es ist zu erwarten, dass dort starke Regenfälle den Transport von Pestiziden von den Feldern in die Oberflächengewässer begünstigen. Aufgrund des geringen wirtschaftlichen Entwicklungsniveaus wird zudem der Umweltüberwachung, Risikobewertung und Umsetzung von Risikominderungsstrategien wenig Aufmerksamkeit geschenkt. Ein Land, das diese Situation veranschaulicht, ist Costa Rica. Ziele dieser Arbeit waren daher, 1) die landwirtschaftlich bedingte Pestizidverschmutzung in tropischen Bächen Costa Ricas zu erfassen, um das Vorkommen, die Konzentrationen und die Verteilung von Pestiziden und Pestizidtransformationsprodukten (PPTP) zu beschreiben; 2) die Risiken durch diese PPTP für aquatische Organismen zu bewerten; und 3) relevante Pfade des PPTP-Transports vom Feld in die Flüsse zu identifizieren, welche als Grundlage zur Risikominderung herangezogen werden können.

1) Das Einzugsgebiet der Tapezco-Bäche wurde als Untersuchungsgebiet ausgewählt. Es handelt sich um ein Gebiet mit intensiver Landwirtschaft, welches durch Felder gekennzeichnet ist, die teilweise an steilen Hängen für den hauptsächlichen Anbau einer Vielzahl von verschiedenen Gemüsesorten angelegt werden. Dieses Einzugsgebiet befindet sich im zentralen Hochplateau in der Provinz Alajuela. In 2015 wurden fünf Standorte über einen Zeitraum von zweieinhalb Monaten und in 2016 acht Standorte über einen Zeitraum von viereinhalb Monaten beprobt. Zur Gewinnung von PPTP-Konzentrationsdaten wurden drei Passivsammler eingesetzt. Zwei davon waren gut bekannte Passivsammler, nämlich Styrol-Divinylbenzol-Disks (SDB) und Polydimethylsiloxan-(PDMS)-Streifen, welche auf Sorption basieren und zweiwöchentlich zeitintegriert-gemittelte Konzentrationen lieferten. Der dritte passive Probennehmer war ein Probenahmesystem (WLPSS), welches abhängig vom Wasserstand fungiert und zweiwöchentliche wasserstands-gewichtete Konzentrationen lieferte. Nach Entnahme der Proben und der Probenextraktion wurden die Extrakte der SDB-Disks und der WLPSS-Wasserproben mittels hochauflösender Flüssigchromatographie-Tandem-Massenspektrometrie analysiert und auf 258 polare und semipolare PPTP, einschließlich Herbizide, Insektizide, Fungizide und einige ihrer TP, untersucht. Die PDMS-Extrakte wurden auf 18 unpolare Insektizide mittels Atmosphärendruck-Chemie-Ionisations-Gas-chromatographie-Tandem-Massenspektrometrie analysiert. Mit den SDB-Disks und dem WLPSS wurde im gesamten Einzugsgebiet ein breites PPTP-Spektrum nachgewiesen. Trotz der unterschiedlichen Probenahmeprinzipien wurde die Mehrzahl der PPTP mit beiden Probennehmer-Typen detektiert; ebenso wurden Pestizide, die die höchsten mittleren Wasserkonzentrationen aufwiesen, sowohl mit den SDB-Disks als auch mit dem WLPSS als solche identifiziert. Für sechs der Pestizide überstiegen die mit dem WLPSS ermittelten Konzentrationen jedoch die Konzentrationen der SDB-Disks. Dieser Befund deutet darauf hin, dass die WLPSS die Pestizidspitzen bei Starkregenereignissen, die mit einem Anstieg des Wasserspiegels verbunden sind, deutlicher erfassen als die SDB-Disks. Die Mehrheit der WLPSS-Proben wurde jedoch nicht im optimalen Bereich beprobt, d. h. sie waren vor der Probenahme vollständig gefüllt, weshalb eine weitere Optimierung der Bedienung des Probennehmers vor weiterem Gebrauch empfohlen wird. Der PDMS-Ansatz ermöglichte die Detektion zusätzlicher, unpolarer Pestizide. Aufgrund der Zuverlässigkeit und des hohen Anteils an gewonnenen Proben wurden die aus Extrakten der SDB-Disks und PDMS-Streifen ermittelten

Zusammenfassung

chemischen Konzentrationen als gemessene Umweltkonzentrationen (engl. MEC-Measured Environmental Concentrations) für eine anschließende Risikobewertung verwendet.

2) Für die Risikobewertung wurden zwei MEC-basierte Ansätze verwendet, die die Identifizierung von Risiken sowohl für einzelne PPTP als auch für PPTP-Gemische ermöglichen. Der erste Ansatz vergleicht die MEC mit chemikalienspezifischen Umweltqualitätsstandards (engl. EQS-Environmental Quality Standards) für Primärproduzenten, Invertebraten und Vertebraten, während der zweite Ansatz die MEC zur Berechnung sogenannter Toxic Units (TU) verwendet, die auf der Toxizität für Invertebraten der zu untersuchenden Chemikalien beruhen. Drei Indizes, die sich auf die Diversität und Abundanz von Makroinvertebraten in den Fließgewässern stützen, wurden zusätzlich angewandt, um den Zustand der Wasserqualität zu untersuchen: der Species at Risk (SPEAR_{pesticide}) Index, der Costaricanische Biological Monitoring Working Party (BMWP-CR) Index und der Ephemeroptera, Plecoptera und Tricoptera (EPT)-taxa richness Index. Mit den EQS und den TU-Ansätzen wurde die Wasserqualität an allen Standorten und in allen Probenahmezeiträumen als schlecht angezeigt; nur wenige der PPTP erklärten das Gesamtrisiko. Invertebraten waren am stärksten betroffen, ohne ein Zeitfenster zur Erholung vom Pestizidstress. Sowohl der SPEAR_{pesticide}, der BMWP-CR, als auch der EPT-Index deuteten darauf hin, dass sich die Wasserqualität trotz der kontinuierlichen Pestizidbelastung an der am weitesten flussabwärts gelegenen Stellen zu verbessern schien, was möglicherweise auf einen großen flussaufwärtgerichteten Abschnitt rückzuführen ist, der einen hohen Anteil an natürlichem Wald besitzt.

3) Um mögliche Maßnahmen zur Risikominderung zu identifizieren, wurde eine Analyse der wichtigsten Pfade für den PPTP-Transport von den Feldern in die Bäche des Wassereinzugsgebietes des Tapezco Flusses durchgeführt. Die Analyse konzentrierte sich auf die Pestizide, die die Gesundheitsrisiken für die aquatischen Organismen dominierten, sowie auf drei ihrer TP und drei weitere Pestizide mit hohen Anwendungsraten. Der erste Pfad umfasste direkte Einträge innerhalb vier Wasserteileinzugsgebiete über die Handhabung, die durch Konzentrationsspitzen identifiziert wurden, die nicht mit dem Anstieg des Wasserstandes zusammenhängen. Solche direkten Einträge konnten für mehrere Pestizide identifiziert werden. Die zweite Art des Pestizidtransports stand im Zusammenhang mit Oberflächenabflüssen, unter der Annahme, dass die Konzentrationen positiv mit dem Anstieg des Wasserspiegels korrelierten und möglicherweise durch hydrologische und topographische Variablen zusätzlich beeinflusst werden. Die Modellierung mittels linearer Regression ergab unter Verwendung der Daten aller Einzugsgebiete, dass der Eintrag von gewissen Insektiziden (Acephat, Cyhalothrin und Thiamethoxam) von Probenorten mit Feldern mit hoher durchschnittlicher Neigung zunahm, während für andere PPTP (2,6-Dichlorbenzamid, Boscalid, Carbofuran, Diazinon, Diuron TP, Linuron und Prometryn + Terbutryn) der Eintrag in Gebieten mit einem hohen Anteil an bewaldeten Bachpufferzonen abnahm. Dies galt aber nicht für alle Pestizide. Für das Fungizid Carbendazim zum Beispiel wurde ein anderes Eintragsmuster beobachtet. Der dritte betrachtete Transportweg von PPTP war die Exfiltration von kontaminiertem Grundwasser durch das Flussufer hindurch, wobei angenommen wurde, dass dies zu konstanten Einträgen führt, die aufgrund von Verdünnung eine inverse Beziehung zu den Wasserständen aufweisen. Solche Einträge waren für mehrere PPTP aufgrund ihres Nachweises in Grundwasserproben prinzipiell möglich, auch wenn solche Beiträge im Vergleich zu den anderen Pfaden als deutlich geringer zu erwarten sind. Obwohl der Datensatz begrenzt war und weitere Untersuchungen erforderlich wären, um die Eintragspfade genauer zu beschreiben, konnten mehrere Strategien zur Verringerung der Einträge vorgeschlagen werden. Dazu gehören zum Beispiel das Angebot von Workshops über den verbesserten Umgang mit Pestiziden; die Vermeidung des Anbaus von Pflanzen auf Feldern an steilen Hängen die einen hohen Einsatz von Insektiziden erfordern; und die Einrichtung von Bachpufferzonen mit natürlichem Wald.

1. Chapter Introduction

1.1 Focus of this thesis

Across the globe, about 4 million tons of pesticides are used each year (Ippolito et al. 2015, Sanchez-Bayo and Hyne 2011) with the current course pointing to a further increase (Food and Agriculture Organization of the United Nations 2016). This intense pesticide use can be traced back to an increasingly intensified worldwide crop production, which is satisfying the needs of higher food demand created by a rapidly and continuously growing world population. As a consequence of this global application, pesticides are found in surface waters all over the world where they can reach peak levels known to pose acute and chronic health risks to aquatic communities. This presents just one of many reasons why water quality improvement and the conservation of freshwater systems are expressed as targets of the sustainable development goals defined by the United Nations (The United Nations 2015). Thus, there is an urgent need to document pesticide pollution in the environment and to mitigate the inputs of those hazardous chemicals into freshwater systems.

Low- and Middle-Income Countries (LAMICS) represent the most agricultural intensively used areas of the world (Food and Agriculture Organization of the United Nations 2013). Especially in tropical regions, the issue of pesticide contamination and threat to aquatic communities is aggravated due to an unfavourable combination of factors. Due to the wet and humid conditions, significant amounts of pesticides are needed year-round. Further, because of low economic levels of development, environmental monitoring and risk assessment receive little attention (Weiss et al. 2016). One country illustrating this perspective is Costa Rica.

This thesis focuses on the assessment of agricultural driven pesticide pollution of the freshwater environment in the tropics. The aim was to characterize the presence, concentrations and distribution of pesticides in a stream network, assess the risks posed by these pesticides to aquatic biota and identify potential mitigation strategies for the investigated region. To accomplish this aim, a thus far little studied but agriculturally intensively used catchment, namely the Tapezeco river watershed of central Costa Rica, was selected as case study.

This introductory chapter provides an overview of the pesticide use in LAMICS in tropical latitudes. It further presents background related to pathways of pesticide transport to water bodies, the challenges faced to detect these pesticides in surface waters and currently applied concepts in risk assessment. Finally, the selected study site is introduced.

Generally, within this thesis the supplementary information (SI) is divided into three parts (SI A, SI B, SI C). For each chapter, SI A section contains background information/data for the reader with quick and easy access added directly after each main chapter. SI B contains raw data, further processed data for analysis, and figures of processed data presented as Excel files. SI C combines the R scripts with information and commands utilized for the statistical analysis. For Chapter 2, SI-2 A, SI-2 B and SI-2 C are available at <https://doi.org/10.25678/0004P2>. For Chapter 3, SI-3 A and SI-3 B can be found at <https://doi.org/10.25678/0004Q3>. The SI information for Chapter 4, SI-4 A, SI-4 B and SI-4 C, are stored under <https://doi.org/10.25678/0004R4>.

1.2 Pesticide situation in Low- and Middle-Income Countries

LAMICS hold ca. 75% of the worldwide available arable land (Food and Agriculture Organization of the United Nations 2013). The tropical, warm and humid climate is beneficial to produce crops year-round. However, this climate provides perfect conditions for spreading of weeds, fungal plant diseases and insect pests, which are conventionally controlled by an intensive application of pesticides. As a consequence, tropical agricultural intensive areas can be considered as pesticide “hot spots” with annually worldwide highest pesticide application rates. Costa Rica especially stands out with reaching up to 80 kg pesticide per hectare (ha), among the highest application rates reported (Carazo-Rojas et al. 2018a, Echeverria-Saenz et al. 2012, Polidoro et al. 2009, Rämö et al. 2018). Other tropical countries with high pesticide application rates (kg/ha and year) include (in descending order): the Bahamas, Mauretania, Colombia, North Korea, Suriname, Belize, Panama, Jordan, Ecuador, Guatemala, Malaysia, Bolivia, and El Salvador (Food and Agriculture Organization of the United Nations (FAO) 2019, Weiss et al. 2016). Due to the high pesticide application rates, combined with the high annual precipitation, Costa Rica is among the countries for which risks due to pesticide pollution in water is estimated to be very high (Ippolito et al. 2015).

Also characteristic for LAMICS is the use of a significant number of pesticides that are banned in higher income regions, such as Europe or North America, due to their persistence and toxicity to non-target biota. This substance list includes compounds such as aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, lindane, and mirex, which are controlled under the Stockholm convention for persistent organic pollutants (POPs) (Dasgupta et al. 2010, Elfvendahl et al. 2004, Stockholm Convention 2013, United Nations 2011). In addition, poor agricultural practices, i.e. improper handling with regard to use, storage and disposal, are commonly found (Figure 1). These evidently result in an increased release and hence exposure of wildlife and humans, raising concerns for environmental and human health (Dawson et al. 2010, de la Cruz et al. 2014a, Kesavachandran et al. 2009, Parsa et al. 2014).



Figure 1: Inappropriate pesticide handling practices. Application of herbicides in ditches next to streets to avoid clogging of the channels which are often directly connected to the stream (left photograph), handling pesticide application equipment near a stream (right photograph). Photos taken by F. T. Weiss.

1.3 Fate of pesticides

After application or improper handling, pesticides may be transported as dissolved and/or particle-bound fractions via the air or water, with important sinks being surface water or ground water aquifers (Figure 2). Transport via surface run-off has been shown to cause the highest input rates from agricultural fields to surface waters (Ammann et al. 2020, Carazo-Rojas et al. 2018a, Dabrowski et al. 2002a, Lalah et al. 2009, Leu et al. 2004a, Thurman et al. 1991). Groundwater is reached via chemical leaching into the ground. Contaminated groundwater can then enter streams through the hyporheic zone (Mechelke et al. 2019) by means of exfiltration.

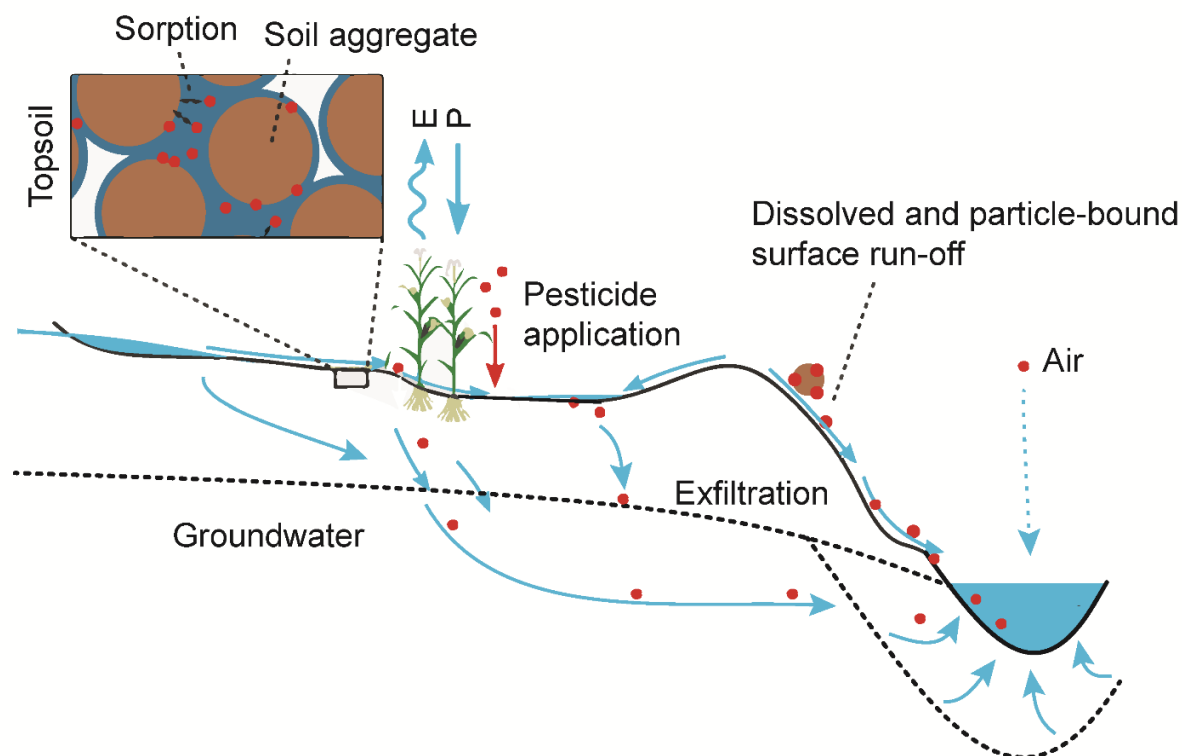


Figure 2: Graphical overview of major transport pathways of pesticides (red) into water bodies after application, with courtesy from Ammann et al. (2020), adapted by F. T. Weiss. Water flow is indicated with blue arrows, air transport with blue dashed arrows. E = evapotranspiration, P = precipitation. The dashed lines beneath the stream represent the hyporheic zone, the zone of ground water exfiltration into the stream.

Once in the environment, pesticides can undergo different transformation processes. These include transformation by abiotic factors, such as photo-degradation or hydrolysis, and biotic processes, such as biotransformation (Boxall et al. 2004a, Kern et al. 2009). Typically, transformation reduces the concentration of the parent compound and creates less concerning transformation products. However, in some cases, transformation products have been shown to be more toxic than the parent compounds and, due to slower subsequent transformations, might be present at even higher concentrations. Thus, the monitoring of transformation products helps to conclude on the past occurrence of pesticides and needs to be included in the assessment of environmental risks (Boxall et al. 2004a, Sinclair and Boxall 2003).

The behaviour and environmental fate of the pesticides and pesticide transformation products (PPTP) depends on their physico-chemical characteristics, as these define e.g. the water solubility or absorption capacity. For example, polar and semi-polar pesticides, such as organophosphates, carbamates and triazines, are more likely to be transported via water (Carter

2000, Pereira et al. 2009) in contrast to non-polar compounds, such as organochlorines and pyrethroids. These non-polar pesticides absorb to particles or organic matter and have an increased potential for bio- and geo-accumulation (Darko et al. 2008, Gan et al. 2005, Xu et al. 2018).

In addition to their physico-chemical properties, region and site-specific knowledge is required to understand the pesticides' capacity to be transported into streams. In this context, local information about the pesticide use, environmental, geological, topographical and hydrological factors needs to be compiled. This includes information about pesticide application practices, the steepness of the area (slopes), the intensity and frequency of rain events, or exfiltration rates of groundwater (Carter 2000, Dabrowski 2013, Dabrowski and Balderacchi 2013, Pehkonen and Zhang 2002). As a result of all these different processes, pesticide concentrations in streams have been shown to be spatially and temporally variable and site specific (Doppler et al. 2012a, Leu et al. 2004b, Spycher et al. 2018, Wittmer et al. 2010a).

Research about the environmental fate and behaviour of pesticides in tropical areas is still lacking behind the knowledge gained in temperate regions (Arbeli and Fuentes 2007, Gentil et al. 2020, Sanchez-Bayo and Hyne 2011). For example, seasonal rain events in tropical regions are extreme and more sudden than in temperate areas. Thus, it is expected that rain-impacted processes cannot be fully understood based on the knowledge about the fate and behaviour of pesticides gained from studies in temperate regions. Further, if available, data are often derived from environmental monitoring studies based on grab sampling, focussing on a small spectrum of pesticides. These studies provide snapshots of pesticide concentrations at a certain location at a specific time point, which are not able to correctly cover e.g. the occurrence of tropical rain event. Thus, these monitoring studies are hardly able to provide for the necessary analysis of the compound spectrum resolved in time and space.

1.4 Water sampling techniques for pesticide monitoring

To monitor pesticides in the environment, a multitude of sampling techniques has been developed. These can be broadly divided into grab sampling, active composite sampling and passive sampling. Grab sampling refers to the practice of taking single water samples, by e.g. simply submerging a container into the water. This method is easy and cheap although it can provide only a snapshot of pollution in terms of time and location as exemplified in the study by Ort et al. (2010). For active automated composite sampling, several grab samples are taken automatically. Combined over time, they allow for a time-integrated assessment of chemicals, which is also referred to as time-proportional sampling (Andersen et al. 2003, Ort et al. 2010). With active automated sampling devices, even flow-proportional sampling is possible which means that the sampled water volume per time unit increases and decreases simultaneously with the water flow. For such flow-proportional sampling, the samplers need to be coupled with a discharge measuring device. Active automated sampling systems collect water by using electrical pump systems; handling and setting up these pumps are technically demanding and electricity is required (Andersen et al. 2003, Ort et al. 2010). The access of electricity or high-capacity batteries is often unavailable in remote tropical sampling areas. For an integrative sampling in such regions, therefore, energy independent sampling techniques are needed (Dabrowski et al. 2002b, Jonsson et al. 2019, Neumann et al. 2002).

A promising, affordable alternative sampling technique to automatic composite water sampling, able to take time-integrated samples without requiring electricity, is a type of water level proportional sampling system (WLPSS) (Schneider et al. in preparation, expected in 2021, Schönenberger et al. 2020). The WLPSS continuously samples water depending on the water level with the help of a capillary or a precision valve as resistant controlling outflow of air and inflow of water. This enables a time-integrated and water level-weighted quantification of

chemicals. The working principle of the WLPSS is based on the continuous intrusion of water into a collecting bottle, where the volume sampled per unit of time is dependent on the hydrostatic pressure. As hydrostatic pressure rises with increasing water levels, the flow rate into the collecting bottle is increased whereas the opposite is true when hydrostatic pressure drops with declining water levels. Under optimal operation, i.e. as long as the sampler is not completely filled, water samples can be collected continuously with an exact measurable volume (Schneider et al. in preparation, expected in 2021, Schönenberger et al. 2020). In the broadest sense, the WLPSS can be described as a passive sampler that functions by equalizing the pressure gradient within the system.

Other more commonly applied types of passive samplers for the aquatic environment are those that rely on the sorption of chemicals to certain materials (Vrana et al. 2005). Chemicals accumulate on these sorbent passive sampling materials over time, which allows for time-integrated sampling and chemical assessment. Due to sorption, chemicals are concentrated on/in the sorbent; hence, even chemicals present at low concentrations in the water can be detected and no large volumes of water samples need to be transported from the field to the laboratory (Gong et al. 2018, Roll and Halden 2016). In addition, enrichment is rarely required, making the approach less lab-intensive and allowing for lower detection limits (Gong et al. 2018, Moschet et al. 2014b, Roll and Halden 2016). As a result, passive sampling systems are affordable and already widely used in temperate regions to obtain time-integrated concentration data of aquatic pollutants (Ahrens et al. 2018, Fernandez et al. 2014, Mechelke et al. 2019, Moschet et al. 2014b), such as, e.g., metals (Allan et al. 2007, Persson et al. 2001), pharmaceuticals, personal care products, pesticides (Gunold et al. 2008, Kaserzon et al. 2014, Morin et al. 2013, Moschet et al. 2015) and halogenated or non-halogenated hydrocarbons like chlorinated biphenyls and polycyclic aromatic hydrocarbons (Monteyne et al. 2013, Pavlova et al. 2016).

The sorbent material of choice depends on the physicochemical properties of the chemicals of interest (Ahrens et al. 2015, Vrana et al. 2005). For monitoring non-polar organic chemicals, such as polychlorinated biphenyls (PCBs) or poly aromatic hydrocarbons (PAHs), the most commonly used non-polar passive sampling methods are low density polyethylene (LDPE) (Lohmann et al. 2012, Rusina et al. 2007), semipermeable membrane devices (SPMD) (Stuer-Lauridsen 2005) and polydimethylsiloxane (PDMS) (Moschet et al. 2014b, Schäfer et al. 2010, Smedes and Booij 2012a). For monitoring semi-polar and polar chemicals, polar organic compound integrative samplers (POCIS) with Oasis hydrophilic-lipophilic balance (HLB) (Ahrens et al. 2018, Kaserzon et al. 2014, Van Metre et al. 2017), or styrene-divinylbenzene reverse phase sulfonated disks (hereafter SDB disks) (Fernandez et al. 2014, Moschet et al. 2015, Mutzner et al. 2019, Schreiner et al. 2021, Vermeirssen et al. 2013) are available. After sampling, time-integrated averaged concentrations (C_{TIA}) in water can then be calculated from the absolute amount of a target chemical collected, combined with compound specific sampling rates (R_S). Such R_S values can be determined by laboratory uptake experiments (Ahrens et al. 2015, Mechelke et al. 2019, Vermeirssen et al. 2013) or in-situ field calibrations (Ahrens et al. 2018, Lehmann et al. 2018, Moschet et al. 2015). Depending on the given conditions (e.g. flow velocities, pHs, temperatures) during calibration, the determined R_S values can vary (Curchod et al. 2019, Gunold et al. 2008, Harman et al. 2012, Moschet et al. 2014b, Vermeirssen et al. 2009). Thus, for some chemicals, different R_S values are available in the literature. If no R_S value is available for the target compound and/or the specific sampling conditions, R_S values accessible for structurally similar chemicals and ideally comparable exposure conditions can be used as alternative, though a greater uncertainty of the resulting time-integrated concentrations needs to be acknowledged in this case (Curchod et al. 2019, Moschet et al. 2014b).

Using these sampling approaches, especially when applied in combination, enables a comprehensive collection of pesticide monitoring data, which helps to understand chemical sources, inputs and distribution patterns. Such data provide an essential base to assess the risks of these pesticides to aquatic biota at the monitored sites in the context of environmental health evaluations.

1.5 Environmental risk assessment

Environmental risk assessment provides a systematic procedure to evaluate the likelihood of chemicals and chemical mixtures to impact organisms in the environment. Specifically, it aims to assess whether a chemical that is currently being used (retrospective risk assessment), or intended to be used in the future (prospective risk assessment), may cause adverse effects (Diamond et al. 2018).

Prospective risk assessment is based on the formation of Risk quotients (RQ). Risk quotients are formed by dividing generally predicted environmental concentration (PEC) by a benchmark concentration reflecting the influence of a chemical on an organism or a community. As such, a benchmark predicted no effect concentrations (PNEC) from laboratory toxicity tests can be used as denominator, which would imply that no negative impact is accepted. In other cases, for example hazardous concentration (HC_x) causing adverse effect to a pre-set percentage of species from one or different organism groups (Figure 3), such as the frequently used HC_5 , can be used as well. In the example of using HC_5 , negative chemical effects up to a level of 5% to the selected species are accepted. RQ larger than 1 indicate that the risk of adverse effects for aquatic organisms is too large and that the chemical should not be accepted for application or only under certain restrictions (Diamond et al. 2018).

Retrospective risk assessment requires quantitative aquatic exposure data from monitoring campaigns to elaborate if environmental levels of chemicals exceed concentrations posing risks to aquatic organisms. For forming retrospective RQ, the use of measured environmental concentrations (MEC) as numerator and the application of Environmental Quality Standards (EQS) as denominator (benchmark concentration) have become broadly accepted. EQS represent a measure of protective threshold concentration, which, when exceeded, indicate that adverse effects on aquatic organisms cannot be excluded. EQS are derived following the technical guideline No. 27 (European Commission 2018) and are compound specific. EQS are mainly based on effect concentrations (EC) or no observed effect concentrations (NOEC) from organisms of different trophic levels. Different trophic levels typically include primary producers and primary, secondary and tertiary consumers. There are different methods to derive EQS, mainly depending on data availability.

For chemicals with small data sets (generally below 10, but at least three different trophic levels), EC data from laboratory studies are used to derive EQS after multiplication of these EC with a safety or so called assessment factor (AF) between 10 and 1000. The AF is used to account for data uncertainty, such as extrapolation from lab to field and high to low exposure concentrations (European Chemicals Agency 2008, Nikinmaa 2014). The closer the test scenario which was used to derive the effect data is to the real environmental scenario, the lower the uncertainty and consequently smaller assessment factors can be applied. For example, data from complex mesocosm studies including chemical effects to communities, are multiplied with lower AF than lab-derived EC values on single species (European Commission 2018). If more data are available, a method described as species sensitivity distribution (SSD) is preferably applied to derive EQS values. The SSD integrates effects of a substance on several species from different trophic levels, represented as the cumulative density distribution (Figure 3, y-axis = cumulative probability) of log transformed effect data (NOEC/EC, Figure 3, x axis), having a sigmoidal relationship. The preparation for such a SSD requires a minimum of 10, but

better > 15 NOEC/EC from species covering at least 8 taxonomic groups, as outlined in the technical guideline No. 27 (European Commission 2018). The derived sigmoidal relationship (Figure 3) is then used to define an HC₅ for 5% of the tested species as EQS. The HC₅, therefore, describes the threshold concentration at which 95% of species are protected. According to the study of Newman et al. (2000), the approximate optimal sample sizes to estimate HC₅ range from 15 to 55 species with a median of 30 species-sensitivity value. The SSD is a standard concept used in the EU, Canada, and the US (Canadian Council of Ministers of the Environment 2007, EFSA Panel on Plant Protection Products and their Residues 2013, U.S. Environmental Protection Agency 2000). To consider the extent of exposure duration, EQS for long-term and short-term effects can be derived. Long-term EQS or annual average concentrations (AA-EQS) are normally based on chronic toxicity data (NOEC or EC₁₀) while short-term EQS or maximum acceptable concentration EQS (MAC-EQS) are based on acute toxicity data (EC₅₀).

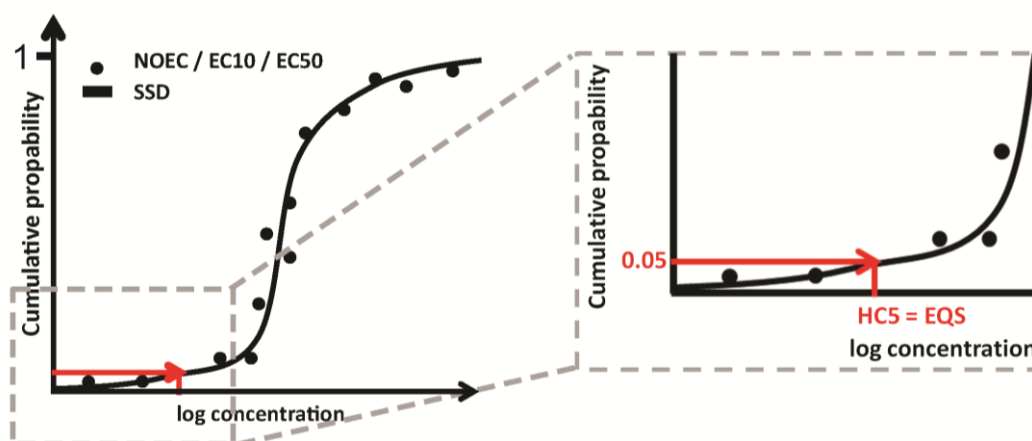


Figure 3: Example scheme of species sensitivity distribution (SSD) for a chemical based on Vighi et al. (2006). The cumulative log₁₀ transformed effect concentrations for different species are plotted on the x-axis versus the cumulative probability of affected species on the y-axis. Here, a value of 1 means that all species are affected at the respective chemical concentration. The HC₅ is derived from this sigmoidal relationship as an EQS that protects 95% of the species (in red). To derive chronic EQS (AA-EQS), NOEC or EC₁₀ is plotted on x axis, for deriving acute EQS (MAC-EQS) EC₅₀ are used.

In cases where only very few effect data are available, Toxic Units (TU) can be calculated to describe risks of chemicals found in the aquatic environment. Here the MEC are compared with laboratory based EC (mainly EC₅₀) from an invertebrate reference species with a broad data set of available EC data, usually *Daphnia magna* (Knillmann et al. 2018, Schäfer et al. 2008). If the EC₅₀ is used, a TU of 1 indicates that 50% of the reference species in the environment are prone to adverse effects.

While the described methods are based on laboratory-derived data, it is often helpful to conduct complementary field evaluations, i.e., biomonitoring. Different methods, which are based on the presence and abundance of macroinvertebrates in the respective environment, are common approaches. Here, for example, the Species at Risk pesticide (SPEAR_{pesticide}) index (Cornejo et al. 2019, Knillmann et al. 2018, Liess and Ohe 2005, Schäfer et al. 2007) and the Ephemeroptera, Plecoptera and Trichoptera (EPT)-taxa richness index (Castillo et al. 2006a, Mertens and Küry 2018, North Carolina Department of Environment 1997) are frequently used.

While the above listed concepts are widely applied in High-Income Countries, application in LAMICS, such as Costa Rica, lags behind. Predominantly, this is due to a lack of pesticide monitoring data and limited biomonitoring. In Costa Rica, for example, instead of deriving

EQS, a substance independent maximum threshold value of 10 µg/L for the sum concentration of organochlorines and organophosphates are used (Mendez et al. 2018). This, however, stands in great contrast to the vast number of pesticides found in surface waters worldwide, some of which are highly bioactive (and hence potentially toxic) at very low levels (pg/L) (Feo et al. 2010, Rämö et al. 2018, Rösch et al. 2019, Swiss Center for Applied Ecotoxicology 2019). Further, threshold values neglect species-specific toxicity. With regard to field-based indices using macroinvertebrates, the EPT-taxa richness index (Castillo et al. 2006a) has been applied in Costa Rica but is not embedded into the regulatory framework yet (La Gaceta Official Newspaper 2007).

In an attempt to describe the status of water pollution by using macroinvertebrates for bio-monitoring, in Costa Rica, the Biological Monitoring Working Party (BMWP-CR) Index (La Gaceta Official Newspaper 2007) was introduced into the regulatory process. For applying the BMWP-CR index, collected macro-invertebrates were identified to the family level. Each family level is assigned to a specific sensitivity value from 1 to 10. The higher this sensitivity value the lower is the tolerance of the family to organic pollution. The values for each family are summed up yielding sensitivity scores. Scores higher than 120 points indicate a natural aquatic system without any anthropogenic influence, while low values (< 16) indicate that the aquatic ecosystem is seriously contaminated. However, the BMWP-CR indicator appears to be a poor predictor of pesticide effects because it is influenced by environmental variables, such as pH, flow velocity and temperature (Böhmer et al. 2004, Liess et al. 2008). From this perspective, a comparison of the previously described SPEAR_{pesticide} index accounting particularly for pesticide as stressor and the BMWP-CR indicator emerged as an interesting field for further research as demonstrated as well in a prior study (Cornejo et al. 2019).

1.6 The pesticide situation in Costa Rica

In Costa Rica, agriculture plays an important socioeconomic role. It creates jobs, and the sale and export of agricultural products on the local and international markets are a solid income source (Ramírez et al. 2016, Ramírez and Ballesteros 2018). About 13% of the labor force were employed in the agricultural sector in 2013 (World Bank 2016) and 10% of the territory, equalling roughly 400 thousand hectares of land, are used for agricultural purposes (de la Cruz et al. 2014a). At the same time, Costa Rica is well-known for its rich biodiversity of natural habitats. Costa Rica contains about ~ 5% of the world's flora and fauna (Kohlmann et al. 2010, Obando 2007) and is well-known for its nature conservation efforts and eco-tourism. Laws and policies need to balance between conserving the environment and keeping the economic productivity of crop production for both national and international markets.

A broad spectrum of about 154 individual pesticides are allowed for use in agriculture (Servicio Fitosanitario del Estado Ministerio de Agricultura y Ganadería 2020), from which about 1/3 are not approved for use on the European market (Lewis et al. 2020). Such banned chemical substance groups include carbamates, organochlorines, pyrethroids, triazines and triazoles. As pointed out by the Inter-American Network of Academies of Sciences (2019), in crop intensive areas, pesticides had even caused pollution of ground water, making this ground water undrinkable. A compilation of monitoring studies illustrates the presence of a broad pesticide spectrum in surface waters and sediments in rivers (Ruepert 2011). For example, pesticides related to the cultivation of pineapple, banana and rice, such as bromacil, chlorpyrifos, diuron, fenbuconazole, ametryn and endosulfan, were detected in the Caribbean zone (Jimenez River, Limon and Madre de Dios River), reaching concentrations that pose risks to aquatic organisms (Arias-Andres et al. 2018, Echeverria-Saenz et al. 2018, Rämö et al. 2018). In South Guanacaste in the Tempisque river basin, environmental risks have been identified due to the exposure to carbendazim, epoxyconazole, diuron, propanil, terbutryn, endosulfan, and triazophos (Carazo-Rojas et al. 2018a). In the Sixaola watershed, pesticide occurrence was directly linked to lethal

effects on crustaceans, reptiles, birds, and fish (Controloria General de la Republica 2013, Polidoro and Morra 2016). Yet, such monitoring studies have mostly been limited to specific areas with large monoculture plantations of, e.g., bananas and pineapples. Examples of such areas are the Caribbean lowlands (Castillo et al. 2006a, Castillo et al. 2000, Diepens et al. 2014, Echeverria-Saenz et al. 2018, Echeverria-Saenz et al. 2012, Mena et al. 2014a, Rämö et al. 2018), Guanacaste in North Western Costa Rica (Carazo-Rojas et al. 2018a, Mena et al. 2014b, O'Neal Coto 2018), the North plain in the Frio river basin (Fournier et al. 2018), and the Sixaola watershed in the South East (Polidoro and Morra 2016). In contrast, occurrence of pesticides in diverse horticultural small scale vegetable farming areas, such as the Tapezco river catchment in the north central highland plateau in the province Alajuela or the agricultural areas in Northern Cartago province, are rarely documented (Ramírez-Morales et al. 2021, Ramírez et al. 2016). Based on grab sampling data, nine pesticides were found in the Tapezco river catchment (Ramírez et al. 2016) to exceed chronic EQS values, and six pesticides in an agricultural catchment in the Cartago province (Ramírez-Morales et al. 2021) exceeded critical ecotoxicological concentrations or limiting values of international Guidelines for Water Quality (Ramírez-Morales et al. 2021).

1.7 Tapezco river study catchment explored in this thesis

The Tapezco catchment represents an important production area for providing mainly vegetables for the national market (Ramírez et al. 2016). It is located in the highland plateau in the province of Alajuela in the Zarcero canton and covers a wide altitude range from 1209 to 2243 meters above sea level. About 20% of the catchment area is intensively used for small-scale horticultural farming to mainly grow potatoes and vegetables such as broccoli, cabbage, carrots, spinach and tomatoes (Ramírez et al. 2016). Crops are mostly cultivated on steep fields via a farming practice similar to contour farming. Average slopes range between 3 and 12%, however, in extreme cases, slopes reach up to a maximum value of 60%. Conventionally in contour farming, land is tilled with furrows along parallel lines of consistent elevation in order to conserve rainwater and to prevent soil losses from erosion (Encyclopædia Britannica 2019). However, on the fields in the given catchment, slope directed paths are added, additionally, between the crops to avoid stagnant waters on the fields during heavy precipitation events (Ramírez et al. 2016). Besides horticultural farming, the majority of the catchment area is covered with forests and pastures used for cattle.

Average pesticide application rates in the Tapezco river catchment are found to be in a similar order of magnitude as in other areas in Costa Rica. Averages of about 22 kg a.i./ha/crop cycle with a maximum of 58 kg a.i./ha/crop cycle were applied in the Tapezco area (Ramírez et al. 2016), vs application rates reaching up to 80 kg pesticide per ha in other, better studied parts of Costa Rica (Carazo-Rojas et al. 2018a, Echeverria-Saenz et al. 2012, Polidoro et al. 2009, Rämö et al. 2018). In the Tapezco river area, chlorothalonil, mancozeb, propineb, and phorate account for the majority of the applied pesticides, potatoes and onions are the crops with the highest pesticide use per ha (Ramírez et al. 2016). As for other areas of Costa Rica, the study conducted by Ramírez et al. (2016) indicated that the Tapezco river catchment can be a potential pesticide hotspot as well. Further, they found that a broad spectrum of pesticides was applied, expected to end up in streams affecting the water quality. Indeed, nine pesticides were found in the Tapezco river catchment (Ramírez et al. 2016) to exceed chronic EQS values. For these reasons, the Tapezco river catchment was selected as study catchment for this thesis. For aqueous pesticide monitoring, the sampling was conducted in two successive years (2015/2016) using SDB disks, PDMS sheets and the WLPSS. Five sites were sampled in 2015 during a course of two and a half months (from ~August to October 2015 $\Delta T1$), and in 2016, eight sites were sampled during four and a half months (~June to August, ($\Delta T2b$), August to October $\Delta T2a$). Four drinking water tanks were grab sampled in three-monthly intervals during the

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environmental sampling campaign. The data of two drinking water tanks located in SC1 (Tpap, tank Asada Palmira) and SC7 (Tpat, tank Asada Palmira Zapezco) were further discussed in Chapter 4.

An overview of the catchment and its eight delineated hydrological sub-catchments (SC, more information, SI-2 B1), along with land uses, streams and drinking water sampling sites (land use: SI-4 A2; drinking water sites: SI-4 B1) used in the research of this thesis, are illustrated in Figure 4. Corresponding to the sampling sites (SC1 - SC8), the hydrological SCs were delineated using the GIS software ArcMap 10.5.1. For doing so, the digital elevation model data with a resolution of 30 x 30 meter was used. Sinks were filled by using the “fill” tool, flow directions of the streams were determined according to the “flow direction” tool and the D8 algorithm setting in ArcMap 10.5.1. The original land use map was obtained from Moraga G., Universidad Nacional, Heredia, Costa Rica. The arable land and forest were manually updated and vectorized by means of available satellite pictures from ArcMap 10.5.1 (Sources of the satellite pictures: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS user Community, last access 25.03.2020). For providing a more detailed picture about the Tapezco catchment, further details about the land use and the climate conditions are described in the following. Especially the meteorological information is relevant for Chapter 3 and Chapter 4 of this thesis in order to understand the rationale behind the temporal division of the monitoring data in three periods ($\Delta T1$, $\Delta T2a$, $\Delta T2b$).

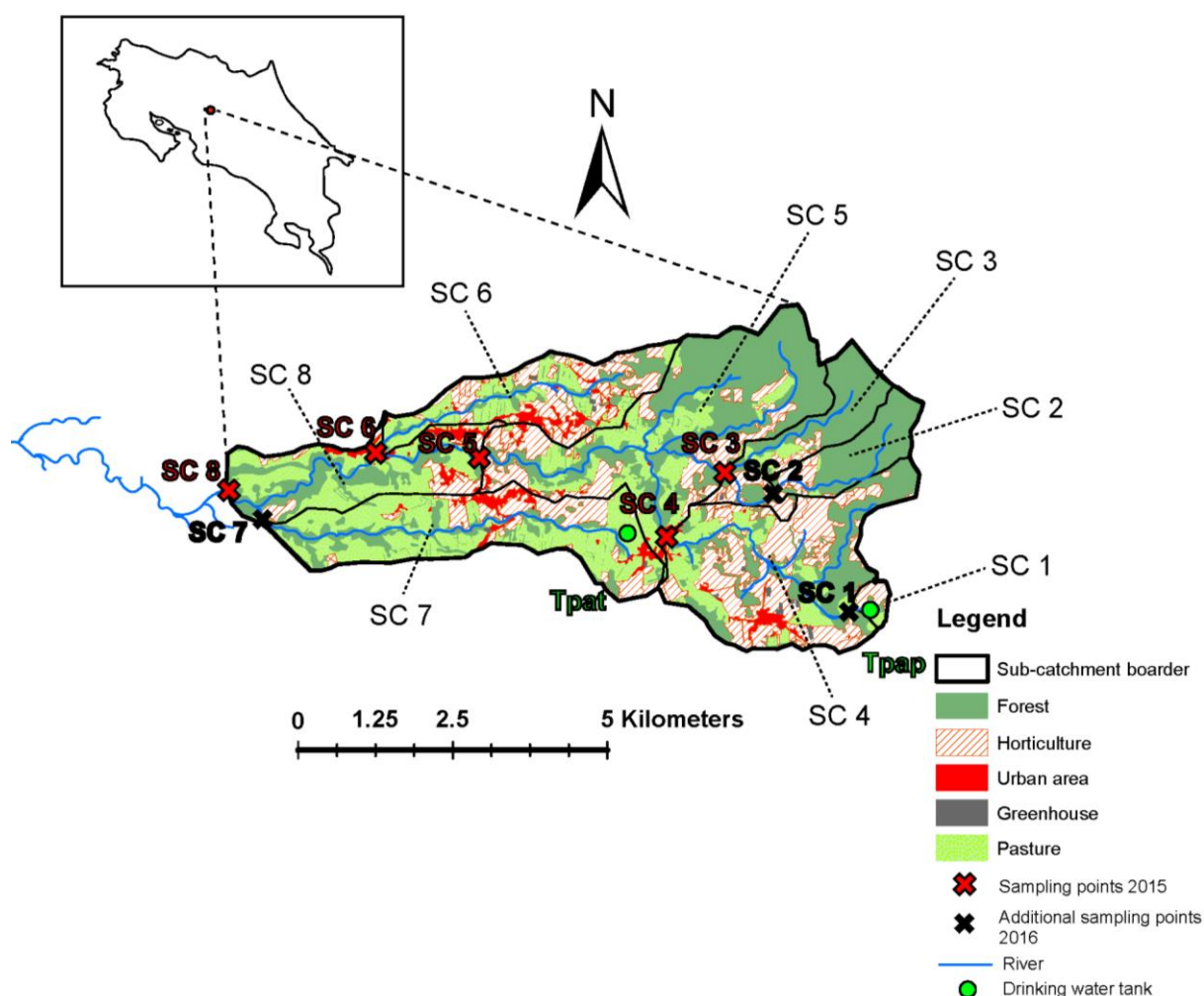


Figure 4: Map of the Costa Rican Tapezco river catchment with its eight sub-catchments (SC1 – SC8), eight sampling sites, land uses and two drinking water tanks (Tpat, Tpap) explored in this thesis. Five sites were sampled in 2015 (red crosses, SC3, SC4, SC5, SC6, SC8), and an additional three sites were sampled in 2016 (black crosses, SC1, SC2, SC7). The original land use map was from Moraga G., Universidad Nacional, Heredia, Costa Rica. For this study the arable land was manually updated and vectorized via available satellite pictures from geographic information system software: ArcMap 10.5.1 (Sources of the satellite pictures: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS user Community, last access 25.03.2020).

Figure 5 illustrates the land use areas of the catchment map to specify the share of each individual land use (forest, horticulture, urban area, greenhouse and pasture) per SC, demonstrating the heterogeneity among the individual SCs. The highest share of horticultural land can be found at SC1, SC4 and SC6.

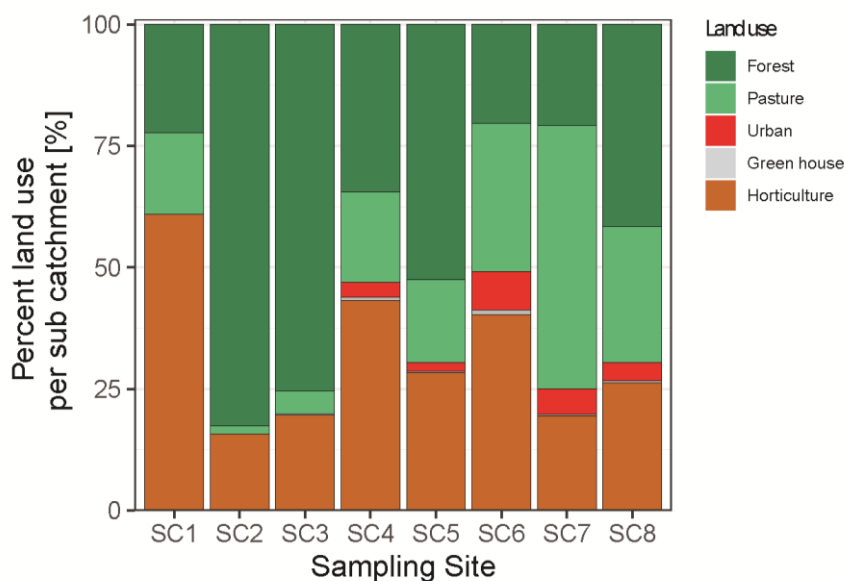


Figure 5: Percentage of land uses among the individual SCs.

With respect to the meteorological conditions, the Tapezco catchment is tropical with an annual rainfall varying between 1500 and 3500 mm/yr (Ramírez et al. 2016). The average yearly cumulative precipitation amounts to 1925 mm/yr, determined from daily precipitation data from 1950 to 2016 (National Meteorological Institute from Costa Rica 1950-2016), compiled in the vicinity of the studied catchment (10°11'31" N, 84°23'35"W; altitude 1736 meters above sea level). The average temperature is 17°C.

Generally, there is a pronounced rainy season from May to October and a dryer period from November to April. However, an El Niño weather phenomenon influenced the precipitation patterns in ~August to October 2015 ($\Delta T1$), leading to a particularly dry rainy season during these months (Figure 6). In this period, the average precipitation was 174 mm/month as opposed to 260 mm/month during the same months in 2016 (August to October 2016 = $\Delta T2a$) (Figure 6). During $\Delta T2a$, the precipitation was more similar to the average precipitation of 310 mm/month from August – October (determined from daily precipitation data of the National Meteorological Institute from Costa Rica 1950-2016) than during the El Niño influenced year, 2015. It was noticeable, however, that in October, monthly precipitation was similar in both sampling years. During ~June to August, which was only explored in 2016 ($\Delta T2b$), the monthly precipitation was 245 mm/month and thus corresponded well to the usual average precipitation of 256 mm/month from June to August (determined from daily precipitation data of the National Meteorological Institute from Costa Rica 1950-2016).

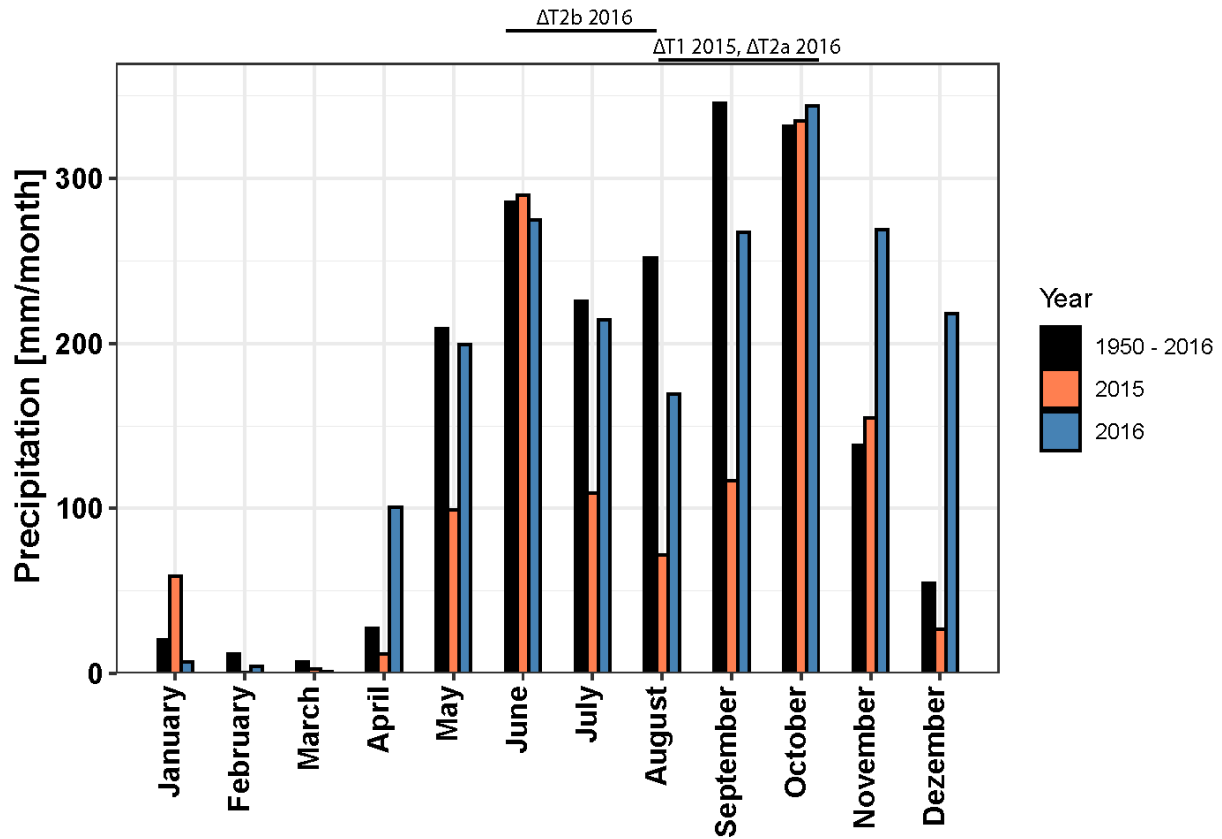


Figure 6: Comparison of monthly precipitations in 2015 (red bars) and 2016 (blue bars); and average monthly precipitation from 1950 to 2016 (black bars). Precipitation data was obtained from a meteorological station next to the investigated study site in Zarcero-Palmira (10°11'31" N, 84°23'35"W at an altitude of 1736 meters above sea level (National Meteorological Institute from Costa Rica 1950-2016).

1.8 Research objectives

In LAMICS, comprehensive water quality assessment programs are lacking. Available pesticide monitoring data rely on grab sampling and a narrow spectrum of analyzed pesticides. Hence, data about the environmental exposure, spatio-temporal distribution and the fate and behavior of pesticides are rare. Focused investigations are required to gain a better systematic understanding of pesticide distribution and associated risks to aquatic organisms. In the Tapezco river catchment, neither a detailed risk assessment has been conducted nor actual effects on macroinvertebrate communities have been summarized and brought into context with pesticide pollution. Without such information, the development of adequate mitigation strategies seems impossible.

To fill these knowledge gaps, the overall aim of this thesis was to provide information on pesticide levels and distribution in the stream network in order to allow for a comprehensive aquatic risk assessment and provide suggestions for mitigation measures. The Tapezco river catchment was targeted as an example for an area with diverse land use in a Middle-Income Country with high, and little controlled, pesticide use.

To achieve this overall aim, the following three approaches were pursued:

- 1) Conducting a targeted, widespread pesticide screening in the study catchment by using a feasible and cost-efficient sampling strategy, which enables a continuous sampling far beyond the conventional snapshot grab sampling.
- 2) Using the obtained pesticide screening data as well as available macroinvertebrate community data to perform an extensive risk assessment to describe the water quality and to evaluate which organism groups (primary producers, invertebrates or vertebrates) are affected the most.
- 3) Identifying the most relevant pesticide input pathways and proposing a set of mitigation measures to reduce the pesticide inputs into the streams.

Accordingly, the original results of this thesis are detailed in Chapters 2-4 as described below. Chapter 5 provides a conclusion and perspective for future research.

Chapter 2: Use of different passive sampling approaches for a comprehensive and time-integrated sampling of pesticides in tropical streams in a vegetable growing area. This chapter describes the application of three passive sampling approaches for time-integrated sampling and the detection of a broad range of pesticides in the Tapecho river catchment and provides a technical comparison among the methods. The three passive samplers used comprised two sorbent based passive samplers, SDB-disks and PDMS-sheets and the non-sorbent based WLPSS to screen for 275 PPTP. Within the study area, 109 PPTP were detected. This study clearly demonstrated that the streams in the catchment are heavily polluted by PPTP –partly surpassing 100 ng/L for individual pesticides. From the hands-on experiences in the field it was found that the SDB and the PDMS sampling led to the highest number of robust data points (ca. 90% of the samples could be used to obtain biweekly averaged pesticide concentration data), while the WLPSS needs further optimization for future sampling. Accordingly, the data of the sorbent-based devices (SDB and PDMS) was applied for the risk assessment analysis performed in Chapter 3.

Chapter 3: Risk assessment for tropical streams of a small-scale horticultural catchment based on spatio-temporal pesticide monitoring data. Risk assessment was conducted using the MEC, obtained in Chapter 2, and compound specific EQS in order to derive RQ which were assigned to different organism group, i.e. primary producers, vertebrates and invertebrates. The RQ-based risk assessment revealed that for 18 pesticides, risks to aquatic organisms are very likely and that invertebrates were prone to the highest risks. Excessive and continuous risks were as well confirmed for invertebrates based on estimated TU results. The actual water quality status was described by utilizing collected macroinvertebrate data and applying the $\text{SPEAR}_{\text{pesticide}}$, the BMWP-CR, and the EPT-taxa richness indices. These indices confirmed as well that the macroinvertebrates suffered on the community level from pesticide exposure. The $\text{SPEAR}_{\text{pesticide}}$ index and BMWP-CR showed a trend of improved water quality at the downstream sites, SC5 and, particularly, SC8. With the EPT-index, an improvement in water quality was likewise indicated but only at the most downstream site, SC8. Thus, the $\text{SPEAR}_{\text{pesticides}}$ index and BMWP-CR reflected a finer gradient than the EPT-taxa richness index with regard to the status of water quality.

Chapter 4: Identification of pesticide input pathways in tropical streams as a basis to propose potential mitigation options. Three main pesticide transportation pathways were considered in this chapter to delineate major input paths of pesticides into streams with a focus on those pesticides that presented the highest risks to aquatic biota (Chapter 3). These pathways comprised: i) direct pesticide inputs, disconnected from hydrology, from inappropriate handling; ii) precipitation driven inputs after surface-runoff events assumed to occur during periods of increased discharge, and iii) possible inputs from exfiltration into streams from contaminated groundwater, leading to dilution effects during discharge events. To identify direct input peaks it was screened for concentration peaks during periods without significant water level increases. For investigating precipitation driven inputs, the influence of explanatory hydrological and topographical variables on percentile concentrations was investigated by applying linear regression models. For identification if inputs via exfiltration are principally possible, the occurrence of PPTP in groundwater samples was investigated and for carbendazim, ratios of the parent carbendazim and its transformation product were used.

Three pesticides showed concentration peaks that were probably associated with direct inputs from handling and for five additional pesticides, the input via inappropriate handling seemed possible. Based on the regression analysis generally precipitation driven inputs seemed to be very compound specific and for the most of the investigated PPTP it was difficult to identify clear input patterns. It seemed that for several PPTP (for instance, boscalid, diazinon, diuron-desdimethyl, linuron and prometryn + terbutryn), high share of forest in the stream buffer zone worked generally as barrier for input via surface run-off. However, this trend was not observed for all PPTP. For example, for the fungicide carbendazim, this trend could not be confirmed. In addition, for a small selection of insecticides (mainly, acephate, cyhalothrin, and thiamethoxam) the inputs were favored and elevated concentrations were observed at sites with horticultural fields with elevated average slopes. The analyses of groundwater-based drinking water samples revealed that for nine PPTP (five parent, four transformation products), a transport via exfiltration seemed possible. Based on these findings, proposed mitigation options range from training workshops for farmers to the installation of biobeds, such as layer-filled pits in the ground to prevent pesticide leaching to the freshwater. Further, it is recommended that areas in proximity to steep slopes should not be cultivated with pesticide-intensive crops. Yet, these suggestions need further confirmation to demonstrate their validity. For example, further investigations are needed to identify so called critical source areas, which represent highly dynamic hydrological pathways connecting the field with the streams.

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2. Chapter Use of different passive sampling approaches for a comprehensive and time-integrated sampling of pesticides in tropical streams in a vegetable growing area

2.1 Abstract

For monitoring of pesticides in tropical streams, cost-efficient and easily applicable approaches are needed. Moreover, to capture short pesticide concentration peaks, a time-integrated sampling is preferable to conventional snapshot grab sampling. Passive sampling approaches fulfil these criteria. Therefore, this chapter focusses on the application of three passive sampling devices to monitor 275 pesticides and pesticide transformation products (PPTP) in the horticultural Tapezco river catchment over several months in two consecutive years. Two of the samplers were sorbent-based: reverse phase sulfonated styrene-divinylbenzene (SDB) disks and polydimethylsiloxane (PDMS) sheets, yielding biweekly integrated averaged PPTP concentrations. The third sampler was a low-cost, non-sorbent-based, water level proportional sampling system (WLPSS), yielding water level-weighted, biweekly integrated PPTP concentrations. The objectives were to (1) test the performance and robustness of these samplers (2) obtain comprehensive quantitative pesticide concentration data and (3) provide recommendations for their field application in future monitoring campaigns.

Of the 275 targeted PPTP, 87 polar and semi-polar PPTP were detected with the SDB method and 99 with the WLPSS, of which 77 were found with both systems. In several cases (10 with SDB, 22 with WLPSS), a pesticide was only detected by one of the set-ups; this exclusive detection could be due to the respective substance concentrations being close to or below the method limit of quantification (MLOQ) for the sampler where it was not detected. Despite the different sampling principles for SDB and WLPSS, the same pesticides (carbendazim and flutolanil) were found with the highest median water concentrations (> 100 ng/L) with both samplers. The complementary PDMS system allowed detection of 11 non-polar pesticides. Among these, cypermethrin, chlorpyrifos and permethrin showed the highest concentrations (> 2 ng/L).

Chlorpyrifos was the only pesticide detected with all three sampling techniques. Standard deviations for detected chlorpyrifos concentrations were the highest for SDB sampling, likely due to a lag-phase in sampling across the membrane covering the sampler due to the chemical's high hydrophobicity. Moreover, derived chlorpyrifos water concentrations were significantly higher using the WLPSS compared to SDB and PDMS sampling. This was also seen for another six pesticides sampled with the WLPSS compared to SDB sampling. Higher concentrations detected via WLPSS can be explained by the ability of the WLPSS to collect pesticide peaks associated with heavy rainfall events and linked to rise of water levels in a more pronounced fashion as compared to the time-integrated sampling manner of the SDB and PDMS samplers. Yet, only a small portion, 15%, of the WLPSS samples collected, could be used to yield water level-weighted, time-integrated concentration (C_{WLW}) data, calling for a need to further optimize and standardize the application of this device.

Of the devices tested, the SDB disks were the easiest to apply and the most cost-efficient for short-term monitoring campaigns. The SDB sampling can be conducted in sparsely equipped laboratory facilities, while for the PDMS sheets and the WLPSS, sample preparation and extraction are technically more demanding.

2.2 Introduction

2.2.1 Current pesticide application and monitoring situation in the Tapezco river catchment

In the Tapezco region, average pesticide application rates of about 22 kg pesticide per hectare (ha) of arable land and cropping cycle, and even maximum application rates of up to 58 kg a.i./ha/crop cycle, were reported (Ramírez et al. 2016). Indeed, the only pesticide grab sample monitoring study conducted, albeit with a limited pesticide spectrum (Ramírez et al. 2016), showed that this region represents a potential pesticide hotspot. Local farmers reported using at least 104 individual pesticides. Out of these, 22 were found in grab samples collected between 2013 and 2016 with concentrations ranging from 0.03 to 6.8 µg/L (Ramírez et al. 2016). It is likely that pesticides were missed because grab sampling only represents a “snapshot” of the pesticide pollution and does not describe the comprehensive general state of pollution. Since pesticides in streams often appear in pulses with short emission peaks (Bundschuh et al. 2014, Doppler et al. 2012a, Leu et al. 2004a, Stehle et al. 2013), approaches that allow sampling in a time-integrative manner are needed to capture such peaks. Passive samplers have been shown to reliably meet this requirement (Ahrens et al. 2018, Fernández et al. 2014, Mechelke et al. 2019, Moschet et al. 2015, Moschet et al. 2014b, Schreiner et al. 2020).

2.2.2 Passive sampling approaches

Passive sampling refers to probing the environment over time intervals for target compounds to obtain time-integrated averaged water concentrations without the necessity of any power supply. Passive samplers can be flexibly deployed in streams in remote or difficult to access areas because they do not require electricity or maintenance during sampling (Lehmann et al. 2018, Mutzner et al. 2019). Other advantages are that they are generally affordable and that their handling is relatively easy. Depending on the type of passive sampler, a broad spectrum of compounds with different physicochemical properties can be sampled (Ahrens et al. 2016, Jonsson et al. 2019, Moschet et al. 2015, Mutzner et al. 2019, Schreiner et al. 2020, Vrana et al. 2005). Within this study, two types of passive samplers were used: sorbent-based (Ahrens et al. 2016, Moschet et al. 2015, Moschet et al. 2014b) and non-sorbent-based (Dabrowski et al. 2002a, Neumann et al. 2002).

The applied sorbent-based samplers were the styrene-divinylbenzene reverse phase sulfonated (SDB-RPS, hereafter: SDB) disks and polydimethylsiloxane (PDMS) sheets. These disks and sheets serve as a material onto which chemicals with an affinity to these materials adsorb or absorb. In the case of SDB disks, these are semi-polar and polar chemicals. Examples of the use of SDB disks include the monitoring of pesticides and pharmaceuticals in streams (Fernández et al. 2014, Lindholm-Lehto 2016, Moschet et al. 2015, Mutzner et al. 2019, Schäfer et al. 2008) and sewers (Mutzner et al. 2019). In the case of PDMS sheets, non-polar chemicals with high PDMS-water partition coefficients can be sampled (Rusina et al. 2010a). Accordingly, previous studies have focused on the application of PDMS to monitor polychlorinated biphenyls (PCB) and poly-aromatic hydrocarbons (PAH) (Pavlova et al. 2016, Rusina et al. 2010b, Schäfer et al. 2010, Smedes and Booij 2012b). They have also been used to sample non-polar pesticides, even at concentration levels as low as pg/L in glacial meltwater and pore water in sediments (Pavlova et al. 2016, Xu et al. 2018) or freshwater streams (Moschet et al. 2014b, Schäfer et al. 2010, Schreiner et al. 2021).

With the sorbent serving as a sink, chemicals can be sampled by the SDB and PDMS material and accumulate over time as long as the sorption capacity of the sorbent material is not surpassed (Camilleri et al. 2012, Vrana et al. 2005). Accordingly, even chemicals that pass the sampler only as short concentration peaks can accumulate in the sorbent material. Time-integrated averaged concentrations (C_{TIA}) in water can be calculated from the absolute amount of a compound collected, combined with compound-specific sampling rates (R_s in L/day),

which can be determined by laboratory uptake experiments (Ahrens et al. 2015, Mechelke et al. 2019, Vermeirssen et al. 2013) or in-situ field calibrations (Ahrens et al. 2018, Lehmann et al. 2018, Moschet et al. 2015). Since the accumulated chemicals are concentrated in the sorbent material, it is not necessary to transport large volumes of water samples from the field to the laboratory (Gong et al. 2018, Roll and Halden 2016). Furthermore, lower detection limits can be achieved compared to the sampling of large water volumes (Gong et al. 2018, Moschet et al. 2014b, Roll and Halden 2016) and chemical enrichment prior to analytical detection is often not required. On the other hand, limitations of these samplers are that only the dissolved fraction of the monitored compounds is captured and that chemical specific R_s values are required to determine C_{TIA} (Moschet et al. 2015, Moschet et al. 2014b).

The non-sorbent-based passive sampler used in this study was the water level proportional sampling system (WLPSS, Schneider et al. unpublished, Schönenberger et al. (2020), illustrated in SI-2 A1). This is a less expensive and less technically demanding alternative to automated water sampling systems, which have been used in studies in well-developed, high-income regions (Lefrancq et al. 2017, Leu et al. 2004a, Wittmer et al. 2010a). The WLPSS was used here to monitor polar and semi-polar pesticides and pesticide transformation products (PPTP).

The working principle of the WLPSS is based on the continuous intrusion of water into a collecting bottle, where the volume sampled per unit of time is dependent on the hydrostatic pressure of the water column above the sampler. As hydrostatic pressure rises with increasing water levels, the flow rate into the collecting bottle is increased whereas the opposite is true when hydrostatic pressure drops with declining water levels. Under optimal operation and sampling conditions, i.e. as long as the sampler is not completely filled, water samples can be collected continuously with an exact measurable volume. This enables a time-integrated, water level-weighted quantification of monitored chemicals – yielding water level-weighted time-integrated concentration (C_{WLW}). In contrast to the passive samplers described above, experimentally determined R_s values are not required. However, for enrichment, the water samples need to be concentrated by solid-phase extraction (SPE) prior analytical detection.

2.2.3 Scope of the study and research questions

To improve knowledge about the occurrence and concentration levels of pesticides in the Tapezco catchment, five stream sampling sites were selected in 2015, and the same sites plus an additional set of three stream sites were selected in 2016, for a time-integrated pesticide monitoring. Samplers were installed over repeated periods of two weeks, over the course of about two months in 2015 and four and a half months in 2016, respectively. The collected sampler extracts were analyzed for 275 PPTP.

The specific questions addressed in this study were:

- a) How is the comparative operability of the selected sampling systems for monitoring polar and semi-polar compounds?
- b) What are the biweekly pesticide concentrations in streams of the studied horticultural catchment, determined with all three passive sampling methods?
- c) How do the quantitative results of the different samplers compare?
- d) Which application recommendations can be provided for the various sampling devices concerning monitoring of pesticides in tropical catchments?

2.3. Materials and Methods

2.3.1 Study catchment

Details about the Tapezco river catchment are provided in Chapter 1 (section 1.7). Two sampling campaigns were conducted: a shorter pilot study in 2015 from July to October with five sampling sites (SC3, SC4, SC5, SC6, SC8); and an extended sampling campaign in 2016, from May to October at the same sites as in 2015 plus three additional sampling sites (SC1, SC2, SC7). GPS locations of the sampling sites and number of collected samples per individual sampling system are shown in (SI-2 B1).

2.3.2 Passive sampler preparation and operation

All three sampler types, SDB disks, PDMS sheets and WLPSS (illustrated in SI-2 A1), were assembled prior to deployment at the Laboratorio de Análisis de Residuos de Plaguicidas (LAREP) of the Universidad Nacional in Heredia, Costa Rica. Conditioning with solvents (to remove impurities and to enable proper absorption of target analytes) was required for the two sorbent-based samplers and was performed at LAREP (SDB disks) and Eawag (PDMS sheets), respectively. SDB disks and PDMS sheets were always deployed on the same day, side-by-side, at the specific sampling sites. In the streams, they were mounted to a brick (SI-2 A1) and exchanged with new samplers every two weeks. The WLPSS was likewise deployed on the same days and locations as the SDB disks and PDMS sheets but was exchanged every week. An operational blank control (i.e. a SDB or PDMS sampler or a sampling bottle filled with 1L nanopure water (NPW) for the WLPSS, going through all procedures from assembly to field exposure until chemical analysis) was carried along for each sampler type and biweekly installations. These blanks were extracted together with the environmental samples to account for possible background contamination. All samples were stored at LAREP at -20°C until shipment on ice to Eawag. At Eawag, samples were placed again at -20°C until work-up for chemical analysis. Further specifications are given for each sampler type below.

2.3.2 a) SDB disks

The SDB disks were applied in polar configuration (reverse phase sulfonated, RPS, Empore™ SDB disk, Modell 2241, Ø 47 mm, thickness: 0.5 ± 0.05 mm, 3M, Switzerland), as described in Moschet et al. (2015) and Vermeirssen et al. (2009). The SDB disks were overlaid by polyethersulfone (PES) filter membranes (Ø 47 mm, pore size: 0.45 µm, Supor, PALL, Switzerland). By using a filter membrane as sorption limiting barrier, the time until the sampler accumulates half of the equilibrium concentration (linear uptake phase, as discussed in detail in section 2.3.4 a) is longer than in “naked” configuration without PES (Endo et al. 2019, Moschet et al. 2015, Sánchez-Bayo and Hyne 2014, Shaw et al. 2009). A top steel plate with a cut-out central hole (area: 12.6 cm²) and a bottom steel plate were used as housing (illustration in SI-2 A1.1).

Conditioning: Before assembly, the SDB disks and the PES filter membranes were conditioned at LAREP. Conditioning started by shaking (velocity: 100 rounds per minute (rpm) = 0.335 relative centrifugal force (RCF), REAX2, Heidolph, Germany), first for 30 min with LC/MS grade methanol (Optima™, Fisher Scientific, Switzerland) and a second time for 30 min with NPW from a lab water purificator system (D11911, Barnstead/Thermo Scientific, USA). The conditioned SDB disks and the overlying PES membrane filter were then fixed between the stainless-steel-holder plates and stored at room temperature in NPW until field deployment (Moschet et al. 2015, Vermeirssen et al. 2009).

Sampling: At the end of each biweekly sampling period, samplers were collected and the overlaying PES filter and the SDB disk were carefully cut-out, on-site, along the central hole with a scalpel. The PES filter was discarded and the SDB disks were transported on ice to LAREP where they were stored at -20°C before shipment to Eawag. In 2015, a total of 24 SDB samples (four to five per site) were collected without any loss of samples. In 2016, a total of 79

SDB samples were collected, of which two were slightly damaged, four had slightly damaged overlying PES filters and three samplers were buried under sediment. One sample was completely lost. For initial qualitative (i.e. absence and presence) analysis, all the SDB samples which could be recovered were used, yielding 103 samples. However, the nine SDB samples that were either damaged or buried under sediment were not utilized for quantitative analysis and comparison among the individual samplers (more information SI-2 B2).

Sample processing: The SDB disks were further processed at Eawag, as previously described (Vermeirssen et al. 2009). Briefly, each SDB disk was extracted with 6 mL analytical LC/MS grade acetone (Merck, Germany) in a 7 mL vial by shaking for 30 minutes (100 rpm = 0.335 RCF). Then, the acetone was transferred into another 7 mL vial and 100 ng per sample of 142 semi-polar and polar isotopically labeled internal standards (ILIS, SI-2 A2.1) were added. Each SDB disk was extracted a second time with 5 mL of methanol under 30 minutes shaking. The two extracts were then blended and filtered through a polytetrafluoroethylene (PTFE) filter (13 mm, 0.45 µm; BGB analytic, Switzerland). The SDB extract was evaporated at 40°C under a stream of nitrogen to 0.1 mL methanol – the acetone was evaporated completely. Then, 0.9 mL of NPW were added to obtain an extract with a methanol-water ratio of 1:10. The extract of each sample was subsequently centrifuged at 4000 rpm (= 3200 RCF, for 30 min at 20°C, Megafuge 1.0R, Heraeus) to deposit particles in the extract in order to avoid a blockage of the HPLC injection system. The supernatant was used for chemical analysis. Extracts were kept at 4°C and analyzed within 2 - 5 days.

2.3.2 b) PDMS sheets

PDMS sheets from Altecweb (AlteSil™, translucent and talc free, 0.5 ± 0.05 mm thick, 60 x 60 cm² area, United Kingdom) with a size of 5 x 10 cm² were used as in Moschet et al. (2014b) (picture in SI-2 A1.1) and according to the guideline for the sampling of non-polar chemicals (Smedes and Booij 2012b). For the selected target pesticides there should be a linear uptake for at least 14 days of sampling (Moschet et al. 2014b).

Conditioning: The sheets were conditioned at Eawag by soxhlet extraction in ethyl acetate (purity > 99.7%, Honeywell, Switzerland) for 100 h to remove oligomers and other impurities, then dried for shipment to LAREP and stored there again in methanol (Moschet et al. 2014b). To transport the PDMS sheets to the field, they were dried at LAREP and wrapped in aluminum foil.

Sampling: The PDMS sheets were bolted next to the SDB disks and fixed with a polyvinyl chloride (PVC) bar. After exposure, the PDMS sheets were collected, transported on ice and stored at -20°C at LAREP, then transported to Eawag on ice and kept again at -20°C until extraction. In 2015, 24 PDMS sheets (four to five per sampling site) were collected, of which one sample of the sites SC3, SC4 and SC5 each had to be discarded because of extraction issues during sample preparation. In 2016, 79 samples were collected. Of those, three were buried under sediment and one had risen above the water level. One PDMS sheet (sample 80) got lost completely during the sampling period. For initial presence/absence analysis of PPTP, all 100 retrievable samples were used (i.e., 21 from 2015 and 79 from 2016). However, the four samples from 2016, which were either buried under sediments or was not completely covered with water throughout the biweekly sampling period, were not included for quantitative analysis and comparison of results among the individual samplers (more information of sorbent-based samples, SI-2 B2).

Sample processing: At Eawag, the sheets were extracted by accelerated solvent extraction (ASE, ASE350, Dionex, USA) in 10 mL ASE cells (Dionex, USA), following a previously established protocol (Moschet et al. 2014b). Briefly, five extraction cycles were carried out at 120°C with methanol, a static time of 10 min, a rinse volume of 75% and a purging of 110 s. After ASE, 10 or 100 ng of six non-polar ILIS (individual ILIS and their corresponding

concentrations are listed in SI-2 A2.2) were added to each extract. The samples were briefly shaken by hand, transferred into Büchi vials (120 mL, Büchi Corporation, Switzerland), and evaporated until dryness in the Büchi Syncore Analyst (Büchi Corporation, Switzerland) at 50°C with 159 mbar and 300 rpm (ca. 4.37 RCF).

The dried extracts were re-dissolved in 1 mL of hexane (purity > 99.7%, Carl Roth AG, Switzerland). For purification and analyte capture, the extracts were filtered through two-layered glass columns (5 mL glass pipette, article number: E945.1, Carl Roth AG, Switzerland, the narrow upper part of the glass pipette was removed to enable its packing with sorbent), filled with 500 mg Isolute C18 (Biotage, USA) and 500 mg pre-activated silica gel (silica gel 60, 0.063 – 0.2 mm, Merck Germany, activated at 130°C for 5 days). Before use, the two-layered columns were conditioned by 6 mL hexane. Subsequently, extracts were passed through the columns and rinsed with 2 mL hexane and then eluted with 10 mL HPLC grade acetonitrile (ACROS organics, Switzerland) as described in Moschet et al. (2014b). The extracts were evaporated again with the Büchi Syncore Analyst until dryness (50°C, 117 mbar, 300 rpm, = ca. 4.37 RCF). The analytes were re-dissolved in 1 mL HPLC grade hexane, centrifuged at 4000 rpm (= 3200 RCF, for 30 min at 20°C) and transferred into vials (1.5 mL short treat amber vials, 32 x 11.6 mm, BGB, Germany) and stored at -20°C until measurement.

2.3.2 c) WLPSS

The WLPSS (for a schematic drawing see SI-2 A1.2) was used in two configurations as suggested by P. Schneider (personal communication) with slight modifications for this study. In 2015, the WLPSS was equipped with an HPLC capillary for resistance (HPLC capillary: Ø 0.13 mm, length: 1.3 m) while in 2016 the HPLC capillary was replaced by a precision valve (Göldi Präzisionsmechanik AG, Schlieren, Switzerland, <https://goeldi-mechanik.ch/kontakt/>). Both the HPLC capillary and the precision valve regulate the outflow of air and the inflow of water in the sampling bottle. The resistance was placed outside the water and was connected to the air-outlet of the sampling flask via a vinyl tube. Furthermore, the 0.5 L high-density polyethylene container used by P. Schneider was replaced by an amber, wide-neck screw thread glass bottle (1 L, Roth AG, Switzerland, order nr. HT12.1) to increase the sample volume capacity and to prevent absorption of pesticides to the inner wall. This 1 L bottle was sealed with a silicone O-ring (Ø 6 mm, Fabrica de Niples Dannis, Heredia, Costa Rica). Lastly, the PVC case for protecting the sampling bottle was lined with foam rubber (22.3 cm height, 45 cm wide, and 1.4 cm thick) and adapted in size (0.8 cm thickness, Ø 16 cm, 30.6 cm height). To keep the WLPSS under water, the PVC case was weighed down with a stainless-steel cylinder (3.3 cm high, 12.7 cm diameter, Acero Roag Almacen S.A., San Jose, Costa Rica).

The basic working principle of the WLPSS is that the volume sampled per time unit is dependent on the water level and the resulting hydrostatic pressure exerted on the WLPSS. This means that at a consistent water level, the water flow into the system is constant. With increasing water levels, the water pressure exerted on the WLPSS system increases, ambient air is pressed out the WLPSS system faster through the resistance (HPLC capillary or the precision valve), resulting in a faster inflow of water into the system as well. If the water level decreases, the hydrostatic pressure imposed on the WLPSS decreases - the outflow of air and the inflow of water slows down.

During initial WPSS deployment, the ambient air in the sampling bottle was compressed and a fixed volume of water per immersion depth was immediately entrained into the sampling bottle until the pressure was equilibrated. This initial volume ranged between 16 to 32 mL at immersion depths of 5 to 20 cm, respectively according to additional laboratory tests (SI-2 A1.3). After this initial sampled amount, the WLPSS directly started sampling continuously with an inflow increasing or decreasing with the water level. Since the described initial leaking volume was small compared to the total volumes sampled (maximum 1 L/week), the initial leaking volume was assumed negligible and is not further discussed within this study.

With the installation described above, the following criteria needed to be fulfilled for optimal performance (= operational range). First, water should be sampled continuously according to hydrostatic pressure but within the volume limits, i.e., without running completely full. Second, biweekly samples needed to be obtained to match the biweekly sampling scheme of the sorbent-based samplers. Third, for optimal enrichment via SPE for chemical analysis, a total volume of 1 L was required per biweekly sample. Thus, to meet these criteria, two successive weekly collected WLPSS samples were always blended together under the condition to yield a 1 L biweekly sample.

Sampling: As stated above, the WLPSS sampling bottles were collected weekly and replaced with empty ones. The collected samples were cooled on ice in the field and transported to LAREP. At LAREP, the weekly samples were then pressure filtrated within 24 h, stored at 4°C in the dark until two-week samples were mixed.

In 2015, 24 biweekly samples (4 to 5 per site) were collected in total, of which only 3 samples for the WLPSS sampled volumes was in the operational range and only these were used for quantitative analysis. For presence/absence control of PPTP, all 2015 samples were taken. In 2016, 80 biweekly samples were obtained (10 per site). For 13 biweekly samples, the WLPSS sampled volumes within the operational range and these were used for quantitative analysis. Thus, overall, only 15% of the WLPSS installed sampled in the optimal range for quantitative PPTP analysis. For 48 samples of the 2016 series, the WLPSS was completely filled in at least one week during the biweekly sampling; these plus the previously stated 13 WLPSS samples were still usable for presence/absence analysis. For 19 samples, the WLPSS did not sample enough water for analysis and were therefore discarded. An overview of obtained samples is provided in SI-2 B3.

Sample processing: Samples were processed at LAREP, as described in Kern et al. (2009) and Ruff et al. (2015). Briefly, the samples were pressure filtered (Grade GF/D, Ø 47 mm, pore size 2.7 µm, Whatman, Huberlab, Switzerland) and stored in the dark at 4°C within 48 h after sample collection. After blending two weekly samples for the biweekly probe, 1 L of each sample was buffered with ammonium acetate and adjusted to a neutral pH by adding ammonia or formic acid (FA). If two subsequent samples were filled completely and 2 L was collected as biweekly sample, 1 L was used as sample and the other 1 L was used for spiking experiments with reference standards to determine matrix effects (SI-2 A2.3). To each sample, 100 ng of 142 semi-polar and polar ILIS were added (SI-2 A2.1) and all the samples were concentrated via SPE with the multilayer cartridges at LAREP.

SPE: Manually packed cartridges were used for SPE as described in Kern et al. (2009) and Vogler (2013). Briefly, 6 mL cartridges (Supelco, Switzerland) with three different layers were used: first, 200 mg of Supelco-Envicarb; second, a mixture of 100 mg Strata-X-AW (Phenomenex, Switzerland), 100 mg Strata-X-CW (Phenomenex, Switzerland) and 150 mg ENV+ (Biotage, United Kingdom); and third, 200 mg OASIS HLB (30 µm, Waters, Switzerland). These cartridges were conditioned with 5 mL of methanol and 10 mL of NPW. After the sample introduction, the cartridges were dried in the SPE manifold via vacuum, and then stored in the freezer at -20°C until transport to Eawag. For a sequentially back-flush elution of the cartridges, 6 mL of methanol/ethyl acetate (v:v 50:50) with 2% of a 25% ammonia solution were used. Then, 3 mL methanol/ethyl acetate (v:v 50:50) containing 1.7% of 99% FA, and finally, 2 mL of methanol were used for rinsing the multilayer cartridge. Afterwards, the extracts were evaporated under a gentle stream of nitrogen to 100 µL and finally reconstituted to a final volume of 1 mL using NPW. Subsequently, the extracts were centrifuged for 30 min at 4000 rpm (= 3200 RCF) to deposit particles and transferred into vials (1.5 mL short treat amber vial, 32 x 11.6 mm, BGB, Germany). The extracts were analyzed within 2-5 days and kept at 4°C until measurement.

2.3.3 Chemical analysis

Targeted screening of 258 polar and semi-polar PPTP in samples obtained with the SDB and WLPSS samplers was conducted via high-resolution liquid chromatography tandem mass spectrometry (LC-HR MS/MS) (Moschet et al. 2013). These PPTP included 247 compounds from previous studies (Moschet et al. 2015, Ruff et al. 2015) plus 11 additional compounds (buprofezin, carbaryl, clethodim, cyazofamid, flutolanil, imazalil, indoxacarb, malathion, propoxur, quizalifop-p, triadimenol), which were added because of previously reported application in the study area (Ramírez et al. 2016). The monitored PPTP spectrum consisted of 55 fungicides and 7 fungicide transformation products (TP), 40 insecticides and 11 insecticide TP, 95 herbicides and 40 herbicide TP and 10 substances from other substance classes (germicides, molluscicides, pharmaceuticals, phyto regulators, preservatives and wood protection agents, shown in (SI-2 B4 and SI-2 B5). Isobaric compounds were counted as one compound since chromatographic separation was not possible (i.e. acetochlor + alachlor; prometryn + terbutryn, acetochlor-ESA + alachlor-ESA, propazine-2-hydroxy + terbutylazine-2-hydroxy).

For detection of non-polar pesticides, 18 insecticides (listed in SI-2 B6) were screened via atmospheric pressure chemical ionization gas chromatography tandem mass spectrometry (GC-APCI-MS/MS) according to Rösch et al. (2019), in PDMS sheet extracts.

The limits of quantification (LOQ, lowest quantifiable mass in ng per L water sample), method limit of quantifications (MLOQ, lowest quantifiable mass in ng per 1 mL sample extract) and recoveries for the different chemical analysis approaches are presented in SI-2 B4 for WLPSS samplers, SI-2 B5 for SDB disks and SI-2 B6 for PDMS sheets. Information about how the absolute and relative recoveries, the MLOQ (ng/mL sample extract) and the LOQ (ng in 1 L sample equivalent) were determined, are collected in section SI-2 A2.3.

2.3.3 a) Analysis of polar and semi-polar PPTP in SDB and WLPSS samples via LC-HR MS/MS

For chromatographic separation, a reversed phase C18 column (XBridge, 3.5 μ m, 2.1 x 50 mm, Waters, Ireland) was used, and a mass spectrometer (QExactive, Thermo Fisher Scientific Corporation, U.S.) was applied for electrospray ionization (ESI) detection (ion source information: SI-2 A2.4). Full scans were acquired with a resolution of 140,000 (at m/z = 200) in the range of 100 to 1000 m/z followed by top five data-dependent MS/MS (resolution 17,500) in positive and negative ionization mode separately. For measuring, 10 μ L of every sample was injected and the gradient was formed using solvent A, NPW, and solvent B, analytical grade methanol, both supplemented with 0.1% FA. The flow rate was 0.2 mL/min (Rheos2200 pump, Flux Instruments, Switzerland) and the chromatographic gradient was set equivalent to Moschet et al. (2013) (details SI-2 A2.4).

Data analysis was realized with TraceFinder (version 3.3, Thermo Fisher Scientific Corporation, U.S.). Chromatographic peaks of target analytes were automatically detected (mass accuracy < 5 ppm, peaks with a minimum of 5 data points) by using the retention times (RT) of the target analytes, confirmed with MS/MS fragments, and comparing them with RT and fragments of analyte identical reference standards (STD). Additionally, for each targeted compound, each peak was reviewed manually in all samples for further quality control. Quantification was then performed with a twelve-point calibration curve using STD together with ILIS as internal standards. ILIS were added to each sample at the beginning of the sample extraction to account for losses during sample preparation. For 44 compounds, structurally identical ILIS were available (SI-2 B4 and SI-2 B5, quantification label: 1). The remaining analytes were quantified using structurally non-identical ILIS with similar RT (SI-2 B4 and SI-2 B4, quantification label: 2).

For the quantification of the masses in the SDB extracts, an external twelve-point serial calibration (0.1, 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000, 2000 ng/mL) was prepared in 1 mL (90:10, methanol: NPW) by using STD mixes with all target PPTP, to which 100 ng (per sample) of the 142 ILIS (details SI-2 A2.1) were added. For the quantification of WLPSS samples, another twelve-point internal serial calibration (0.1, 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000, 2000 ng/L) was prepared in 1 L NPW. The WLPSS calibration samples were then enriched via SPE (enrichment factor: 1000) and extracted in the same way as the environmental samples (see above, 2.3.2 c). Before SPE, 100 ng (per sample) of the 142 ILIS were added to these calibration samples as well. The ratio of the peak area of the analytes and the corresponding ILIS were used for each substance and compared to those in the respective calibration curve. The calibration curves were obtained conducting a linear least square regression with a weighting factor 1/concentration. For the compounds without structurally identical ILIS, the concentrations were corrected by relative recovery (SI-2 A2.3).

2.3.3 b) Atmospheric pressure chemical ionization (APCI) gas chromatography tandem mass spectrometry

For chromatographic separation, a fused silica column (Rtx-5MS, 30 m, 0.25 µm film thickness, 0.25 mm i.d., Restek, BGB, Switzerland) and a mass spectrometer (triple quadrupole, MS/MS, Agilent 6495, Switzerland) were used as described by Rösch et al. (2019). The oven temperature gradient was applied as shown in detail in SI-2 A2.5. For measuring, 3 µL of each sample were injected using a deactivated liner (borosilicate glass, 4 mm i.d., Restek) at 250 °C. As carrier gas, helium (99.99%, Carbagas, Switzerland) was used with a flow of 3 mL/min. Information about the APCI Ion source are listed in the table in SI-2 A2.5.

The substances were measured in positive ionization mode with NPW as a modifier. The NPW was pumped constantly (50 µL/min) into a small open vial, placed in the ionization source. The mass spectrometer was used in dynamic multiple reaction monitoring (MRM) mode. The cycle time was 250 ms, the mass resolution was 1.2 Da (quadrupole 1 and 3, wide isolation mode). N₂ was used as collision gas, (99.999%, Carbagas, Switzerland). For each target substance and ILIS, a minimum of two transitions were measured, from which the most sensitive transition was used as quantifier and the remaining transition as qualifier in agreement with Rösch et al. (2019). Main information about the GC-APCI-MS/MS method applied in this study are briefly summarized in SI-2 A2.5.

For peak integration, the Masshunter Qualitative and Quantitative analysis software (version: B.07.00, Agilent, Switzerland) was used (Rösch et al. 2019). For quantification of the environmental samples, a matrix-matched ten-point calibration series was prepared (0.2, 1, 5, 10, 20, 50, 100, 200, 500, 1000 ng/mL) using STD. Ten conditioned PDMS sheets were spiked with the individual amounts of STD via pipetting. Afterwards, the spiked sheets were extracted via ASE, 10 or 100 ng non-polar ILIS (SI-2 A2.2) were added, and the calibration samples were processed equivalently to the environmental samples. The quantification was based as well on internal standard calibration as described previously (in section 2.3.3 a); ILIS are listed in SI-2 A2.2.

2.3.4 Back-calculation of water concentrations

2.3.4 a) Calculating C_{TIA} from chemical amounts extracted from SDB disks and PDMS sheets

The masses absorbed to the sorbent-based samplers, $m_{sorbent}$, were used to calculate environmental C_{TIA} in water as described in Camilleri et al. (2012) and Vrana et al. (2005). To directly relate the $m_{sorbent}$ [ng/sorbent-based sampler] with C_{TIA} [ng/L], the sorbent material needs to act as an infinite sink for the target compounds throughout the sampling period, t [d]. Under this assumption, the passive samplers act as a linear accumulating device. The

assumption of linear accumulation is only satisfied if the concentration in the receiving phase is less than half of its equilibrium value. Based on this assumption, Equation 2.1 becomes valid.

$$C_{TIA} = \frac{m_{absorbent}}{R_S * t} \quad [\text{Eq. 2.1}]$$

where R_S is the sampling rate [L/d]. R_S values are material-, compound- and environmental condition-dependent and can be determined via uptake experiments (Ahrens et al. 2015, Gunold et al. 2008, Mechelke et al. 2019, O'Brien et al. 2011) or *in-situ* calibrations (Ahrens et al. 2018, Moschet et al. 2015). For 68 polar and semi-polar PPTP, such experimentally determined R_S values were available (SI-2 B10). If more than one R_S value per target compound was found, the average was used as previously suggested (Curchod et al. 2019). For all PPTP without available R_S values, the average R_S , 0.094 L/d, for all 68 available PPTP was used as an approximation. The enrichment factor of PPTP during SDB sampling was on average 150 (based on Eq. 2.1: $1/R_S * \text{deployment time} = 1/0.094 * 14$). More details about the average R_S values are given in SI-2 A4, Eq. SI-2A (5). Finally, it is important to note that R_S values can vary with sampling site specific conditions, such as pH, temperature, water flow velocities (Curchod et al. 2019, Gunold et al. 2008, Harman et al. 2012, Mechelke et al. 2019, Moschet et al. 2014b, Vermeirssen et al. 2009). Thus, a suggested uncertainty factor of about one-order of magnitude (i.e., R_S multiplied and divided by a factor of three) was applied to all R_S values used in this study as previously described (Curchod et al. 2019, Moschet et al. 2014b).

For the target analytes monitored with the PDMS sheets, no compound-specific R_S values were available from the literature. Therefore, in order to determine C_{TIA} , the average R_S value of PCBs and PAHs of 5.83 L/d for PDMS sheets of 50 cm² size was used (Rusina et al. 2010a, Smedes and Booij 2012b) as described in a previous study (Moschet et al. 2014b). This was done under the assumption that the strong relationship between the water-PDMS partition coefficients and $\log K_{OW}$ for PCBs and PAHs (Rusina et al. 2010b) applies also to the non-polar pesticides analyzed in this study (Moschet et al. 2014b).

2.3.4 b) Deriving C_{WLW} from WLPSS samples

For back-calculating the amounts of the target analytes from the WLPSS sample extract, a dilution factor of 1000 was applied to yield C_{WLW} . This was done because 1 L water samples were concentrated into 1 mL sample extract during SPE (Enrichment factor: 1000).

2.4 Results and discussion

From the 275 chemicals targeted for screening, 99 and 87 polar to semi-polar PPTP were detected with the WLPSS and the SDB disks, respectively (see tables, SI-2 B4 and SI-2 B5), with an overlap of 77 chemicals, belonging to all pesticide classes. Moreover, 11 non-polar pesticides were captured with the PDMS sheets of which one pesticide, chlorpyrifos, was also detected with the SDB and WLPSS.

2.4.1 Monitoring of polar and semi-polar PPTP with the WLPSS and SDB disks

2.4.1 a) Absence/presence analysis and comparison

A comparison of the number of detected PPTP for each pesticide type (herbicides, insecticides, fungicides and their TP) with the WLPSS and the SDB sampler revealed that, in each year and with both sampling systems, the pesticide type fungicides was the highest in number, followed by insecticides and herbicides with similar coverage (Figure 1, SI-2 B4 and SI-2 B5). Importantly, the number of compounds per individual pesticide type and sampling year were not significantly different between the two sampler types (Chi-squared test: p values > 0.9 for both years, R-script: SI-2 C1). Accordingly, it can be stated that both WLPSS and SDB efficiently sampled a similar number of PPTP. These results underline the application of the WLPSS and the SDB sampler for a robust detection of PPTP with regard to chemical coverage in remote tropical areas. Moreover, the results obtained demonstrate that in both sampling years a similar number of PPTP per pesticide type were released into the streams.

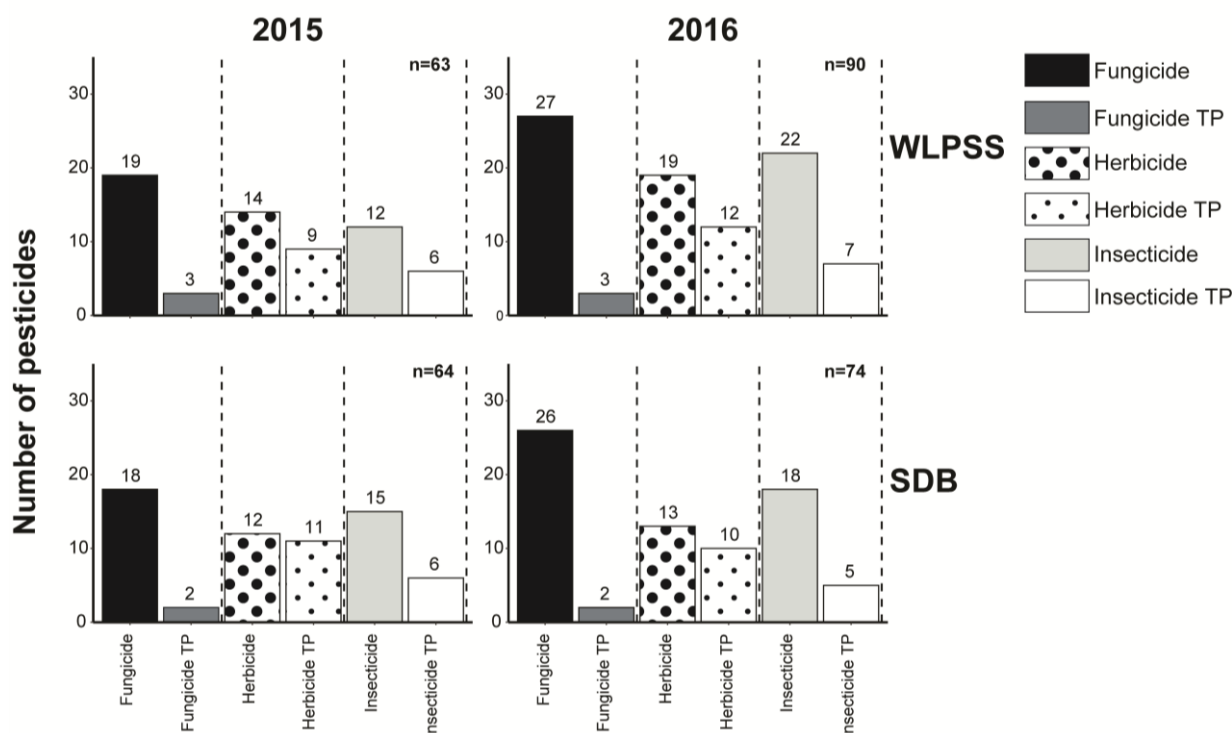


Figure 1: Number of PPTP detected during the two sampling campaigns in the Tapezco river catchment with the WLPSS and the SDB sampling approaches. The compounds were divided into different pesticide types: fungicides, fungicide TP, herbicides, herbicide TP, insecticides, insecticide TP.

The current study complements previously published data (Ramírez et al. 2016) concerning the PPTP spectrum detected in the Tapezco river catchment. They reported 22 pesticides based on three monthly grab samples from 2013 to 2016 (SI-2 B7) using LC with an ultraviolet photodiode array detector and a gas chromatography MS/MS method. Of these 22 pesticides,

13 were also detected with both WLPSS and SDB together, three were not quantifiable and six pesticides (five non-polar polar and one polar pesticide) were not included in the chemical methods applied in this study. A further development of the chemical analysis method to broaden the analyzed spectrum was not conducted because it was not the main focus of this study and because method development is very time consuming. Yet, the current study expanded the previously detected spectrum by another 83 PPTP. Thus, of the 104 pesticides described by farmers to be used in the Tapezco river area (Ramírez et al. 2016), 44% were confirmed in this monitoring campaign, in contrast to 18% (19 of the 22 detected pesticides) detected in the prior grab sampling study (Ramírez et al. 2016).

In total, 109 polar and non-polar PPTP were detected in this study (SI-2 B8) with the WLPSS and SDB disks compared to 146 PPTP by Moschet et al. (2015), who used similar approaches, i.e. the same type of SDB disks and a time proportional automated water sampler instead of the WLPSS. Of the 146 PPTP detected in their study in five medium-sized Swiss rivers, 79% (116 pesticides) were detected in both the SDB disks and the water samples, compared to an overlap of 71% (77 out of 109) between the WLPSS and SDB here. Moreover, 63 of the PPTP reported by Moschet et al. (2015) were detected in the WLPSS and 53 with the SDB disks employed in the Tapezco river catchment (see SI-2 B9 for comparison). In both studies, a similar number of fungicides was detected, whereas in the Swiss rivers the numbers of herbicides was 2-fold higher and that of insecticides 2-fold lower than in the Tapezco river catchment.

Even though in the present study, the majority of PPTP was found with both the SDB and the WLPSS, some PPTP were detected only with one sampling method, as also previously described (Moschet et al. 2015). Specifically, nine compounds (acetochlor and alachlor isobar) were only found with the SDB approach (Figure 2A, red points), and 22 compounds exclusively with the WLPSS (Figure 2B, SI-2 A3).

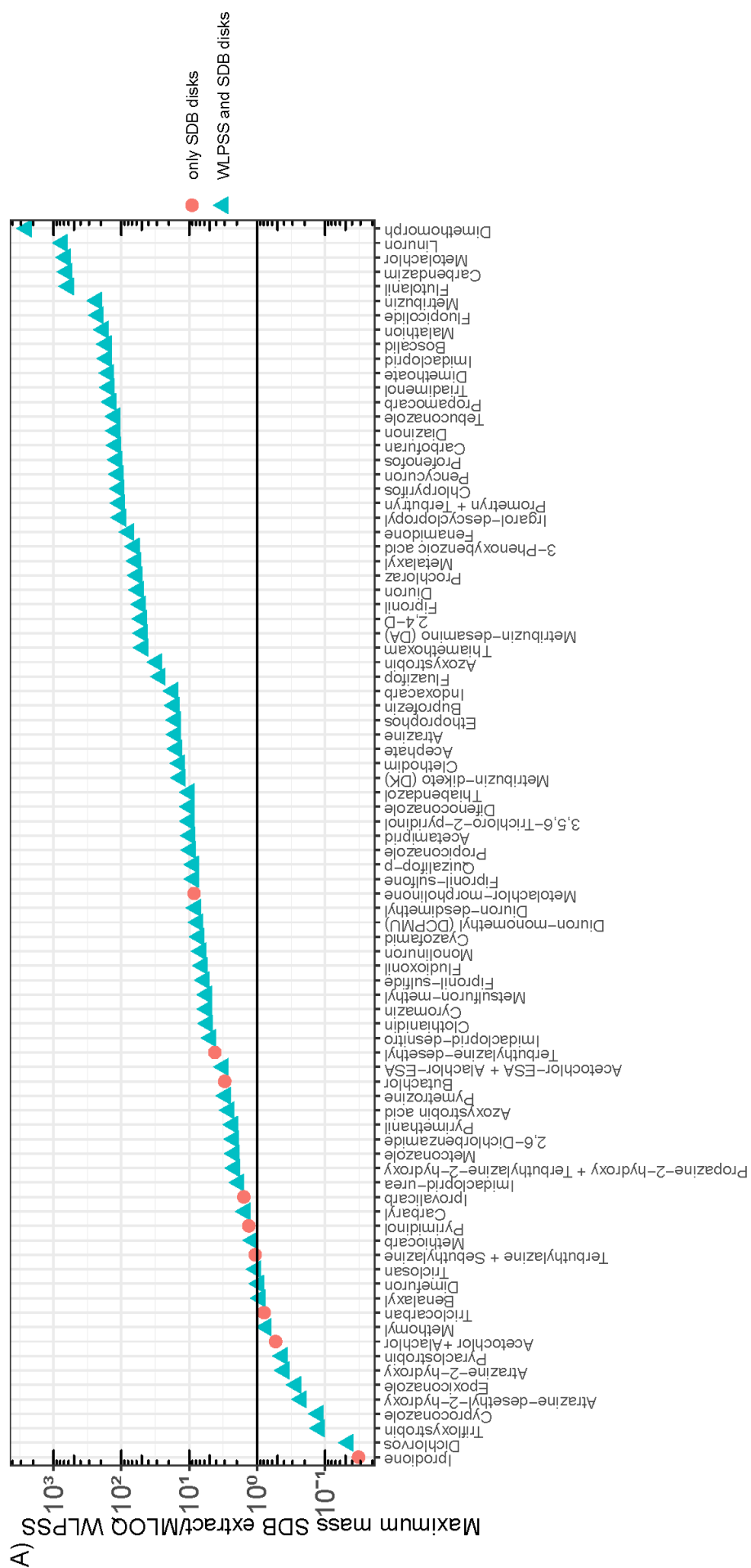
The selective detection of most of the PPTP can be explained by low exposure levels and resulting low masses accumulated in the samplers. This becomes apparent by comparing the maximal masses of the PPTP detected in the SDB disk extracts with the MLOQ for the corresponding PPTP in the WLPSS extracts (Figure 2A, red points: selective detected PPTP with SDB disks, blue triangles: PPTP detected with both approaches) and vice versa (maximum masses in WLPSS samples/MLOQ of SDB, Figure 2B, red points: selective detected PPTP with WLPSS, blue triangles: PPTP detected with both approaches).

As can be seen from Figure 2A, the maximum masses of the PPTP selectively sampled with the SDB are similar or below the MLOQ of the WLPSS extracts. Similarly, as seen in Figure 2B, the maximum masses of the selectively sampled PPTP with the WLPSS are similar or below the MLOQ of the SDB disk extracts. Of the PPTP selectively detected with the WLPSS, particularly seven stood out which should be detectable with both approaches (maximum masses in WLPSS extracts exceeded MLOQ of SDB extracts by factors between 10 and 100). Of these seven PPTP, three, namely flusilazole, prometon and bentazon, occurred at very low levels (between 3.5 and 8.8 ng/mL) in the WLPSS extracts, which is close to their MLOQs in the SDB extracts (ranging between 0.2 – 0.75 ng/mL). For three of the remaining four chemicals (fluroxypyr, propachlor-OXA and 5-chloro-2-methyl-4-isothiazolin—3-one (CMI)), the determined maximum concentration in the WLPSS extract must be treated with caution. For fluroxypyr, the RT of the chromatograms were slightly shifted and an unambiguous allocation was not possible; for propachlor-OXA, the recovery was poor though RT and peaks fragments were confirmed in 2015, while in 2016, the calibration curve was not linear; CMI occurred only at very low levels as well in some extracts close to the MLOQ with the WLPSS method. It might be that CMI was able to enter some samples as background at low levels during preparation since it is used in paints as preservative. Along these lines, CMI was confirmed as traces as well in several field blinds though below MLOQ. All of these latter named compounds did not pass the criteria to be considered for final quantitative analysis.

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With the WLPSS approach, more PPTP were selectively detectable than with the SDB approach. This could be due to the differences between the enrichment factors of both approaches (Moschet et al. 2015). With the WLPSS approach, all compounds had an enrichment factor of 1000 during sample preparation (1 L concentrated to 1 mL). The enrichment factor of PPTP during SDB sampling was generally lower, i.e. on average 150 (see 3.3.4 a). This could also explain why pyroxsulam, the final of the seven PPTP with WLPSS-derived maximum masses exceeding the SDB-MLOQ (Figure 2B), was only detected with the WLPSS and not with the SDB disk approach.

In addition, low exposure levels and resulting low (maximum) masses accumulated in the samplers did not always though in the most cases explain the selective/exclusive detection of PPTP. Only a small selection of PPTP were exclusively detected despite their accumulation to high (maximum) masses, exceeding the MLOQ of the corresponding sampling method. Moreover, it was noticeable that the PPTP detected in both systems had maximum mass (of one system)/MLOQ (of the opposite sampling system) ratio distribution along the y-axes (see Figure 2) that were significantly shifted upwards compared to those PPTP only detected with one sampling system. To test this, the distribution of maximum amount/MLOQ ratios for selective and non-selective PPTP was tested by one-way ANOVA, Welch test ($p \leq 0.001$, SI-2 C2).



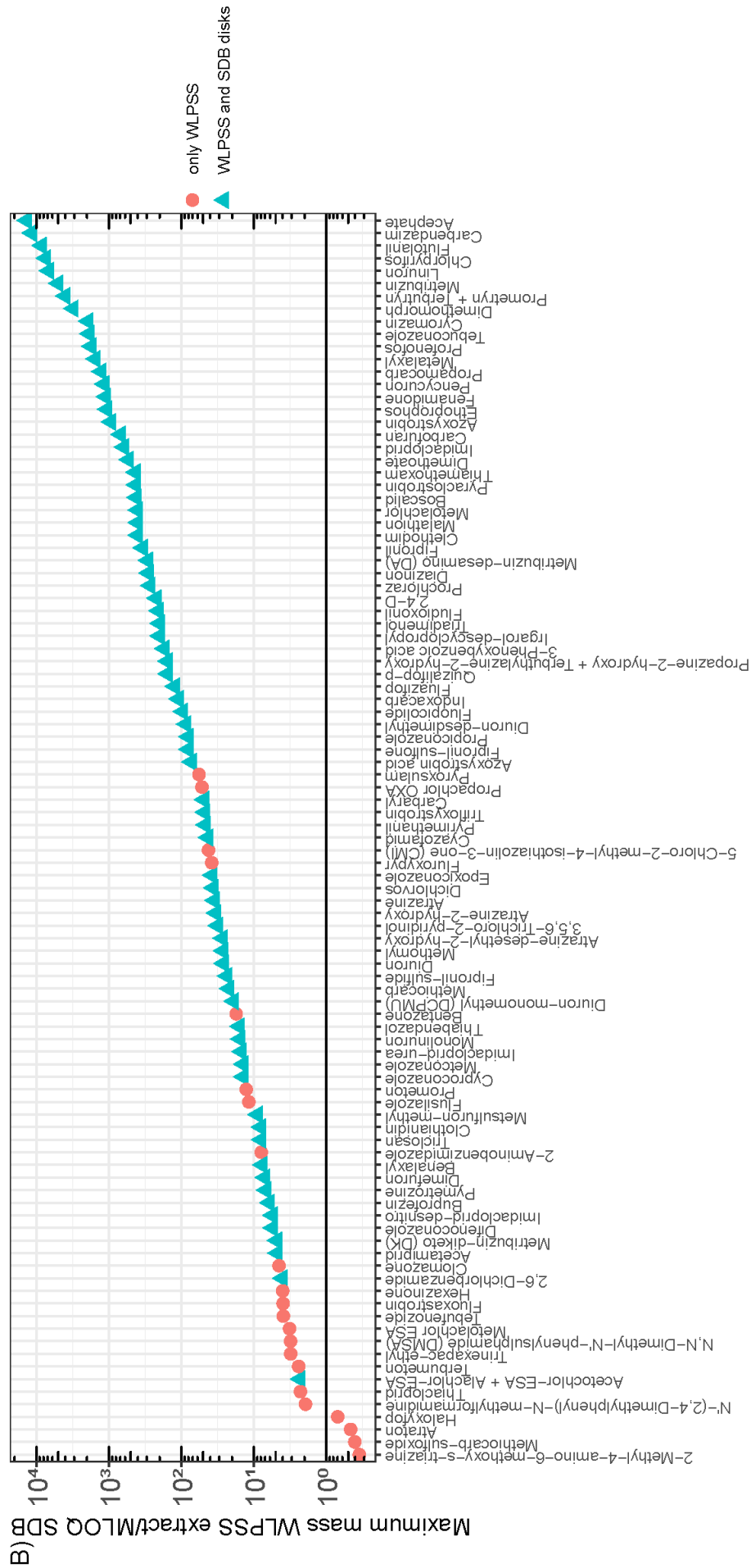


Figure 2: Differentiation among selectively and non-selectively detected PPTP. Selectively detected PPTP have low ratios between the maximum masses in the selective sampler and the MLOQ of the non-selective sampler. Ratios of the highest detected amount in SDB disk extracts and the MLOQ for the PPTP of the corresponding WLPSS sampling method (A). Ratios of the highest detected amount in WLPSS extracts and the MLOQ for the PPTP of the corresponding SDB sampling method (B). Black line represents 1:1 ratio.

2.4.1 b) Quantitative analysis – detected concentration ranges

Several criteria were applied to determine if further quantitative interpretation would be justifiable. For some of the PPTP for which the presence in the environmental samples was confirmed, their concentrations could not be determined due to unsatisfactory linear calibration curves ($R^2 \leq 0.95$, SDB samples, SI-2 B5), as for iprodione and metolachlor-morpholine, or due to poor recoveries as for N'-(2,4-dimethylphenyl)-N-methylformamidine (WLPSS samples, SI-2 B4). Only samples without sampling issues, as described in 2.3.2, were applied. All WLPSS and SDB samples used for quantitative analysis are highlighted in SI-2 B3 and SI-2 B2, respectively.

Following these considerations, C_{TIA} of PPTP were calculated using the amounts absorbed to the SDB disks along with the R_S values as described in the material and method (section 2.3.4 a). Resulting concentrations are shown in SI-2 B11.2. The concentration ranges of the 20 PPTP with the highest determined concentrations are presented in Figure 3 (based on SI-2 B11.1). Collating them along the level of determined concentrations indicates that carbendazim, flutolanil and dimethomorph reached highest concentrations with the median surpassing 100 ng/L.

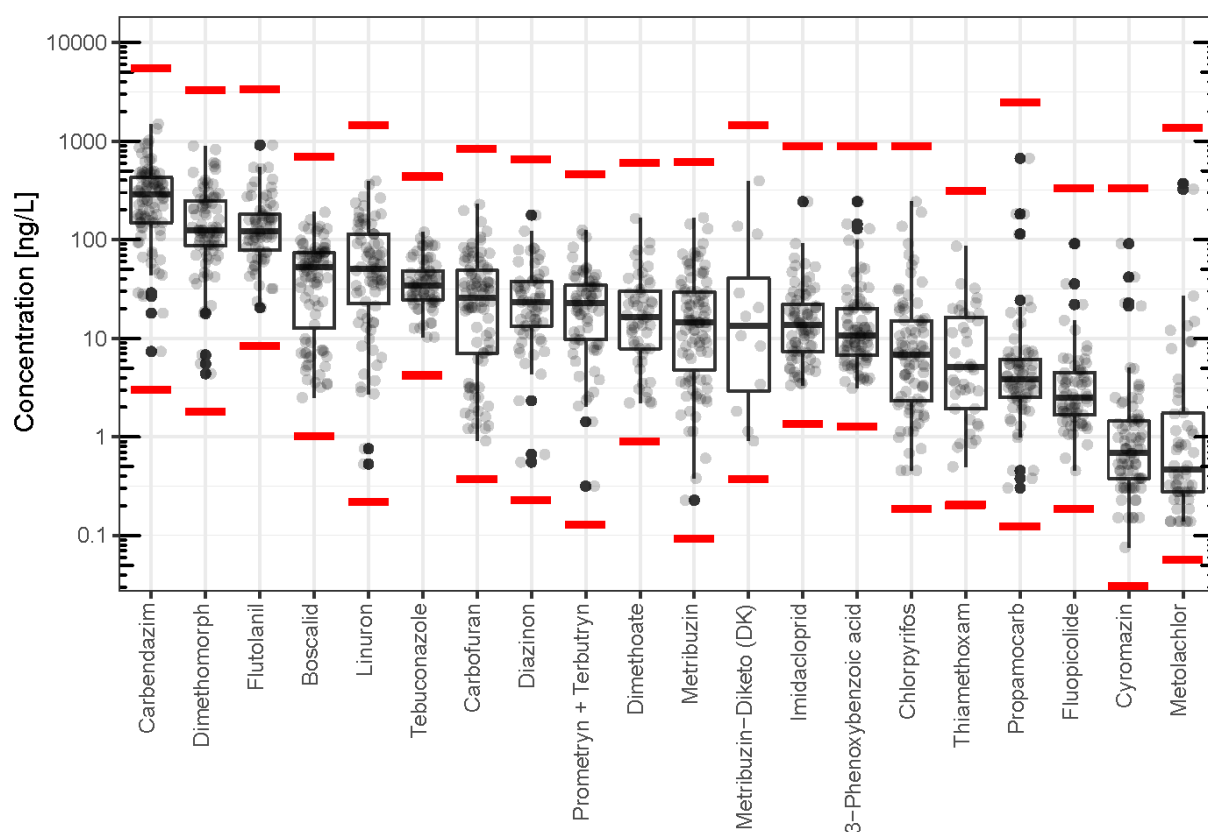


Figure 3: The 20 PPTP with the highest maximum water concentrations, monitored with SDB disks, in the Tapezco river catchment in descending order. Data are for both sampling periods in 2015 and 2016. Boxplots represent first and third quartiles (outer box) and medians (thick lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of $1.5 \times$ the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of $1.5 \times$ the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers, the grey (staggered) dots represent individual concentration data points, indicating how the data is distributed (standardized boxplot using R ggplot2 package). Red lines represent uncertainties of minima and maxima values based on a factor of three for the R_S values in both directions according to Curchod et al. (2019) and Moschet et al. (2014b).

For WLPSS derived samples, C_{WLW} of PPTP were determined directly from their amounts in the sample extracts as described (section 2.3.4 b). The resulting concentrations are presented in SI-2 B12.2. The concentration range of the 20 PPTP with the highest concentrations is presented in Figure 4 (based on SI-2 B12.1). Chemicals surpassing the median of 100 ng/L concentration were carbendazim, flutolanil, and linuron.

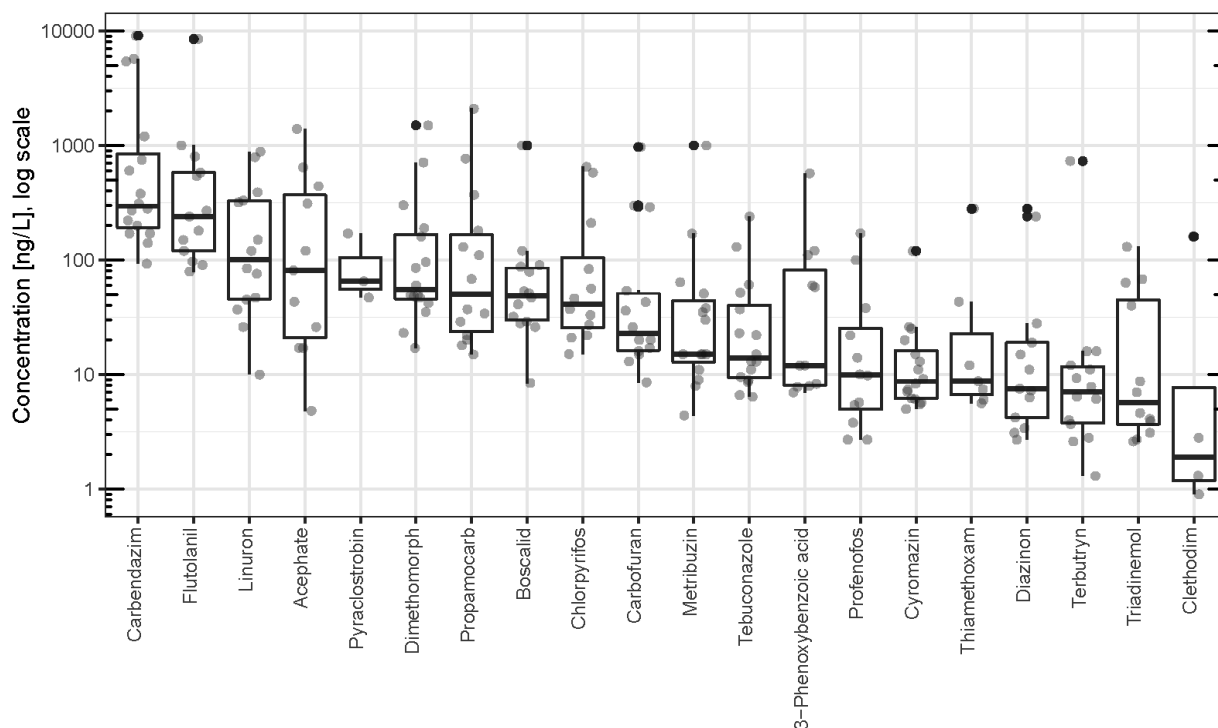


Figure 4: Concentration ranges of the 20 PPTP with the highest concentrations, detected with the WLPSS in descending order. Data are for both sampling periods in 2015 and 2016. Boxplots represent first and third quartiles (outer box) and medians (thick lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of 1.5 * the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of 1.5 * the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers, the grey (staggered) dots represent individual concentration data points, indicating how the data is distributed (standardized boxplot using R ggplot2 package).

While the concentration data provide a broad overview of pesticide pollution in the Tapezco river catchment, some uncertainties need to be kept in mind. For the SDB disk-derived C_{TIA} , R_S values were collected from the literature, which means that they may not fully account for each individual chemical and the special situations at the site. Therefore, the three-fold uncertainty range in both directions, according to the recommendations by Curchod et al. (2019) and Moschet et al. (2014b), was applied (Figure 3). To reduce these uncertainties, R_S values would need to be determined empirically for all targeted PPTP. This would have been possible by laboratory uptake experiments in flow channels or water tanks according to Ahrens et al. (2015), Schreiner et al. (2020) or Mechelke et al. (2019), performed under conditions similar to those experienced in the tropic stream e.g. in terms of temperature (15 to 20 °C). However, due to the broad target spectrum and limitations in time, this was not feasible. Another option would have been to conduct a calibration in the field by taking, for at least some overlapping time periods, automated time-proportional samples and compare the concentrations obtained with masses absorbed to the SDB disks to estimate R_S values (according to [Eq. 2.1]) as conducted by Moschet et al. (2015). Since both approaches sample in a time-weighted averaged manner, such

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a comparison would be possible. Using such an automated, energy-demanding composite sampler, however, was not possible at the remote Tapezco river sampling sites with difficult access. Hence, the WLPSS was applied.

The WLPSS was used here for the first time to monitor PPTP. This study demonstrated that there is a need to investigate the sampling behavior of the WLPSS in more detail to improve the adjustment of the sampling volume at a given field site. The water level proportional concentrations in the WLPSS extracts were derived as described in 2.3.4 b) by considering the known sample volume. The data of the WLPSS that were obtained within the optimal sampling range were compared to the SDB data. According to the different sampling principles (the biweekly integrated water level-weighted sampling of the WLPSS vs. the biweekly integrated averaged sampling of the SDB sampling), one could postulate that, if pesticide concentrations increase together with water level and discharge, in the WLPSS, they would exceed those of the SDB disks, because the sampled volume increases simultaneously with increasing water levels based on the working principle of the WLPSS explained in 2.3.2 c) (more details about the WLPSS sampling behavior, see SI-2 A4.2).

For seven pesticides (pyraclostrobin, clethodim, epoxicoazole, acephate, chlorpyrifos, propamocarb, and cyromazin), the WLPSS indeed provided water concentrations that were 10-fold higher than with the SDB disk sampling. One caveat of this analyses is that only one or two data points were available for clethodim, epoxiconazole, pyraclostrobin (Figure 5, SI-2 A4.3, based on data SI-2 B11.1 and SI-2 B12.1). However, despite the different sampling principles, in the majority of cases (52 out of 59 PPTP), the quantitative data differed less than one order of magnitude between the WLPSS and the SDB. It has to be pointed out, however, that for 11 of the 52 PPTP (Figure 5, SI-2 A4.3, comparison C_{TIA} and C_{WLW}) only one or two data points were available.

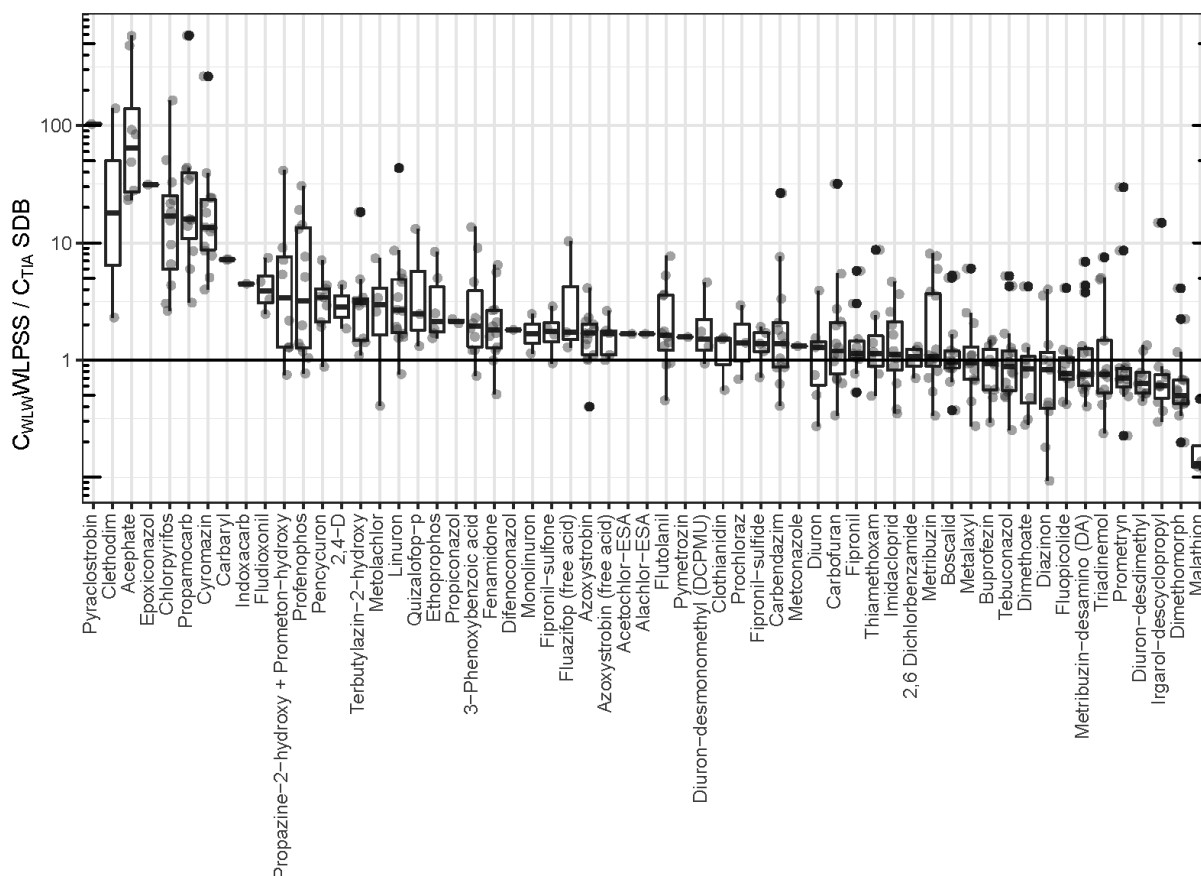


Figure 5: Ratios of the CWLW derived from the WLPSS and CTIA derived from SDB disks. Boxplots represent first and third quartiles (outer box) and medians (thick lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of $1.5 \times$ the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of $1.5 \times$ the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers, the grey (staggered) dots represent individual concentration data points, indicating how the data is distributed (standardized boxplot using R ggplot2 package).

Among possible input pathways (Chapter 1, Section 1.3), surface runoffs after heavy rain events, associated with water level and discharge increases, are described as major sources of pesticides in streams (Castillo et al. 2000, Doppler et al. 2012a, Echeverria-Saenz et al. 2018, Lefrancq et al. 2017, Mendez et al. 2018, Mortensen et al. 1998). Given the water level-weighted sampling principles in the WLPSS, it seems likely that short and high surface-runoff pesticide peaks, occurring with water level rises, are sampled proportionally more than base flow concentrations. During rain-event driven pesticide fluxes into streams, the WLPSS samples with a rapid, direct response. In contrast with the SDB disks approach, the PPTP first have to permit through the filter membrane and become absorbed to the receiving phase. Hence, a peak becomes evened out with time. In this context it is possible that the seven pesticides with elevated concentrations determined with the WLPSS entered the streams at least partially via surface runoff events. An alternative explanation would be that there are systematic, compound-specific biases in the sampling methods causing these differences between PPTP concentrations measured with both methods.

On the other hand, for PPTP with a ratio of C_{WLW}/C_{TIA} closer to one or below, one could conclude that for these PPTP not only rain-driven event inputs might be relevant. It might be possible that PPTP were more constantly released into surface waters, e.g. when they are

applied with high frequencies or enter streams through bank filtration. Direct PPTP inputs from handling, independent from precipitation and hydrology (water levels), are possible as well. Such peaks could be expected to lead to similar concentration data with both sampling approaches. These results indicate that further investigations about the input patterns would be an important aspect to consider (more see Chapter 4). Additionally, further experiments with documented pesticides application amounts, and pesticide concentration measurements with a high temporal resolution right before and after rain events (Doppler et al. 2012a, Lefrancq et al. 2017, Leu et al. 2004a), could shed light on the transportation pathways of individual PPTP from the fields into surface waters.

2.4.2 Monitoring of non-polar compounds with the PDMS sheets

2.4.2 a) Absence/presence analysis

A total of eleven insecticides were detected with the PDMS sheets in the Tapezco river catchment (SI-2 B13.2). Thus, the monitored pesticide spectrum could be extended successfully to non-polar insecticides.

2.4.2 b) Quantitative analysis

As expected from the hydrophobicity of the non-polar insecticides sampled with the PDMS sheets, their aqueous concentrations were lower than for the polar- and semi-polar PPTP detected with the WLPSS and SDB approach. Among the PDMS data, chlorpyrifos was detected at the highest concentrations, i.e., median concentration above 10 ng/L and a range from 4.1 to 34 ng/L (Figure 6, based on SI-2 B13.1). This is in the same order of magnitude as in a prior grab water sampling study (Ramírez et al., 2016) where chlorpyrifos concentrations ranged between 10 to 60 ng/L. As well, cypermethrin was detected in the present study at 87 ng/L while a structural analogue, permethrin, was detected once at a concentration of 20 ng/L by Ramirez et al. (2016). The remaining eight insecticides had not been detected before this current research study.

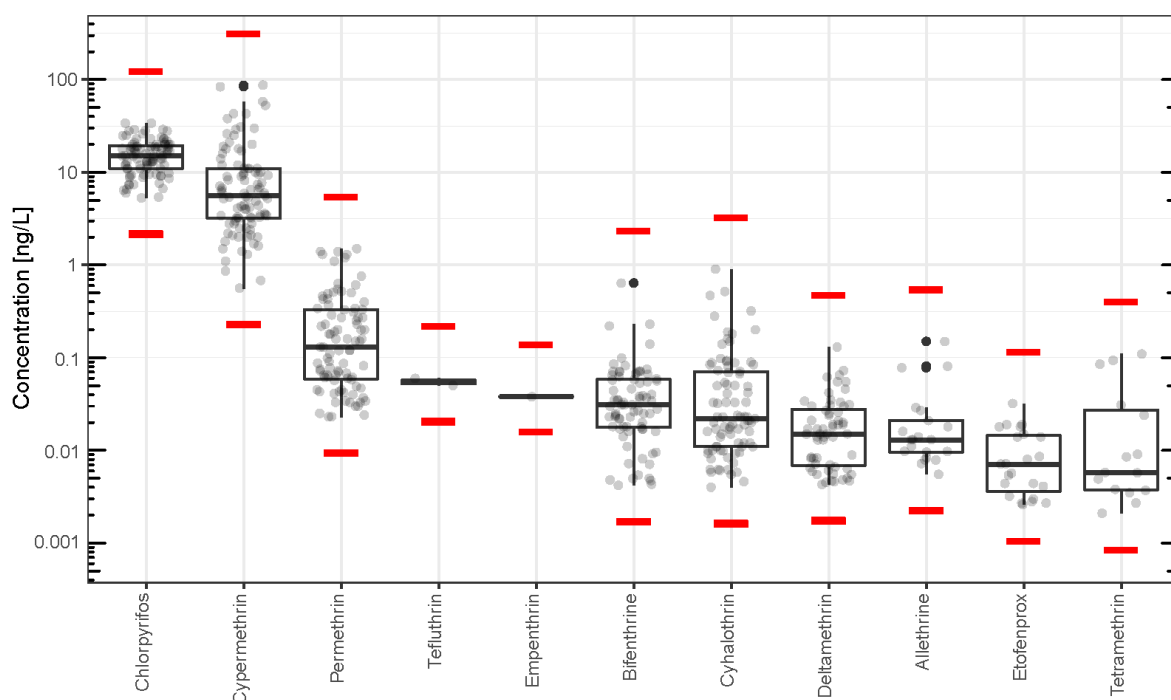


Figure 6: Non-polar pesticides detected with the PDMS sheets and their estimated water concentration range [ng/L], monitored in the Tapezco river catchment, 2015 and 2016 together, in descending order. Boxplots represent first and third quartiles (outer box) and medians (thick lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of 1.5 * the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of 1.5 * the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers, the grey (staggered) dots represent individual concentration data points, indicating how the data is distributed (standardized boxplot using R ggplot2 package). Red lines represent uncertainties of minima and maxima values based on a factor of three for the R_s values in both directions according to Curchod et al. (2019) and Moschet et al. (2014b).

2.4.3 Comparing all samplers based on chlorpyrifos concentrations

Chlorpyrifos was the only compound detectable with all three sampling approaches, allowing an across-sampler comparison, using the concentrations obtained. Therefore, the determined aqueous chlorpyrifos concentrations were compared among the individual passive samplers first, followed by investigating spatial exposure trends within the Tapezco river catchment.

All quantitative chlorpyrifos data from 2015 and 2016 and all sites combined showed that the WLPSS-derived chlorpyrifos concentrations were significantly higher than the concentrations obtained with SDB disks and PDMS sheets (Figure 7). Indeed, chlorpyrifos was also among the seven chemicals for which the ratio of C_{WLW}/C_{TIA} was greater than ten (Figure 5). These differences in the determined aqueous water concentrations may be explained by differences in the sampling mode: sorbent-based vs. non-sorbent-based, where again the WLPSS appears to capture exposure peaks during water level rises in a more distinct manner than the sorbent-based samplers. Aqueous concentrations determined with the SDB disks and the PDMS sheets were as well significantly different from each other (Figure 7) and the spread of data for the SDB was much larger than for the PDMS (Figure 7, Figure 8). Individual water concentrations for chlorpyrifos from SDB disks and PSMD sheets were only weakly correlated (Figure 8, $R^2 = 0.26$). Considering that both samplers are based on the same principle, this weak correlation was unexpected and is therefore further discussed below.

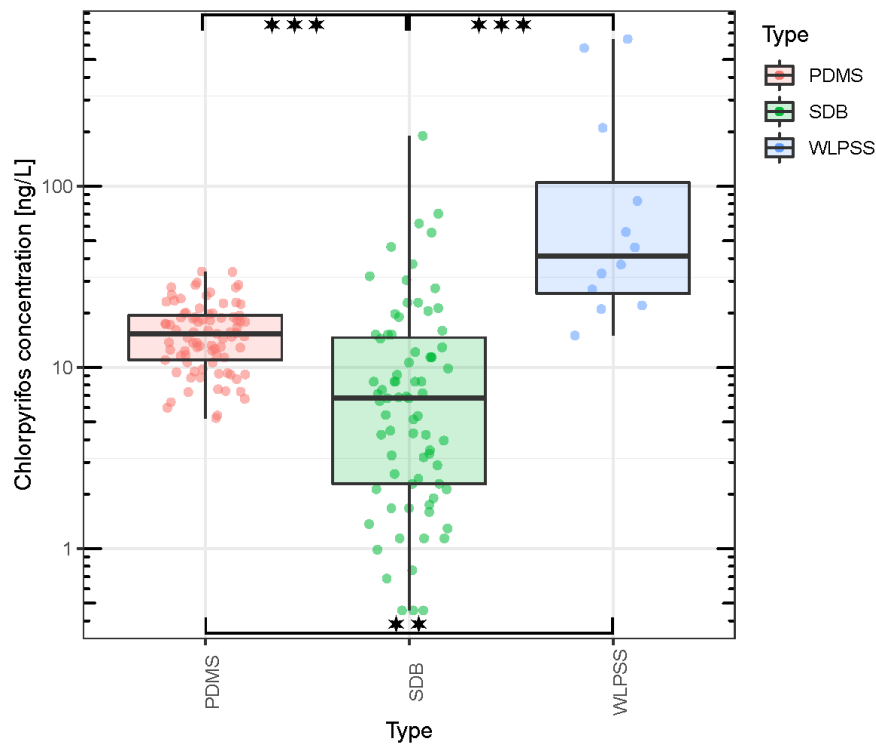


Figure 7: Concentration range of chlorpyrifos detected with the PMDS, SDB and WLPSS (Statistic significance levels: **, $p < 0.01$; ***, $p < 0.001$, One-way ANOVA, Games-Howell post hoc test in R with no assumption of equal variances, SI-2 C3). Boxplots represent first and third quartiles (outer box) and medians (thick lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of $1.5 \times$ the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of $1.5 \times$ the interquartile range. The dots represent individual concentration data points (standardized boxplot using R ggplot2 package).

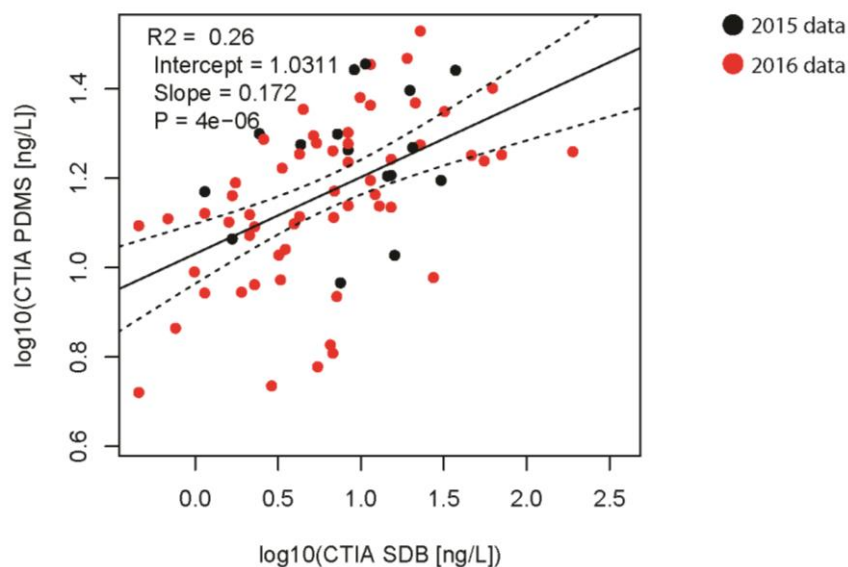


Figure 8: Correlation of the C_{TIA} data of chlorpyrifos derived from the SDB disks and the PDMS sheets during the sampling campaigns of 2015 and 2016 together.

Despite the technical aspects of a larger spread of the SDB disk-derived chlorpyrifos concentrations and the weak correlation to concentrations from the PDMS sheets, the sampling behavior of the SDB disks was not random. By distributing the data among the individual sampling sites, it was shown that the highest median concentrations were observed with both approaches at the same sampling site (SC2, see Figure 9). Only at three sites (SC3, SC4 and SC8) were the concentrations significantly different between both methods.

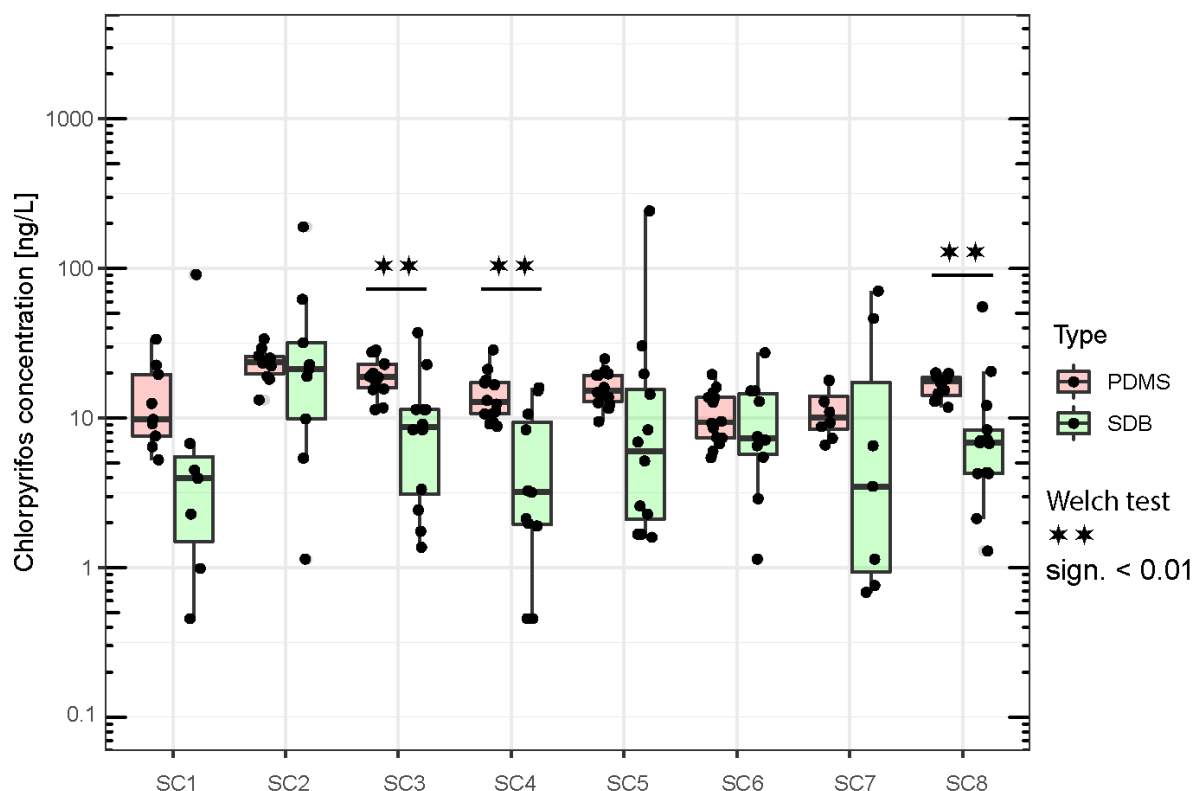


Figure 9: Concentration range of chlorpyrifos detected with the PMDS and SDB approach per individual sampling site (Statistic significance level: ** = $p < 0.01$; one-way ANOVA, Welch Test in R, with no assumption of equal variances, SI-2 C4). Boxplots represent first and third quartiles (outer box) and medians (thick lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of 1.5* the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of 1.5 * the interquartile range. The (dodged) dots represent individual concentration data points, indicating how the data is distributed (standardized boxplot using R ggplot2 package).

The higher variability in the SDB-derived concentrations and the poor correlation with the PDMS concentration data may be due to technical issues of the SDB sampling for chlorpyrifos. Compounds with $\log K_{ow}$ values in the range of chlorpyrifos i.e. ≥ 5.1 ([EPISuite4.1.](#)), absorb to the PES membrane and then diffuse only slowly through this membrane onto the SDB disks, leading to an increased so-called lag-phase (Vermeirssen et al. 2012). Depending on the time at which chlorpyrifos entered the streams during the biweekly sampling intervals, this lag-phase might have led to increased technical variability and particularly an underestimation in concentration in case that chlorpyrifos reached the streams later in the sampling period. From PPTP monitored with the SDB disk, only difenoconazole and pencycuron had $\log K_{ow}$ values comparable to chlorpyrifos (i.e., above 5.1, [EPISuite4.1.](#)) and thus might have been prone to a lag-phase effect as well. Within this study, the extraction and analysis of PPTP in the PES membrane was omitted, because water soluble chemicals were not expected to accumulate in the membrane (Moschet et al. 2015). However, such an analysis could have helped to better understand the lag-phase. For the majority of the PPTP, however, a lag phase phenomenon can be excluded since the SDB concentrations fitted very well with the concentrations determined with the WLPSS.

Chlorpyrifos has previously been described to be a difficult compound for detection with the SDB disks due to its hydrophobic character. For example, an R_S value could not be determined for chlorpyrifos during laboratory uptake experiments, likely owing to a greater partitioning of

the chemical to container walls (Ahrens et al. 2015, Shaw et al. 2009). Given these circumstances, the direct comparison of determined chlorpyrifos water concentrations from SDB disks with PDMS sheets needs to be treated with caution.

Since a membrane was not necessary during the PDMS sampling, such a lag-phase effect for hydrophobic compounds could not have occurred. Two studies showed that log PDMS-water partition coefficients of accumulated hydrophobic compounds correlate well with their $\log K_{OW}$ values (Ahrens et al. 2015, Rusina et al. 2010b). Accordingly, the rationale behind using the average R_s of PAH and PCBs for chlorpyrifos and pyrethroids with the PDMS sheets seems reasonable (Moschet et al. 2014b). Since for chlorpyrifos, the data seemed to be influenced by the lag-phase phenomenon in the SDB, the chlorpyrifos concentrations derived from the PDMS sheets were used for further quantitative investigations and the risk assessment presented in Chapter 3. The use of the chlorpyrifos PDMS data for the risk assessment is also justified because, with any sampler type, the environmental chronic quality standard of 0.46 ng/L (SI-3.3.1) was severely surpassed. In this sense, regardless of the chlorpyrifos data used, the risk for aquatic organisms due to chlorpyrifos exposure would be judged to be high (SI-2 A4.4).

2.4.4 Recommendation for use of the SDB disks, PDMS sheets and WLPSS

The experience gathered in handling the three sampling systems both in the laboratory and the field was evaluated in order to help prospective users to choose the most suitable system for their monitoring study. Evaluation criteria were i) level of standardization, ii) properties of chemicals and data obtained, iii) handling in the laboratory and field, and iv) costs for equipment and consumables for sample preparation and extraction. For the cost evaluation, it was assumed that other prerequisites, such as chemical analysis devices, solvents, and trained personnel are available. An overview of this analysis is provided in Table 1.

Use of both the SDB disks and PDMS sheets is well established. Accordingly, the current study benefited from procedures previously applied (Gunold et al. 2008, Rusina et al. 2010b, Shaw et al. 2009, Vermeirssen et al. 2012). Testimony to this status of development are studies carried out in different geographical and climate regions, such as South Africa (Curchod et al. 2019), West Africa (Chepchirchir et al. 2017, Sheikh et al. 2020), Australia (Novic et al. 2017, Tran et al. 2007), and Europe (Moschet et al. 2015, Moschet et al. 2014b, Münze et al. 2015, Mutzner et al. 2019, Schäfer et al. 2008, Schreiner et al. 2021, Townsend et al. 2018). Moreover, for the PDMS sheets, there is a guideline for the sampling of non-polar chemicals (Smedes and Booij 2012b). In contrast, the WLPSS is at an early stage of development. In fact, no publications are available yet, and, as identified in this study, details on optimal testing and calibration of the sampling volume still need to be established.

Yet, one advantage of the WLPSS is that, compared to the SDB and PDMS sampling, no chemical-specific uptake experiments for determination of R_s values are required. Under optimal operation, a water level dependent specific volume is sampled with the WLPSS, yielding concentrations for the collected pollutants without further conversion steps.

Although there is a broad overlap in terms of $\log K_{OW}$ of chemicals reported to be collectable with all three methods, with the PDMS approach, highest $\log K_{OW}$ chemicals were detected within this study. However, by using solvent-based liquid-liquid extraction procedure with water-immiscible organic solvents, e.g. n-hexane (Albaseer et al. 2010, Feo et al. 2010, Rösch et al. 2019), an extraction of hydrophobic compounds ($\log K_{OW}$: 3-7) would even be possible from WLPSS samples. Compared to the PDMS sheets, as for the SDB, the WLPSS is still at an earlier stage of development.

Depending on the desired monitoring data, to obtain C_{TIA} to describe the general water pollution state, the SDB disks and the PDMS sheets should be used. For the detection of concentration peaks after surface run-off events, the WLPSS is the best choice. This is mainly because, during surface run-off, the water level increases and with that, the sampled volume increases

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simultaneously (see 2.4.1 b and 2.3.2 c). By changing the SDB disk configuration such that sampling is done without the overlayed PES membrane, the SDB disks can function as an event driven sampler as well. Without the PES membrane, compounds are taken up faster by the SDB disks. As a consequence, however, saturation is reached faster and, therefore, the disks should be collected directly after the precipitation event (Mutzner et al. 2019, Schreiner et al. 2021). So far no study demonstrated the comparability of the WLPSS and the SDB disk sampler without a PES membrane in monitoring event-driven inputs from surface run-off.

According to the hands-on experience in the laboratory, the handling of the SDB disks was the least technically demanding and chemicals were extracted the fastest. Therefore, SDB sampling is suitable for minimally equipped laboratories. The WLPSS and the PDMS approaches are more technically demanding and a solid knowledge about extraction procedures is needed. In the field, the SDB disks and the PDMS sheets were the easiest to deploy. In comparison, the WLPSS needs a greater depth of the water column for installation and, especially in rocky uneven riverbeds, the installation was difficult.

When considering costs, the SDB approach is the most cost-efficient procedure if only a few monitoring campaigns are planned because it does not require the up-front investment needed for the PDMS and WLPSS. The longer the monitoring campaigns are, the more the costs among the different approaches are balanced out (SI-2 A5). The fact that the WLPSS are re-usable, and that the price of the PDMS sheets is very low contribute to this increasing cost efficiency.

In summary, as these three different samplers currently stand and with the experience gathered in this study, the SDB and the PDMS approaches were the most robust with respect to the number of successfully retrieved samples with a sample recovery of 90% for SDB disks and 92% for PDMS sheets. Additionally, with the use of the PDMS sheets, the compound spectrum monitored was successfully extended to the non-polar insecticides, which were frequently detected in the studied catchment. To enable a comprehensive risk assessment for the study catchment, the SDB and PDMS-derived chemical concentrations will be used in Chapter 3. Generally, each type of sampling device has its advantages and limitations which need to be critically evaluated prior to use. Even though the WLPSS needs to be studied further to ensure that its operational range can be met under the conditions of the respective study, it has the potential to serve as an alternative to expensive and energy-intensive automated water sampling systems especially in low income and difficult to access regions.

Table 1: Overview about the level of standardization, sampling capabilities and mode, handling and costs of the SDB, PDMS and the WLPSS samplers.

CRITERIA	SDB disks	PDMS sheets	WLPSS
LEVEL OF STANDARDIZATION			
Commonly agreed upon protocols available?	YES	YES	NO
Compound-specific sampling rates needed?	YES	YES	NO
CHEMICALS AND DATA			
Supported <i>log K_{ow}</i> range	<ul style="list-style-type: none"> • -1.5 – 5.5 (Ahrens et al. 2015, Charriau et al. 2016) • -0.9 to 5.51 in the present study 	<ul style="list-style-type: none"> • 0.53 to 8 (Ahrens et al. 2015, Moschet et al. 2014, Rusina et al. 2010a) • 5.11 to 8.15 in the current study 	<ul style="list-style-type: none"> • 3 to 6.8 via SPE (Kern et al. 2009, Vogler 2013) • 3-7 via liquid-liquid extract (Rösch et al. 2019) • -0.9 to 5.51 in the current study
Information obtained	<ul style="list-style-type: none"> • Time-integrated averaged concentrations 	<ul style="list-style-type: none"> • Time-integrated averaged concentrations 	<ul style="list-style-type: none"> • Water level-weighted concentrations • Time-integrated averaged concentration possible
HANDLING			
Conditioning	<ul style="list-style-type: none"> • Easy, largely unsupervised • 1 hour 	<ul style="list-style-type: none"> • Easy, occasional check required • 100 hours 	<ul style="list-style-type: none"> • SPE cartridge (see extraction) • 0.2 hours
Deployment	<ul style="list-style-type: none"> • Simple stainless-steel holding system • Installable to steel rods, rocks, bricks 	<ul style="list-style-type: none"> • Simple holding system, PVC bar • Installable to steel rods, rocks, bricks 	<ul style="list-style-type: none"> • Complex, especially in rivers with rocky, uneven riverbeds • Minimum depth of 35 cm water required

CRITERIA	SDB disks	PDMS sheets	WLPSS
Extraction	<ul style="list-style-type: none"> No enrichment step required Simple: extracted via shaking with acetone and ethanol, purification via filter syringe 1 hour / sample 	<ul style="list-style-type: none"> No enrichment step required Technically demanding: accelerated solvent extraction, purification with self-packed glass columns 4 hours / sample 	<ul style="list-style-type: none"> Installable to walls or rods Enrichment via SPE required Technically demanding: pressure filtration, pH adjustment, SPE, elution with methanol and water 2 hours / sample
• COSTS (in CHF)			
Upfront investment	NONE	<ul style="list-style-type: none"> Soxhlet extractor 950 Accelerated solvent extractor 20,000 	<ul style="list-style-type: none"> SPE manifold 500
Reusable parts	<ul style="list-style-type: none"> Steel housing 5 	<ul style="list-style-type: none"> Glass column for purification 42 	<ul style="list-style-type: none"> WLPSS with HPLC capillary 205 WLPSS with precision valve 550
One-way consumables per sample	<ul style="list-style-type: none"> Filter syringe 1 SDB disk 16 PES membrane 2 	<ul style="list-style-type: none"> PDMS sheet 2 Sorbent for purification 2 	<ul style="list-style-type: none"> Glass filter 1 Self-packed multilayer cartridge 17

2.5 Conclusion

This study set out to test a combination of the three sampling methods, i.e. using SDB disks, WLPSS and the PDMS sheets, as a comprehensive strategy for monitoring of a broad spectrum of polar, semi-polar and non-polar PPTP in a time-integrative manner. The large overlapping spectrum detected with the SDB and the WLPSS approach (77 PPTP), together with a similar distribution in pesticide types in two subsequent years, showed two aspects. Firstly, both approaches were well suited for a presence/absence control of a broad variety of different PPTP from different pesticide types. Secondly, in both sampling years, a similar number per each pesticide type reached the streams. With the addition of the PDMS sheets, the compound spectrum was broadened to non-polar pesticides, of which most would not have been found with the applied SDB disks or the WLPSS.

This research has also shown that pesticide concentrations of biweekly samples, simultaneously collected via SDB disks and the WLPSS, were overall comparable. For chlorpyrifos, the only compound detectable with all sampling methods applied, the concentrations between the PDMS, SDB disk and WLPSS sampling were statistically different, with highest concentrations detected with the WLPSS. The SDB disk-derived chlorpyrifos data showed a larger spread, probably because of a lag-phase effect occurring during the sampling of the non-polar chlorpyrifos ($\log K_{ow} = 5.1$, determined with [EPISuite4.1.](#)) via SDB disk with PES membrane cover. Nevertheless, for both, the PDMS sheets and the SDB disks, highest median concentrations (exceeding 20 ng/L) were observed at the same site. This finding indicates that both sorbent-based sampler data are useful to investigate spatial pollution trends. Further investigations about the uptake behavior of chlorpyrifos and other non-polar pesticides by the SDB disks overlayed with PES membrane and the PDMS sheets are necessary. On the one hand, additional studies are necessary to obtain more compound-specific R_s values, not only for non-polar pesticides. On the other hand, further research is needed to understand if the lag-phase phenomenon can influence the quantitative analysis of the SDB sampling or if other environmental factors need to be considered as well.

This monitoring study clearly showed a heavy PPTP pollution in the streams within the Tapezco river catchment, partly surpassing 100 ng/L for individual pesticides. This raises the question whether adverse effects to aquatic organisms can be expected. Therefore, in the next chapter, the almost gapless biweekly chemical concentration data obtained with the SDB disks and the PDMS sheets are further investigated for an assessment of water quality in the context of risks to aquatic organisms in space and time.

2.6. Literature

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Chapter 2

Use of different passive sampling approaches for a comprehensive and time-integrated sampling of pesticides in tropical streams in a vegetable growing area

SI-2 A1 Passive samplers

SI-2 A1.1 Sorbent-based passive samplers

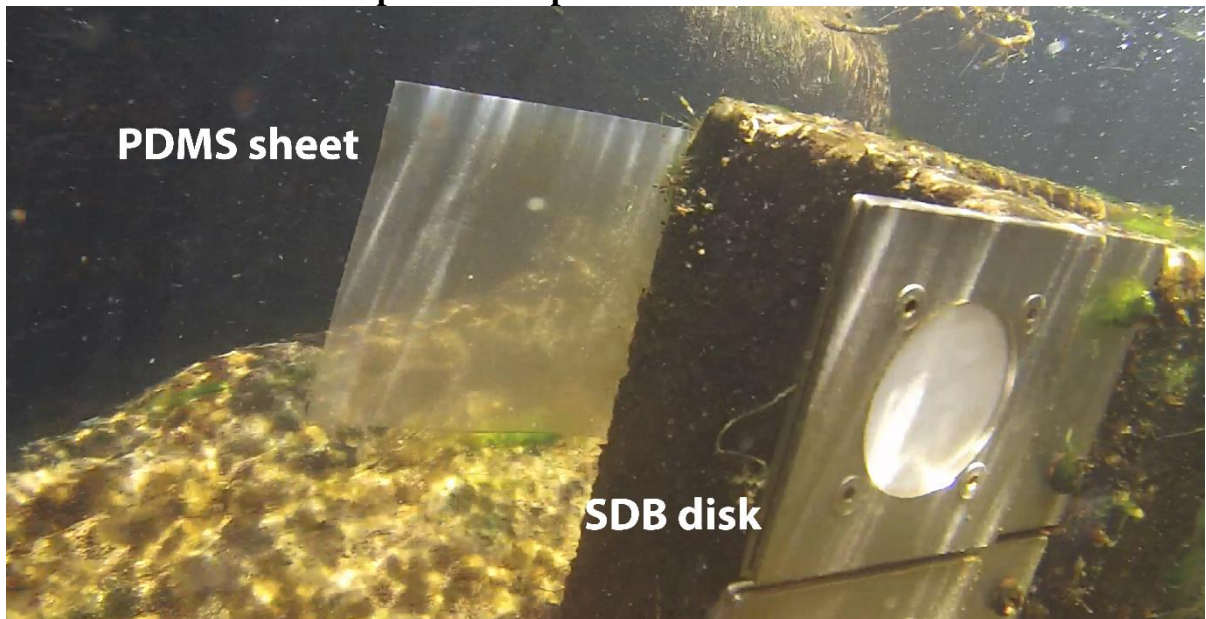


Figure SI-2 A1: Deployment of a PDMS sheet and a SDB disk.

SI-2 A1.2 Water level proportional sampling system (WLPSS)



Figure SI-2 A2: Deployed of the water level proportional sampling system (WLPSS). For more details, see description and Figure SI-2 A3 below.

The WLPSS sampler is composed of three main elements (Figure SI-2 A2, Figure SI-2 A3):

- (1) **A sampling flask:** 1 L wide-neck screw thread glass bottle (Roth AG, Switzerland).
The flask has a curved steel water inlet (\varnothing 6 mm, 14.6 cm length) and an air outlet (2m vinyl tube, \varnothing 6 mm).
- (2) **A resistance** to regulate the outflow of air and the inflow of water: As resistance an HPLC capillary (PEEK tubing 1/16"OD x \varnothing 0.13mm, length: 1.3 m, BGB, Switzerland) was used in the Tapezco river catchment in 2015 (according to Schneider unpublished). Additionally the resistance was replaced by a more easily adjustable precision valve (Göldi Präzisionsmechanik AG, Schlieren, Switzerland, <https://goeldi-mechanik.ch/kontakt/>) during the monitoring campaigns in the Tapezco river catchment in 2016. To keep the HPLC capillary dry, Teflon flasks with activated silica gel (2 - 5 mm, silica gel orange, Carl Roth AG, Switzerland) were attached to both ends of the capillary (Figure SI-2 A3). The precision valve can be disassembled, cleaned with methanol and dried in the air. The resistance of the HPLC capillary can be set manually by changing the length and diameter of the HPLC capillary. For the precision valve the resistance can be more easily adjusted than with the HPLC capillary system by adapting the screw cap setting.
- (3) **A PVC case** to protect the glass sampling flask. The case was kept weight down underwater with a stainless-steel cylinder (3.3 cm high, 12.7 cm diameter, Acero Roag Almacen S.A., San Jose, Costa Rica). For installation, an iron rod (\varnothing 2 cm, length about 1.20 m) was mounted into the river sediment to attach the PVC protection case with the empty sampling flask by using large zip ties.

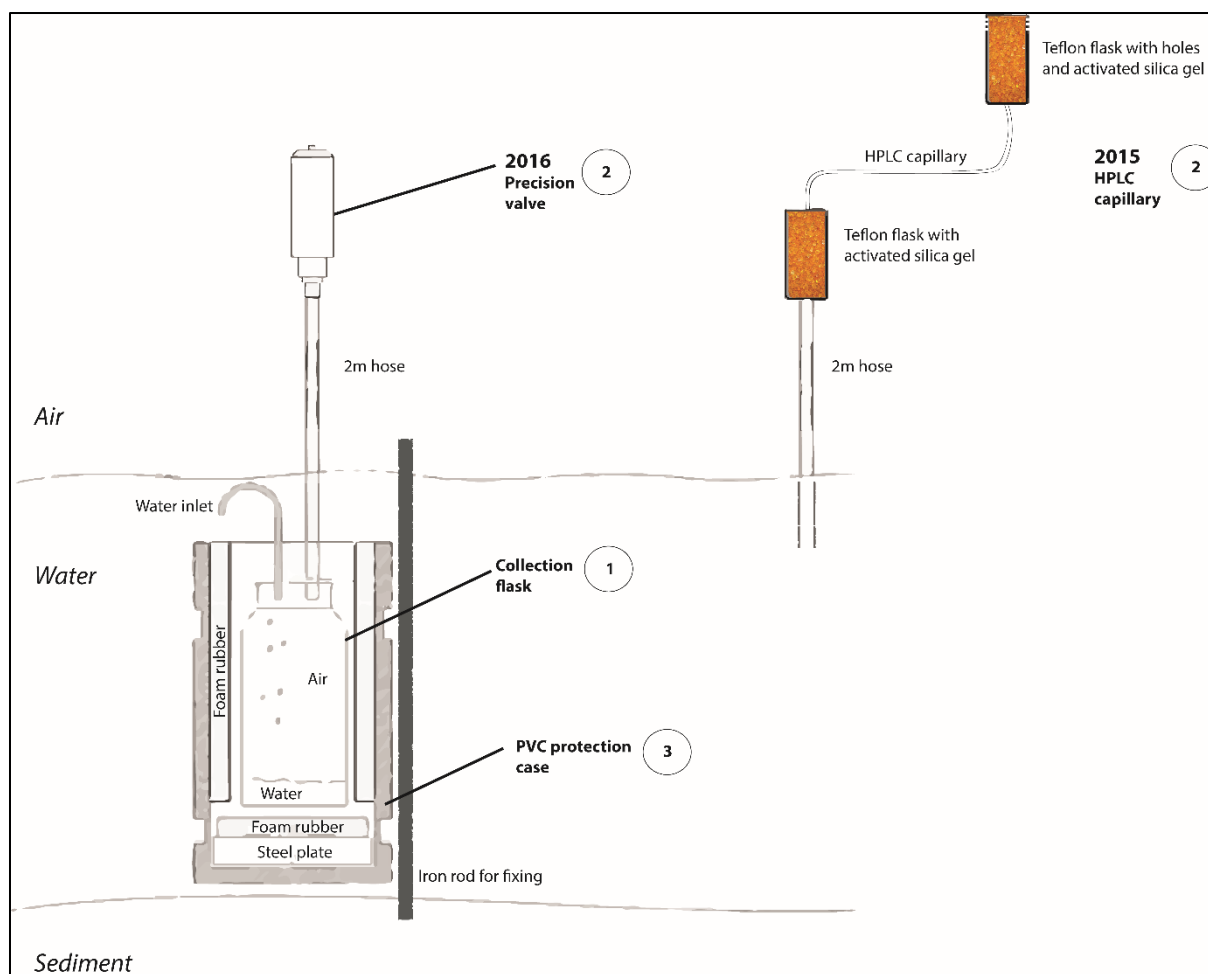


Figure SI-2 A3: Water level proportional sampling sytem (WLPSS) with: (1) collection flask, (2) precision valve (left) or an HPLC capillary (right) for regulation of the water inflow rate, and (3) the PVC protection case (S. R. Blatter and F. T. Weiss).

SI-2 A1.3 Initial collected sampling volumes after installing the WLPSS at different water depths
Table SI-2 A1: Initial sampling volume (two replicates) per three different immersions depth by using the WLPSS in HPLC capillary and precision valve configuration.

Immersion depth	WLPSS + HPLC capillary		WLPSS + precision valve		Average initial water volume \bar{x}	Average initial water volume \bar{x}
[cm]	[mL]		[mL]		[mL]	[mL]
5	15.8	15.5	15.8	15.8	15.7	15.8
10	20.8	20.4	22.1	20.9	20.6	21.5
20	30.7	31.5	31.9	33.8	31.1	32.9

SI-2 A2 Chemical analysis

SI-2 A2.1 Isotopically labeled internal standards (ILIS) used for samples detected via high resolution mass spectrometry coupled to liquid chromatography (LC-HR MS/MS)

Table SI-2 A2: isotopically labeled internal standards (ILIS) used for SDB disk and WLPSS samples with 100 ng absolute.

	Isotopically labeled internal standard	Category
1	2,4-D D3	Pesticide
2	2,6-Dichlorbenzamid-3,4,5-D3	Pesticide
3	Alachlor D13	Pesticide
4	Aldicarb (N-methyl-13C-D3-carbamoyl-13C)	Pesticide
5	Atrazine D5	Pesticide
6	Atrazine-2-hydroxy D5	Pesticide
7	Atrazine-desisopropyl D5	Pesticide
8	Azoxystrobin D4	Pesticide
9	Bentazone D6	Pesticide
10	Carbendazim D4	Pesticide
11	Chloridazon D5	Pesticide
12	Chloridazon-desphenyl-15N2	Pesticide
13	Chloridazon-methyl-desphenyl-D3	Pesticide
14	Chlorotoluron D6	Pesticide
15	Chlorpyrifos D10	Pesticide
16	Chlorpyrifos-methyl D6	Pesticide
17	Chlothianidin D3	Pesticide
18	Cyprodinil D5	Pesticide
19	Desethylatrazine 15N3	Pesticide
20	Diazinon D10	Pesticide
21	Dicamba D3	Pesticide
22	Dichlorprop D6	Pesticide
23	Diiflufenican D3	Pesticide
24	Dimethenamid D3	Pesticide
25	Dimethoate D6	Pesticide
26	Diuron D6	Pesticide
27	Epoxiconazole D4	Pesticide
28	Fipronil-13C2 15N2	Pesticide
29	Imidacloprid D4	Pesticide
30	Irgarol D9	Pesticide
31	Isoproturon D6	Pesticide
32	Linuron d6	Pesticide
33	MCPA D3	Pesticide
34	MCPB D6	Pesticide
35	Mecoprop D6	Pesticide
36	Mesotrion D3	Pesticide
37	Metalaxyl-D6	Pesticide
38	Acetaminophen-glutathione-D3	Pesticide
39	Methiocarb D3	Pesticide

	Isotopically labeled internal standard	Category
40	Metolachlor D6	Pesticide
41	Metolachlor -ESA D11	Pesticide
42	Metsulfuron-methyl D3	Pesticide
43	N,N-diethyl-3-methylbenzamide-D10 (DEET-D10)	Pesticide
44	Nicosulfuron-D6	Pesticide
45	Octilinone-D17	Pesticide
46	Pirimicarb D6	Pesticide
47	Prochloraz D7	Pesticide
48	Propamocarb free base D7	Pesticide
49	Propazin D6	Pesticide
50	Propiconazol D5	Pesticide
51	Pyrimethanil D5	Pesticide
52	Simazin D5	Pesticide
53	Sulcotrion D3	Pesticide
54	Tebuconazole D6	Pesticide
55	Tebutam D4 (5 time less)	Pesticide
56	Terbutryn D5	Pesticide
57	Terbuthylazine D5	Pesticide
58	Thiamethoxame D3	Pesticide
59	Triclosan-D3 (8 times more)	Biocide
60	2',2'-Difluoro-2-deoxyuridine-13C,15N2	Pharmaceutical
61	5-Fluorouracil-13C15N2	Pharmaceutical
62	5-Methyl-Benzotriazol-D6	Anti-corrosive
63	Amisulpride-D5	Pharmaceutical
64	Atazanavir-D5	Pharmaceutical
65	Atenolol-acid D5	Pharmaceutical
66	Atenolol-D7	Pharmaceutical
67	Atomoxetine-D3	Pharmaceutical
68	Atorvastatin-D5	Pharmaceutical
69	Azithromycin-D3	Pharmaceutical
70	Benzotriazol-D4	Anti-corrosive
71	Bezafibrat-D4	Pharmaceutical
72	Bicalutamide-D4	Pharmaceutical
73	Bisphenol-A D16	Plasticizer
74	Candesartan-D5	Pharmaceutical
75	Carbamazepin 10,11-epoxide-C13,D2	Pharmaceutical
76	Carbamazepin-D8	Pharmaceutical
77	Cetirizine-D8	Pharmaceutical
78	Citalopram-D6	Pharmaceutical
79	Clarithromycin-D3	Pharmaceutical
80	Climbazol-D4	Preservative
81	Clofibric acid-D4	Pharmaceutical
82	Clopidogrel-(+/-)-D4	Pharmaceutical
83	Clotrimazol-D5	Pharmaceutical
84	Clozapine-D8	Pharmaceutical

	Isotopically labeled internal standard	Category
85	Codein-13C,D3	Pharmaceutical
86	Coffein-D9	Pharmaceutical
87	Cyclophosphamide-D4	Pharmaceutical
88	Darunavir-D9	Pharmaceutical
89	Diazepam-D5	Pharmaceutical
90	Diclofenac-D4	Pharmaceutical
91	Emtricitabine-13C,15N2	Pharmaceutical
92	Eprosartan-D3	Pharmaceutical
93	Erythromycin-13C2	Pharmaceutical
94	Fenofibrate-D6	Pharmaceutical
95	Fluconazol-D4	Pharmaceutical
96	Fluoxetine-D5	Pharmaceutical
97	Furosemid-D5	Pharmaceutical
98	Gabapentin-D4	Pharmaceutical
99	Gemcitabine-13C,15N2	Pharmaceutical
100	Hydrochlorothiazide-13C-D2	Pharmaceutical
101	Ibuprofen-D3	Pharmaceutical
102	Indomethacin-D4	Pharmaceutical
103	Irbesartan-D3	Pharmaceutical
104	Lamotrigine-13C3,D3	Pharmaceutical
105	Levetiracetam-D3	Pharmaceutical
106	Lidocaine-D10	Pharmaceutical
107	Meclizine-D8 (=Meclozine)	Pharmaceutical
108	Mefenamic acid-D3	Pharmaceutical
109	Metformin-D6	Pharmaceutical
110	Methylprednisolol-D3	Pharmaceutical
111	Metoprolol-D7	Pharmaceutical
112	Metronidazol-D4	Pharmaceutical
113	Morphin-D3	Pharmaceutical
114	N4-Acetylsulfamethoxazol-D5	Pharmaceutical
115	N4-Acetyl-Sulfathiazol-D4	Pharmaceutical
116	Naproxen-D3	Pharmaceutical
117	Nelfinavir-D3	Pharmaceutical
118	O-Desmethylvenlafloxin-D6	Pharmaceutical
119	Oxazepam-D5	Pharmaceutical
120	Oxcarbazepine-D4	Pharmaceutical
121	Paracetamol-D4	Pharmaceutical
122	Phenazon-D3 (Antipyrin-D3)	Pharmaceutical
123	Pravastatin-D3	Pharmaceutical
124	Primidon-D5	Pharmaceutical
125	Propranolol-D7	Pharmaceutical
126	Ranitidine-D6	Pharmaceutical
127	Ritalinic acid-D10	Pharmaceutical
128	Ritonavir-D6	Pharmaceutical
129	Sotalol-D6	Pharmaceutical
130	Sulfadiazine-D4	Pharmaceutical

	Isotopically labeled internal standard	Category
131	Sulfadimethoxine-D4	Pharmaceutical
132	Sulfamethazine-13C6	Pharmaceutical
133	Sulfamethoxazole-D4	Pharmaceutical
134	Sulfapyridin-D4	Pharmaceutical
135	Sulfathiazole-D4	Pharmaceutical
136	Tramadol-D6	Pharmaceutical
137	Trimethoprim-D9	Pharmaceutical
138	Valsartan-15N,13C5	Pharmaceutical
139	Valsartan acid-D4	Pharmaceutical
140	Venlafaxine-D6	Pharmaceutical
141	Venlafaxin-N,O-didesmethyl-D3	Pharmaceutical
142	Verapamil-D6	Pharmaceutical

SI-2 A2.2 ILIS used for compounds detected via atmospheric pressure chemical ionization gas chromatography tandem mass spectrometry (GC-APCI-MS/MS)

Table SI-2 A3: ILIS used for PDMS samples

	Isotopically labeled internal standard	Amount absolute [ng]	Category
1	Bifenthrin-D5	100	Pesticide
2	Chlorpyrifos-D10	10	Pesticide
3	Chlorpyrifos-methyl-D6	100	Pesticide
4	Cypermethrin-trans-D6	10	Pesticide
5	Deltamethrin-D5	100	Pesticide
6	Etofenprox-D5	10	Pesticide
7	Fenvalerat-D7	10	Pesticide

SI-2 A2.3 Recoveries and limits of quantification*Relative recovery determination*

For analytes without a structure identical ILIS, the final analyte concentrations needed to be corrected by the relative recovery. To calculate the relative recoveries, the concentration, C in spiked and not spiked samples were used and divided by the spiked concentrations according to Equation SI-2A (1):

$$\text{Relative recovery [\%]} = \frac{(C_{\text{spiked sample}} - C_{\text{not spiked sample}})}{C_{\text{spiked}}} * 100 \quad \text{Eq. SI-2A (1)}$$

Limit of Quantification (LOQ) – HR-LC MS/MS

The Method Limit of Quantification in nanopure water ($MLOQ_{NPW}$), was defined as the lowest calibration standard (1 mL extract) with chromatic peaks with a minimum of five data points in the MS1 full scan mode (and signal-to-noise (S/N) ratios of at least 10); and a peak area ratio of the analyte against the ILIS of at least double as high as the peak area ratio in the blank samples, if signals were found in blank samples. Accordingly, the $MLOQ$ take into consideration the amounts in field blanks and variations during chemical analysis (e.g. variations in performance and accuracy if the samples are not measured at the same day, or variations between different sampling methods and chemical analysis methods). The $MLOQ$ referring to limit of ng found in the 1 mL sample extract. LOQ refers to the limit of ng found in 1 L water sample equivalent. The $MLOQ$ for each detected compound can vary among the WLPSS and the SDB samples (LOQ for WLPSS samples are shown in SI-2 B4, and $MLOQ$ for SDB disk are presented in SI-2 B5).

For taking matrix effects into account for pesticides without structurally identical ILIS, the $MLOQ_{NPW,LC}$ was divided by the absolute recovery as seen in Equation SI-2A (2):

$$MLOQ_{\text{Matrix}} = \frac{MLOQ_{NPW}}{\text{Absolute recovery}} \quad \text{Eq. SI-2A (2)}$$

Absolute recovery

For compounds with structurally identical ILIS, the absolute recovery was determined, by using the peak area of the ILIS in the environmental samples (with matrix), and dividing it by the median peak areas of the ILIS in NPW water of all calibration standards as shown in Equation SI-2A (3):

$$\text{Absolute recovery}_{\text{structurally identical ILIS}} = \text{median} \frac{\text{peak area ILIS}_{\text{matrix}}}{\text{median (peak area ILIS}_{\text{NPW}})} \quad \text{Eq. SI-2A (3)}$$

For compounds with assigned structurally not identical ILIS, the absolute recovery was estimated, by using the peak area of the analyte in the spiked sample and subtracting the peak area in the not spiked sample. Then the peak area of the analyte in the calibration standard of the corresponding spiking level was divided, as seen in Equation SI-2A (4):

$$\text{Absolute recovery}_{\text{no structurally identical ILIS}} = \frac{\text{peak area}_{\text{spiked sample}} - \text{peak area}_{\text{not spiked sample}}}{\text{peak area}_{\text{calibration standard}}} \quad \text{Eq. SI-2A (4)}$$

For the WLPSS samples, the determined Method Limits of Quantification ($MLOQ_{WLPSS}$) (e.g. 1 ng in mL extract) can be converted to LOQ found in 1 L environmental water samples equivalent ($LOQ_{WLPSS, WS}$) by considering an enrichment factor of 1000 due to the SPE (1 ng/L). To convert the $MLOQ_{SDB}$ from the SDB sample extracts (in [ng/mL] = [ng/disk]) into $LOQ_{SDB, WS}$ in [ng/L], the $MLOQ_{SDB}$ (per disk or mL sample extract) need to be divided by the compound-specific R_s and the deployment time (14 days) of the disks. For both types of samples the $MLOQ$ describe the lowest calibration standard concentrations, detected in 1 mL sample extracts with our analytical method.

Limit of Quantification (LOQ) – GC-APCI MS

For the PDMS sheet samples, the MLOQ in 1 mL hexane extracts (MLOQ_{hexane, PDMS}), was defined by the concentration of the calibration standards with analyte peaks with signal-to-noise (S/N) ratios of at least 10 for the quantifier ion. When signals of analytes were found in blank samples, the highest detected peak area in the blank samples was doubled and compared to the analyte peak areas detected in the calibration standards. The MLOQ_{PDMS}, determined in the PDMS extracts (in [ng/mL] = [ng/sheet]) are listed in SI-2 B6. To calculate LOQ_{PDMS, WS} from the environmental water samples in concentrations per liter [ng/L], the MLOQ_{PDMS} from the sample extract need to be divided by the R_s value and deployment time (14 days) of the PDMS sheets.

SI-2 A2.4 Details about the method used for LC-HR MS/MS analysis

Table SI-2 A4: Overview on instrumental analysis method used to analyze SDB and WLPSS samples via LC-HR MS/MS.

High resolution mass spectrometry coupled to liquid chromatography (LC-HR MS/MS)

Sample type	SDB disks and composite WLPSS water samples				
Instrument	QExactive				
Ion source	Heated ESI, spray voltage: 4,000 V(+) / 3,000 V (-), sheat gas flow: 40 arbitrary units, capillary temperature: 350 °C, heater temperature: 40°C				
MS scans	FullMS + Top5 data dependent (DD) MS/MS				
Mass resolution	MS1: 140,000 MS/MS: 17,500				
Electrospray ionization	pos/neg separate				
Mass range (m/z)	100 to 1,000				
Injection volume	10 µl				
Column	Xbridge C18, 2.1x50 mm, 3.5 µm, Waters, Ireland				
Eluents	A: NPW, 0.1% FA; B=Methanol, 0.1% FA				
Chrom. gradient	No. Time A% B% flow [µL/min]				
	0 0.00 90% 10% 200				
	1 4.00 50% 50% 200				
	2 17.00 5% 95% 200				
	3 25.00 5% 95% 200				
	4 25.10 90% 10% 200				
	5 29.00 90% 10% 200				
Detection	0.5 to 27 min				
Calibration levels	0.1, 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000, 2000				
Concentration unit	[ng/mL] for SDB samples, [ng/L] for WLPSS samples				
ILIS [ng] on column	100 ng				

SI-2 A2.5 Details about the method used for GC-APCI-MS/MS analysis

Table SI-2 A5: Overview on instrumental analysis method used to analyze PDMS sheet samples via GC-APCI-MS/MS.

Monitoring via atmospheric pressure chemical ionization gas chromatography tandem mass spectrometry

Sample type	PDMS sheet extracts			
Instrument	Agilent GC7890B gas chromatograph; Agilent MS/MS 6495			
MS Mode	dynamic multiple reaction monitoring mode			
Mass resolution	1.2 Da			
MS cycle time	250 ms			
APCI	Positive mode, APCI interface heated to 280 °C, Capillary voltage 1000 V, ion funnels 100/40 V for high-pressure/low pressure radio frequency (RF)			
Carrier gas	He (99.999%, Carbagas, Switzerland)			
Collision gas	N ₂ (99.999%, Carbagas, Switzerland)			
Source gas	N ₂ (99%, generator), flow 11 L/min , 150 °C			
APCI corona discharge current	1 µA			
Mass range (m/z)	100 to 1,000			
Injection volume	3 µL			
Column	RTX-5ms: 30m, 0.25 µm film, 0.25 mm ID, Restek, BGB, Switzerland			
Temp gradient	No.	Time	Temperature [°C]	flow [mL/min]
	0	0.00	100°C	3
	1	1.00	100°C	3
	2	3	25°C per min to 150°C	3
	4	18	10°C per min to 300°C	3
Detection	0 to 18 min			
Calibration levels	0.2, 1, 5, 10, 20, 50, 100, 200, 500, 1000			
Concentration unit	[ng/mL] for PDMS samples			
ILIS [ng] on column	10 or 100 ng			

SI-2 A3 Qualitative data

SI-2 A3.1 Compounds only detected with the SDB or the WLPSS sampler and their $\log K_{OW}$ values, biodegradation half-lives and hydrolysis half-lives

Table SI-2 A6: Compounds only detected with the SDB or the WLPSS sampler and their $\log K_{OW}$, biodegradation half-lives and, hydrolysis half-lives.

Compound	Method	$\log K_{OW}^*$	Biodegradation, half-lives [days] [#]	DT_{50} aqueous hydrolysis (20°C, pH7) ^{\$}
Acetochlor	SDB	-0.47	3.7	stable
Alachlor	SDB	3.52	3.4	0.5
Butachlor	SDB	4.5	3.6	-
Iprodione	SDB	3	3.0	4.5
Iprovalicarb	SDB	3.33	3.7	stable
Metolachlor-morpholinone	SDB	2.54	3.6	NA
Pyrimidonil	SDB	1.95	3.8	NA
Terbutylazine	SDB	3.4	2.9	stable
Terbuthylazine-desethyl	SDB	1.94	3.0	stable
Triclocarban	SDB	4.9	2.9	NA
2-Aminobenzimidazole	WLPSS	0.91	3.5	-
2-Methyl-4-amino-6-methoxy-s-triazine	WLPSS	1.26	3.5	NA
5-Chloro-2-methyl-4-isothiazolin-3-one (CMI)	WLPSS	-0.34	3.5	NA
Atraton	WLPSS	2.69	3.3	-
Bentazone	WLPSS	2.34	3.5	stable
Clomazone	WLPSS	2.5	3.2	stable
Fluoxastrobin	WLPSS	2.86	3.2	stable
Fluroxypyr	WLPSS	2.2	3.5	223

Compound	Method	Log K_{OW}^*	Biodegradation, half-lives [days] [#]	DT_{50} aqueous hydrolysis (20°C, pH7) ^{\$}
Flusilazole	WLPSS	3.87	3.4	stable
Haloxypop	WLPSS	3.38	3.4	stable
Hexazinone	WLPSS	1.85	3.5	56
Methiocarb-sulfoxide	WLPSS	0.7	3.6	-
Metolachlor-ESA	WLPSS	1.69	3.6	NA
N'-(2,4-Dimethylphenyl)- N-methylformamide	WLPSS	2.23	3.7	NA
N,N-Dimethyl-N'-phenylsulphamide (DMSA)	WLPSS	1.67	3.6	stable
Prometon	WLPSS	2.99	3.3	stable
Propachlor-OXA	WLPSS	0.6	4.1	NA
Pyroxsulam	WLPSS	1.94	3.2	stable
Tebufenozide	WLPSS	4.25	3.0	stable
Terbumeton	WLPSS	3.1	3.2	-
Thiacloprid	WLPSS	2.33	3.3	stable
Trinexapac-ethyl	WLPSS	1.6	3.8	868

* determined with [EPISuite4.1](#).

[#] determined with BIOWIN4 v.4.10 primary biodegradation tool from EpiSuite 4.1.

^{\$} [PPDB dataBase](#) (Lewis et al. 2020).

NA = Not available in PPDB dataBase.

SI-2 A4 Quantitative data – determination of environmental concentrations

SI-2 A4.1 Sampling rates for available compounds detected with SDB disks

For compounds without any sampling rate (R_S), the total arithmetic mean (\bar{x}_{Total}) from all available sampling rates was estimated according Equation SI-2A (5):

$$\bar{x}_{\text{Total}} = \frac{\sum_{i=1}^N \bar{x}_i * n_i}{\sum_{i=1}^N i * n_i} \quad \text{Eq. SI-2A (5)}$$

Where N is the maximum number of compounds with available sampling rates; n the amount of the available R_S values for each compound, i .

From all pesticides together the estimated R_S value was 0.094 L/d.

SI-2 A4.2 Sampling behavior of the composite WLPSS

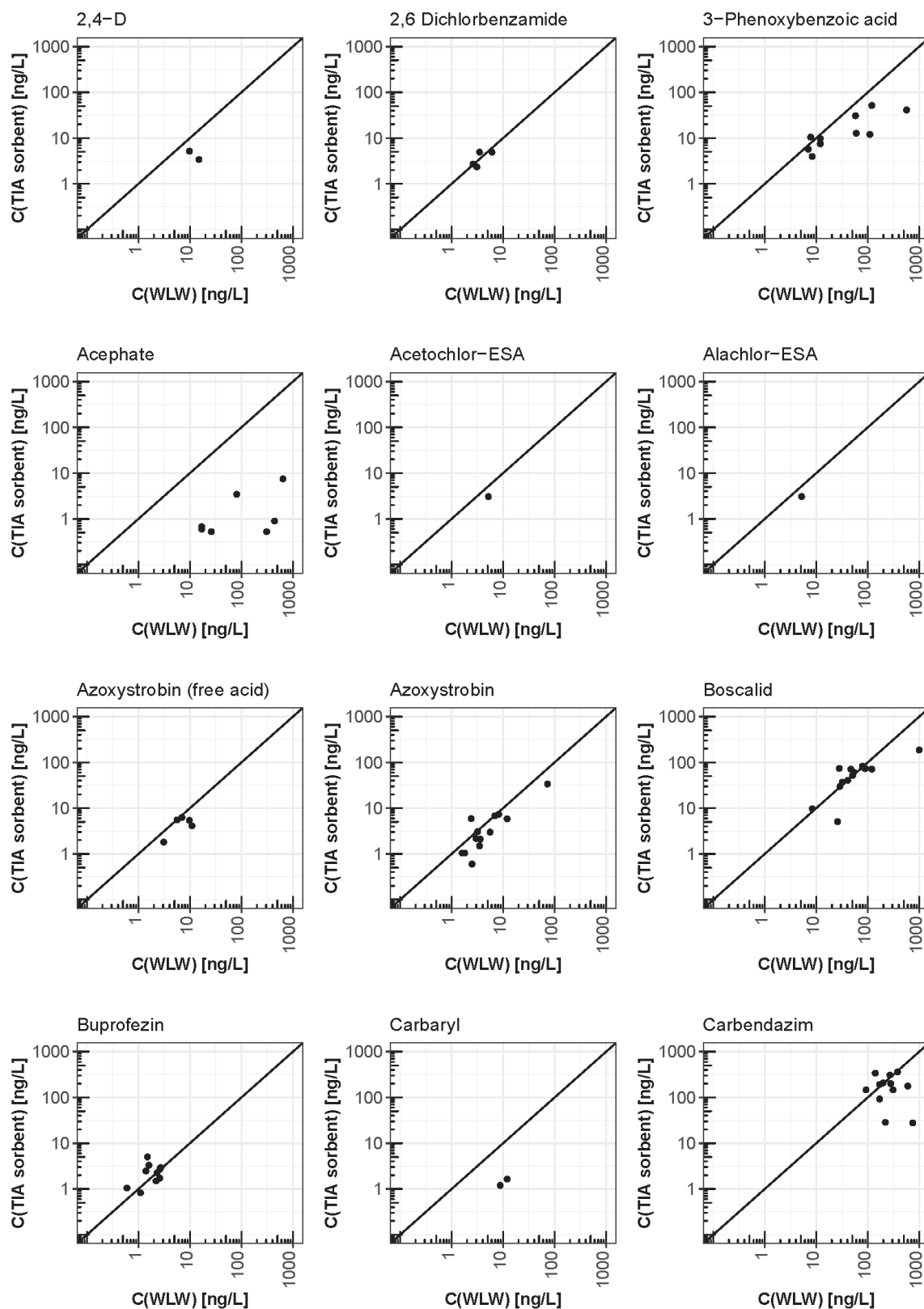
The WLPSS functions as described in Schneider et al. (unpublished) and Schönenberger et al. (2020). Briefly, for the WLPSS the inflow volume of water and the masses of the pesticides in the samples water in the sampling flasks per specific time point are described in SI-2A Equation (6) and (7):

$$v_{\text{WLPSS}}(t) = \alpha \times (L(t) - L_0) = \alpha \times L^*(t) \quad \text{Eq. SI-2A (6)}$$

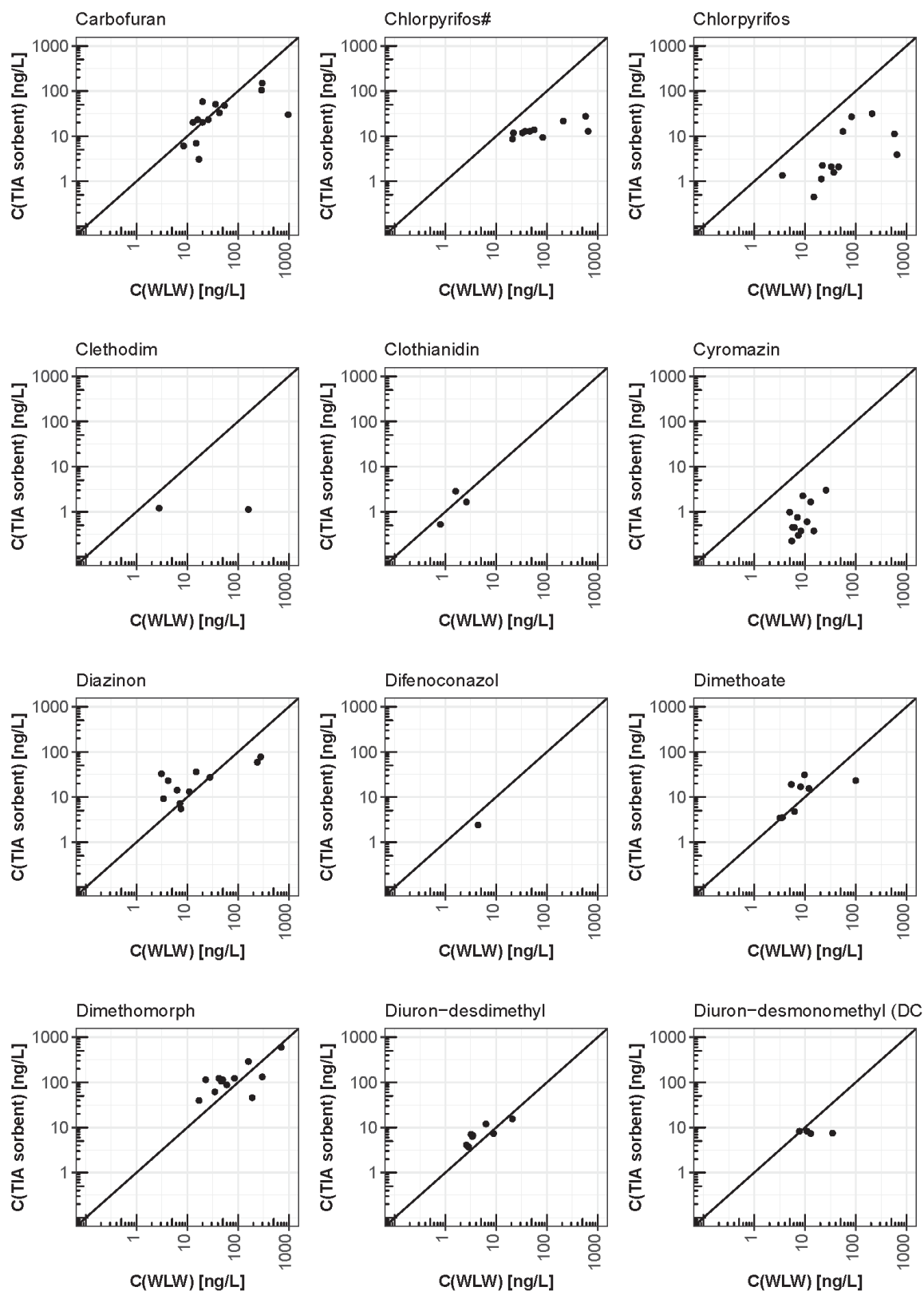
$$m_{\text{WLPSS}}(t) = \alpha \times (L(t) - L_0) \times C_w(t) = \alpha \times L^*(t) \times C_w(t) \quad \text{Eq. SI-2A (7)}$$

Where, $v_{\text{WLPSS}}(t)$ describes the instantaneous water volume influx into the sampler per specific time point [L], $m_{\text{WLPSS}}(t)$ is the instantaneous pesticide mass influx into the sampler [ng]. C_w is the pesticide concentration in the water, α is the flow resistance parameter of the capillary or the precision valve regulating the outflow volume of air out of the system. $L(t)$ is the water level of the stream [m] per a specific time point; L_0 the water level of the water inlet [m]; and $L^*(t)$ represents the river stage above the water inlet of the WLPSS sampler.

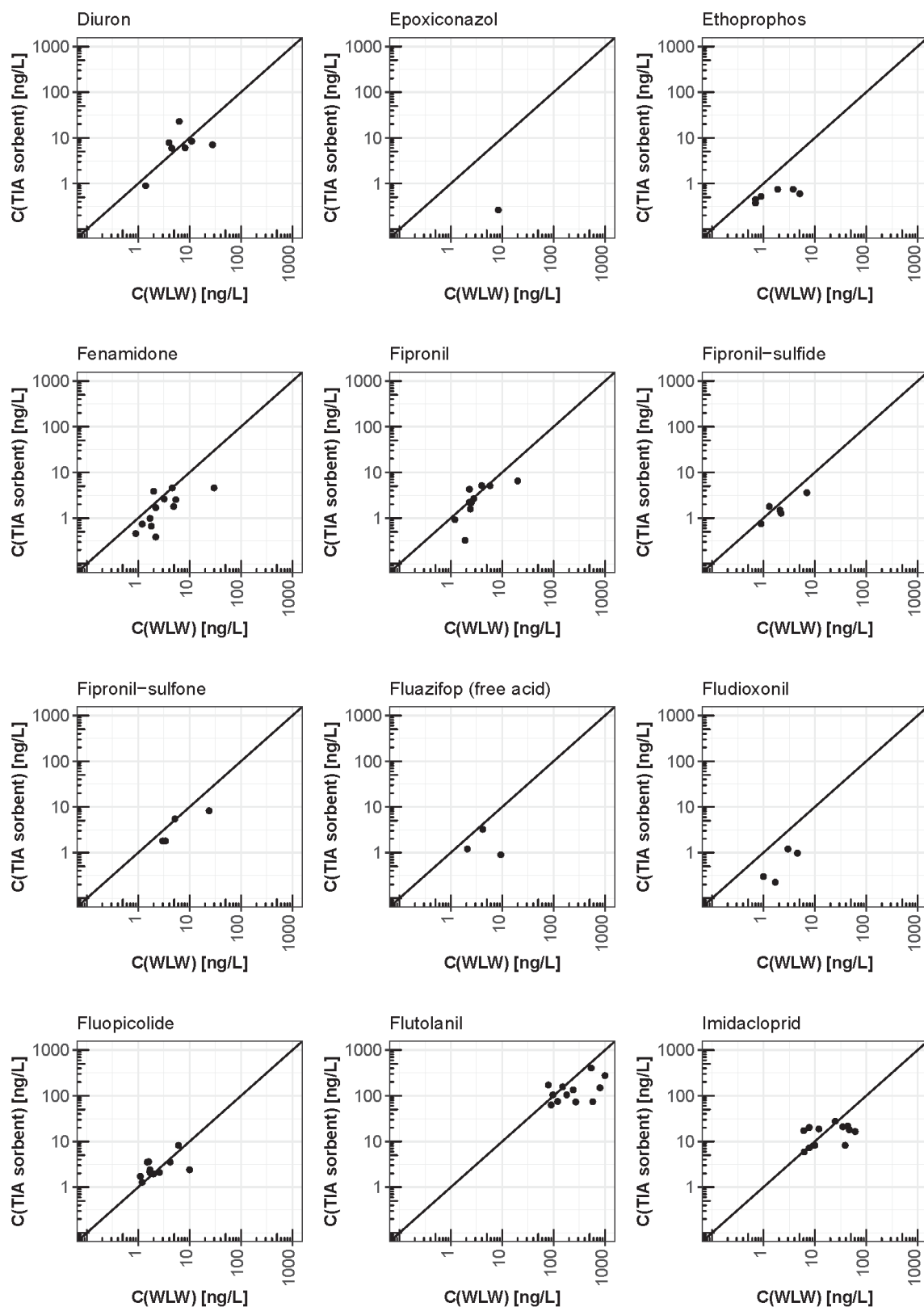
SI-2 A4.3 Comparison CTIA from SDB disks/PDMS sheets and CWLW from WLPSS



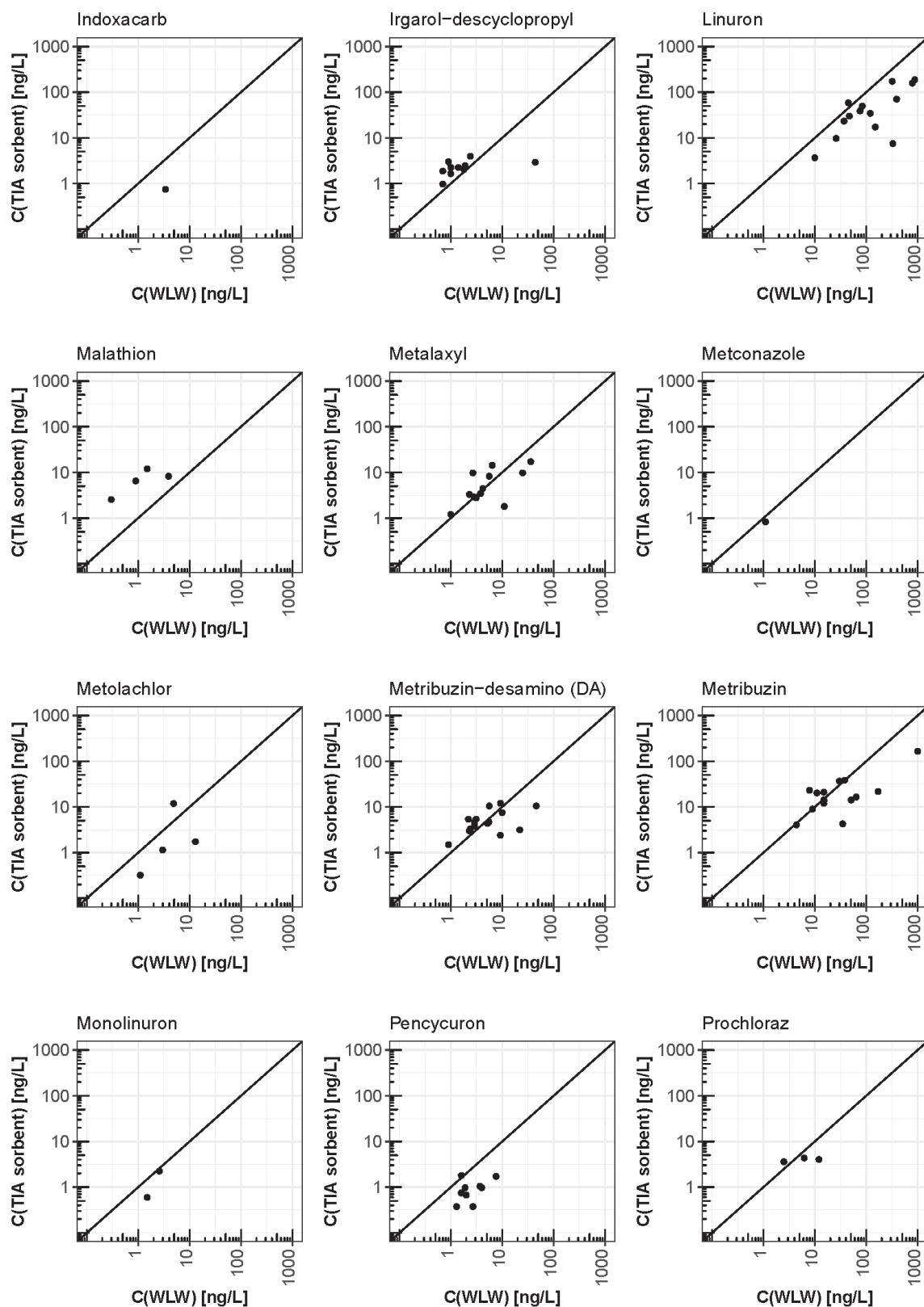
Chapter SI 2-A



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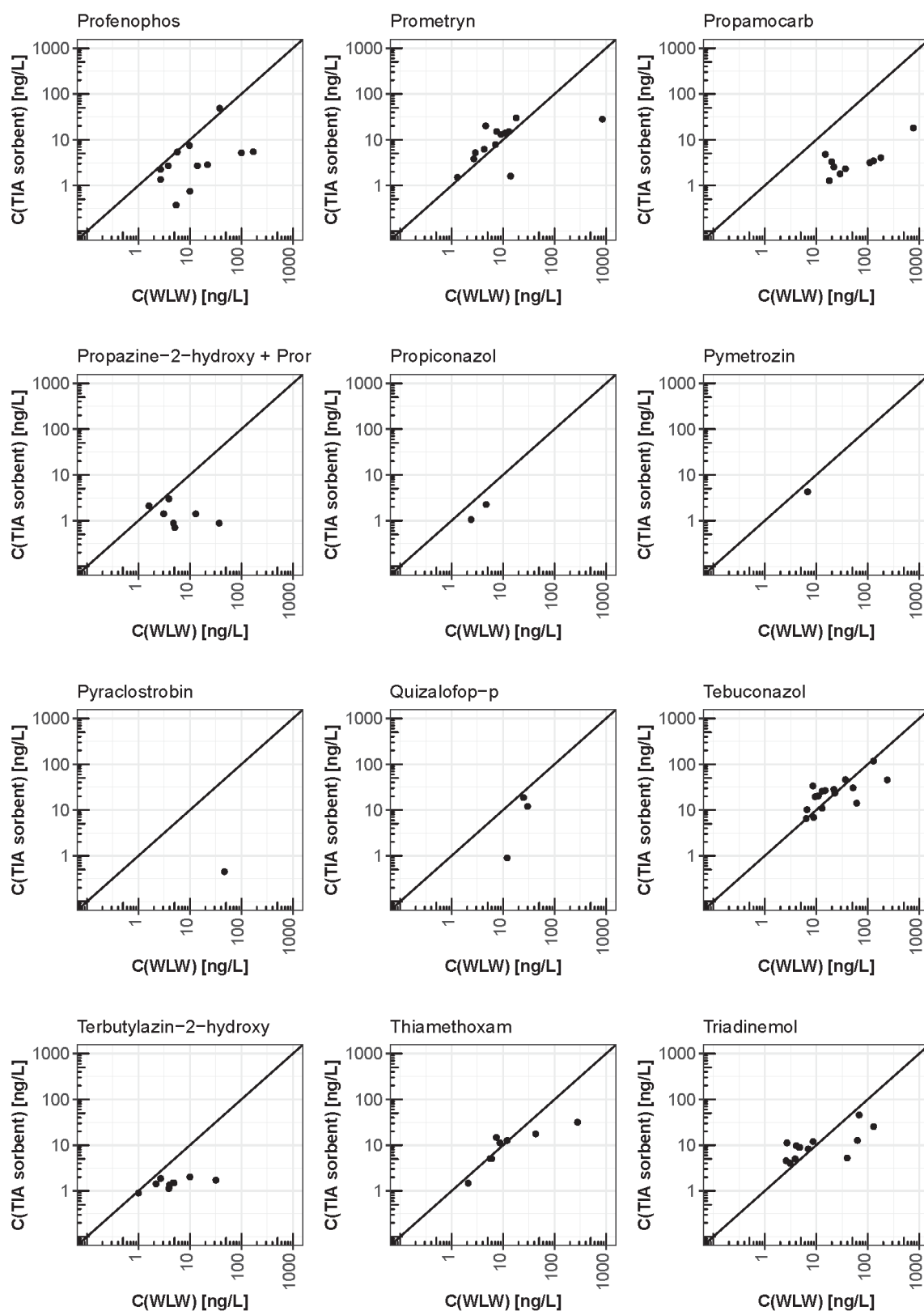


Figure SI-2 A4: Comparison of the C_{TIA} in the sorbent-based samplers and C_{WLW} of the WLPSS. # C_{TIA} determined with PDMS sheet data. Diagonal line = 1:1 line.

SI-2 A4.4 Comparison of chlorpyrifos concentrations per site determined either with the SDB and the PDMS approach with the chronic environmental quality standard.

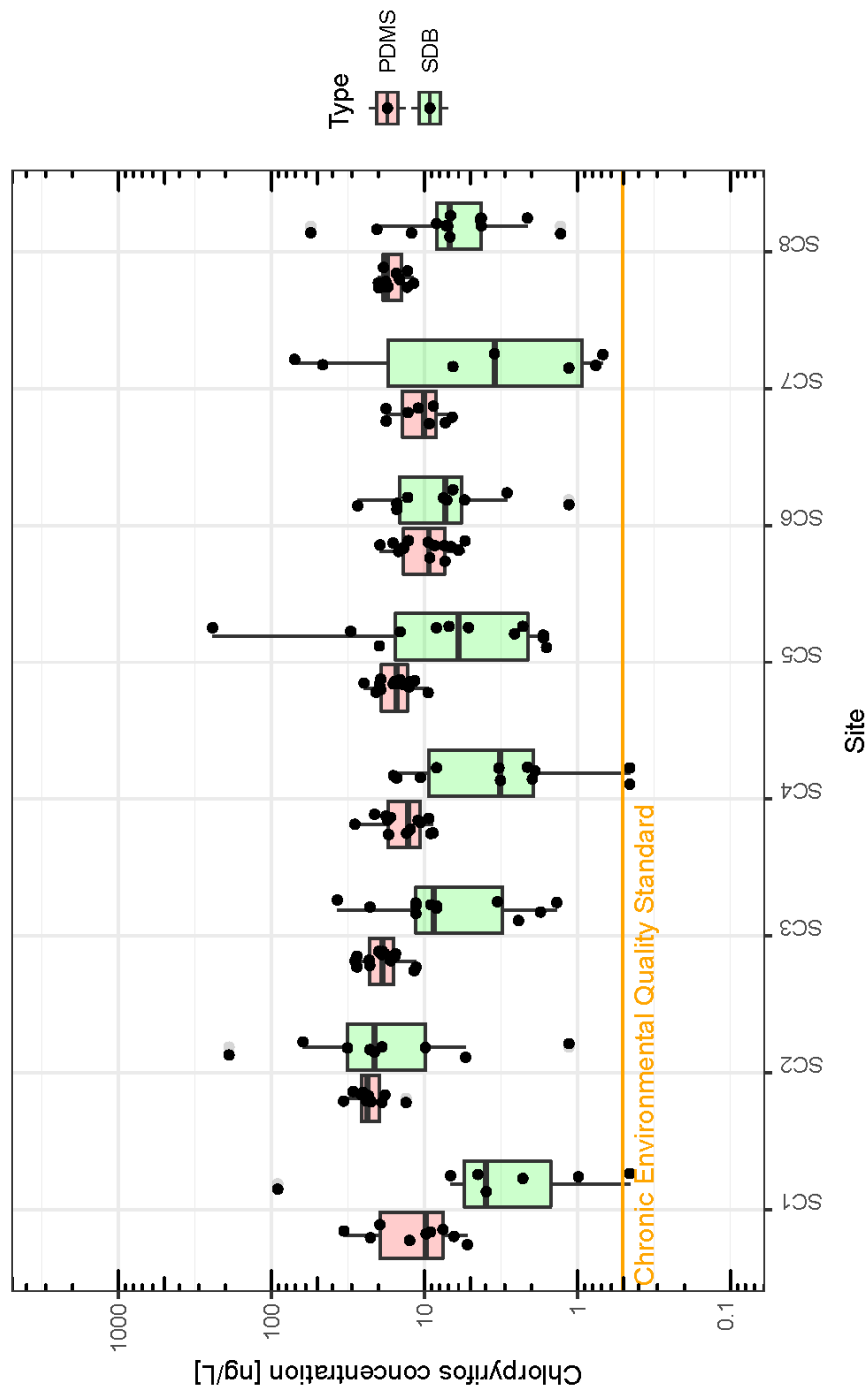


Figure SI-2 A5: Concentration range of chlorpyrifos detected with the PDMS and SDB approach per individual sampling site and their comparison with the chronic Environmental Quality Standard. Boxplots represent first and third quartiles (outer box) and medians (thick lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of 1.5* the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of 1.5 * the interquartile range. The (dotted) dots represent individual concentration data points, indicating how the data is distributed (standardized boxplot using R ggplot2 package). Chronic Environmental Quality Standard of 0.46 ng/L; orange line (Swiss Center for Applied Ecotoxicology 2019).

SI-2 A5 Experiences with the SDB disks, PDMS sheets and WLPSS in the field and laboratory and recommendations for other users

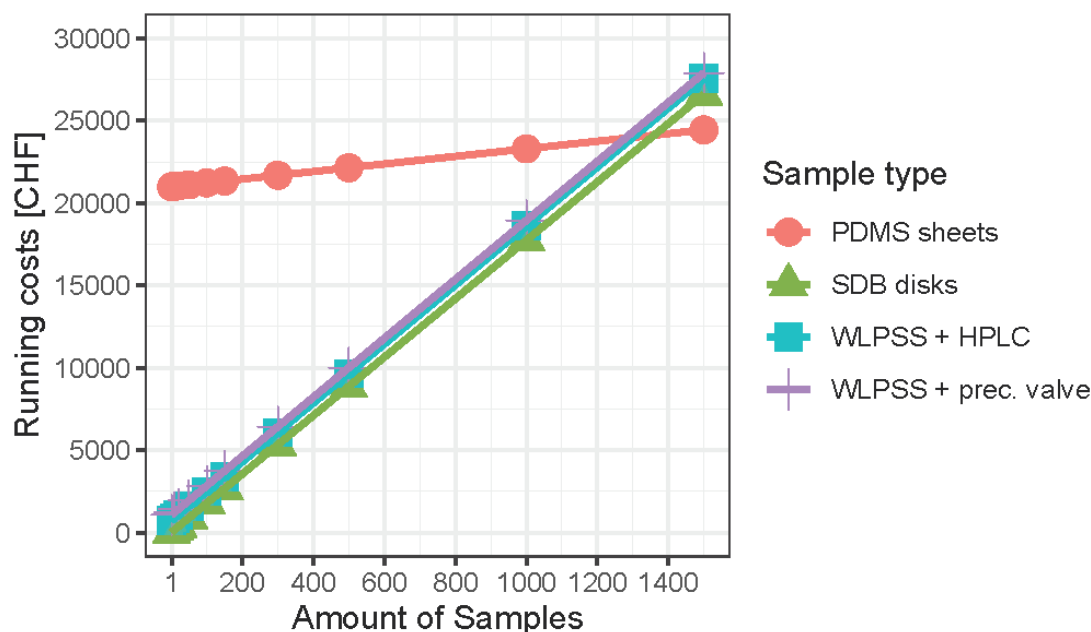


Figure SI-2 A6: Running costs for PDMS sheets, SDB disks, and WLPSS sampling.

SI-2 A6 Literature

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3. Chapter Risk assessment for tropical streams of a small-scale horticultural catchment based on spatio- temporal pesticide monitoring data

3.1. Abstract

A pesticide monitoring in the Tapezco river catchment region in two subsequent years (2015/2016) revealed that intensive pesticide use leads to contamination of streams. As shown in Chapter 2, 87 pesticide and pesticide transformation products (PPTP), comprising insecticides, herbicides, fungicides and several of their transformation products (TP) were identified by applying sorbent-based passive sampling approaches at the five (2015), respectively eight (2016), sub-catchment (SC) sites.

Using these monitoring data as a basis, the first aim of this study was to exploit the measured environmental concentrations (MEC) of the PPTP with regard to their spatio-temporal distribution among the different sampling sites in the Tapezco river catchment. To enable a comparison between the two sampling years, of the 87 detected PPTP, the data set was narrowed down to those which were found in both sampling years, leading to a subset of 62 PPTP. Two MEC-based risk assessment approaches, one relying on Environmental Quality Standards (EQS) and the other on the Toxic Units (TU) concept focusing on invertebrates, were used to identify if the PPTP pose health risks to aquatic biota either singly or in mixture. As well, available macroinvertebrate data for four sites (SC1, SC4, SC5 and SC8) was evaluated in view of the indicated water quality, applying the Species at Risk pesticide (SPEAR_{pesticide}), the Costa Rican Biological Monitoring Working Party (BMWP-CR) Index, and the Ephemeroptera, Plecoptera and Trichoptera (EPT)-taxa richness indices.

For the 62 considered PPTP, spatial trends were observed. In more detail, at two connected sites (SC2 and SC3), the average number of PPTP was 2-fold lower compared to the six remaining sites. At all sites, insecticides had the broadest detected spectrum as opposed to the numbers of individual herbicides and fungicides. Conversely, at all sites and periods, fungicides had the highest average %-contribution of the average sum-concentration among the individual detected pesticide types. Independent of the risk assessment approach applied, the quality of the water was indicated to be generally poor, pointing at chronic, and even acute effects to be expected for aquatic communities at all sampling sites. Invertebrates were the most affected organism group based on EQS and TU without any apparent time window to recover from pesticide stress during both sampling years. The SPEAR_{pesticide} and the BMWP-CR indices both indicated that, despite the continuous pesticide pollution stress at all sites, water quality seemed to be improved at SC5 and reached even a good to regular water quality at the most downstream site (SC8) compared to the other remaining sites (SC1 and SC4) for which macroinvertebrate data was available. The EPT-taxa richness index showed as well an improvement in water quality at SC8. This finding could be due to a larger river stretch upstream to the sampling site with no horticultural land and high share of natural forest.

Given that all applied approaches confirmed substantial risks, there is an urgent need for a reduction of pesticides in streams of the Tapezoco catchment to improve the water quality in order to protect aquatic communities in these streams.

3.2. Introduction

Information about pesticide levels in streams in Costa Rica is limited, particularly in the central horticultural area, a gap that Chapter 2 of this thesis is beginning to fill. This Chapter 3 applies the data on the concentrations of pesticides and pesticide transformation products (PPTP) reported in Chapter 2 to investigate their spatial distribution among five sites sampled in 2015 and eight sites sampled in 2016 and to retrospectively assess the risks associated with PPTPs at the sites in the Tapezco river catchment. The catchment with sampling sites is illustrated in Chapter 1 (section 1.7).

3.2.1. Aquatic environmental risk assessment of pesticides

Retrospective risk assessment, as conducted in this chapter, is applied when chemicals have been approved for application and have already entered ecosystems, such as surface waters. It is applied in order to safeguard good water quality (Diamond et al. 2018, European Commission 2018). One risk assessment approach involves the quantification of chemicals in water to derive measured environmental concentrations (MEC), which are put into context with toxicological information to elaborate if these levels exceed those posing risks to aquatic organisms. Toxicological information is expressed as Environmental Quality Standards (EQS), defined by the Water Framework Directive and derived following the technical guideline No. 27 (European Commission 2018). EQS represent maximum acceptable concentrations and/or annual average concentrations, which, if met, allows the chemical status of the waterbody to be described as good. EQS are compound-specific and mainly based on laboratory-derived effect concentrations (EC) from organisms of different trophic levels (primary producers, invertebrates, vertebrates). Deriving EQS values from field and mesocosm studies is possible as well; however, such data are less commonly available. More details about the derivation of EQS values are described in Chapter 1 (section 1.5). EQS for describing short-term effects are based on acute EC data and EQS for describing long-term effects are based on chronic EC data. Risks of single chemicals are assessed by dividing the MEC by its compound-specific EQS value forming risk quotients (RQ). Risks of chemical mixtures are determined by summing all RQ of the chemicals found in the sample.

Another retrospective approach to assess risks to organisms in freshwater streams is the determination of Toxic Units (TU) (Knillmann et al. 2018, Liess and Ohe 2005, Schäfer et al. 2007). TU for individual PPTP are described as the logarithmic transformation of the MEC of individual PPTP, divided by their median EC for 50% (EC₅₀) of a reference species. To determine TU for mixtures of PPTP, all the single TU of the PPTP in the samples are summed up. The application of maximum TU values to describe risks is possible as well, though was not used within this thesis. To determine the mixture TU, the planktonic arthropod *Daphnia magna* was mainly used within this thesis as reference species because of the wealth of toxicity data available for this species. If no *Daphnia magna* data was available, *Ceriodaphnia dubia* toxicity data was utilized instead. Besides these species, toxicity data of other organisms, such as *Hyalella azteca* for freshwater invertebrates and *Pimephales promelas* for fish can be applied as well (Schäfer et al. 2013), though again was not considered in this thesis. The usage of TU enables the interpretation and risk evaluation for aquatic invertebrates, for compounds without established EQS values. Equivalent to the RQ, TU can be determined for single chemicals as well as for chemical mixtures.

While the above described approaches assess the risk by combining MEC with toxicity effect data from model species, the status of the water quality can as well be described by the community composition of species in the monitored streams, which is commonly done based on macroinvertebrate data. Thus, macroinvertebrate species are collected and their diversity and abundance evaluated. Two indices that have been developed on the basis of such macroinvertebrate data are the Species at Risk pesticide (SPEAR_{pesticide}) index (Knillmann et al.

2018, Liess and Ohe 2005, Schäfer et al. 2007) and the EPT-taxa richness index (Castillo et al. 2006b, Mertens and Kürý 2018). The determination of the $\text{SPEAR}_{\text{pesticide}}$ index is based on macroinvertebrate abundance and biological trait information of taxa. Since the sensitivity of the collected macroinvertebrate taxa to pesticides is evaluated relative to the sensitivity of *Daphna magna*, the $\text{SPEAR}_{\text{pesticide}}$ is indirectly linked with the TU (both include sensitivity of *Daphna magna*). Moreover, a correlation between the $\text{SPEAR}_{\text{pesticide}}$ and TU data was confirmed (Knillmann et al. 2018). Other biological trait based information, such as generation time of each taxa, e.g. to know if an aquatic life stage exists during periods with intensive pesticide exposure, and the ability of the macroinvertebrates to protect themselves in refuge areas, is considered as well in the $\text{SPEAR}_{\text{pesticide}}$ index. On the other hand, the EPT-taxa richness index is estimated by adding up the number of taxa in the insect orders ephemeroptera, plecoptera and trichoptera present at the site (Castillo et al. 2006b, Mertens and Kürý 2018). This index has been developed as a relatively simple strategy for water quality assessment. Though not specific to pesticides, its ease of application has led to its use for describing the water quality also in tropical regions where toxicological data about the prevailing tropical species is rare. Indeed, the EPT-taxa richness indicator has been applied in Costa Rica to determine the water quality (Castillo et al. 2006b).

3.2.2. Status of pesticide risk assessment in Costa Rica

Comprehensive, compound specific limit values comparable to the European EQS values are not yet established for Costa Rica. So far, the only available threshold value for managing pesticide residues in surface water bodies is 10 µg/L for the sum concentration of organochlorines and organophosphates. Additionally, this threshold is applied only in surface waters which are used for human consumption or running into naturally protected areas (Mendez et al. 2018) as described in Decree N° 33903-MINAE-S (La Gaceta Official Newspaper 2007). However, pesticides from other classes than organochlorines and organophosphates have been detected in surface waters, as demonstrated, e.g., in Chapter 2. These pesticides are not covered by the current limiting threshold even though they have been repeatedly associated with adverse effects on aquatic organisms (Arias-Andres et al. 2018, Carazo-Rojas et al. 2018a, de la Cruz et al. 2014b, Diepens et al. 2014, Echeverría-Sáenz et al. 2018, Rämö et al. 2018).

Nevertheless, some risk assessments have been performed for large monoculture areas in the province Limon and in South Guanacaste. For instance, in the River Madre de Dios, five herbicides and five insecticides reached environmentally hazardous concentration levels, based on the species sensitivity distribution (SSD; for details on this approach see Chapter 1, section 1.5.) (Arias-Andres et al. 2018, Echeverría-Sáenz et al. 2018, Rämö et al. 2018). Additionally, according to determined RQ, chronic risks have been identified based on two fungicides, three herbicides and two insecticides, in South Guanacaste in the Tempisque river basin (Carazo-Rojas et al. 2018a). In the same study, even acute risks had been predicted at one of the sampling sites.

To describe the status of water pollution by using macroinvertebrates, the Costa Rican Biological Monitoring Working Party (BMWP-CR) Index (La Gaceta Official Newspaper 2007) was introduced into the regulatory process (see Chapter 1, section 1.5 for more details). Accordingly, the BMWP-CR Index was presented within this study (Echeverría-Sáenz and Weiss 2021). Additionally the previously described European $\text{SPEAR}_{\text{pesticide}}$ index was utilized as well and compared with the BMWP-CR results (Cornejo et al 2019). The $\text{SPEAR}_{\text{pesticide}}$ index particularly accounts for pesticide as stressor (Böhmer et al. 2004, Liess et al. 2008). Given the few reports about risks to aquatic organisms in large monoculture areas, it can be hypothesized that aquatic organisms are at risk as well in small-scale horticultural areas, where pesticide application has been described to be extensive though comprehensive risk assessments have not been conducted yet (Ramírez-Muñoz et al. 2014, Ramírez et al. 2016).

3.2.3. Aim of the study

Based on the comprehensive monitoring data presented in Chapter 2, the aim of this chapter was to use the MEC of PPTP to investigate their spatial distribution within the catchment and to employ these MEC for a comprehensive risk assessment at individual sites of the Tapezco river catchment. The data was separated into three periods, one with low precipitation, $\Delta T1$ in 2015, and two with usual precipitation, $\Delta T2a$ and $\Delta T2b$ (2016) (precipitation shown in Chapter 1, section 1.7), to investigate if the risks vary among these periods. The risk assessment using MEC was based on the derivation of RQ and of TU as means to link exposure levels to laboratory based toxicity data from different trophic levels (primary producers, invertebrates, vertebrates) and for determining chronic and acute risks for mixtures and individual PPTP. Complementary approaches to describe the status of the water quality and to investigate if direct adverse effects can be observed, were the SPEAR_{pesticide}, the BMWP-CR and EPT-taxa richness indices using macroinvertebrate abundance data measured at four main stream sites of the Tapezco river.

3.3 Materials and Methods

3.3.1. The Tapezco river catchment

The study catchment, its eight sampling sites and its division into eight hydrological sub-catchments (SCs) is presented in Chapter 1 (section 1.7; Figure 4). The eight sampling sites comprise four headwater catchments sites (SC1, SC2, SC6 and SC7) which are nested into four other SCs (i.e. SC3 is downstream of SC2; SC4 downstream of SC1; SC5 is downstream of both SC4 and SC3; and SC8 is furthest downstream). Section 1.7 of Chapter 1 contains as well information about the meteorological conditions and land use within the study catchment. The highest share of horticultural land is present in SC1, SC4 and SC6, the lowest share in SC2, SC3 and SC7 while SC5 and SC8 lie in between.

3.3.2 Monitoring strategy

All the data was collected at five sampling sites between 30-Jul and 07-Oct in 2015, and at eight samplings sites from 25-May to 11-Oct in 2016. A total of 62 PPTP were identified in both sampling years and were thus included in the analyses for the risk assessment. Details about these 62 PPTP, along with information about nutrients and other physical water quality parameters measured at the SC, are listed in SI-3 A1.

As described in Chapter 2 (section 2.3.2), sampling was conducted by using two sorbent-based passive samplers: the reverse phase sulfonated styrene-divinylbenzene (SDB) disks and the polydimethylsiloxane (PDMS) sheets. The passive samplers were deployed at the sites and replaced by a time course of two weeks, extracted and analyzed. Among the individual sampling years, different precipitation patterns have been observed. In 2015, the rainy season was much drier as in 2016 (Chapter 1, Section 1.7). Consequently, to enable comparison among similar periods of time among the years, the biweekly averaged MEC data of the detected PPTP was divided into three time periods as follows: periods $\Delta T1$ and $\Delta T2a$ cover the nearly synchronized time period from 30-Jul to 07-Oct, 2015 and 02-Aug to 11-Oct, 2016, respectively; and period $\Delta T2b$ contains the data from the sampling campaign in 2016, i.e., from 25-May to 02-Aug (SI-3 A1.1). Treatment of MEC data in terms of uncertainty is described below in section 3.3.3.

Benthic macroinvertebrates were collected by personnel of the Instituto Regional de Estudios en Sustancias Tóxicas (IRET), Costa Rica, Heredia, for six months from August 2013 to February 2016 for a total of six sampling campaigns. The first three sampling campaigns included SC1, SC4 and SC5. From August 2014 on, SC8 was additionally included. Macroinvertebrates were collected by sampling all available habitats within the streams using a D net (250 μ m) for a period of 5 minutes. Organisms were preserved in ethanol (75%), and identified by IRET to the family and/or genus level (macroinvertebrate data is presented in

Echeverría-Sáenz and Weiss (2021)). For identification, regional taxonomical keys were applied (Merritt et al. 2008, Pennak 1989, Springer et al. 2010). The taxa richness per individual sampling site is presented in SI-3 B2.

3.3.3 Uncertainty of the MEC

The determined MEC used in this risk assessment study carry a level of uncertainty. As described in Chapter 2 (sections 2.3.4 a), uncertainty stems from the R_S values, which were taken from the literature, and from variations due to environmental parameters, such as varying flow conditions, varying pH, biofilm growth and sediment deposition. Thus, in an attempt to account for this uncertainty, the R_S values were divided and multiplied by a factor of three, an approach previously suggested by Curchod et al. (2019) and Moschet et al. (2014a). This uncertainty has been shown to cover 90% of the empirical R_S -variance amongst compounds in a previous field study (Moschet et al. 2014a). During the conversion of the masses sorbed to the SDB or PDMS samplers into MEC, the uncertainty factor of three is transferred to the MEC as well.

Taking this uncertainty factor into account, three MEC scenarios were distinguished: i) Minimum risk scenario: MECs of each compound for each sample divided by a factor of 3; ii) Measured risk scenario: MECs with no change; iii) Maximum risk scenario: MECs multiplied by a factor of 3.

3.3.4 Risk assessment approaches based on pesticide exposure data and lab-based effect data

Two risk assessment approaches based on pesticide exposure data (i.e. the MEC) were applied. In the first approach, the MEC of the PPTP were divided by EQS values forming RQ. In the second approach, the MEC were divided by effect-related concentrations of *Daphnia magna*, or *Ceriodaphnia dubia* if no *Daphnia magna* data was available, to derive TU.

3.3.4 a) Derivation of RQ

Within the EU Water Framework Directive, RQ are determined using MEC and chronic-EQS for identifying long-term risks and maximum acceptable concentration or acute EQS for describing short-term risks (European Commission 2018). The applied acute and chronic EQS values with their references are presented in SI-3 B3. All EQS values were obtained according to the Technical Guidance for deriving Environmental Quality Standards, No. 27 (European Commission 2018). The majority represent established EQS values, a minor part are ad hoc EQS values which were not yet officially approved by the Water Framework Directive.

For a risk assessment of single PPTP, RQ were determined using the individual MEC (three case scenarios, section 3.3.3) divided by the compound specific chronic or acute EQS (SI-3 B3) as presented in Equation 3-(1) (EFSA Panel on Plant Protection Products and their Residues 2013). If no EQS value was available (18 PPTP), the compound was excluded from this risk assessment.

$$RQ = \frac{MEC}{EQS} \quad \text{Eq. 3-(1)}$$

For describing the water quality, the RQ classification was applied such that an $RQ \geq 1$ indicates that negative impacts on water organisms cannot be excluded as follows (Junghans 2013):

- $0 < RQ < 0.1$: water quality is very good
- $0.1 \leq RQ < 1$: water quality is good
- $1 \leq RQ < 2$: water quality is moderate
- $2 \leq RQ < 10$: water quality is unsatisfactory
- $10 \leq RQ < 100$: water quality is bad

- Given some of the very high RQ obtained in this study, an additional category was added for $100 \leq RQ < 1000$: water quality is very bad.

To account for the presence of pesticides in mixtures, mixture RQ (RQ_{mix}) were determined as well for each sample by summing all RQ of each PPTP using its MEC and its corresponding EQS as described in Equation 3-(2) (Junghans 2013):

$$RQ_{mix} = \sum_i \frac{MEC_i}{EQS_i} \quad \text{Eq. 3-(2)}$$

where, MEC_i is the MEC for each detected PPTP, i , and EQS_i the corresponding EQS for each detected PPTP. RQ_{mix} were estimated also separately for organism groups of different trophic levels. Accordingly, RQ_{mix} were determined by clustering the RQ for each individual pesticide according to the most effected organism group before accumulating them (Junghans 2013). For substances affecting more than one organism group, the EQS values were labelled with the most affected organism groups (i.e. vertebrates (V), primary producers (P), and invertebrates (I)). These V, P, I labels, assigned for the EQS values, are presented in SI-3 B3. The RQ_{mix} of all detected compounds, i , for each trophic organism group, j (P, I, V), were estimated according to Equation 3-(3) (Junghans 2013):

$$RQ_{mix,j} = \sum_{i \text{ element of } j} \frac{MEC_i}{EQS_i} \quad \text{Eq. 3-(3)}$$

where, $RQ_{mix,j}$ represents the RQ_{mix} of each trophic organisms group (j).

3.3.4 b) Calculation of TU

Single chemical TU were determined by dividing the compound-specific MEC by the compound specific EC_{50} (median effect concentrations for 50% of the tested species) according to Equation 3-(4) (Liess and Ohe 2005):

$$TU = \log_{10}\left(\frac{MEC}{EC_{50}}\right) \quad \text{Eq. 3-(4)}$$

As test species *Daphnia magna* was used; in a few cases, where no *Daphnia magna* data was available, data from *Ceriodaphnia dubia* were used if available. The list with available EC_{50} is presented in SI-3 B4 with references – this list was provided by the Ecotox centre (Contact: Junghans M. marion.junghans@cluteroekotoxzentrum.ch). Only EC_{50} values from freshwater laboratory experiments on mortality, immobility and population endpoints in short-term experiments were considered as reference for describing acute risks. This procedure is very similar to that utilized within the European Commission (2018). Only the EC_{50} concentrations were applied instead of predicted no effect concentrations (PNEC) to describe acute risks and the quotient was log transformed in order to improve the readability of the data (EC_{50} data: SI-3 B4).

The TU for the mixture of PPTP (TU_{mix}) for each sample was calculated according to Equation 3-(5) deduced from the European Commission (2018) and on the basis of Eq. 3-(4):

$$TU_{mix} = \sum_n TU_n \quad \text{Eq. 3-(5)}$$

Here, TU_{mix} is the sum of TU for each pesticide contained in the sample; n is the total number of pesticide per sample. Available EC_{50} of the detected pesticides were used for the calculation. Compounds without an available EC_{50} value were excluded from the risk assessment (20 PPTP).

The following TU classification was applied according to Schäfer et al. (2007):

- $TU < -4$ are not contaminated
- $-4 \leq TU < -2$ are slightly contaminated

- $-2 \leq TU < 0$ are heavily contaminated
- Given some of the very high TU obtained in this study, an additional category was added for $0 < TU < 2$: are very heavily contaminated.

It is important to note that the TU and the RQ classifications are somewhat inconsistent. With the RQ classification, log transformed RQ data > 1 indicate an unsatisfactory water pollution whereas with the TU classification, $TU > -2$ indicate heavily contaminated water quality. This difference equals a safety factor of 1000 to the TU, i.e. to consider that some invertebrates are more sensitive to pesticides than *Daphnia magna*.

3.3.5 Approaches describing water quality status based on macroinvertebrate data

To estimate if the PPTP had an impact on macroinvertebrates, the macroinvertebrate data were used to calculate the $SPEAR_{pesticide}$, the EPT-taxa richness index and the BMWP-CR index.

3.3.5 a) Determination of $SPEAR_{pesticide}$

The $SPEAR_{pesticide}$ index was determined based on the most recent estimations of Knillmann et al. (2018) and Liess and Ohe (2005), as described in Equation 3-(6) and according to the formula applied within the freely available “Indicate” software to determine $SPEAR_{pesticide}$ data (Version 2.0.0, <http://www.systemecology.eu/indicate/>):

$$SPEAR_{pesticide} = \frac{\sum_{i=1}^n \log(x_i + 1) \times y}{\sum_{i=1}^n \log(x_i + 1)} \quad \text{Eq. 3-(6)}$$

Here, n is the total number of taxa in each sample, x_i the abundance of taxon i (Echeverría-Sáenz and Weiss 2021) and y is set to 1 if taxon i is classified as “at risk” dependent on its biological trait information, specifically the physiological sensitivity to organic toxicants, generation time, presence of aquatic stage in the water during the maximum pesticide usage and migration abilities (Knillmann et al. 2018, Liess and Ohe 2005, Schäfer et al. 2008). The abundance data is $\log(x + 1)$ -transformed in order to avoid the undefined $\log(0)$ (Knillmann et al. 2018). The biological trait information, used for the calculation of the $SPEAR_{pesticide}$, are presented in Echeverría-Sáenz and Weiss (2021). The taxonomic data is provided as well (Echeverría-Sáenz and Weiss 2021). Based on the determined $SPEAR_{pesticide}$ values, five environmental quality classes are distinguished, which refer to ecological status classes according to the European Water Framework Directive and have normative character. Essentially, the $SPEAR_{pesticide}$ index “calibrates” the macroinvertebrate data from the respective sampling sites to macroinvertebrate data expected in reference streams, namely European reference streams without pollution.

The derived environmental quality classes are:

- $SPEAR_{pesticide} \geq 0.80$: High (I)
- $0.60 \leq SPEAR_{pesticide} < 0.80$: Good (II)
- $0.40 \leq SPEAR_{pesticide} < 0.60$: Moderate (III)
- $0.20 \leq SPEAR_{pesticide} < 0.40$: Poor (IV)
- $SPEAR_{pesticide} < 0.20$: Bad (V)

Knillmann et al. (2018) demonstrated that there was a correlation ($R^2 = 0.57$, explained variance 54.83%) between their $SPEAR_{pesticide}$ data and TU. By utilizing their correlation, and considering the relation between $SPEAR_{pesticide}$ and TU of Liess et al. (2021), applied within the “Indicate” software (version 2.0.0, <https://www.systemecology.de/indicate/>), the $SPEAR_{pesticide}$ data can be converted into $TU_{estimated}$ as described in Equation 3-(7):

$$TU_{estimated} = \frac{(0.17502 - SPEAR_{pesticide})}{0.13012} \quad \text{Eq. 3-(7)}$$

TU_{estimated} were calculated for comparison with TU_{mix} within this study.

3.3.5 b) Calculation of the EPT-taxa richness indicator

The EPT-taxa richness index is based on the added up numbers of taxa of the insect orders ephemeroptera (E), plecoptera (P) and tricoptera (T) (Castillo et al. 2006b, Mertens and Küry 2018). The EPT abundancy data applied in this thesis is provided in Echeverría-Sáenz and Weiss (2021). The water quality classification scheme described by Mertens and Küry (2018) and the North Carolina Department of Environment (1997) was used as it was suggested for streams of similar size as the streams of the Tapezco catchment. This was done because it has to be considered that the size and width of the streams might influence the classification range (Paller et al. 2006).

- Number EPT-taxa ≤ 6: poor water quality
- 6 < number EPT-taxa ≤ 13: fair water quality
- 13 < number EPT-taxa ≤ 20: moderate water quality
- 20 < number EPT-taxa ≤ 27: good water quality
- number EPT-taxa >27: highest water quality

3.3.5 c) Calculation of the BMWP-CR index

To describe the status of water pollution by using macroinvertebrates, BMWP-CR Index (La Gaceta Official Newspaper 2007) was introduced into the regulatory process. The BMWP-CR index was applied as described in Chapter 1, section 1.5 and Echeverría-Sáenz and Weiss (2021).

The defined BMWP-CR classes according to the sensitivity score were:

- Points > 120: Excellent quality waters
- Points between 101 and 120: Good quality waters, not contaminated
- Points between 61 and 100: Regular quality waters, eutrophic, moderately contaminated
- Points between 36 and 60: Bad quality waters, contaminated
- Points between 16 and 35: Bad quality waters, very contaminated
- Points ≤ 15: Very bad quality waters, extremely contaminated

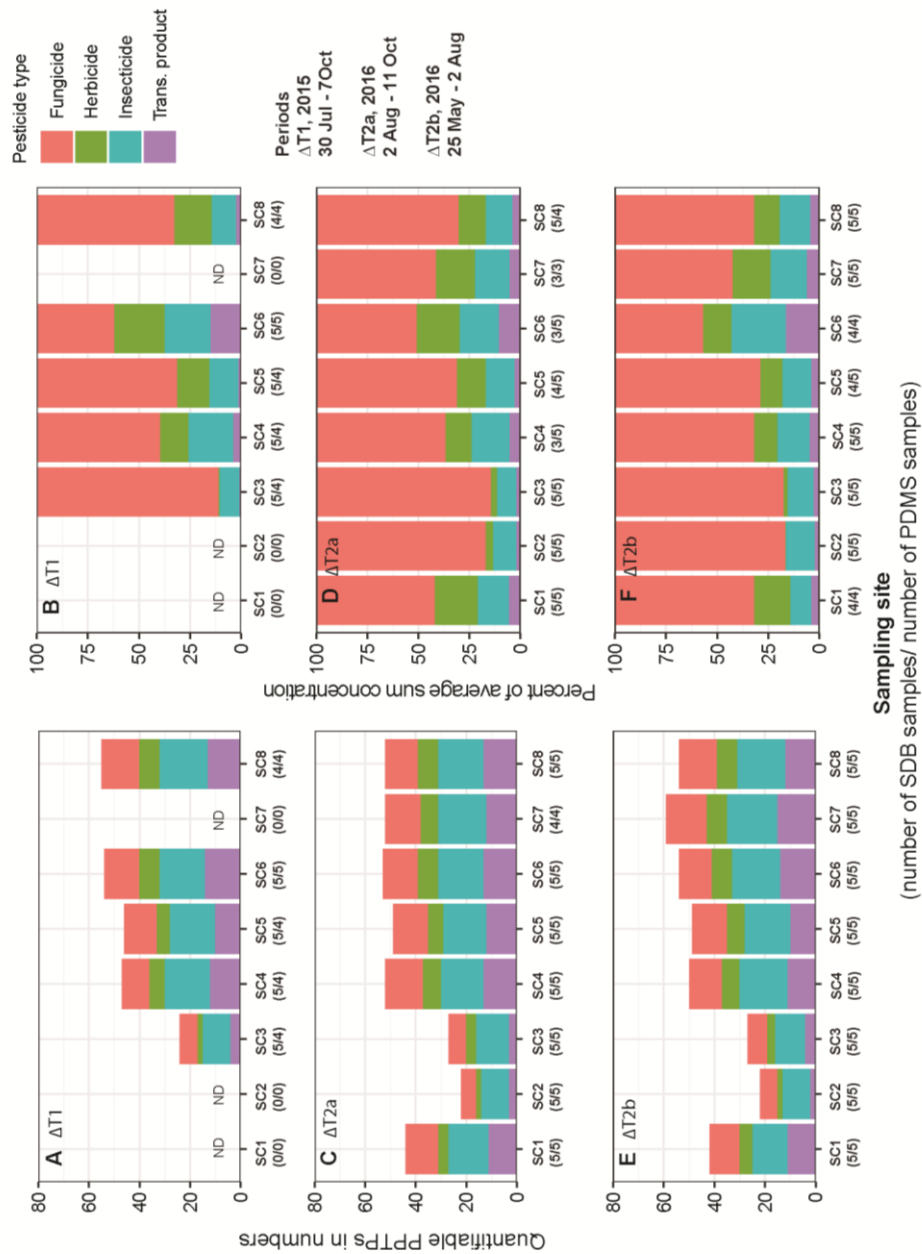
3.4 Results

The overall aim of this study was to perform an aquatic risk assessment for eight sub-catchments (SC1 to SC8) within the Tapezco river watershed, a tropical small-scale horticultural area, and to investigate if the risks differ among the individual sampling periods and sites. Risk assessment was based on pesticide biweekly MEC data of 62 PPTP, obtained as described in Chapter 2. Additionally, the determined pollution status from the MEC of PPTP was compared with the determined water quality derived from macroinvertebrate data via SPEAR_{pesticide}, BMWP-CR indices and the EPT-taxa richness indicator.

3.4.1 Spatial distribution of PPTP during the sampling years 2015 and 2016

Overall, the PPTP data of this study showed that at the headwater site SC2, and the site SC3 (downstream of SC2), the average number of detected PPTP was about 2-fold lower than at the other SCs (Figure 1, left-hand site, panels A, C, E). It stood out that, from the individual pesticide types, i.e. insecticides, fungicides, herbicides and TP, the insecticides had the broadest detected compound spectrum at all individual sites, followed by fungicides, TP and herbicides. For each sampling site, the total number of PPTP remained similar from $\Delta T1$, $\Delta T2a$ to $\Delta T2b$; as well, the share of the different PPTP per pesticide type remained similar over the three periods.

A somewhat different pattern emerged when the concentrations of all detected PPTP per each sample were added together and expressed as average %-contribution of the total sum concentration per pesticide type and sampling site for each sampling period (Figure 1, right-hand site, panels B, D and F). First, while again sites SC2 and SC3 were distinct from the other sites, fungicides were dominant %-contribution-wise by far at SC2 and SC3. Even though total fungicide %-contributions were as well the highest for the other sites (SC1, SC4-SC8), these other sites had more significant contributions also from insecticides and herbicides. The average %-contribution of the total sum concentration per pesticide type and site remained very similar during the three sampling periods. For instance, in both years (i.e. seen in all three periods), the average %-contribution of fungicides was the highest at SC3, and the lowest at SC6. The individual spatio-temporal distribution of the biweekly averaged concentration data of each quantifiable PPTP per SC is presented in SI-3 B5.



3.4.2 Environmental risk assessment based on RQ

Chronic RQ (CRQ) and acute RQ (ARQ) were calculated based on the MEC and available EQS. For the pesticide data used in this study, chronic EQS were available for 44 PPTP and acute EQS for 42 PPTP (SI-3 B3). Such RQ were determined first for single PPTP. However, since PPTP are present in streams mostly as complex mixture, the RQ of the individual compounds were as well added up, forming the RQ_{mix} . The RQ_{mix} were, moreover, determined per each individual organism group. To do so, each RQ of the individual pesticides affecting primary producers, vertebrates or invertebrates, respectively, were added. Information about which PPTP affects which organisms group the most is provided in SI-3 B3.

3.4.2 a) Spatial and temporal distribution of chronic and acute risks

Calculation of RQ revealed frequent exceedance of both CRQ (Figure 2, top left) and ARQ (Figure 2, top right) above the threshold of one, for all sampling sites and periods of sampling. As expected, CRQ surpassed the threshold of one more frequently than the ARQ. The fewest exceedances were consistently seen for SC2 and SC3. Overall, when considering time, exceedances were similar for both CRQ and ARQ during the synchronized periods of $\Delta T1$ (2015) and $\Delta T2a$ (2016) and during $\Delta T2b$ (2016). Only at SC5 and SC8, the CRQ exceedances increased by about 1/3 and 2-fold, respectively, during $\Delta T2a$ and $\Delta T2b$ compared to $\Delta T1$. Additionally at SC4 and SC7, the number of CRQ and ARQ exceedances were elevated in $\Delta T2b$ compared to the numbers in $\Delta T2a$. At SC7 the number of chronic RQ exceedances are higher during $\Delta T2b$ as opposed to $\Delta T2a$ most likely due to the loss of two samples during $\Delta T2a$. The fact that, during $\Delta T2b$, the number of exceedances was similar to $\Delta T2a$, showed that aquatic organisms were at continuous risk, at least from May to October. The actual CRQ_{mix} and ARQ_{mix} values (Figure 2, bottom, median values) were greatest for SC2, despite the lower frequency of exceeding the CRQ and ARQ value, followed by SC1 and SC3 during $\Delta T2a$, and SC3 and SC8 during $\Delta T2b$. Here it is important to note that the results of SC3 are influenced by SC2. The RQ exceedances and the RQ_{mix} ranges per site (chronic and acute) for the best and worst case scenario are presented in SI-3 A2.2.

The RQ results for the different scenarios (explained in section 3.3.3) are not discussed in detail in the main text, since the distribution of the numbers of RQ exceedances remained similar among the individual sites in consideration of the worst and best case scenario.

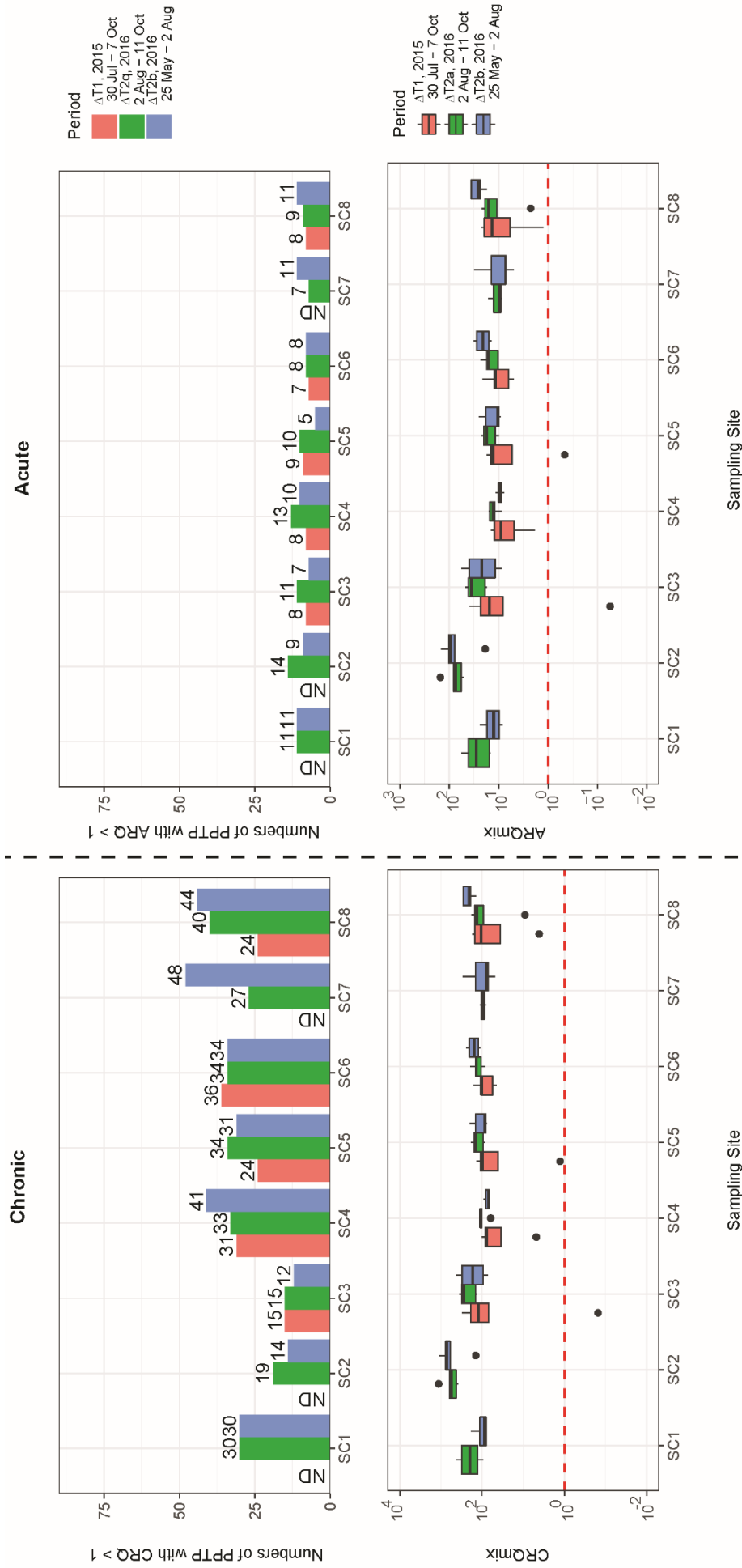


Figure 2: Chronic and acute risks, expressed as RQ, observed at the individual sampling sites during three sampling periods. The numbers of PPTP with CRQ and ARQ > 1 are shown in the upper two graphs. The magnitude of CRQ_{mix} and ARQ_{mix} are presented in the two bottom graphs. The factor of three of uncertainty is not applied here. Boxplots represent first and third quartiles (outer box) and medians (fat lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of 1.5* the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of 1.5 * the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers (standardized boxplot using R ggplot2 package). ND = not determined.

3.4.2 b) Temporal distribution of chronic and acute risks for different organism groups

Based on RQ calculated for the organism groups most commonly investigated in regulatory aquatic risk assessment (vertebrates, primary producers, invertebrates), the data of this study over all sites showed that invertebrates were at risk. Considering even the best case scenario (Figure 3, lowest dashed line), continuous risks can be expected for invertebrates in the Tapezco river catchment. Vertebrates and primary producers were at no or moderate/high risk (moderate/high water quality) and were so at comparable levels between these organism groups (Figure 3). In 2015 ($\Delta T1$), the water quality decreased with respect to chronic risk from bad to very bad for invertebrates, whereas the water quality was generally very bad for 2016 ($\Delta T2a/\Delta T2b$). An important caveat, however, is that the PDMS sheets could not be properly extracted and could not be analyzed for the first biweekly interval in $\Delta T1$ (samples with issues are listed in SI-2 B2). This means that the CRQ_{mix} values during the first biweekly interval in $\Delta T1$ do not include data for the pyrethroid and chlorpyrifos insecticides. The exact same pattern was observed for the ARQ_{mix} though shifted by one category, i.e., water quality for invertebrates in $\Delta T1$ was generally unsatisfactory to bad rather than bad to very bad as for the CRQ_{mix} . The water quality for invertebrates in $\Delta T2a$ was generally bad instead of very bad as for the CRQ_{mix} .

Risks to vertebrates and primary producers were significantly lower for chronic effects compared to invertebrates. In this case, the trend for increasing risks (decreasing water quality) during 2015 was not affected by the missing insecticide data from PDMS sheets as they were not considered for the determination of the CRQ_{mixed} for vertebrates and primary producers. In 2016, water quality for chronic effects to vertebrates and primary producers fluctuated between being moderate to unsatisfactory.

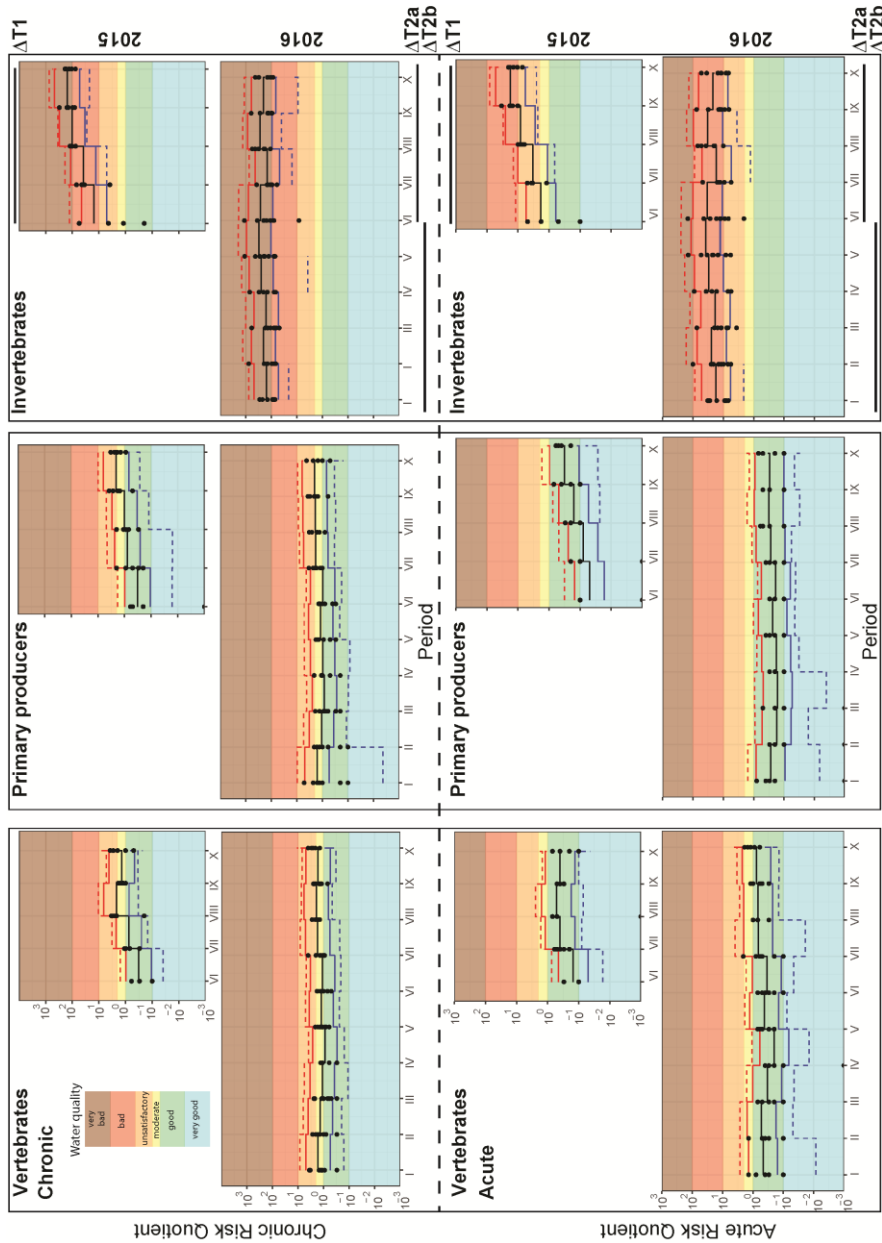


Figure 3: Temporal chronic and acute risk trends from mixtures of pesticides for vertebrates, primary producers and invertebrates within the Tapezco river catchment. RQ_{mix} for the different organisms groups were determined per biweekly sampling interval (Roman numbers on x-axis represent biweekly sampling intervals explained in SI-3 A1.1 with starting in 2015 at the 30 July – 13 Aug (V) and in 2016 at the 24 May to 7 June (I)). CRQ_{mix} are shown in the upper part, ARQ_{mix} in the lower part. The solid black lines represent the average RQ_{mix} from data of five sites in 2015 and eight sites in 2016 during the measured scenario. The upper solid red lines represent the average RQ_{mix} according to the worst case scenario; the lower solid blue lines represent the average RQ_{mix} according to the best case scenario. To illustrate the range of uncertainty, the upper standard deviation of the worst case scenario is presented as dashed, red lines and the lowest standard deviation of the best case scenario is shown as dashed, blue lines. In some cases the lowest standard deviation could not be shown due to the log scale (non-logarithmic data would be negative).

3.4.2 c) Spatial distribution of risks from individual pesticides

To understand which pesticides pose the highest risks at which site, those pesticides exceeding CRQ and ARQ were identified along with their frequencies of exceedance for all periods ($\Delta T1$, $\Delta T2a$ and $\Delta T2b$) (Figure 4). The full data set of ARQ and CRQ per each PPTP in biweekly samples per each SC is provided in SI-3 B5. The frequencies of RQ exceedances in the measured scenario are illustrated for simplification, representing intermediate risk assessment data between the two extreme cases, the best and worst case scenario (scenarios are explained in section 3.3.3).

For a total of 18 pesticides, chronic risks were indicated by CRQ above one considering the measured risk scenario (shown Figure 4). Insecticides posed the highest risks, i.e. CRQ for chlorpyrifos and cypermethrin were exceeded almost continuously (in $\geq 95\%$ of the samples) at all sampling sites. Comparable, albeit lower, frequencies of exceedance were also found for carbendazim, deltamethrin, imidacloprid and metribuzin without a clear trend per periods and sites. The frequencies of exceedance for bifenthrin, carbofuran, diazinon and fipronil was the highest at sites SC1 and SC4 – SC8, singling out SC2 and SC3 as somewhat less affected. Cyhalothrin, thiamethoxam, dimethoate, diuron, linuron and tebuconazole exceeded CRQ without showing a clear trend over space and time. According to the minimum risk scenario, for eleven out of the 18 pesticides, CRQ were exceeded. Here again exceedances for chlorpyrifos and cypermethrin almost continuous (SI-3 A2.1). With the maximum risk scenario, three additional pesticides (methiocarb, metolachlorand metsulfuron-methyl), i.e. for total 21 pesticides, CRQ were exceeded (SI-3 A2.1).

Seven of the pesticides exceeded the ARQ of one. Chlorpyrifos and cypermethrin again posed the highest potential risk with an overall higher frequency of exceedance in 2016 than in 2015. For carbendazim, cyhalothrin, imidachloprid and diazinon ARQ were exceeded without a clear pattern; fipronil-ARQ were only exceeded in $\Delta T2b$. Considering the minimum risk scenario, three pesticides (cyhalothrin, cypermethrin and diazinon) exceeded the ARQ of one (SI-3 A2.1). Cypermethrin exceeded ARQ at all sites as well. With the maximum risk scenario, eleven pesticides (four additional: carbofuran, deltamethrin, diuron, prometryn + terbutryn) exceeded the ARQ of one sporadically (SI-3 A2.1).

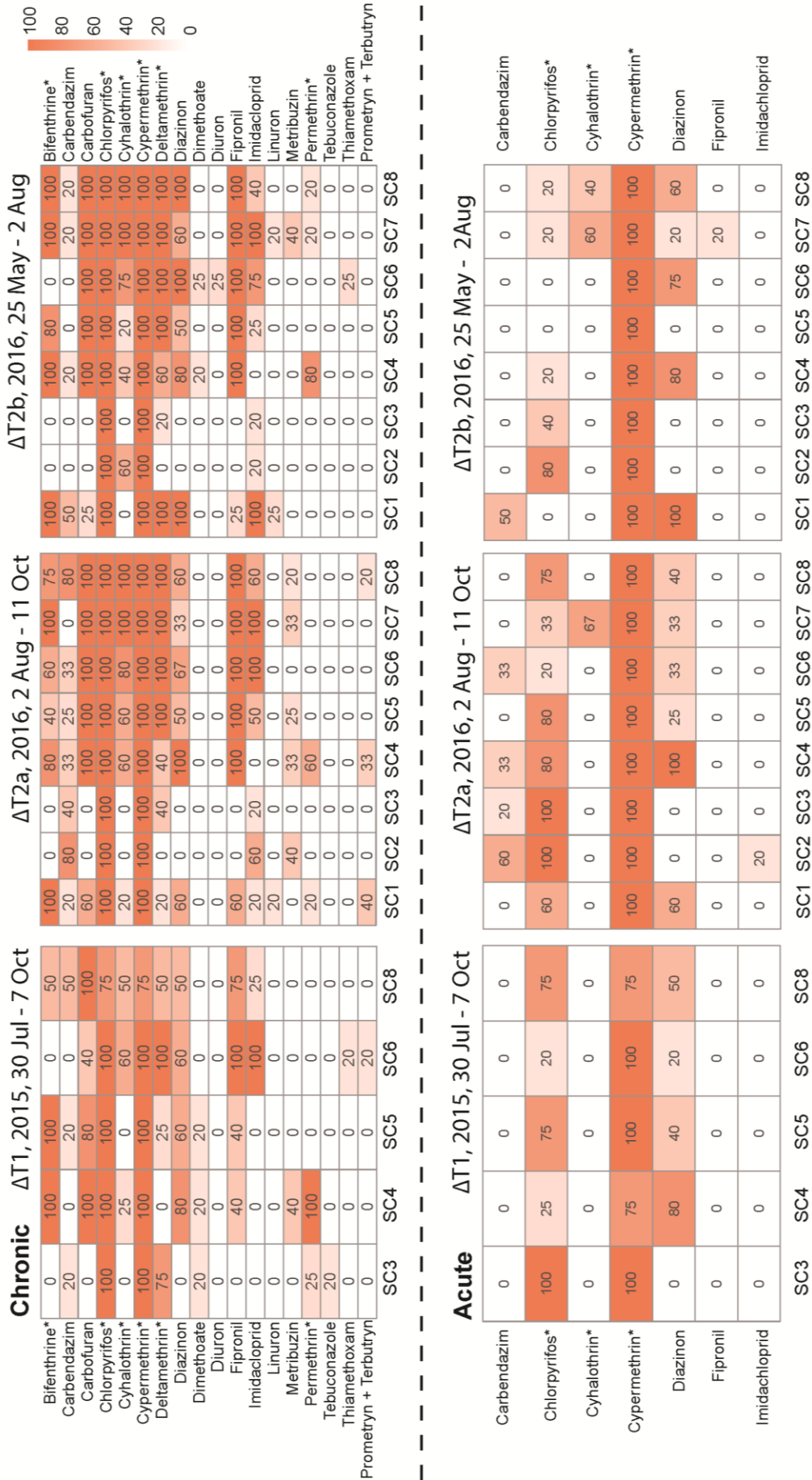


Figure 4: Frequencies of individual pesticides indicating chronic and acute risks at the different sampling sites and sampling years. Percentages of CRQ exceedance for individual pesticides during ΔT1, ΔT2a and ΔT2b are presented in the upper part. Percentages of ARQ exceedances are shown in the lower part. *Data from PDMS approach, otherwise from SDB approach. The PDMS sheets for the first biweekly interval in ΔT1 were not properly extracted and could not be analyzed. The heatmap was created with pheatmap package of R Studio Version 1.25001.

3.4.3 Environmental risk assessment based on TU

The TU approach uses the same experimental data (MEC) as in the RQ approach but evaluates the risks based on the sensitivity of *Daphnia magna* or *Ceriodaphnia dubia* for individual PPTP or PPTP-mixtures, instead of using EQS. Because of this difference and because EC_{50} for acute exposures were available only for 42 of the 62 PPTP analyzed (SI-3 B4), the TU_{mix} and RQ_{mix} values are not directly comparable as pointed out as well in section 3.3.4 b.

3.4.3 a) Spatial distribution of acute risks

Equivalent to the ARQ data (Figure 2, top right), the TU data show as well that all sites were heavily contaminated during all periods (Figure 5, upper part). At SC7, the number of $TU > -2$ was about 2-fold higher during $\Delta T2b$ compared to $\Delta T2a$ (likely due to the loss of two samples during $\Delta T2a$). Similar absolute values were found for TU_{mix} across all sites (Figure 5, lower part), again confirming a heavy contamination of the water. TU exceedances and TU_{mix} ranges according to the best and worst case scenario are shown in SI-3 A3.2.

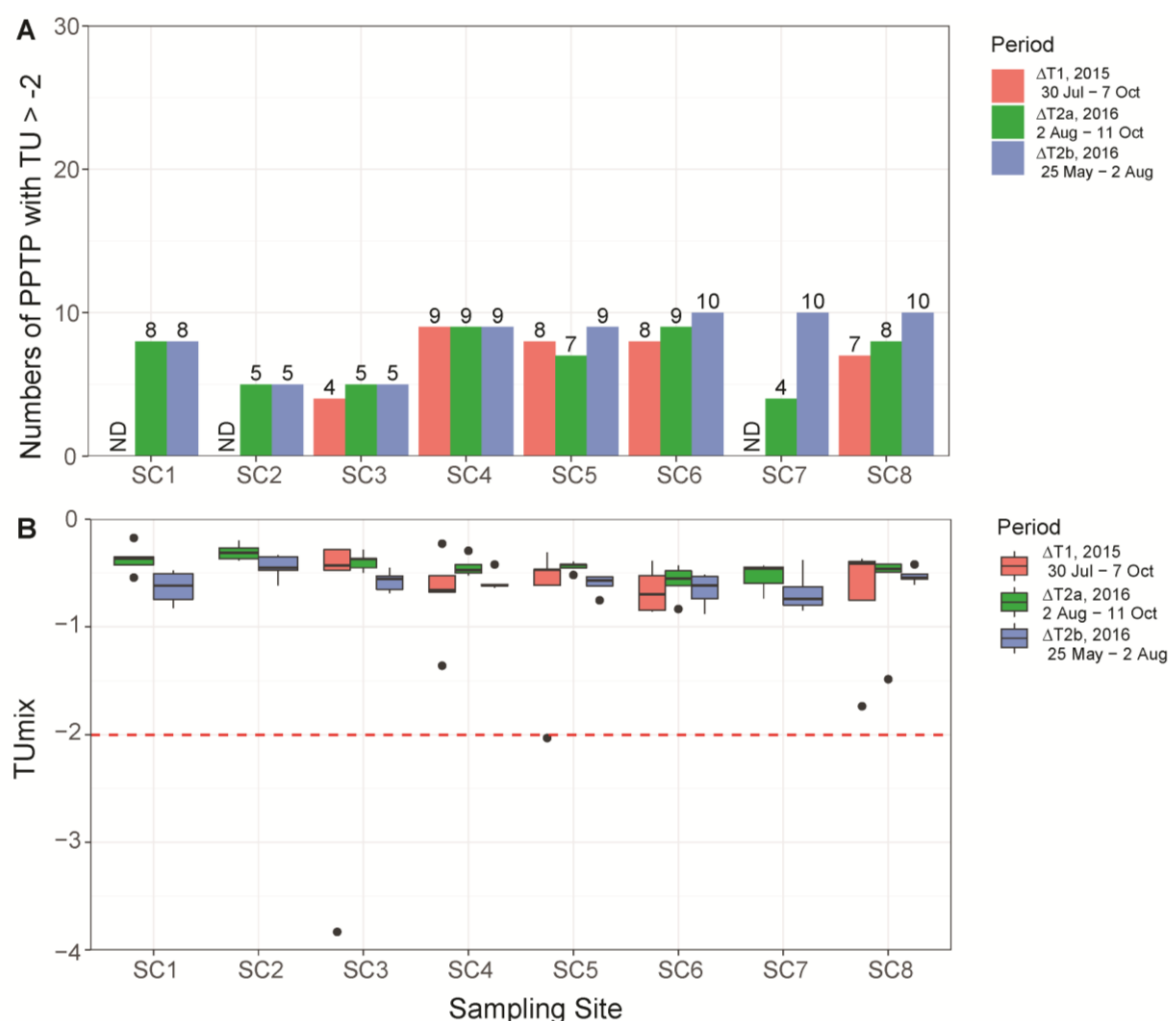


Figure 5: Acute risks based on TU, observed at the individual sampling sites during the three sampling periods. The numbers of PPT with $TU > -2$ are shown in the upper graph. The magnitude of TU_{mix} are presented in the bottom graphs. Boxplots represent first and third quartiles (outer box) and medians (fat lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of 1.5* the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of 1.5 * the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers (standardized boxplot using R ggplot2 package). Red dashed line indicate the environmentally critical TU_{mix} value of -2. ND = not determined.

3.4.3 b) Temporal distribution of acute risks

TU_{mix} above -2 were found at all sites throughout all sampling campaigns, underlining the continuity of heavy water contamination even in the best case pollution scenario (Figure 6, lower dashed lines). The lower TU for the first biweekly interval in 2015 ($\Delta T1$) is likely again influenced by the missing insecticide data from the PDMS sampling approach (SI-2 B2).

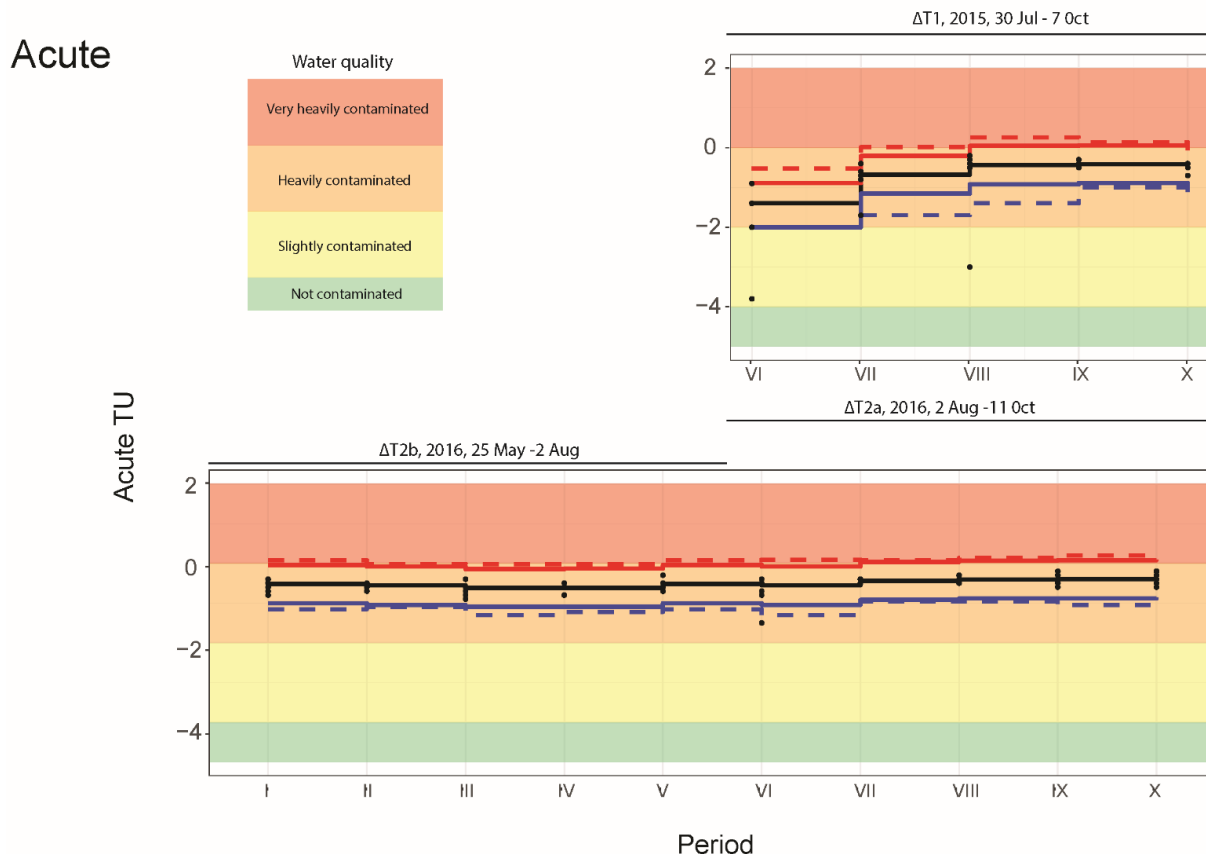


Figure 6: Temporal acute risk trends from mixtures of pesticides based on TU_{mix} for invertebrates within the Tapezco river catchment. TU_{mix} for invertebrates were determined per biweekly sampling interval (Roman numbers on x-axis represent biweekly sampling intervals explained in SI-3 A1.1 with starting in 2015 at the 30 July – 13 Aug (V) and in 2016 at the 24 May to 7 June (I)). The solid black lines represent the average TU_{mix} from data of five sites in 2015 ($\Delta T1$) and eight sites in 2016 ($\Delta T2a$ and $\Delta T2b$) during the measured scenario. The upper solid red lines represent the average TU_{mix} according to the worst case scenario; the lower solid blue lines represent the average TU_{mix} according to the best case scenario. To illustrate the range of uncertainty, the upper standard deviation of the worst case scenario is presented as dashed, red lines and the lowest standard deviation of the best case scenario is shown as dashed, blue lines. In 2015, the lowest standard deviation could not be shown into the sampling period VI due to the log scale (non-logarithmic data would be negative).

3.4.3 c) Spatial distribution of acute risks from individual pesticides, based on $TU > -2$

Three compounds exceeded critical levels according to the TU approach indicating heavy pollution (Figure 7, measured scenario). Chlorpyrifos and diazinon exceeded critical TU levels indicating acute risks, which was observed as well with the previously used ARQ approach (Figure 4, lower panel). In contrast, carbofuran exceeded critical TU levels at SC 4 and SC6 posing acute risks which was not observed with the previous ARQ approach (Figure 4). Cypermethrin did not seem to pose acute risks based on the TU approach, though posed continuous risks with the ARQ method. The spatial and temporal TU data is shown in SI-3 B5.

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A heatmap showing the spatial and temporal distribution of TU exceedances is presented in SI-3 A3. Considering the minimum risk scenario, TU values showed continuous risks for chlorpyrifos and sporadic risks for diazinon (SI-3 A3.1). According to the maximum risk scenario, TU values indicated partially risks due to carbendazim and cyhalothrin exposure, additionally (SI-3 A3.1).

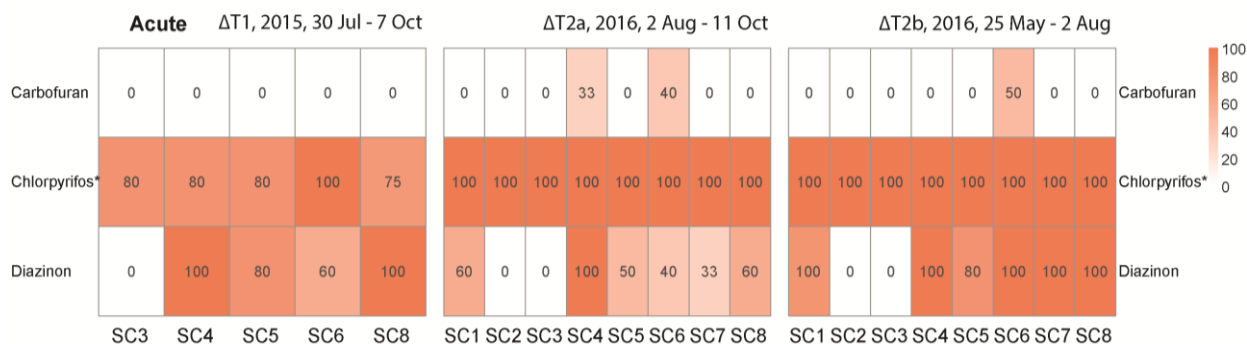


Figure 7: Frequencies of individual pesticides indicating acute risks ($TU > -2$), based on TU, at the different sampling sites and three sampling periods. *Data from PDMS approach otherwise from SDB approach. The PDMS sheets for the first biweekly interval in $\Delta T1$ were not properly extracted and could not be analyzed. The heatmap was created with pheatmap package of R Studio Version 1.25001.

3.4.4 Comparison of the ARQ_{mix} and the TU_{mix}

The ARQ_{mix} for invertebrates correlated well with the TU_{mix} ($R^2 = 0.47$, Figure 8). Results were similar if the overall ARQ_{mix} (considering EQS data affecting all trophic levels, invertebrates, vertebrates and primary producers) were plotted vs. the TU_{mix} (SI-3 A4.1) to using only ARQ_{mix} for invertebrates (Figure 8). This supports the dominating role of insecticides posing a risk to aquatic organism in the Tapezco river catchment. The ARQ_{mix} for invertebrates showed a moderate to very bad water quality vs. the TU_{mix} showing a very heavy contamination of the water. This demonstrates that both approaches lead to conclude that acute risks to invertebrates can be expected by using varying reference values. However, the TU_{mix} is more sensitive than the ARQ_{mix} for invertebrates (see also 3.3.4. b).

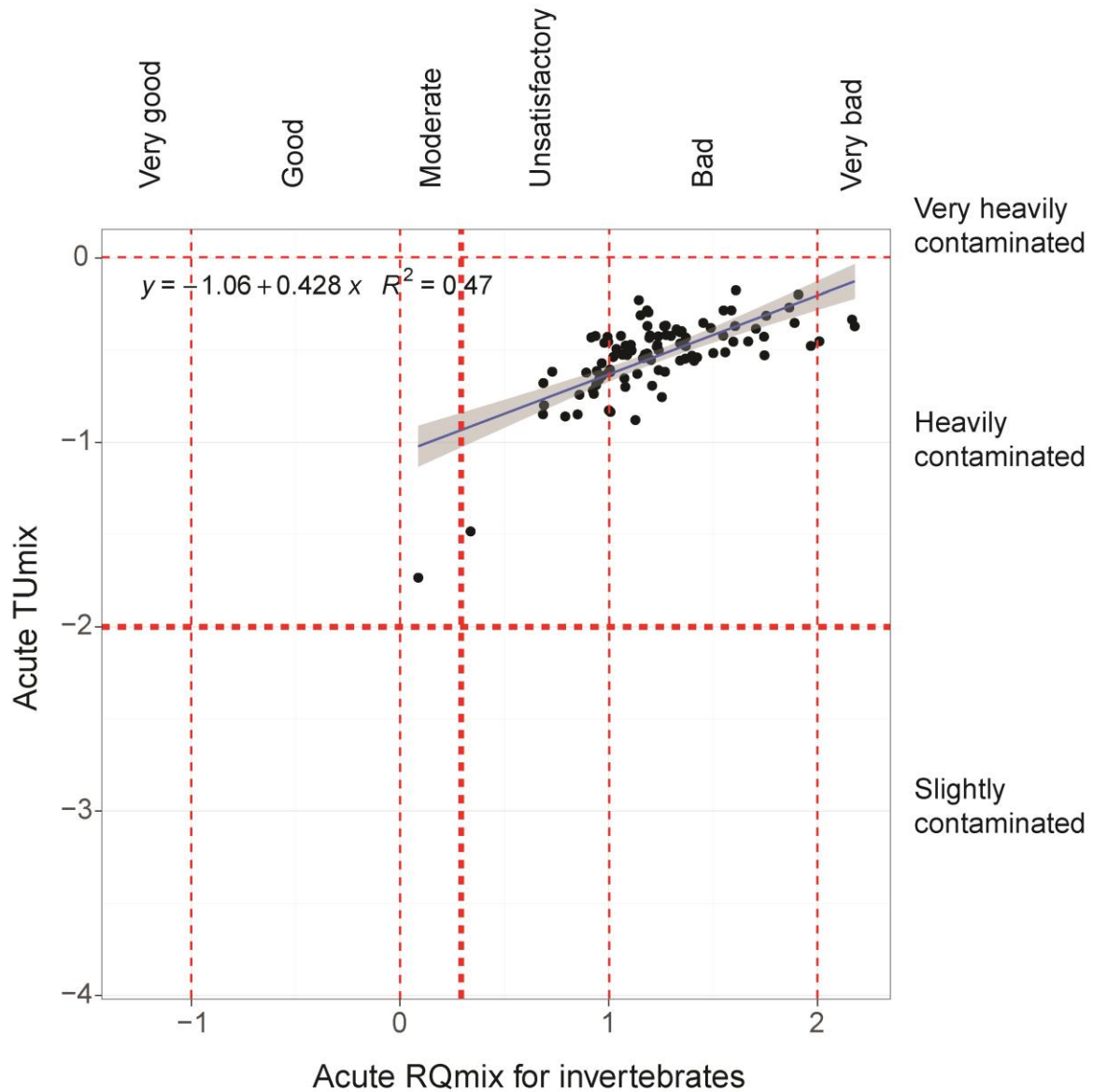


Figure 8: Correlation between acute TU_{mix} and ARQ_{mix} (x-axis log transformed) for invertebrates for mixture of pesticides for each sample with 95% confidence interval, all data log10 transformed. For linear regression, only TU data was considered from samples where both SDB disks and PDMS sheets data was available. The horizontal dashed lines represent the boundaries of the TU classification (water quality: right y-axis), the thick, dashed horizontal line the critical TU pollution level. The vertical dashed lines represent the boundaries of the ARQ classification (water quality: upper x-axis), the thick, dashed vertical line the critical ARQ pollution level.

3.4.5 Application of the SPEAR_{pesticide}, the BMWP-CR and the EPT-taxa richness index for describing the water quality status

To assess the exposure of mixtures of PPTP in relation to invertebrate occurrence in the streams, the SPEAR_{pesticide}, the EPT-taxa richness index and the BMWP-CR index were determined via collected macroinvertebrate spot samples at four sites of the Tapezco main river (Echeverría-Sáenz and Weiss 2021).

The SPEAR_{pesticide} indicates the worst water quality (“bad”) for the most upstream site, SC1, with an apparent improvement downstreams at SC5 and even good water quality for SC8 (Table 1, upper part). The improved water quality at SC5 and SC8 occurred mainly due to the high abundances of species with the orders Ephemeroptera and Trichoptera (with maximal abundances per species of 300 and 20, respectively (Echeverría-Sáenz and Weiss 2021)). The EPT-taxa richness index provides a much coarser scale, showing similarly poor water quality for all sites toward a borderline improvement to “fair” at SC8 (Table 1, middle part) and indicates that, even though the abundances of Ephemeroptera and Trichoptera-taxa seemed high, their taxa richness (of individual species) was low. The water quality as defined by the BMWP-CR index was in agreement with the SPEAR_{pesticide} results, indicating improved water quality at SC5 and, even more so, at SC8 (Table 1, bottom part). The SPEAR_{pesticide} and the BMWP-CR data correlated significantly ($R^2 = 0.65$, $p < 0.00001$ as shown in SI-3 B6).

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Table 1: Water quality assessment of the four main stream sites of the Tapezco river catchment by using macroinvertebrate data from spot sampling. The upper part refers to applying the biological trait-based SPEAR_{pesticide} index, the middle part refers to the EPT-taxa richness index, while the lower part shows the BMWP-CR results according to Echeverría-Sáenz and Weiss (2021). ND = not determined.

SPEAR _{pesticide}	26-Aug, 2013	24-Feb, 2014	25Aug, 2014	23-Feb, 2015	31-Aug, 2015	22-Feb, 2016
SC1	0.0	0.41	0.11	0.0	0.0	0.31
SC4	0.41	0.41	0.41	0.46	0.25	0.36
SC5	0.40	0.39	0.53	0.33	0.40	0.68
SC8	ND	ND	0.74	0.71	0.66	0.71

EPT-taxa richness	26-Aug, 2013	24-Feb, 2014	25Aug, 2014	23-Feb, 2015	31-Aug, 2015	22-Feb, 2016
SC1	0	2	1	0	0	2
SC4	2	1	1	3	2	1
SC5	2	2	1	3	3	5
SC8	ND	ND	6	7	7	7

BMWP-CR	26-Aug, 2013	24-Feb, 2014	25Aug, 2014	23-Feb, 2015	31-Aug, 2015	22-Feb, 2016
	16	49	53	23	27	53
	45	43	37	56	35	29
	35	48	40	36	37	64
	ND	ND	62	70	73	64

SPEAR _{pesticide}	Environmental quality pesticides	EPT- taxa richness	Water quality	BMWP- CR	Water quality
≥ 0.80	I High	> 27	I High	> 120	Excellent
≥ 0.60 - 0.80	II Good	21 - 27	II Good	101 - 120	Good
≥ 0.40 - 0.60	III moderate	14 - 20	III moderate	61 - 100	Regular
≥ 0.20 - 0.40	IV Poor	7 - 13	IV fair	36-60	Bad, contaminated
< 0.34	V: Bad	0 -6	V: poor	16-35	Bad, very contaminated
				≤ 15	Very bad

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In temperate regions, the $\text{SPEAR}_{\text{pesticide}}$ index is found to correlate well with TU as described in Eq. 3-(7) (Knillmann et al. 2018). With this relation from the yielded $\text{SPEAR}_{\text{pesticide}}$ values of this study, $\text{TU}_{\text{expected}}$ were estimated. This enables a comparison of the observed water quality status from the macroinvertebrate data with the chemical water quality status determined with TU_{mix} (Table 1). The $\text{TU}_{\text{expected}}$ show a very similar gradient as the $\text{SPEAR}_{\text{pesticide}}$ index with the worst pollution (“heavy”) for the most upstream site, SC1, and with an improvement downstream towards moderately to no pollution for SC8 (shown in SI-3 A5.1). For comparison of the $\text{TU}_{\text{expected}}$ with TU_{mix} , however, only a small set of overlapping data from August to September 2015 was available (Table 2). The TU_{mix} data indicated no differences, though the $\text{TU}_{\text{expected}}$ (and $\text{SPEAR}_{\text{pesticide}}$) results showed differences among sites. The calculated $\text{TU}_{\text{expected}}$ was similar as the TU_{mix} at SC4, one order different at SC5 and even three orders different at SC8 (Table 2), demonstrating as well the site dependent differences observed with the $\text{SPEAR}_{\text{pesticide}}$ data. TU_{mix} did not indicate an improvement of the water quality at SC8 as it was the case for the $\text{TU}_{\text{expected}}$.

Table 2: Direct comparison of TU_{mix} determined from pesticide exposure data and $\text{TU}_{\text{estimated}}$ from the $\text{SPEAR}_{\text{pesticide}}$ data according to the “Indicate” software (<https://www.systemecology.de/indicate/>, version, 2.0.0), based on Liess et al. (2021) and Knillmann et al. 2018. ND = not determined. The TU values are presented on basis of log10. Only pesticide monitoring data from 2015 (sites: SC3, SC4, SC5, SC6 and SC8) and macroinvertebrate data from end of August 2015 were compiled simultaneously and could be utilized for deriving TU_{mix} or $\text{TU}_{\text{estimated}}$ for comparison.

Site	Date _{macroinvertebrates} / Date _{passive sampling}	TU_{mix} from pesticide data	$\text{TU}_{\text{expected}}$ from $\text{SPEAR}_{\text{pesticide}}$ values
SC3	31 Aug 2015 / 27 Aug – 10 Sep 2015	-0.28	ND
SC4	31 Aug 2015 / 27 Aug – 10 Sep 2015	-0.23	-0.6
SC5	31 Aug 2015 / 27 Aug – 10 Sep 2015	-0.31	-1.7
SC6	31 Aug 2015 / 27 Aug – 10 Sep 2015	-0.52	ND
SC8	31 Aug 2015 / 27 Aug – 10 Sep 2015	-0.43	-3.7

3.5 Discussion

3.5.1 Spatial distribution of PPTP among the sampling years 2015 and 2016

The average number of pesticides per type was comparable among the sites during all periods, with one notable exception: at one upstream tributary, with SC2 feeding into SC3, the number of fungicides and herbicides was lower as opposed to the other sites. These observations show that in the SC1, SC4, SC5, SC6, SC7 and SC8 in both years, a similar spectrum (42 to 59) of PPTP was transported from the fields into the streams (Figure 1, left side). Thus it can be suggested that especially in the headwater catchments SC1, SC6, SC7, a similar compound spectrum was applied, ending up in the streams. The spectrum detected in SC4, SC5 and SC8 could enter the stream from the fields or from the connected rivers. The fact that the pesticide spectrum is smaller in SC2 and SC3, might be due to the fact that these sites have the lowest share of horticultural areas (Chapter 1, section 1.7).

In terms of %-contribution of pesticide type, fungicides were strongly dominating at all sampling sites (Figure 1, right side). At SC2 and SC3, even though the number of fungicides was lower than at the other sites, the total fungicide %-contribution of the concentrations were the highest overall. In this area, the cultivation of potatoes was observed during field visits – potatoes require a high amount of fungicides (Ramírez-Muñoz et al. 2014). Additionally, since the horticultural areas are owned by different farmers, pesticides might be applied differently (frequencies and quantities) in the individual SCs which could lead to different pesticide inputs among the different sites. A more detailed analysis of the type of crops grown, pesticides applied and susceptibility of the areas to surface run-off would allow to shed some light on the specificities of sites SC2 and SC3. Such maps with different crop uses are not available yet. However, information about pesticide application and handling practices were collected by surveys with farmers of the Tapezco region (Staudacher et al. 2020), as discussed in more detail in Chapter 4.

Not only the number and types of pesticides but also the %-contributions of concentrations per PPTP type were overall similar between the sampling periods and sites. Accordingly, it can be suggested that, within the studied catchment, precipitation alone cannot be the main driver for pesticide inputs into streams. Handling, application practices and disposal of leftovers could lead to a significant pesticide input into streams, even during dryer periods as shown by (Wittmer et al. 2010b) and further discussed as well in Chapter 4.

Overall, as already stated in Chapter 2, the pesticide results of this study support the observation of Ramirez et al 2016 and Ramírez-Muñoz et al. 2014 that horticultural areas can be pesticide hotspots and a broad spectrum of pesticides can be expected to end up in streams posing risks to aquatic organisms.

3.5.2 Risks due to PPTP exposure at the individual SCs based on RQ and TU

Risk assessment based on RQ revealed a high likelihood that aquatic organisms are chronically and even acutely affected by the PPTP that occurred in streams of the individual SC. With the continuity of the passive sampling data it was demonstrated that this risk persists over months. It is a strength of the passive sampling strategy applied in Chapter 2 that time-integrated information can be obtained.

Among the sites, the number of CRQ exceedances was the lowest at SC2 (in $\Delta T2a$) and at SC3 ($\Delta T1$, $\Delta T2a$ and $\Delta T2b$, Figure 2, upper panel) even though determined risks due to the mixture of PPTP, presented as CRQ_{mix} , were highest (in median) at the same sites (Figure 2, lower panel). These results show that even if only a few pesticides are found in streams, these can dominate the risk. Overall, the CRQ_{mix} for the organisms groups of different trophic levels showed that invertebrates were affected the most, thus RQ were dominated by insecticides (Figure 3).

Eleven insecticides, three fungicides, and four herbicides defined the chronic risk (CRQ for single PPTP, Figure 4, upper panel). Several of the monitored pesticides with CRQ > 1 confirm the findings of Ramirez et al (2016), obtained for the same study area via grab sampling. For instance, chlorpyrifos, carbofuran, cypermethrin, diazinon, dimethoate, permethrin and tebuconazole and prometryn + terbutryn exceeded CRQ in both studies. Particularly chlorpyrifos posed a high risk according to Ramirez et al. (2016) as well. In their study, chlorpyrifos was detected in 48% of the stream samples (19/39) and in 19 samples (48%) CRQ were exceeded. Within this current study, chronic risks for chlorpyrifos were exceeded nearly continuously at all SC. Compared to Ramirez et al. (2016), CRQ could now be obtained for ten more pesticides covered in this study.

In addition to the CRQ, also the ARQ and the TU showed that acute risks for invertebrates can be expected at all sites based on the same experimental MEC data set (Figure 4, lower panel, Figure 7). According to the two approaches taken together, seven insecticides and one fungicide (Figure 4, ARQ exceedances and Figure 7, TU exceedances) dominated the acute risks assessment. The ARQ approach was more sensitive for carbendazim, cyhalothrin, fipronil, imidacloprid and cypermethrin due to the use of EQS as references. The TU approach was more sensitive for chlorpyrifos, carbofuran and diazinon due to their high toxicity to *Daphnia magna*. For chlorpyrifos, cypermethrin, diazinon, ARQ were also exceeded in the study by Ramirez et al (2016), with chlorpyrifos contributing most strongly. In their study, chlorpyrifos was detected in 19 out of 39 samples and exceeded ARQ in 18 samples (46%). Within this current study, ARQ for chlorpyrifos was exceeded in 44% of the samples. Further within this study, four additional compounds (carbendazim, cyhalothrin, fipronil, imidacloprid) were identified posing acute risks (Figure 4, lower panel and Figure 7).

The high risk to aquatic organisms by pesticides determined in this study adds to prior knowledge for other regions of Costa Rica where partly similar chemicals were associated with acute risks. For example, risks to aquatic organism, including fish killings, have been associated with exposure to carbendazim, tebuconazole, diuron, carbofuran, chlorpyrifos, diazinon, dimethoate, fipronil, and cypermethrin (de la Cruz et al. 2014b). Moreover, CRQ for aquatic organisms (based on SSD), ranging between 1.5 and 36.4, were determined in streams near agricultural areas in the vicinity of Limon with large monocultures carrying diuron, carbofuran, chlorpyrifos and diazinon (Arias-Andres et al. 2018, Diepens et al. 2014, Rämö et al. 2018). Further, RQ >1 (based on no observed effect concentrations (NOEC) or EC₅₀ if no NOEC was available) were reported for carbendazim and diuron in South Guanacaste in the Tempisque river basin (Carazo-Rojas et al. 2018a). Hence it is evident that in both large monoculture fields as well as in smaller horticultural areas of Costa Rica, the same pesticides are posing high risks. Pesticide management, leading to a reduction of input to the environment, or the use of alternative methods, could lead to a significant improvement of the water quality and thus reduced risk to aquatic biota.

3.5.3 Occurrence of PPTP and macroinvertebrate abundance

The description of the water quality status based on the presence of macroinvertebrates (SPEAR_{pesticide}, BMWP-CR and EPT-taxa richness) pointed at two sites of particularly poor water quality (SC1 and SC4, Table 1). For the remaining SC, the SPEAR_{pesticide} and BMWP-CR index showed a trend of improving water quality at SC5 and particularly SC8. With the EPT-taxa richness approach, an improvement in water quality was likewise indicated but only at the most downstream site, SC8. Thus, the SPEAR_{pesticide} and BMWP-CR index reflected a finer gradient than the EPT-taxa richness index with regard to the status of water quality.

The indications for improved water quality based on macroinvertebrate abundance using the SPEAR_{pesticide} index is interesting as it contrasts the high pesticide levels measured and high risks observed at all Tapezco catchment test sites determined with RQ_{mix} and TU_{mix}. The fact

that upstream of SC8 there is a main river section of about 3.5 km with almost no horticultural land and high share of natural forest in the vicinity of the river (Chapter 1, section 1.7) could explain these observations. According to Echeverría-Sáenz et al. (2018) and Knillmann et al. (2018), a riparian area with natural vegetation can act as refuge area for different organisms and compensate to some degree the impact of chemical pollution. Stream sections with natural vegetation can particularly attract semi-aquatic organisms such as ephemeroptera, trichoptera and libellula for mating and reproduction. Such organisms, which are characterized by a terrestrial adult stage, can recover, recolonize affected sections and become further distributed by downstream drifting. Beyond this aspect, a pronounced natural forest zone next to the streams may act as barrier and mitigate the input of surface run-off into streams (Rasmussen et al. 2011). For example the particle-bound pesticide fraction might be retained in the thick undergrowth and, as a consequence, the pesticide stress to soil fauna could be reduced. In that respect, habitat characteristics appear to play at least as large a role as pesticide exposure in water quality.

Another reason explaining this discrepancy might be that the $SPEAR_{\text{pesticide}}$ index was dominated by the occurrence of several ephemeroptera species i.e. camelobaetidiid and baetodes of the baetidae family at SC5, and baetodes, tricorythodes and leptohyphes of the families baetidae and leptohyphidae at SC8 (Echeverría-Sáenz and Weiss 2021), leading to an improved water quality compared to the remaining sites, SC1 and SC4. It is possible that mass reproduction events of these species indicated improvements in water quality due to their high abundances. Even though numbers of several sensitive species seemed high, the EPT-taxa-richness was low at all investigated sites with macroinvertebrate data showing a poorer water quality than with the other macroinvertebrate approaches. At status quo it remains unclear why at SC5 the water quality seemed partly improved ($SPEAR_{\text{pesticide}}$ and BMWP-CR data) and more investigations would be required to better understand this observation. A more detailed habitat analysis of the riparian area could help to better interpret these results as conducted in previous studies (Cornejo et al. 2019, Schreiner et al. 2021).

An improvement of water quality from SC1 and SC4 to SC5 and SC8 was neither indicated by the RQ_{mix} nor the TU_{mix} risk approach. It has to be kept in mind that these approaches, as well as the sensitivity to pesticides described by the $SPEAR_{\text{pesticide}}$ index, rely on an elaborated data set of toxicological information. They are based on model organisms that might not be the most representative in the tropical Tapezco catchment. The RQ_{mix} and the TU_{mix} are much more specific to the toxicity of the measured pesticides while macroinvertebrate abundance depends on many other factors, such as suspended solids, pH, flow velocity, nutrient levels, the availability of refuge areas and temperature (Knillmann et al. 2018, Liess et al. 2008). Compared to other macroinvertebrate-based water quality indices, such as the BMWP-CR index (La Gaceta Official Newspaper 2007), the $SPEAR_{\text{pesticide}}$ has the advantage of including risks specifically derived from pesticides (Knillmann et al. 2018, Liess et al. 2008). Moreover, even though other relevant information, e.g. if the taxa has an aquatic life stage during the main application season in Europe, if the taxa can recover in refuge areas, and their relative toxicity to pesticides related to the one of *Daphnia magna* (Knillmann et al. 2018), is included - the results of the $SPEAR_{\text{pesticide}}$ index were in agreement with the BMWP-CR index and correlated significantly ($R^2 = 0.65$, $p = 0.00001$, see SI-3 B6). This correlation is in contrast to Cornejo et al. (2019) who showed that the pesticide toxicity, expressed as maximum TU, affected BMWP, but not $SPEAR_{\text{pesticide}}$. This discrepancy might be explained by the limited spectrum of detected pesticides accounted for and the grab sampling technique used in the study by Cornejo et al. (2019) which might not present the full picture of pesticide pollution and the related toxic effects.

Besides these differences it is worthy to mention that the actual MEC is not included either in the $SPEAR_{\text{pesticide}}$ or the BMWP-CR method. A combination of different risk assessment

approaches, as done here, therefore, allows for a more differentiated picture of pesticide exposure and associated risks in the studied areas.

3.5.4 Limitations of the current study

Despite the comprehensive nature of the risk assessment carried out, several limitations of this study need to be considered. With respect to the chemical sampling strategy it has to be taken into account that it could not record the highest peak concentration of pesticides reaching the streams via short pulses because the peaks were averaged over the sampling period. To be able to fully record such peak concentrations, deployment of automated time-proportional samplers could be useful (Doppler et al. 2012b, Leu et al. 2004a) but such installations are elaborate and not yet applicable to many field sites simultaneously, especially in remote regions such as the Tapezco river catchment. If such peak concentrations were taken into account, even higher RQ and TU values would be expected temporarily.

During gathering EQS and effect concentration data it was notable that toxicity information for several pesticides was non-existent or rare, particularly also for transformation products. Accordingly, the risks for aquatic organisms due to exposure to such pesticides and their transformation products might be underestimated.

Another limitation is that the RQ, TU and SPEAR_{pesticide} indices are adapted to temperate regions rather than to the specific situation in Costa Rica. However, thus far, no comprehensive toxicological pesticide data is available for endemic tropical species (Arias-Andres et al. 2014, Castillo et al. 1997, Daam and Van den Brink 2009, Rämö et al. 2018). Even though a recent study showed that sensitivities to toxic chemicals of species in temperate or tropical regions were not fundamentally different (Rämö et al. 2018), more research on the responses of tropical species to pesticides should be conducted to further test if risk assessment approaches need to be adapted for tropical regions.

Until now, the SPEAR_{pesticide} index is exclusively calibrated to the sensitivity of *Daphnia magna*, a species from temperate regions. Also, the index relies on normalization based on aquatic life cycles of species during periods where pesticides are applied intensively in Europe (Knillmann et al. 2018). For adapting the SPEAR_{pesticide} to tropical regions, several important factors need to be considered. For instance, a tropical species living in streams could be used as a reference but gathering such data will be a tremendous effort. Additionally, the generation cycle for the taxa considered in the SPEAR_{pesticide} index might be different in tropical compared to temperate zones. It is, for example, possible that the reproduction of specific taxa is not synchronized as it is the case after the winter in temperate zones. Therefore, especially for taxa having a non-aquatic adult life cycle stage, in the tropics a continuous reproduction might be possible and thus recovery even after intense pesticide peaks. Such species are prone to reduction or elimination if high pesticide peaks occur during the aquatic larval stage, where in temperate regions, no possibility for reproduction in the same season exists (Jackson and Sweeney 1995). In addition, one has to consider that also the cropping seasons and hence the pesticide applications are very different in the tropics where farming is basically carried out year-round. Site specific adjustments of the SPEAR_{pesticide} index would make this index even more powerful. In any case, adapting the SPEAR_{pesticide} index for tropical risk assessment could be an interesting field for further research. For doing so, more macroinvertebrate data from unpolluted tropical reference areas would be necessary to further calibrate this index.

3.6 Conclusion

This study has shown that PPTP are widely distributed in the Tapezco catchment with overall rather small differences between the sampling sites and years. Risk assessment based on MEC of mixtures of PPTP (RQ_{mix} and TU_{mix}) revealed that chronic and even acute risks to aquatic organisms are to be expected. Particularly invertebrates carried the most of the PPTP exposure

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burden without having any periods for recovering from pesticide exposure. For vertebrates and primary producers, expected chronic risks were lower with sporadic periods for potential recovery. Acute risks for vertebrates occurred occasionally but seemed to be low for primary producers. Application of concepts describing the actual status of water quality that rely on macroinvertebrate data from the impacted streams indicated that, at the downstream site, the water quality seemed to be improved; an alternative explanation would be that a zone with riparian vegetation and absence of horticultural areas helped the macroinvertebrate community to recover. By using a combination of risk assessment approaches, it was possible to perform a more differentiated analysis. Such a strategy could be even more powerful if the approaches would be specifically adapted to the tropical regions. Finally, the fact that a relatively low number of pesticides apparently drives the risk provides a starting point for risk mitigation measures. This becomes the more tangible as partly the same pesticides were previously identified as risky to aquatic organism in streams affected by large monoculture areas. Along these lines, it is advisable to include these compounds into the current regulation of pesticide residues in surface waters in Costa Rica.

3.7 Literature

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Supporting information 3. Chapter

Risk assessment for tropical streams of a small-scale horticultural catchment based on spatio-temporal pesticide monitoring data

SI-3 A1 Monitoring: time periods, chemicals, nutrients and physicochemical properties

SI-3 A1.1 Time periods, $\Delta T1$, $\Delta T2a$ and $\Delta T2b$

Table SI-3 A1: Biweekly time sampling intervals during the three time periods $\Delta T1$, $\Delta T2a$ and $\Delta T2b$.

Sampling period	Period $\Delta T1$ in 2015	Period $\Delta T2a$ in 2016	Period $\Delta T2b$ in 2016
I	NA	NA	24 May – 7 Jun
II	NA	NA	7 Jun – 21 Jun
III	NA	NA	21 Jun – 5 Jul
IV	NA	NA	5 Jul – 19 Jul
V	NA	NA	19 Jul – 2 Aug
VI	30 Jul – 13 Aug	2 Aug – 16 Aug	
VII	13 Aug – 27 Aug	16 Aug – 30 Aug	
VIII	27 Aug – 10 Sep	30 Aug – 13 Sep	
IX	10 Sep – 24 Sep	13 Sep – 27 Sep	
X	24 Sep – 7 Oct	27 Sep – 11 Oct	

SI-3 A1.2 PPTP detected in the Tapezco watershed at all three periods $\Delta T1$, $\Delta T2a$ and $\Delta T2b$

Table SI-3 A2: PPTP detected during the sampling campaigns in 2015 and 2016.

Compound	CAS	Molecular formular	Type [#]
2,4-D	94-75-7	C ₈ H ₆ Cl ₂ O ₃	H
2,6-Dichlorobenzamide	2008-58-4	C ₇ H ₅ Cl ₂ NO	HTP
3-Phenoxybenzoic acid	3739-38-6	C ₁₃ H ₁₀ O ₃	ITP
Alachlor-ESA + Acetochlor-ESA	142363-53-9/187022-11-3	C ₁₄ H ₂₁ NO ₅ S	HTP
Allethrine*	584-79-2	C ₁₉ H ₂₆ O ₃	I
Atrazine	1912-24-9	C ₈ H ₁₄ Cl ₁ N ₅	H
Atrazine-desethyl-2-hydroxy	19988-24-0	C ₆ H ₁₁ N ₅ O	HTP
Azoxystrobin	131860-33-8	C ₂₂ H ₁₇ N ₃ O ₅	F
Azoxystrobin (free acid)	1185255-09-7	C ₂₁ H ₁₅ N ₃ O ₅	FTP
Bifenthrine*	82657-04-3	C ₂₃ H ₂₂ ClF ₃ O ₂	I
Boscalid	188425-85-6	C ₁₈ H ₁₂ Cl ₂ N ₂ O	F
Carbendazim	10605-21-7	C ₉ H ₉ N ₃ O ₂	F
Carbofuran	1563-66-2	C ₁₂ H ₁₅ NO ₃	I
Chlorpyrifos*	2921-88-2	C ₉ H ₁₁ Cl ₃ NO ₃ PS	I
Clothianidin	210880-92-5	C ₆ H ₈ ClN ₅ O ₂ S	I
Cyhalothrin*	91465-08-6	C ₂₃ H ₁₉ ClF ₃ NO ₃	I
Cypermethrin*	52315-07-8	C ₂₂ H ₁₉ Cl ₂ NO ₃	I
Cyproconazole	94361-06-5	C ₁₅ H ₁₈ ClN ₃ O	F
Cyromazin	66215-27-8	C ₆ H ₁₀ N ₆	I
Deltamethrin*	52918-63-5	C ₂₂ H ₁₉ Br ₂ NO ₃	I

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Compound	CAS	Molecular formular	Type [#]
Diazinon	333-41-5	C ₁₂ H ₂₁ N ₂ O ₃ P ₁ S ₁	I
Dichlorvos	62-73-7	C ₄ H ₇ Cl ₂ O ₄ P	I
Difenoconazole	119446-68-3	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₃	F
Dimethoate	60-51-5	C ₅ H ₁₂ NO ₃ PS ₂	I
Dimethomorph	110488-70-5	C ₂₁ H ₂₂ ClNO ₄	F
Diuron	330-54-1	C ₉ H ₁₀ Cl ₂ N ₂ O ₁	H
Diuron-desdimethyl	2327-02-8	C ₇ H ₆ Cl ₂ N ₂ O	HTP
Diuron-desmonomethyl (DCPMU)	3567-62-2	C ₈ H ₈ Cl ₂ N ₂ O	HTP
Epoxiconazole	133855-98-8	C ₁₇ H ₁₃ ClFN ₃ O	F
Ethoprophos	13194-48-4	C ₈ H ₁₉ O ₂ PS ₂	I
Etofenprox*	80844-07-1	C ₂₅ H ₂₈ O ₃	I
Fenamidone	161326-34-7	C ₁₇ H ₁₇ N ₃ OS	F
Fipronil	120068-37-3	C ₁₂ H ₄ Cl ₂ F ₆ N ₄ O ₁ S ₁	I
Fipronil-sulfide	120067-83-6	C ₁₂ H ₄ Cl ₂ F ₆ N ₄ S ₁	ITP
Fipronil-sulfone	120068-36-2	C ₁₂ H ₄ Cl ₂ F ₆ N ₄ O ₂ S ₁	ITP
Fluazifop (free acid)	69335-91-7	C ₁₅ H ₁₂ F ₃ NO ₄	HTP
Fludioxonil	131341-86-1	C ₁₂ H ₆ F ₂ N ₂ O ₂	F
Fluopicolide	239110-15-7	C ₁₄ H ₈ Cl ₃ F ₃ N ₂ O	F
Imidacloprid	138261-41-3	C ₉ H ₁₀ ClN ₅ O ₂	I
Imidacloprid-urea	120868-66-8	C ₉ H ₁₀ ClN ₃ O	ITP
Iprovalicarb	140923-17-7	C ₁₈ H ₂₈ N ₂ O ₃	F
Irgarol-descyclopropyl	30125-65-6	C ₈ H ₁₅ N ₅ S	FTP
Linuron	330-55-2	C ₉ H ₁₀ Cl ₂ N ₂ O ₂	H
Metalaxyl	57837-19-1	C ₁₅ H ₂₁ NO ₄	F
Methiocarb	2032-65-7	C ₁₁ H ₁₅ NO ₂ S	I
Metolachlor	51218-45-2	C ₁₅ H ₂₂ ClNO ₂	H
Metribuzin	21087-64-9	C ₈ H ₁₄ N ₄ O ₁ S ₁	H
Metribuzin-Desamino (DA)	35045-02-4	C ₈ H ₁₃ N ₃ OS	HTP
Metsulfuron-methyl	74223-64-6	C ₁₄ H ₁₅ N ₅ O ₆ S	H
Pencycuron	66063-05-6	C ₁₉ H ₂₁ ClN ₂ O	F
Permethrin*	52645-53-1	C ₂₁ H ₂₀ Cl ₂ O ₃	I
Profenophos	41198-08-7	C ₁₁ H ₁₅ BrClO ₃ PS	I
Prometryn + Terbutryn	7287-19-6 / 886-50-0	C ₁₀ H ₁₉ N ₅ S ₁	H
Propamocarb	24579-73-5	C ₉ H ₂₀ N ₂ O ₂	F
Propazine-2-hydroxy + Terbutylazine-2-hydroxy	7287-19-6 / 886-50-0	C ₁₀ H ₁₉ N ₅ S ₁	HTP
Propiconazole	60207-90-1	C ₁₅ H ₁₇ Cl ₂ N ₃ O ₂	F
Pyraclostrobin	175013-18-0	C ₁₉ H ₁₈ ClN ₃ O ₄	F
Tebuconazole	107534-96-3	C ₁₆ H ₂₂ ClN ₃ O	F
Terbutylazine	5915-41-3	C ₉ H ₁₆ ClN ₅	H
Terbutylazine-desethyl	30125-63-4	C ₇ H ₁₂ Cl ₁ N ₅	HTP
Tetramethrin*	7696-12-0	C ₁₉ H ₂₅ NO ₄	I
Thiamethoxam	153719-23-4	C ₈ H ₁₀ ClN ₅ O ₃ S	I

*detected with PDMS approach, otherwise detected with SDB approach.

H = herbicide, I = insecticide, F = fungicides and TP = transformation product.

SI-3 A1.3 Information about nutrient measurements and physicochemical parameters

Table SI-3 A3: Detected water quality parameter and devices.

Parameter	Working device, company, country		Details
Ammonium [NH ₄ ⁺]	colorimetric Ammonium test kit,	VWR, Switzerland	concentrations: 0.5-8 mg/L; catalog Nr.: 1.14423.0002
Total dissolved phosphorous [PO ₄ ³⁻]	colorimetric phosphate test kit,	VWR, Switzerland	concentrations: 0.046-0.43 mg/L; catalog Nr.: 1.18394.0001
Nitrate [NO ₃ ⁻]	colorimetric nitrate test kit,	VWR, Switzerland	concentrations: 5-90 mg/L; catalog Nr.: 1.18387.0001
Dissolved oxygen [mg/L]	HQ30D Flexi meter, pH and oxygen, Hach, Switzerland		
pH	Catalog Nr.: HQ30D.99.101301		
Temperature [°C]			
Conductivity [µS/cm]	IntelliCal conductivity electrode, Hach, Switzerland		Catalog Nr.: CDC40101

SI-3 A1.4 Water quality according to nutrients and physicochemical data

The 7 quality classes of the water quality classification system used by the EU (Umweltbundesamt 2016):

- Quality class I: no anthropogenic pollution: geogenic background value
- Quality class I-II: lightly polluted up to half value of class II
- Quality class II: moderately polluted target value complied with
- Quality class II-III: critically polluted up to twice value of class II
- Quality class III: heavily polluted up to four times values of class II
- Quality class III-IV: very heavily polluted up to eight times values of class II
- Quality class IV: Excessively polluted more than eight times values of class II” as cited at the official web page of the Federal Environmental Agency of Germany (Umweltbundesamt 2016).

For quality class II the limiting values are: ≤ 3 mg/L for total nitrogen; ≤ 0.15 mg/L for total phosphorus; ≤ 0.1 for ammonium nitrogen (comparison value for each nutrient: 90 percentile); and > 6 mg/L for dissolved oxygen (comparison value 10 percentile).

SC 6 was classified as excessively polluted and was the most polluted SC (excessively polluted, elevated NH₄⁺ values above 2.4 mg/L, PO₄³⁻ values exceeding the detectable maximum of 0.43 mg/L, Table SI-3 A4). SC: 1, 3, 4 and 7 were heavily polluted (maximum PO₄³⁻ levels ranging between 0.14 and 0.43 mg/L). The SC 5 and SC8 were critically polluted (elevated PO₄³⁻ levels up to 0.25 mg/L). The remaining SC2 was moderately polluted and therefore the least polluted SC (max PO₄³⁻ levels 0.14 mg/L). Dissolved oxygen was in an acceptable range between 3.9 and 8.9 mg/L at all sampling sites, whereas the minimum of 3.9 mg/L was reached in the excessively polluted SC6. Other parameters measured during our sampling campaign such as pH, conductivity and temperature are not considered in this water quality classification approach (Table SI-3 A4).

In the SC: 1, 2, 3, 4, 5, 7, 8, the pH ranged between 5.9 and 8.4; only in SC 6, the pH fluctuated higher between 5 and 10.6. The conductivity was only elevated in SC 6, ranging between 122 and 566 $\mu\text{S}/\text{cm}$. In the other SC, the conductivity was lower and more constant (20-149 $\mu\text{S}/\text{cm}$). The temperature was slightly lower at the upstream SC: 1, 2 and 3 ranging between 14.6 and 17.6 °C than at the downstream situated SC. At the downstream SC 4,5,6,7 and 8, the temperature was ranging between 15.1 and 20.4 °C (Table SI 3.5).

Table SI-3 A4: Average Nutrient and physicochemical data collected during the field work in 2015 and 2016.

Sub catchment	NH ₄ ⁺ [mg/L]	PO ₄ ³⁻ [mg/L]	NO ₃ ⁻ [mg/L]	O ₂ [mg/L]	Temperature [°C]	pH	Conductivity [μS/cm]	Chemical water quality														
SC1	0.20	-	0.80	0.09	-	0.34	5.00	-	7.5	6.0	-	81	-	137	III							
SC2	<LOQ	<LOQ	0.05	-	0.14	<LOQ	-	2.50	7.8	-	8.3	14.6	-	17.6	6.8	-	8.4	34	-	77	II	
SC3	<LOQ	-	0.20	0.05	-	0.14	<LOQ	-	2.50	6.2	-	8.4	14.7	-	16.7	5.0	-	10.6	20	-	82	II
SC4	<LOQ	-	0.20	0.07	-	0.43	<LOQ	-	5.00	6.2	-	8.9	15.1	-	19.6	6.0	-	8.3	74	-	149	III
SC5	<LOQ	-	0.20	0.09	-	0.18	<LOQ	-	5.00	6.5	-	8.6	16.0	-	19.4	6.0	-	7.9	44	-	97	II-III
SC6	0.16	-	6.50	0.18	-	>0.43	<LOQ	-	7.50	3.9	-	8.6	17.2	-	20.1	6.5	-	8.0	122	-	566	IV
SC7	<LOQ	<LOQ	0.34	-	0.43	<LOQ	-	2.50	7.6	-	8.4	17.8	-	20.4	6.3	-	8.2	102	-	129	III	
SC8	<LOQ	-	0.20	0.14	-	0.25	<LOQ	-	2.50	7.5	-	8.6	17.2	-	19.9	5.9	-	8.2	53	-	133	II-III

SI-3 A2 Spatio temporal risk assessment based on CRQ and ARQ

SI-3 A2.1 Frequencies of CRQ and ARQ exceedances of single PPTP for each sampling site and period (minimum and maximum concentration scenario)

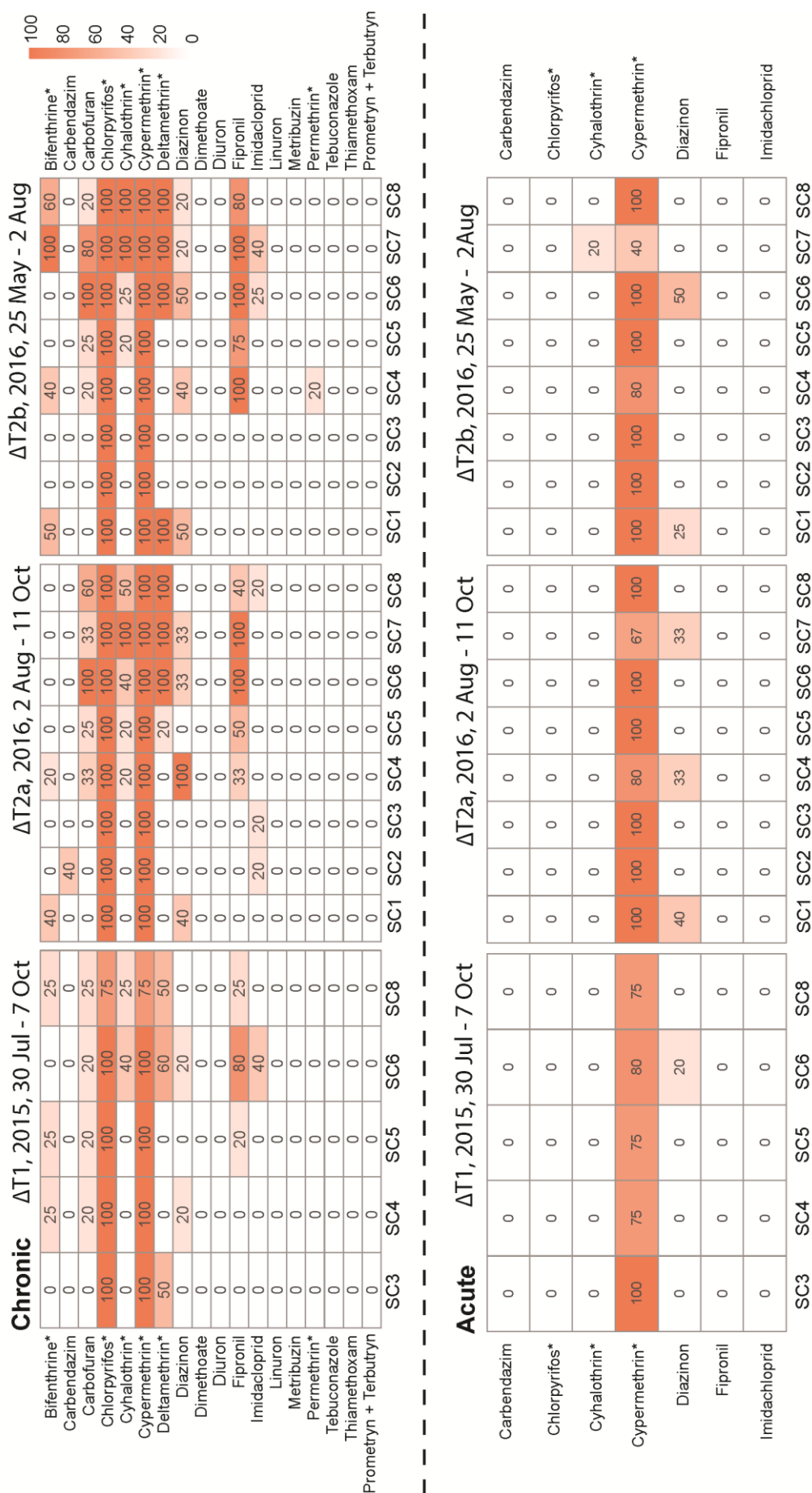


Figure SI-3 A1.1: Frequencies of individual pesticides indicating chronic and acute risks at the different sampling sites and sampling years – minimum risk scenario. Percentages of CRQ exceedance for individual pesticides during $\Delta T1$, $\Delta T2a$ and $\Delta T2b$ are presented in the upper part. Percentages of ARQ exceedances are shown in the lower part. *Data from PDMS approach, otherwise from SDB approach. The PDMS sheets for the first biweekly interval in $\Delta T1$ were not properly extracted and could not be analyzed. The heatmap was created with pheatmap package of R Studio Version 1.25001.

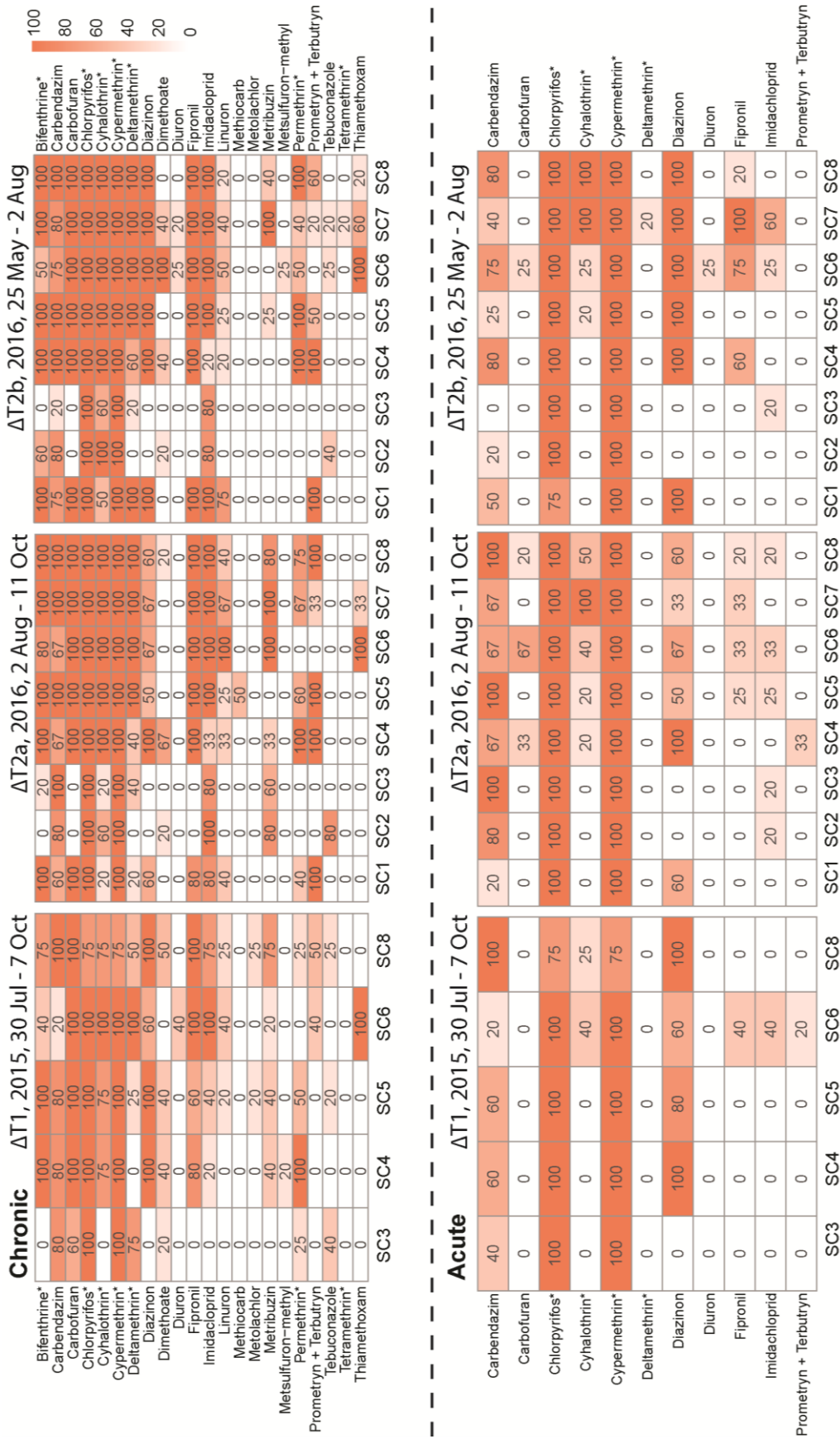


Figure SI-3 A1.2: Frequencies of individual pesticides indicating chronic and acute risks at the different sampling sites and sampling years – maximum risk scenario. Percentages of CRQ exceedance for individual pesticides during $\Delta T1$, $\Delta T2a$ and $\Delta T2b$ are presented in the upper part. Percentages of ARQ exceedances are shown in the lower part. *Data from PDMS approach, otherwise from SDB approach. The PDMS sheets for the first biweekly interval in $\Delta T1$ were not properly extracted and could not be analyzed. The heatmap was created with pheatmap package of R Studio Version 1.25001.

SI-3 A2.2 CRQ and ARQ exceedances of single PPTP and magnitudes of CRQ_{mix} and ARQ_{mix} for each sampling period

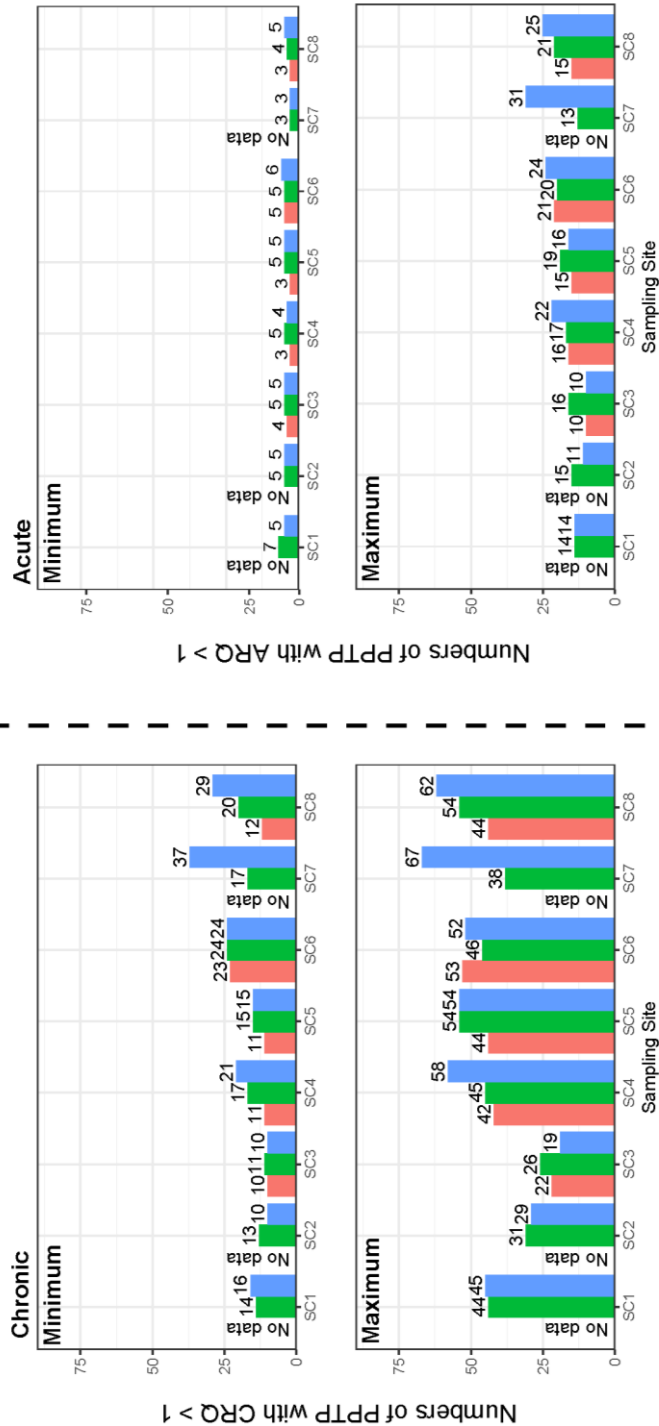


Figure SI-3 A2.1: Chronic and acute risks, expressed as exceeded RQ, observed at the individual sampling sites during three sampling periods. The numbers of PPTP with CRQ and ARQ > 1 are shown in the upper two graphs considering the best case scenario (MEC / 3 used for calculation). The numbers of PPTP with CRQ and ARQ > 1 are shown in the bottom graphs considering the worst case scenario (MEC * 3). Red bars = $\Delta T1$, green bars = $\Delta T2a$, blue bars = $\Delta T2b$.

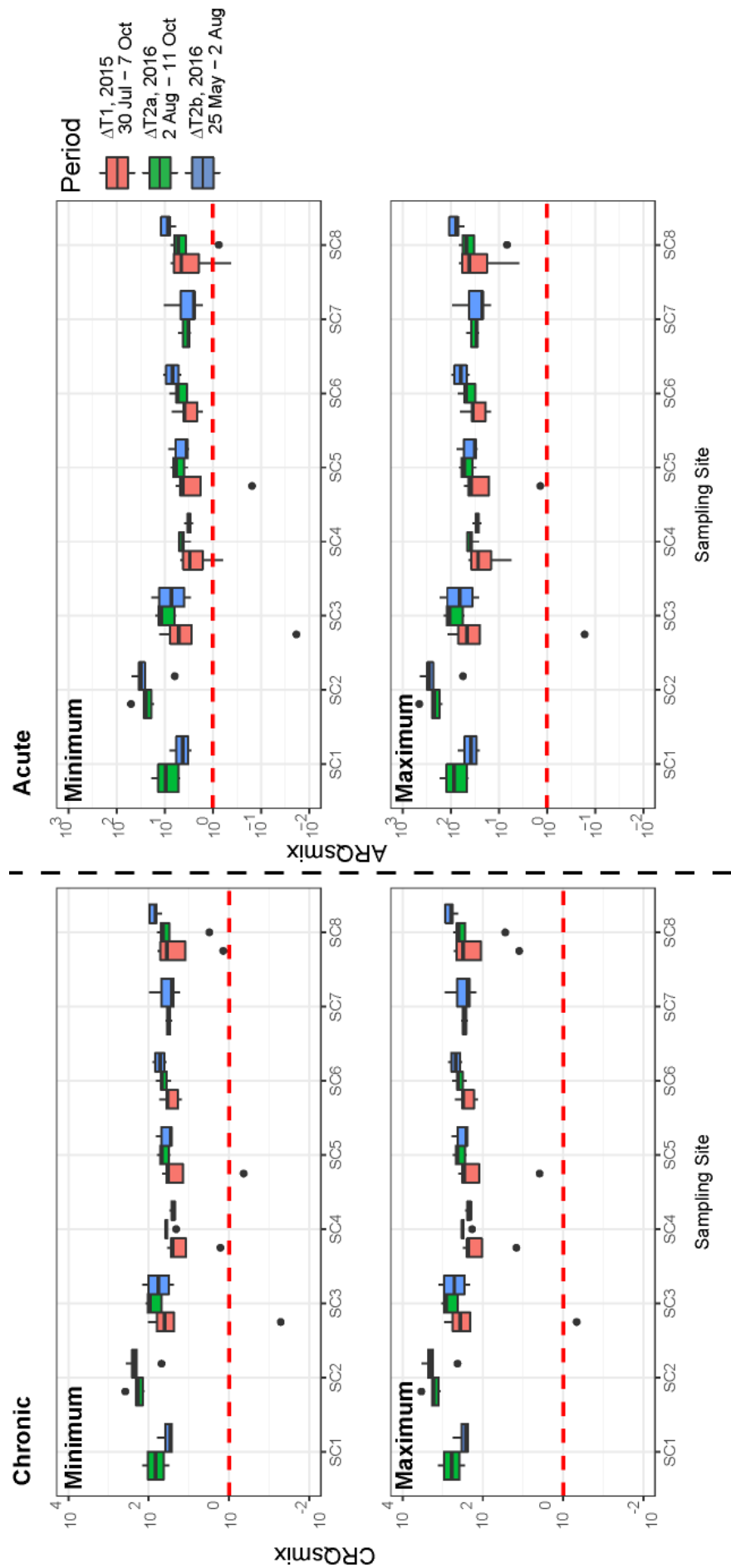


Figure SI-3 A2.2: Chronic and acute risks, expressed as RQ_{mix} , observed at the individual sampling sites during three sampling periods. The magnitude of CRQ_{mix} and ARQ_{mix} according to the best case scenario ($MEC / 3$ are used for calculation) are presented in the two top graphs. The magnitude of CRQ_{mix} and ARQ_{mix} according to the worst case scenario ($MEC * 3$ used for calculation) are presented in the two bottom graphs. Boxplots represent first and third quartiles (outer box) and medians (fat lines). The lower whiskers show the minimum values not falling below the first quartile more than a factor of 1.5* the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of 1.5 * the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers (standardized boxplot using R ggplot package).

SI-3 A2.3 CRQ_{mix} per individual organisms groups (V, P, I) sampling site and each biweekly sampling interval 2015/2016

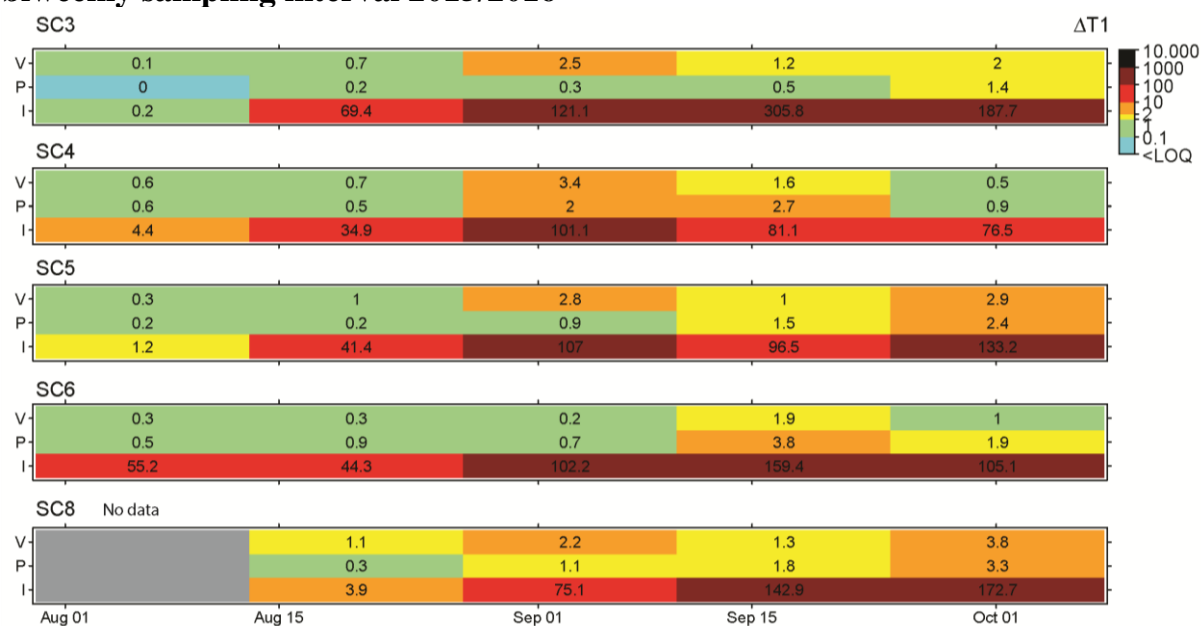


Figure SI-3 A3.1: CRQ_{mix} timeline for the different taxonomic groups: vertebrates (V), primary producers (P) and invertebrates (I), based on pesticide and monitoring data collected at five sampling sites of the Tapezco river catchment (order: upstream to downstream), 2015. Grey area: no monitoring data available. Numbers represent CRQ_{mix}.

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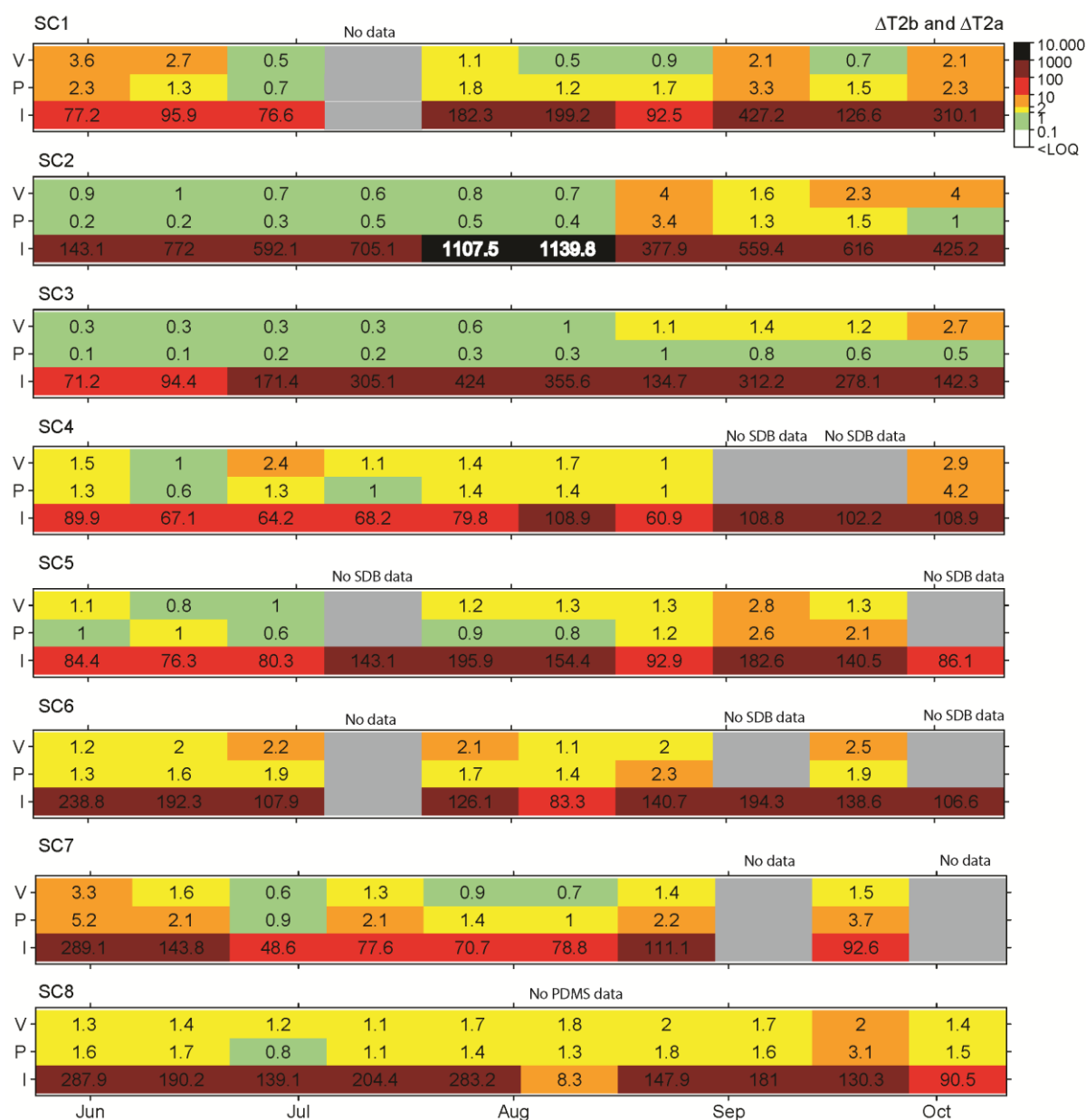


Figure SI-3 A3.2: CRQ_{mix} timeline for the different taxonomic groups: vertebrates (V), primary producers (P) and invertebrates (I), based on the pesticide and monitoring data collected at eight sampling sites of the Tapezco river catchment (order: upstream to downstream), 2016. Grey areas: no monitoring data available. Numbers represent CRQ_{mix}.

SI-3 A2.4 ARQ_{mix} per individual organisms groups (V, P, I) sampling site and each biweekly sampling interval 2015/2016

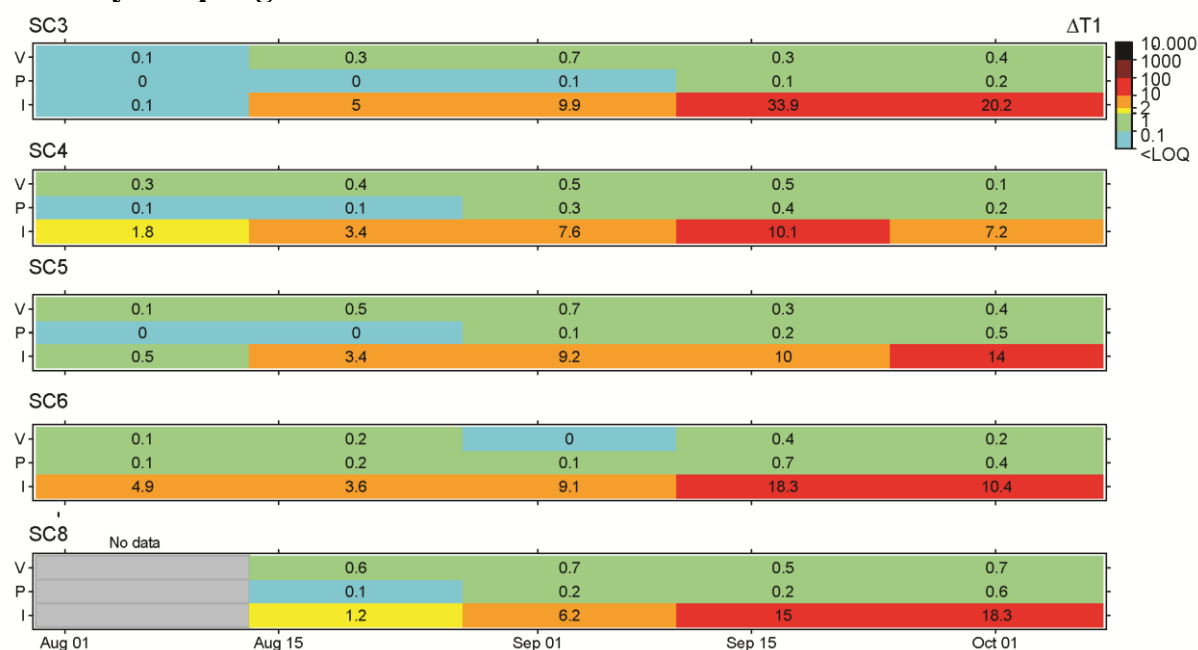


Figure SI-3 A4.1: ARQ_{mix} timeline for the different taxonomic groups: vertebrates (V), primary producers (P) and invertebrates (I), based on the pesticide and monitoring data collected at five sampling sites of the Tapezco river catchment (order: upstream to downstream), 2015. Grey area: no monitoring data available. Numbers represent ARQ_{mix}.

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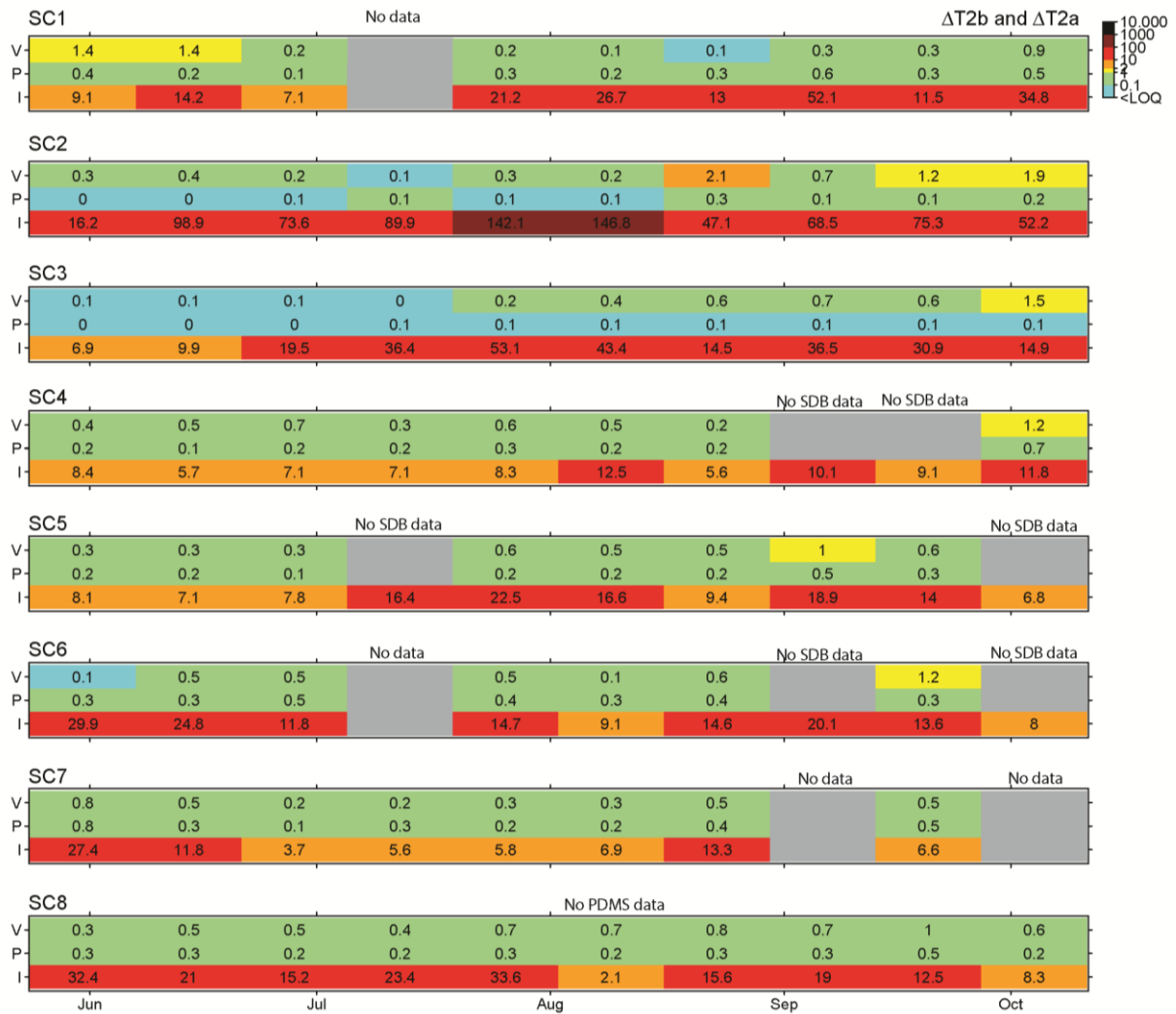


Figure SI-3 A4.2: ARQ_{mix} timeline for the different taxonomic groups: vertebrates (V), primary producers (P) and invertebrates (I), based on the pesticide and monitoring data collected at eight sampling sites of the Tapezco river catchment (order: upstream to downstream), 2016. Grey areas: no monitoring data available. Numbers represent ARQ_{mix}.

SI-3 A3 Risk assessment based on the determination of TU

SI-3 A3.1 Frequencies of individual pesticides indicating acute risks ($TU > -2$), from 2015 ($\Delta T1$) and 2016 ($\Delta T2a$ and $\Delta T2b$) at all sites (minimum and maximum concentration scenario)

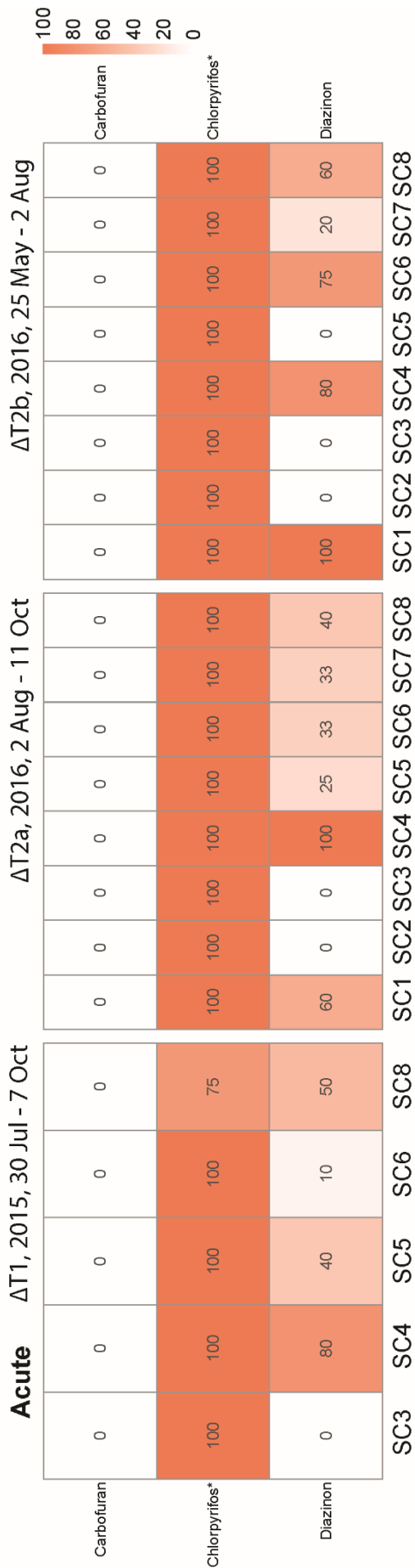


Figure SI-3 A5.1: Frequencies of individual pesticides indicating acute risks (TU > -2), based on TU of minimum risk scenario, at the different sampling sites and three sampling periods. *Data from PDMS approach otherwise from SDB approach. The PDMS sheets for the first biweekly interval in ΔT1 were not properly extracted and could not be analyzed. The heatmap was created with pheatmap package of R Studio Version 1.25001.

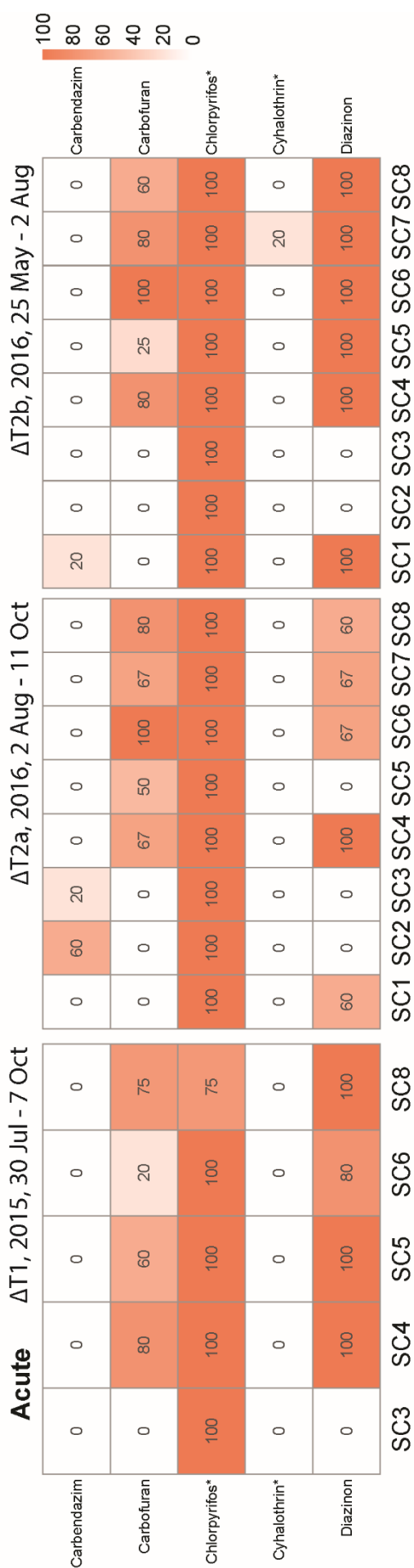


Figure SI-3 A5.2: Frequencies of individual pesticides indicating acute risks ($TU > -2$), based on TU of maximum risk scenario, at the different sampling sites and three sampling periods. *Data from PDMS approach otherwise from SDB approach. The PDMS sheets for the first biweekly interval in $\Delta T1$ were not properly extracted and could not be analyzed. The heatmap was created with pheatmap package of R Studio Version 1.25001.

SI-3 A3.2 Number TU > 0.01 and mixture TU, from 2015 ($\Delta T1$) and 2016 ($\Delta T2a$ and $\Delta T2b$)

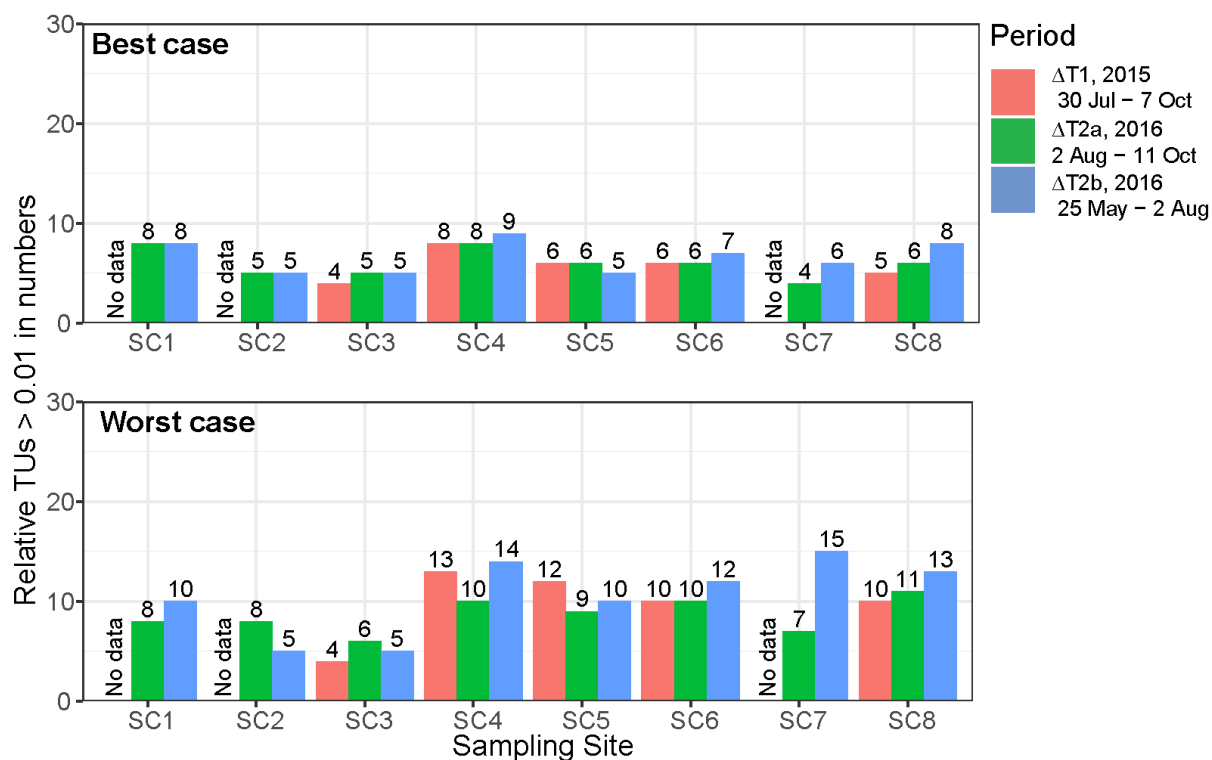


Figure SI-3 A6.1: Acute TU exceedances, observed at the individual sampling sites during three sampling periods based. The relative TU > -2 in numbers for the best case scenario is shown in the upper graph. The relative TU > -2 in numbers for the worst case scenario is shown in the bottom graph.

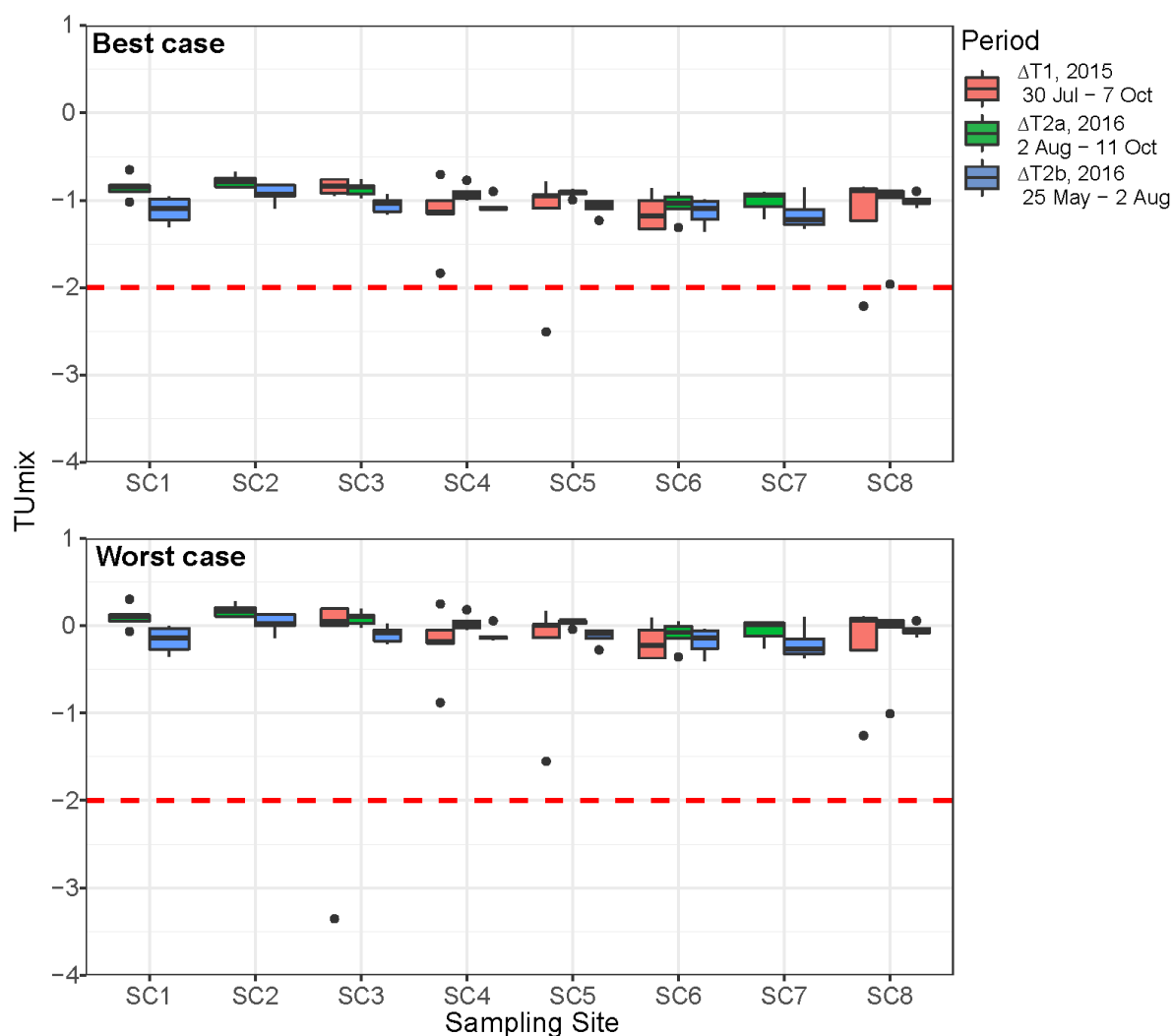


Figure SI-3 A6.2: Acute risks based on TU_{mix} , observed at the individual sampling sites during three sampling periods based. The magnitude of TU_{mix} for the best case scenario is presented in the upper graphs. The magnitude of TU_{mix} for the worst case scenario is shown in the bottom graphs. The lower whiskers show the minimum values not falling below the first quartile more than a factor of $1.5 \times$ the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of $1.5 \times$ the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers (standardized boxplot using R ggplot package).

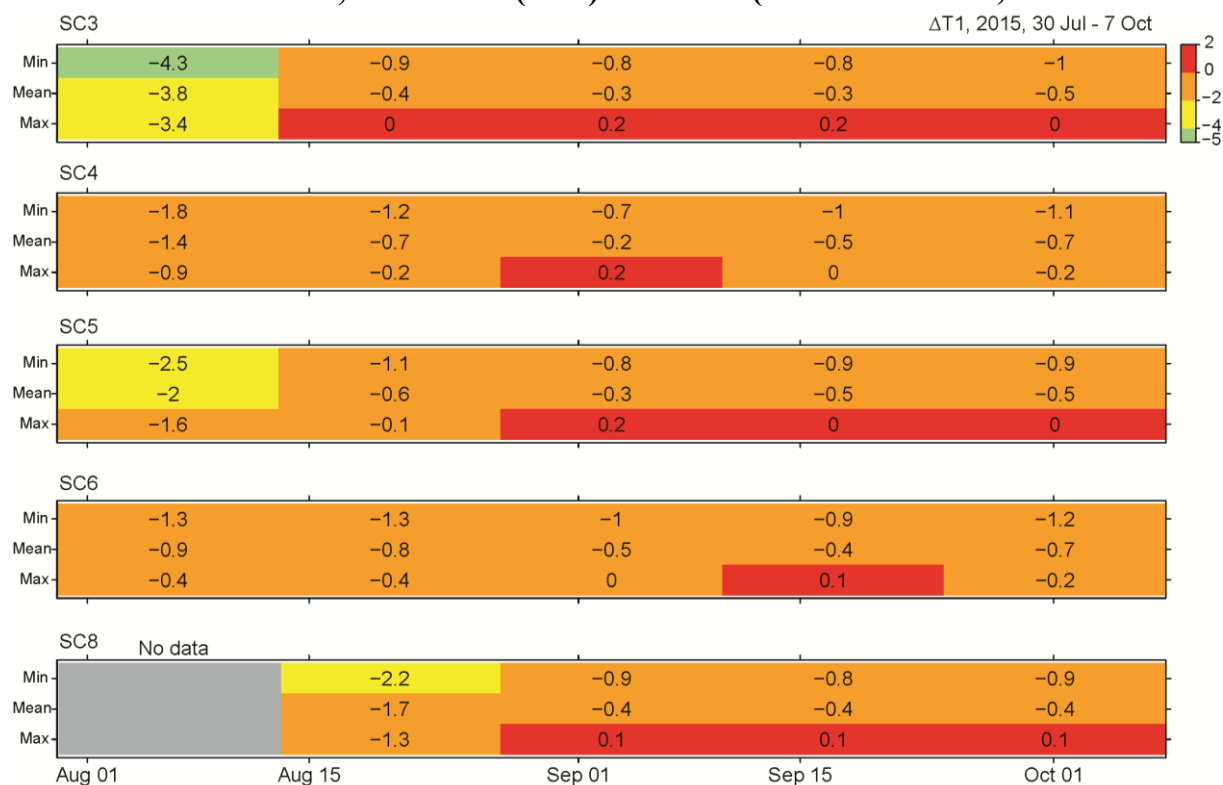
SI-3 A3.3 Mixture TU, from 2015 ($\Delta T1$) and 2016 ($\Delta T2a$ and $\Delta T2b$)

Figure SI-3 A7.1: Mixture TU for the 2015 data between the 30.7 to the 7.10. 2015 ($\Delta T1$) in biweekly intervals in SCs 3, 4, 5, 6 and 8 for three different scenarios (Min = TU_{mix} divided by an uncertainty factor of three; mean = no adjustment, and max = TU_{mix} multiplied by an uncertainty factor of three). The uncertainty factors represent the uncertainties of the environmental concentrations obtained by the absorbent based passive samplers. Grey area: no samples collected.

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Figure SI-3 A7.2: Mixture TUs for the 2016 data between the 25.5 to the 11.10. 2016 ($\Delta T2b$, $\Delta T2a$) in biweekly intervals in SCs 1, 2, 3, 4, 5, 6, 7 and 8 for three different scenarios (Min = TU_{mix} divided by an uncertainty factor of three; mean = no adjustment, and max = TU_{mix} multiplied by an uncertainty factor of three). The uncertainty factors represent the uncertainties of the environmental concentrations obtained by the absorbent based passive samplers. Grey area: no samples collected.

SI-3 A4 Comparison of ARQ_{mix} (vertebrate, invertebrate and primary producer data together) and TU_{mix}.

SI-3 A4.1 Correlation of the ARQ_{mix} (vertebrate, invertebrate and primary producer data together) and the TU_{mix}.

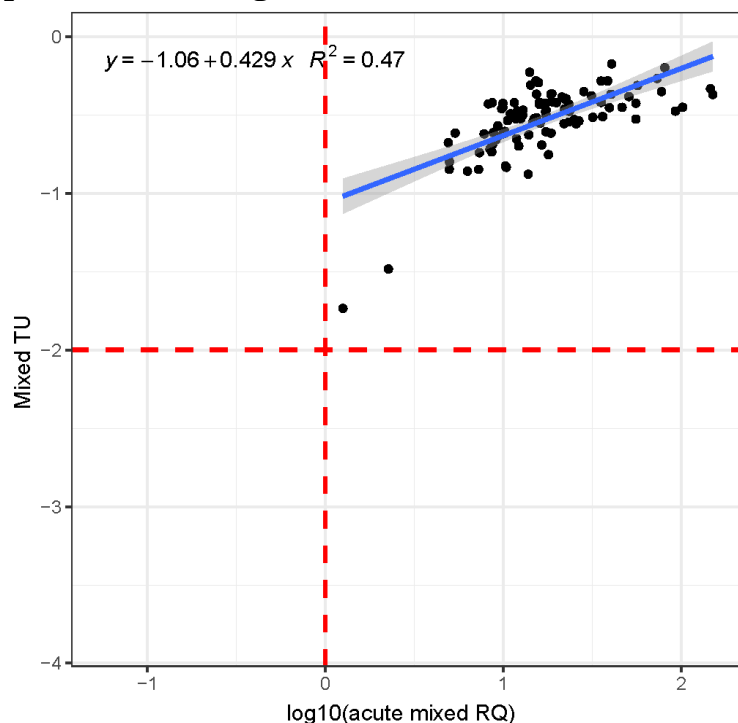


Figure SI-3 A8: Correlation between acute TU_{mix} and ARQ_{mix} for mixture of pesticides for all trophic groups for each sample with 95% confidence interval. For linear regression, only TU_{mix} and ARQ_{mix} data was considered from samples where both SDB disks and PDMS sheets data was available. The dashed lines represent the critical TU levels (horizontal) and critical ARQ levels (vertical) indicating heavy pollution or moderate water quality, respectively. Data of TU_{mix} and ARQ_{mix} for invertebrates \log_{10} transformed.

SI-3 A5 Estimated TU_{expected} deduced from $SPEAR_{\text{pesticide}}$ data

SI-3 A5.1 Estimated TU_{expected}

Table SI-3 A5: TU_{expected} converted from the $SPEAR_{\text{pesticide}}$ data according to Liess et al. (2021, submitted) and Knillmann et al. (2018) as applied within the indicate software (version 2.0.0). The values are presented on basis of \log_{10} .

$TU_{\text{estimated}}$	26-Aug, 2013	24-Feb, 2014	25Aug, 2014	23-Feb, 2015	31-Aug, 2015	22-Feb, 2016
SC1	1.3	-1.8	0.5	1.3	1.3	-1.0
SC4	-1.8	-1.8	-1.8	-2.2	-0.6	-1.4
SC5	-1.7	-1.6	-2.7	-1.2	-1.7	-3.9
SC8	NA	NA	-4.3	-4.1	-3.7	-4.1

TU_{expected}	Water quality
$TU_{\text{expected}} < -4$	High - not contaminated
$-4 \leq TU_{\text{expected}} < -2$	Moderate - slightly contaminated
$-2 \leq TU_{\text{expected}} < 0$	Bad - heavily contaminated
$0 < TU_{\text{expected}} < 2$	Very bad - very heavily contaminated

SI-3 A6 Literature

Knillmann, S., Orlinskiy, P., Kaske, O., Foit, K. and Liess, M. (2018) Indication of pesticide effects and recolonization in streams. Science of the Total Environment 630, 1619-1627.

Umweltbundesamt (2016) Chemical Quality Standards and Assessment.

<https://www.umweltbundesamt.de/en/topics/water/rivers/assessment-of-watercourses/chemical-quality-standards-assessment#textpart-1>.

4. Chapter Identification of pesticide input pathways in tropical streams as a basis to propose potential mitigation options

4.1. Abstract

Finding targeted strategies to mitigate entry of pesticides into surface waters in areas of intense agriculture is challenging. This holds especially true in little studied areas with very distinct topographic characteristics and unconventional field cultivation practices, such as in the tropical Tapezco river catchment in Costa Rica. Within this catchment, areas with steep slopes are used for intense horticultural farming of mainly vegetables. This is exclusively done by a farming practice similar to contour farming, the practice of tilling land with furrows along parallel lines of consistent elevation in order to conserve rainwater and to prevent soil losses by erosion. At the same time, slope-directed paths are implemented to act as drainage system to avoid stagnant water on the fields during heavy rain events, though as well connecting the fields directly with the streams, which enable a fast pesticide transport. Indeed, a significant contamination of streams with pesticides and pesticide transformation products (PPTP) throughout the Tapezco river catchment has been confirmed, leading to considerable toxicological risks to aquatic communities, urgently calling for effective mitigation strategies to reduce PPTP inputs.

To identify how PPTP are transported from horticultural areas into streams of the Tapezco river catchment, different PPTP transportation pathways were considered. The first investigated pathway was via handling practices of pesticides by farmers and field workers, where inappropriate handling was proposed to lead to sporadically distributed pesticide inputs unrelated to hydrology. The second studied pathway was surface run-off. Typically, heavy precipitation events are found to be important drivers for the surface-based transport of pesticides into the streams. Thus, such pesticide inputs can be assumed to correlate positively with water levels in the receiving streams. Surface run-off is additionally favored by the slope-directed paths on the fields, which directly connect fields with the streams. Therefore, the influence of prevalent topographical and hydrological variables on PPTP inputs via surface run-off were studied within this thesis. The third potential investigated input pathway was the leaching of pesticides into the ground from where pesticides can enter streams via exfiltration through river banks. This path would be expected to lead to a constant input that is negatively correlated with water levels.

To investigate the role of these pathways in transporting PPTP into the streams, pesticide peaks unrelated to hydrology were identified based on measured environmental concentrations (MEC) of PPTP and compared with water level time series. Survey data about pesticide handling practices were evaluated additionally. Temporal PPTP distributions were investigated during three sampling periods ($\Delta T1$, $\Delta 2a$, $\Delta 2b$) within 2015 and 2016 and spatial trends were studied at eight sub-catchment (SC) sites. In addition, knowledge on the topography (share of horticultural land, share of forest in the 100 m stream buffer zone, average slopes of the horticultural fields) and hydrology (median water level factors) was considered. These variables were referred to as explanatory variables while 20-, 50- and 80-percentiles of MEC were considered dependent variables. The explanatory and dependent variables were correlated via linear regression modelling for identifying the most important determinants of PPTP transport. There, 20-percentiles represent a scenario with low precipitations, no or little surface run-off and low PPTP inputs; 50-percentiles a scenario with medium precipitations, resulting in moderate surface run-off and PPTP inputs; and 80-percentiles a scenario with high precipitations, pronounced surface run-off and high PPTP inputs into streams. With a focus on potential mitigation measures achieving the highest effectiveness for reducing risks to aquatic biota, analyses were performed on a sub-set of PPTP that dominated the risks to aquatic organisms, along with three transformation products (TP) to calculate TP/PPTP ratios as a measure of pesticide residence time. The correlation analysis of the PPTP input pathways was again based on eight SC sites.

The input of three pesticides were very likely due to inappropriate handling. For five additional pesticides, the input via inappropriate handling seemed probable. Temporal exposure trends were observed by comparing the MEC during the sampling period with reduced precipitation ($\Delta T1$, in 2015) with the MEC detected at periods with normal precipitations ($\Delta 2a$, $\Delta 2b$, in 2016). In addition, spatial trends were investigated by conducting a cluster analysis with the MEC PPTP data (20-, 50- and 80-percentiles) among the different sites. Particularly the pesticide distributions at SC2 and SC3 were different compared to other sites (SC1, SC4, SC6, SC7 and SC8). However, except for the 20-percentile scenario, the pesticide distribution at SC5 was similar compared to that at SC2 and SC3, forming one sub-cluster. Linear regression models helped to find relationships between two explanatory variables, namely, the share of forest in the buffer zone, and mean slopes of horticultural fields, and the dependent variable, MEC percentiles in streams. For five PPTP, boscalid, diazinon, diuron-desdimethyl, linuron and prometryn + terbutryn the percentile concentrations decreased significantly with increasing share of forest in 100 m river buffer zone considering all scenarios. With regard to the horticultural mean slope, for cyhalothrin and thiamethoxam, the percentile concentrations increased with increasing mean slopes of the horticultural areas for all three scenarios. A high share of forest in the buffer zone worked generally as barrier for input via surface run-off, but not for all PPTP. For the fungicide carbendazim increased average slopes did not favor the input into the streams and inputs were low even at sites with horticultural areas with a high mean slope (80 percentile scenario). By analyzing groundwater samples it became apparent that, especially in SCs with horticultural fields with low average slopes, a leaching of PPTP into groundwater and further transport into the streams via exfiltration might be possible.

Based on this assessment, three avenues for mitigating input of PPTP into the streams could be deduced: to provide training workshops for better handling as well as biobeds for proper disposal; to avoid cultivation of crops with high insecticide needs on steep slopes; and to establish forested buffer zones between the fields and the streams.

4.2. Introduction

4.2.1 Pesticide pollution and aquatic health risks in the Tapezco river catchment

Streams of the horticultural Tapezco river catchment in Costa Rica are severely polluted by a wide spectrum of pesticides. In total, 109 pesticides and pesticide transformation products (PPTP) were identified throughout eight sub-catchment sites (SC1 – SC8) over several months in two consecutive years (Chapter 2). A retrospective risk assessment revealed that these pesticide inputs into streams are likely to endanger aquatic communities, especially invertebrates (Chapter 3). Within all of the eight analyzed SCs, chronic continuous risks had been observed during all sampling periods ($\Delta T1$, $\Delta T2a$ and $\Delta T2b$), although the exposure patterns at SC2 and SC3 of several pesticides seemed to be distinct compared to those of the remaining sites. It can therefore be hypothesized that input pathways at the SC2 and SC3 might be different from the other sites, calling for a more detailed spatio-temporal distribution analysis of the pesticides dominating the risks. Indeed, 18 of the detected pesticides, specifically 12 insecticides, four herbicides and two fungicides (SI-4 A1) were identified to mainly drive the chronic health risks to aquatic invertebrate communities (Chapter 3). A similar observation, i.e. that risks are often caused by a smaller set of pesticides, has been made repeatedly in various prior studies (Echeverría-Sáenz et al. 2018, Munz et al. 2017, Rämö et al. 2018, Sangchan et al. 2014, Schreiner et al. 2021).

Knowledge about the pesticides posing the highest risks in a catchment can help define targeted mitigation strategies for improving water quality because focus on selected priority PPTP may offer feasible measures of input prevention with high effectiveness. Equally important for designing risk mitigation measures is an understanding of seasonal and spatially distributed inputs of PPTP and to shed light on how these PPTP migrate from the usage sites into the surface waters.

4.2.2 Knowledge about pesticide input pathways

Pesticides can be transported via various mechanisms from the site of application to off-target sites, such as rivers and streams (see Chapter 1.3). Based on knowledge gained in prior studies, three major mechanisms of transport and/or inputs of PPTP into streams are hypothesized to be of possible relevance in the Tapezco river catchment: i) direct inputs due to inappropriate handling (Leu et al. 2004a, Wittmer et al. 2010), ii) surface transport during rain events (Doppler et al. 2012, Lalah et al. 2009, Lefrancq et al. 2017, Leu et al. 2004a, Thurman et al. 1991); and iii) exfiltration of groundwater, indicating possible transport via bank filtration (Mechelke et al. 2019, Romero et al. 2010, Verstraeten et al. 2003).

The first mechanism of direct input falls under the generic term “inappropriate handling of pesticides”, such as the washing of pesticide application equipment where washing water might be disposed directly into streams or into drain ditches connected to streams (Staudacher et al. 2020). This type of input would be expected to be independent of rain events. Indeed, direct peaks from inappropriate handling practices have previously been indicated by high concentration peaks unrelated to precipitation, water level and discharge changes (Wittmer et al. 2010) as conceptualized in Figure 1A. Inappropriate handling might include as well inputs of pesticides from spray drift, if pesticides were sprayed in the vicinity of streams, leading as well to pesticide peaks unrelated to hydrological parameters as described before. In the context of the Tapezco river catchment, such inputs can be identified as concentration peaks occurring during dry periods. These inputs are expected to occur suddenly and with a short residence time in the environment; thus extensive transformation of the pesticides is not likely. Therefore, sharply decreased transformation product (TP) and parent pesticide ratios have been reported as indicators for handling related pesticide peaks (Leu et al. 2004a, Wittmer et al. 2010).

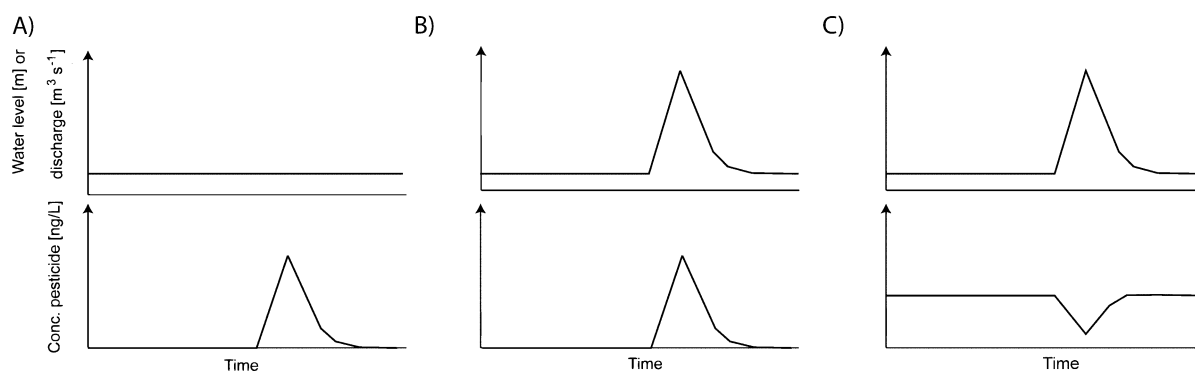


Figure 1: Conceptual presentation of the relationship between water levels or discharges (upper row) and pesticide inputs in streams (bottom row). A) Pesticide inputs from inappropriate handling of pesticides – pesticide peaks are not related to water level and discharge. B) Pesticide inputs from rain events - pesticide peaks correlate with water level and discharge changes. C) Pesticide inputs from groundwater exfiltration into streams - pesticide peaks correlate negatively with water level and discharge changes.

The second mechanism of pesticide input is transport due to rain. PPTP could be transported into the streams during rain events by surface run-off. In fact, due to heavy tropical rainfalls with values above 200 mm/month (National Meteorological Institute from Costa Rica 1950-2016), pesticides can be washed from the crops and fields and be transported to the streams as over land flow. The presence of over-ground slope-directed pathways or manmade surface sealing can moreover favor the fast transportation of PPTP into streams and act as so called “shortcuts” (Schönenberger and Stamm 2021). However, on the fields within the Tapezco river catchment, only slope-directed over-ground pathways are present, no tile drains have been observed. Pesticide inputs from surface run-off generally lead to pesticide concentration peaks in streams which correlate with discharges and water levels (Doppler et al. 2012, Lalah et al. 2009, Lefrancq et al. 2017, Leu et al. 2004a, Schriever et al. 2007, Thurman et al. 1991) as depicted in Figure 1B. In such situations, increased concentrations would be accompanied by heavy precipitation only if the increase in flux outweighs the dilution due to increased precipitation. It moreover has to be considered that surface-runoff may represent fluxes of pesticides applied on the fields but as well non-direct inputs from handling – with the biweekly concentration data available (Chapter 2), a further differentiation of the surface run-off peaks is not possible.

The third mechanism of pesticide transport explored for its relevance for the Tapezco river catchment is the exfiltration of PPTP from contaminated groundwater into streams. Leaching of pesticides into the ground is known to potentially lead to contamination of groundwater (Dores et al. 2008, García de Llasera and Bernal-González 2001, Tariq et al. 2004). Contaminated groundwater can then reach the streams through exfiltration through the river bank via the hyporheic zone (Mechelke et al. 2019, Romero et al. 2010, Verstraeten et al. 2003). This latter process causes a constant input of PPTP into affected streams, leading to concentrations that are negatively correlated with water levels and discharges as illustrated schematically in Figure 1C.

Experience from former studies (Leu et al. 2004a, Wittmer et al. 2010) showed that the flux of pesticide inputs into streams by each of the three mechanisms can vary not only in a compound but also a catchment specific manner. Additionally, under field conditions, input of an individual pesticide via different mechanisms is possible resulting in an overlay of different concentration patterns.

4.2.3 Pesticide source identification

Different pesticide input mechanisms lead to different pesticide fluxes into the streams and hence are expected to result in varying concentration patterns (Figure 1). Conversely, identified concentration patterns in the streams can be used as a basis to deduce specific pesticide input mechanisms and to better understand the driving factors of the mass flow of pesticides from the fields into the streams (Ammann et al. 2020, Doppler et al. 2012, Doppler et al. 2014, Leu et al. 2004a, Morselli et al. 2018, Sangchan et al. 2012, Schriever et al. 2007). As elucidated in these studies, there are several obstacles environmental modelers have to face for the derivation of key pesticide sources and to determine mass flows. The fluxes of the PPTP into the streams do not only relate to the physicochemical characteristics of the PPTP. Other variables are relevant to understand the conditions in the application area, including pesticide application practices, topography, land use and hydrology. It has been shown that the effect of these variables on the pesticide fluxes can even dominate over the influence of their physicochemical properties, referring to fast direct inputs from handling or surface run-off (Leu et al. 2004b, Schriever et al. 2007). Bringing such inputs into the context of the research of this thesis, special topographic characteristics of the Tapezco river catchment are discussed in the following. A farming practice similar to contour farming is common in the Tapezco river catchment. This type of farming means that land with slopes is tilled with furrows along parallel lines of consistent elevation in order to conserve rainwater and to prevent soil losses from erosion (Encyclopædia Britannica 2019). In addition, these parallel contour lines are frequently intersected with slope-directed paths, which directly connect the fields with the streams in order to avoid stagnant water on the fields after heavy rain events (Ramírez et al. 2016). An example of contour lines and a slope-directed paths is shown in Figure 2.



Figure 2: Parallel contour farming lines and the slope-directed surface run-off path which connects fields with the streams at SC1 in the Tapezco river catchment (Photograph from F. T. Weiss).

Very small fractions of a catchment area, such as the previously described slope-directed pathways, may contribute substantially to the pesticide pollution via surface run-off into streams (Doppler et al. 2014). Such areas can be described as critical source areas, characterized by three main criteria: i) they present areas where pesticides are applied, ii) they are

hydrologically active, i.e., mobilization and fast transport into the stream is possible and iii) they are well connected to the streams (Doppler et al. 2014, Pionke et al. 2000). A major advantage that prior studies on critical source area identification had was the availability of highly resolved sets of data. For example, to describe the dynamic pesticide fluxes, pesticide concentration data originated from up to 15 minutes time-proportional automated sampling (Doppler et al. 2012, Doppler et al. 2014, Leu et al. 2004a, Sangchan et al. 2014). Likewise, very detailed data on topography (Doppler et al. 2012), soil composition or hydrology existed (Ammann et al. 2020, Doppler et al. 2014, Morselli et al. 2018, Sangchan et al. 2012). Such level of detail is not as of yet available for the Tapezco river catchment (Calvo-Alvarado et al. 2014, Ramírez et al. 2016, Sangchan et al. 2014).

Conscious of these obstacles, a simplified approach to derive pesticides input pathways and to determine the driving variables had to be developed. Hence, investigation about which topographical and hydrological variables explain elevated pesticide concentrations from surface run-off was conducted with the limited available data set by correlating explanatory topographical and hydrological variables with different percentiles of MEC as dependent variables. Regression analysis by the so-called elastic net regularisation (Zou and Hastie 2005) previously helped to identify the most important drivers of pesticide input under conditions of limited available data in a little studied agricultural area in Romania (Schreiner et al. 2021). The advantage of using the linear regression approach within this thesis instead of an elastic net approach is that linear regressions can be applied with an even more limited data set as those available in Schreiner et al. (2021).

4.2.4 Data sources for explaining pesticide inputs

Pesticide application practices depend on the level of training and care exerted by the personnel. Prior studies showed that the inappropriate handling of pesticides by poorly trained farmers and field workers may lead to occupational exposure causing adverse health effects (Dinham 2010, Fieten et al. 2009, Khan and Damalas 2014, Mejía et al. 2014, Polidoro et al. 2008, Wesseling et al. 1993) or favor release of pesticides into aquatic systems, causing a deterioration of water quality (Leu et al. 2004a, Ramírez et al. 2016, Ruepert et al. 2014). Therefore, to mitigate pesticide inputs from handling, it is important to provide a clear description of the pesticide application situation and of common pesticide handling practices in the field. Such information is generally gathered by means of surveys (Dinham 2010, Hashemi et al. 2009, Matthews et al. 2003, Staudacher et al. 2020).

The input of pesticides via surface run-off associated with heavy rainfall events is dependent on hydrological and topographical variables. Water level and discharge are hydrological variables that can help to understand input of PPTP into streams based on rain (Leu et al. 2004a, Szöcs et al. 2017, Wittmer et al. 2010). By measuring the hydrostatical pressure in the streams with technical devices, such as pressure loggers, water level data can easily be collected. To describe topographical attributes, i.e. slopes influencing surface run-off, Geographical Information System (GIS) based data constitute a solid base. For example, digital elevation model data allow to determine slopes, which can have an influence on the intensity of the surface run-off and the associated transport of pesticides (Müller et al. 2004). Satellite images can help localize areas with farming and for identifying sections with different land uses. Furthermore, the distance between fields and streams can be a useful variable to describe the connectivity of the fields to the open surface water bodies (Doppler et al. 2012). Along these lines, natural buffer zones between the fields and the streams can be identified. Strips with planted trees or natural forest zones are known to be especially efficient in mitigating the transport of PPTP into the streams (Parkyn 2004, Reichenberger et al. 2007).

Finally, groundwater exfiltration is driven by irrigation or precipitation and is dependent on several factors, such as precipitation, land use, evapotranspiration and soil characteristics, such

as soil porosity or water absorption capacity (Ammann et al. 2020, Doppler et al. 2012). Yet, such specific soil properties are not commonly available aside from the generally heterogeneous nature of soil. Thus, a relatively simple way to investigate qualitatively if groundwater exfiltration may occur is the monitoring of groundwater samples (Dores et al. 2008, García de Llasera and Bernal-González 2001, Tariq et al. 2004). If PPTP are found in groundwater samples, it is possible that these PPTP also leach via exfiltration through river banks into streams.

4.2.5 Research aim and hypothesis

The aim of this study was to identify input paths of risk-dominating PPTP into the streams of the Tapezco river catchment in order to identify their sources and to better understand important input drivers. Based on the result of this analysis, this study additionally aimed at deducing possible mitigation options to reduce pesticide concentrations in the streams.

To follow these aims, the assessment relied on the biweekly MEC to provide insights about the spatio-temporal pesticide distribution and on pesticide user information, hydrological, topographical, land use and groundwater PPTP data to help identify the relevant input pathway(s). More specifically, the focus was on 18 PPTP that were found to dominate the risk to aquatic communities, as described in Chapter 3, along with the transformation products (TP) for three of them. Three additional pesticides (i.e. acephate, boscalid and propamocarb) were added due to their known high application volume in the Tapezco river catchment (Ramírez et al. 2016, Staudacher et al. 2020). For the spatio-temporal analysis and the evaluation of the driving variables with the linear regression, data of all eight SCs was used. In order to avoid bias due to interdependencies (spatial overlay of concentrations and hydrological signals) from nested SCs (SC3, SC4, SC5, SC8; sites are illustrated in Chapter 1.7) in the linear regression analysis, weighted linear correlations were applied, considering the ratio among the unnested area and total area of each respective catchment. A comparison of observed data with modelled data was conducted as well by using the determined correlation parameters of the weighted linear model for testing the robustness of the model. For identification of peaks from inappropriate handling, concentration and water level time series were analyzed visually and statistically only from headwater SCs to clearly identify such peaks and to avoid a possible input from upstream SC locations. For finding patterns between PPTP concentrations and the variables, catchment attributes and hydrological data were utilized by applying weighted linear regression models. Groundwater samples of drinking water tanks were collected at headwater SC, SC1 and SC7, and screened for PPT to investigate if a leaching of PPTP and their exfiltration into streams is in principle possible. The hypothesis was that the dominating input paths could be elucidated by means of an array of information and analysis approaches geared toward the overall limited data pool.

4.3 Material and methods

4.3.1 Pesticide concentration data

The biweekly-integrated pesticide MEC data from sorbent-based passive sampling (SDB disk and PDMS sheets), evaluated in detail in Chapter 2, was used. It is important to note that these sorbent-based passive sampling approaches allow for analysis of the dissolved but not particle-bound fraction of the PPTP; thus, the input of the particle-bound fraction is not considered here. Pesticide concentration data were collected in two consecutive years. Of the detected PPTP, a set of parent pesticides was prioritized which (i) dominated the risks to aquatic organisms as demonstrated in Chapter 3 and (ii) were known for their high application rates in the Tapezco river catchment according to previous studies (Ramírez et al. 2016, Staudacher et al. 2020). For two parent pesticides (diuron and carbendazim), TP data (of diuron-desdimethyl, diuron-desmonomethyl and 2,6-dichlorbenzamide) were used as well to enable the calculation of TP/parent compound ratios. Since for diuron, two TP were detected, their sum concentration

were used forming these ratios (more information about the TP and parent pesticide ratio, section 4.3.5). The final list of the 24 PPTP considered is shown in SI-4 A1. For the general spatial distribution analysis and for further investigations about the pesticide pathways, PPTP data of all SCs was used. For the application of weighted linear regression, 20-, 50- and 80-percentile concentrations were used from each SC as dependent variable to describe MEC inputs from different scenarios. For the determination of the percentiles, all MEC data < LOQ were replaced by LOQ/2 according to U.S. Environmental Protection Agency (2000) and U.S. Environmental Protection Agency (2021) to account for the PPTP analyzed though not detected in the samples. As explanatory variables for the weighted linear modelling, catchment attributes (e.g. slopes, land use, data of stream buffer analysis) and hydrological data based on water levels were utilized.

In addition to these data, PPTP analyses of groundwater from drinking water tanks, sampled in SC1 (Asada Palmira, Tpap) and SC7 (Asada Palmira Tapezco, Tpat), were used (for more detail see SI-4 B1). For analyses, 1 L grab samples were collected and then processed and analyzed as described for the water level proportional samples in Chapter 2.3.2 and Chapter 2.3.3. These samples were screened for 258 polar and semi-polar PPTP.

4.3.2 Catchment characterization

The sub-catchments and land use data: The delineation of the eight SCs (SC1-SC8) and the origin of the land use data is described in Chapter 1.7. The land use was distinguished between: forest, horticultural areas, pasture, urban area and greenhouses (SI-4 A2 and SI-4 B2).

The average and maximum slopes of horticultural areas were determined by using the vectorized horticultural area and land use data and digital elevation model data (with a resolution of 30 x 30 meter, section 1.7) using the “slope” tool in ArcMap 10.5.1.

For the stream buffer zone analysis, a radial buffer zone around the streams was considered. Based on a literature search, no explicit regulatory value could be found in Costa Rica that describes the legally required distance between fields and streams. Therefore, a radial buffer zone of 100 m was used in this study. This 100 m radial buffer zone referred to the actual Costa Rican regulatory framework including the presence of a 100 m natural forest buffer zone radial from water springs (Law N° 6425 2020). With such a buffer area around the streams containing a high share of natural forest, it can be assumed that pesticide inputs into the streams are low (Parkyn 2004, Reichenberger et al. 2007). The buffer zone was mapped within ArcMap 10.5.1 around the stream network with the “buffer” tool. Land use in the 100 m buffer zone was obtained by using the river course and the vectorized land use data and by applying the “proximity” and the “buffer” tools in ArcMap 10.5.1 (Schaub 2016).

The connectivity of the horticultural fields to the river network depends on prevailing surface structures (roads, ditches, slope-directed paths on the fields). However, insufficient surface structure data was available for the Tapezco river catchment. Therefore, the radial distance of the streams containing 75% of horticultural land was selected as SC dependent explanatory variable to describe the connectivity between the streams and the fields (example presented in Figure 3, more data see: SI-4 B3). If there is no relationship between the concentrations and this radial distance, this would indicate that even distant fields are well connected with the streams. This can be expected due to the slope-directed paths on the fields. A complete overview of the catchment attributes is given in SI-4 B2 and SI-4A2.

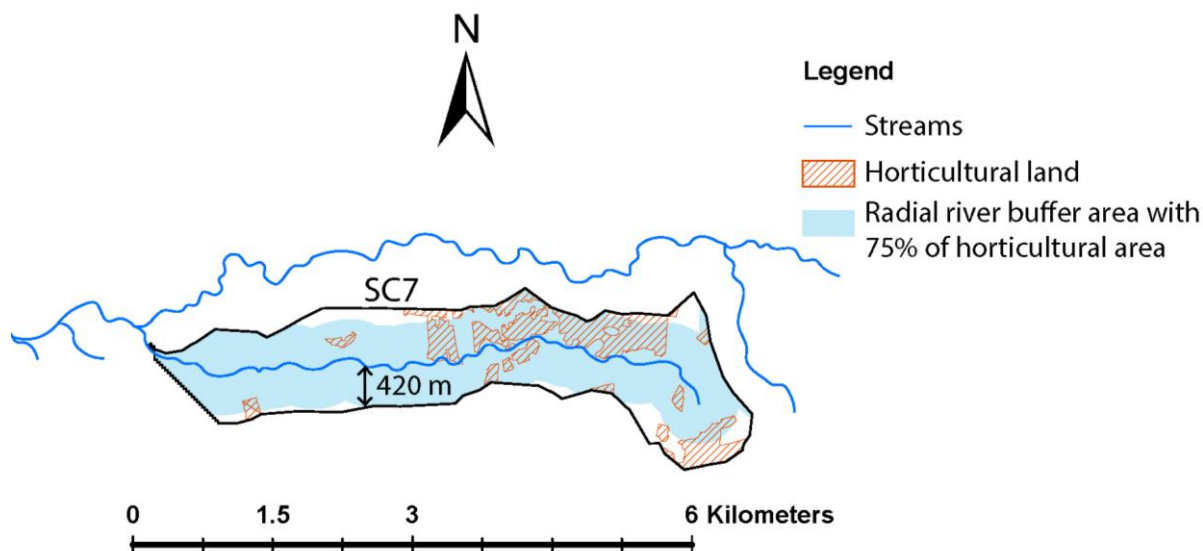


Figure 3: Radial buffer area from streams of SC7 with 75% of horticultural land. The radial distance (here 420 m) from the streams containing 75% of horticultural land is marked with an arrow (data SI-4 B3).

4.3.3 Hydrological data and derived variables

Precipitation samples were collected by using pluviometers (TFA Dostmann 47.1008 pluviometer, Conrad, Switzerland, European article number: 4009816018458). To make the precipitation data comparable with the pesticide concentrations, cumulated precipitation samples of two successive weeks were always combined forming biweekly samples. An overview of collected data is provided in SI-4 A3. The pluviometers were placed in the vicinity of the sampling sites (sampling site locations, SI-2 B1). It has to be noted that a preliminary investigation showed that the precipitation data did not correlate with the water level data (SI-4 A3.3, Figure SI-4 A6 and Hannah Wey (2016)). During the field work, very local precipitation events had been observed explaining this poor correlation. Based on this knowledge, precipitation data from the pluviometers, while fully depicted in SI-4 A3.1 and SI-4 A3.2, was neglected for further analysis and only the water level variables were used for modelling.

Water levels were measured in 2015 continuously in 5 minute intervals during the sampling at SC3, SC4, SC5, SC6 and SC8 (SI-4 B4) by using HOBO® U20L water level loggers (Onset, Switzerland). In 2016, water levels were measured in 15 minutes intervals at SC1 – SC8 by using the same loggers (SI-4 B4). Available hydrological information, including water level and precipitation data from both years are presented in SI-4 A3.

Precipitation events can lead to rapid water level peaks in the nearby streams. To parametrize the effects of such events numerically, first the factors of water level peak maxima vs base water levels (minimum weekly water levels) were determined with the water level time series for each biweekly interval (SI-4 A3.1 and SI-4 A3.2) according to Equation 4.1:

$$\text{Water level factors} = \frac{\text{Water level peak maxima}}{\text{Water level minimum per biweekly intervall}} \quad [\text{Eq. 4.1}]$$

To enable a direct comparison of these water level factors with biweekly concentrations of the monitored PPTP, in a second step, these water level factors were summed up for each biweekly period to yield biweekly water level factors. Water level factors above a variation of 30% from

the base water level (water level factor > 1.3 as relative values) were taken to determine biweekly water level factors according Equation 4.2:

$$\text{biweekly water level factor} = \sum_{d=1}^{14} \left(\frac{\text{Water level peak maximum}_{n,d}}{n * \text{Water level minimum per biweekly interval}} \right),$$

[Eq. 4.2]

if Water level factors were > 1.3,

where n is the number of water level peaks per day and d are the days (biweekly intervals, d , 1-14, for each period). Water level factors > 1.3 were selected because only those could be clearly visually determined as water level peak in the water level time series and not as baseline noise. Therefore, only water level factors above 1.3 could be considered large enough to lead to a sufficient flux of pesticides from the field to the streams. For describing the responses of the water levels to precipitation (duration of water level increases and duration of declines of water level), daily average water levels were deduced and the minimum biweekly water level was subtracted from the daily average water levels (used as well in Eq. 4.2). These daily water levels were cumulated over 14 days according Equation 4.3:

$$\text{Biweekly cumulative water level} = \sum_{d=1}^{14} (\text{average water level}_d - \text{Water level minimum per biweekly interval})$$

[Eq. 4.3]

The biweekly water level factors and the biweekly cumulative water levels are shown in the water level and precipitation time series in SI-4 A3.1 and SI-4 A3.2 and in SI-4 B5, respectively. The water level raw data is presented in SI-A B4. It is hypothesized that low cumulative water level values indicate that the streams respond quickly in terms of water levels after precipitations – water level changes appear and disappear fast. High cumulative water level values demonstrate that the duration of the water level peaks is longer and the water level responses to the precipitation are slower. This cumulative water level approach can only be used as approximation for describing responses of water level peaks after rain because the intensity of the water level changes are as well dependent on the topography. For conducting more accurate investigations about the responses of the water level to precipitation, and to enable a more accurate comparison of the responses among the sites, discharge measurements would be necessary and so called “flashiness” indices would need to be determined (Baker et al. 2004).

4.3.4 Identification of spatio-temporal pesticide inputs

For temporal distribution, PPTP concentrations (\geq LOQ) of the individual periods, $\Delta T1$, $\Delta T2b$ and $\Delta T2a$, were compared. During $\Delta T1$, a particularly low precipitation was observed, attributed to an El Niño weather phenomenon. Accordingly, concentrations during $\Delta T1$ are expected to be lower than during $\Delta T2a$ and $\Delta T2b$. $\Delta T1$ and $\Delta T2a$ cover the nearly same time period in consecutive years from 30-Jul to 07-Oct, 2015 and 02-Aug to 11-Oct, 2016, respectively; period $\Delta T2b$ contains the data from the sampling campaign in 2016, from 25-May to 02-Aug (time periods SI-3 A1.1, PPTP concentration data SI-3 B5, statistical analysis SI-4 C1). For investigating the spatial variability of the detected PPTP, the 20-, 50- and 80-percentile concentrations of the PPTP were determined. The 20-percentile concentrations are expected to describe more constant PPTP inputs without high dynamics with no or low precipitation, no or weak surface run-off events and no inputs via handling. The 50-percentile concentrations represent a medium input scenario with medium precipitation and surface run-off. The 80-percentile concentrations represent high PPTP input scenarios with high precipitation and surface run-off. The specific selection of the percentiles is subjective but their plausibility relies on the PPTP concentration to water level relations as explained in section 4.2.2. For the determination of the percentiles, data of samples with sampling issues were excluded (see SI-4 C2). In addition it was assumed that all concentration < LOQ were equal to the LOQ/2 according to U.S. Environmental Protection Agency (2000) and U.S. Environmental Protection Agency (2021). The percentiles were scaled (normalized) via scale function in R

prior clustering to avoid that large values dominate the clustering. The scaled percentiles were then plotted as a heatmap for each compound and site to provide general exposure trends. The plotting was conducted via the *pheatmap* package in R; for clustering, a hierarchical clustering, using euclidean distance and complete linkages, was applied.

4.3.5 Identification of direct pesticide inputs from inappropriate handling

Pesticide peaks during dry periods without relevant water level increases were determined as indicator of inputs from inappropriate handling at headwater SC sites (SC1, SC2, SC6 and SC7). Four strategies were applied.

First, time series were prepared containing the biweekly-integrated pesticide concentration data and the water level data (see SI-4 B6.1 and SI-4 B7.1). For each PPTP considered in this study, the concentration and water level time series were scanned visually to find elevated concentrations during biweekly periods with no or low water level increases, similar to the procedure described in a previous study (Wittmer et al. 2010).

Second, as a statistical approach for confirming the visually identified concentration peaks, an outlier analysis was conducted (SI-4 C3). It was assumed that these peaks exceeded, or were equal, to the 95% concentration quantile, and occur simultaneously during periods with a low hydrological dynamics, defined as periods with biweekly water level factors below, or equal to their 25% biweekly water level factor quantile. If both assumptions were fulfilled, the PPTP input was assumed to stem from inappropriate handling (overview SI-4 A4.3). A peak was defined as definitive from handling if the peak could be determined with both the visual and statistical approach, or if the visual peak was very distinct (see SI-4 B7.1 and SI-4 B7.2). These concentration peaks from handling were then removed for the following model-based analysis of rain driven pesticide inputs (SI-4 C5).

Third, to indicate direct inputs from handling, the ratios of the TP of diuron and carbendazim and their respective parent pesticide were used. As described in previous studies, a sharp decrease in TP and parent pesticide ratios can be used to indicate direct inputs of handling (Leu et al. 2004a, Wittmer et al. 2010). This is because, during direct pesticide inputs from handling, the parent pesticide has a short environmental residence time and hence a very limited timeframe for possible biotransformation.

Last, survey data from a collaboration study was exploited. The survey data concerned all relevant SCs to obtain an overview about local pesticide handling practices. Detailed information about the interviews conducted and the compiled data are available from previous studies (Fuhriemann et al. 2020, Fuhriemann et al. 2019, Staudacher et al. 2020). Shortly, for the interviews, 300 farmers and fieldworkers from 90 farms participated in two interview rounds in 2016, simultaneously to the environmental pesticide monitoring ($\Delta T2b$ and the first interval of $\Delta T2a$). In their surveys, farmers and field workers were asked multiple choice questions about where they dispose pesticide residual water during the cleaning of pesticides application equipment. The possible answers were: “I don’t apply pesticides”, “In the courtyard of the house”, “Next to the farms”, “specific place where pesticides are mixed”, “into the drain”, “in the garbage”, “in the river”, “in a biobed”, and “other”. Moreover, farmers were asked whether they apply a subset of seven pesticides (yes/no), namely acephate, boscalid, carbendazim, carbofuran, chlorpyrifos, cypermethrin and propamocarb, which were detected as well in this study (SI-4 A1).

4.3.6 Identification of important drivers of rain driven pesticide inputs

Individual explanatory catchment and hydrological variables were derived from the available catchment attributes and water level data, as described above (sections 4.3.2 and 4.3.3, respectively). The log transformed 20-, 50- and 80-percentiles of the PPTP-MEC were used as dependent variables. To investigate the relationships between the dependent variable and each

explanatory variable, a linear regression was performed between the dependent variable and each individual explanatory variable (according to SI-4 C5).

The advantages of using percentile concentrations for the linear regression model are that i) outlier concentrations give less weight to the regressions; ii) hydrological interpretation of the data is possible. The 80-percentile concentration was selected to be below the 95% quantile, which explained direct inputs from handling (described in section 4.3.5). The linear regression modelling is based on two assumptions: first that the discharge at the outflow of each SC is proportional to the catchment area; and second that the load of pesticides at the outflow of each SC is proportional to the horticultural area in the respective catchment (percent horticultural area see SI-4 A2, SI-4 B2 and Table 2). Based on these two assumptions, the pesticide concentrations at the outflow of each SC are expected to be proportional to the ratio between horticultural area and the total area of the respective catchment. Therefore, this ratio was used as first explanatory variable for the regression analysis (variables see SI-4 B2). As second and third explanatory variable, maximum slope and average slope of the horticultural areas were used because the higher the slopes the more intense is the intensity of the surface run-off and the associated transport of pesticides (Müller et al. 2004). As forth explanatory variable the radial distance of the streams containing 75% of horticultural land per each SC was selected and as fifth the share of forest in 100 m stream buffer as explained in section 4.3.2 (details SI-4 A2). As hydrological explanatory variables, the median biweekly water level factor and the median biweekly cumulative water level per period were applied based on the biweekly water level factors and the biweekly cumulative water levels described in section 4.3.3.

For modelling using the five catchment attributes (share of horticultural fields per SC, maximum slopes in percent of horticultural fields, average slopes in percent of horticultural fields, the share of forest in the 100 m stream buffer zone and the radial distance of the streams containing 75% of the horticultural fields) and the two hydrological explanatory variables (median biweekly water level factors and median biweekly cumulative daily water levels), only those explanatory variables were selected that showed no significant inter-correlation among each other (all pairwise $-0.7 < R < 0.7$, correlations shown in SI-4 A6 similar to Schreiner et al. (2021)).

While some of the SCs are headwater catchments and provide independent concentration data, other SCs are nested catchments, and are therefore not providing independent data. In the linear regression, therefore, the SCs were weighted proportional to their area fraction not nested in other catchments. Accordingly, for headwater SCs (SC1, SC2, SC6 and SC7) the weighting factor 1 was assigned; for the nested SCs (SC3, SC4, SC5 and SC8) the weighting factors 0.58, 0.4, 0.64 and 0.12 were assigned, respectively (SI-4 B2). In this sense, the independent headwater catchment were weighted stronger during the regression analysis than the remaining nested catchments. The modelling was conducted using the R Software (version R-3.6.1) as presented in SI-4 C5.

The determined correlation parameters, significances of the regression coefficients and residual, and normal Q-Q plots of the weighted linear regression are presented in SI-4 B8.1, SI-4 B8.2 and SI-4 B8.3. The plots were created according SI-4 C5 and SI-4 C6.

In summary, the weighted linear regression modelling will provide different outputs explaining effects of the explanatory variables on the percentile concentrations. The different MEC PPTP percentiles (20, 50 and 80) were selected to represent general inputs from different input scenarios (scenarios are described in section 4.3.4). However, it needs to be considered that, due to the biweekly time-integrated averaged characteristic of the MEC data and the use of 20-, 50- and 80-percentile concentrations, it was not clearly possible to distinguish direct pesticide inputs, pesticide spills next to the fields and inputs from surface run-off during wet periods with water level increases. In addition, random effects of sites, sampling periods and interactions

among the different explanatory variables could not be determined by using the weighted linear regression approach. Nevertheless, this simplistic weighted linear correlation analysis was applicable for the restricted data set available within this study.

4.3.7 Identification of inputs via exfiltration of contaminated groundwater

Besides the results of the groundwater samples indicating if a leaching of PPTP into the ground, and further transport into the streams through the hyporheic zone, is principally possible, TP/parent ratios were applied. Since TP have longer half-lives than their parent counterparts (Boxall et al. 2004, Sinclair and Boxall 2003), elevated TP/parent ratios could indicate inputs of contaminated groundwater/bank filtration water because parent pesticides have a residence time long enough to become bio-transformed.

Finally, to identify inputs from exfiltration, it was assumed as explained in section 4.2.2, Figure 1C, that such an input would lead to concentration inputs negatively correlating with water level changes. Accordingly, it was evaluated with weighted linear regression (explained 4.3.6) if increased median biweekly water level factors had negative estimated effects on the concentrations.

4.4 Results

4.4.1 Spatio-temporal pesticide distribution

To investigate if input patterns by individual PPTP were discernibly and significantly different over time, the concentration range of each of the 24 PPTP was compared between the periods $\Delta T1$, $\Delta T2a$ and $\Delta T2b$ (Figure 4). For the majority of the PPTP (14), the concentration ranges were not significantly different among the periods. Significantly lower concentrations in the period with less precipitation ($\Delta T1$) as opposed to one of the other periods with usual precipitations ($\Delta T2a$ and $\Delta T2b$) were observed for carbendazim, linuron, metribuzin, cypermethrin, diuron-desdimethyl, thiamethoxam and fipronil. However, these findings could not be linked to specific physicochemical properties. Indeed, these chemicals cover the range from polar to non-polar. Water solubility of these substances ranges from 0.002 to 17710 mg/L, $\log K_{ow}$ from 0.8 – 6.4 and $\log K_{oc}$ from 2 – 5.2 (SI-4 A4.1). For two semi-polar chemicals, diuron and propamocarb, with $\log K_{ow}$ of 2.7 and 1.13, respectively, and a water solubility above 151 mg/L (SI-4 A4.1), concentrations during $\Delta T1$ were higher than in $\Delta T2a$ or $\Delta T2b$ despite the lower precipitation.

An overview of the spatial distribution of the 24 PPTP is shown in Figure 5. Different clusters can be observed among the PPTP at the different SCs by using 20-, 50- and 80-percentile concentrations. With the 20-percentile clusters (Figure 5A), two main clusters were distinguished with similar percentile concentration patterns. One main cluster contained SC6 and SC7, representing the highest PPTP inputs. The other main cluster contained SC2, SC3, SC5, SC1, SC4 and SC8, which could further be divided into two groups. The first sub-group, including SC2, SC3 and SC5, represents the group with the most PPTP with the 20-percentile below or equal to LOQ/2. Within the second sub-group, with SC1, SC4 and SC8, the inputs among the individual PPTP seemed to vary the most.

The clustering of the 50-percentile and the 80-percentile data (Figure 5B and C) lead to similar clusters. Here, specifically two main clusters emerged. One was for SC2 and SC3, which are interconnected. This cluster (with SC2 and SC3) had most PPTP (10 - 13) with 50- and 80-percentiles below or equal the LOQ/2. The other main cluster comprised SC1 and SC4 - SC8, where SC1, SC4, SC5 and SC8 are interconnected and whereas SC6 and SC7 stem from headwaters. This cluster with SC1 and SC4 - SC8, could further be divided into two sub-groups. The first sub-group, including SC6 and SC7, had the most PPTP with highest inputs; and the second sub-group including the sites SC1, SC4, SC5 and SC8, had medium to high PPTP inputs (sites presented in Chapter 1.7). The fungicide, carbendazim, stood out with the highest percentile concentrations at all sites (49 – 650 ng/L).

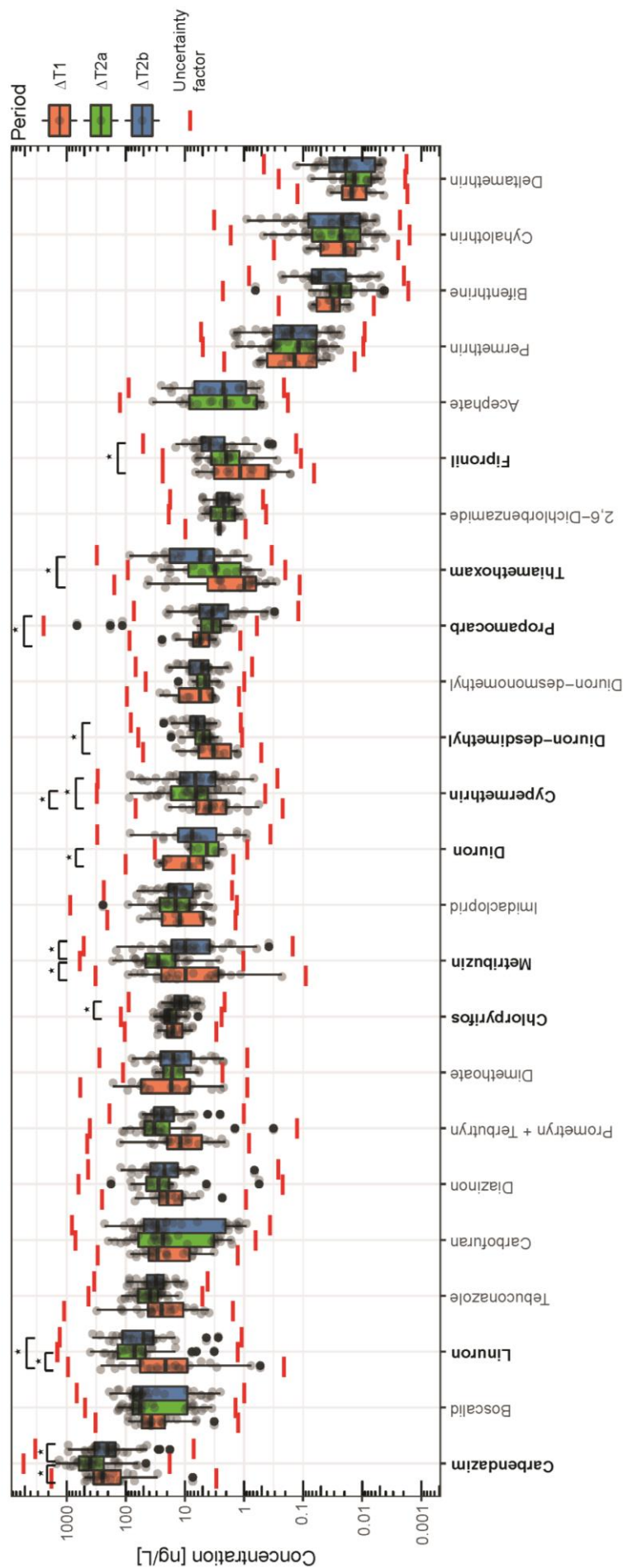


Figure 4: Overview about the spatio-temporal distribution of the 24 PPTP selected for this study. A) Concentration ranges of the considered PPTP detected at all sites within the sampling periods $\Delta T1$, $\Delta T2a$ and $\Delta T2b$. Boxplots represent first and third quartiles (outer box) and medians (thick lines). Statistical significance levels: *, $p < 0.05$, by using a one-way ANOVA, Games-Howell post hoc test in R with no assumption of equal variances, log10 transformed concentrations. The lower whiskers show the minimum values not falling below the first quartile by a factor of $1.5 \cdot$ the interquartile range. The upper whiskers show the maximum values not exceeding the third quartile by a factor of $1.5 \cdot$ the interquartile range. The black dots (vertical to whiskers) represent outliers which fall below or above the whiskers, the grey (staggered) dots represent individual concentration data points, indicating how the data is distributed (standardized boxplot using R ggplot2 package). Red lines represent uncertainties of minima and maxima values based on a factor of three for the sampling rate (R_S) values in both directions according to Curchod et al. (2019) and Moschet et al. (2014). PPTP names written in bold indicate significant differences of the concentrations among at least two of the periods.

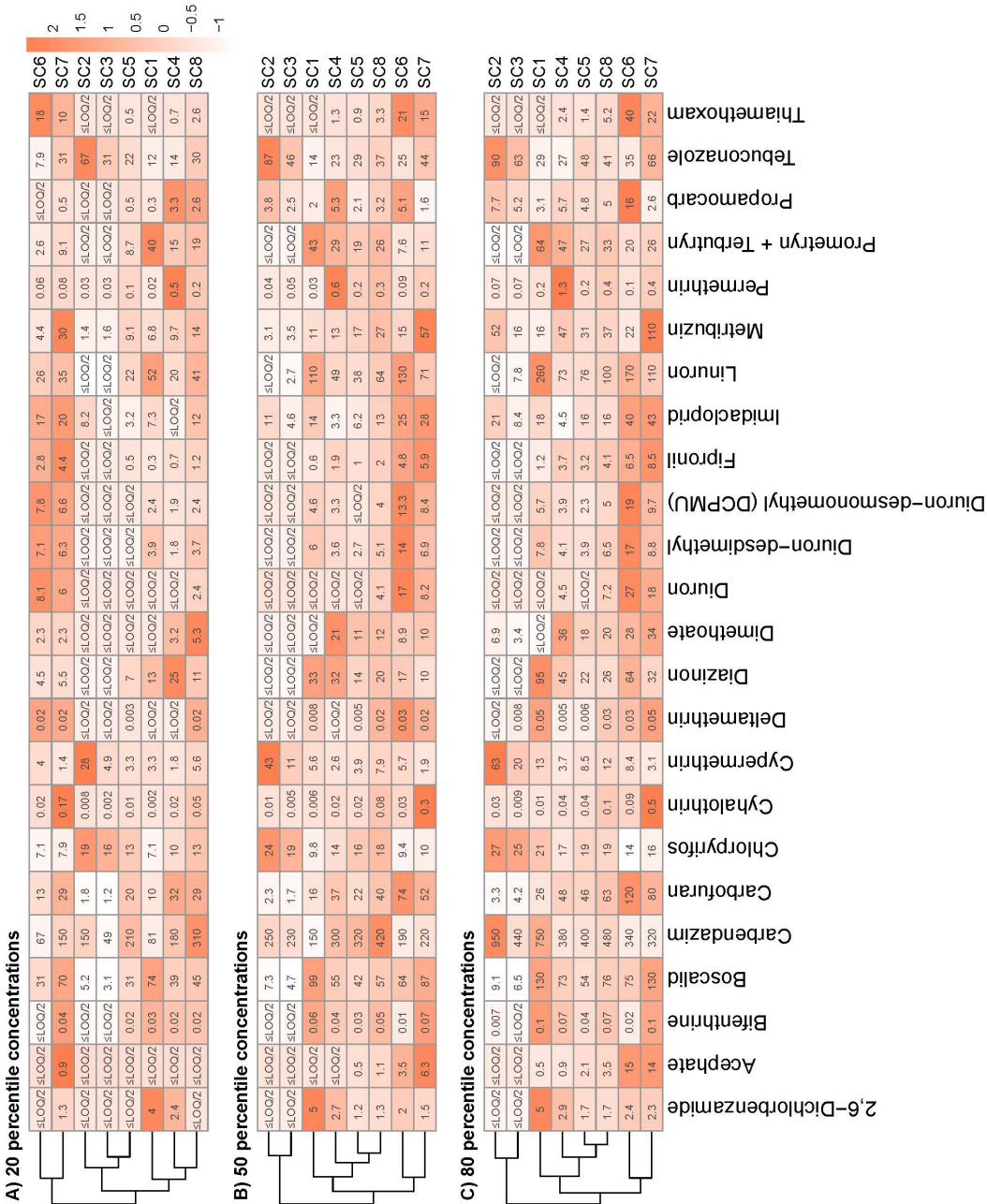


Figure 5: The 20- (A), 50- (B) and 80- (C) percentile concentrations detected at all eight sites. Percentile concentrations were scaled and clustered (hierarchical clustering, using euclidean distance and complete linkages) according to sites by using the pheatmap package in R. The numbers represent the unscaled percentiles.

During the survey that was carried out in 2016 (Staudacher et al. 2020), farmers were asked for application of different pesticides (yes/no). For a subset of seven pesticides, which were detected as well in this thesis, namely acephate, boscalid, carbendazim, carbofuran, chlorpyrifos, cypermethrin and propamocarb, survey data was available. This survey covered $\Delta T2b$ in addition to the first biweekly sampling period of $\Delta T2a$ (as described in section 4.3.5). An example of the results of these surveys, combined with the MEC, is shown in Figure 6, focusing on cypermethrin (results of remaining pesticides presented in SI-4 A4.2, Figure SI-4 A7). Cypermethrin was selected as an example of a pesticide that was frequently detected at all sites in order to depict if its broad detection is reflected with its application patterns. Indeed, the application of cypermethrin was confirmed in seven of the eight SCs according to the survey data. For acephate, chlorpyrifos and cypermethrin, the application was confirmed by the survey data at seven of the eight SCs, for boscalid and carbendazim at six of the eight SCs and for carbofuran only at SC2. Therefore, these application data showed that these pesticides (except for carbofuran) were applied from June to mid-August without a visible seasonal trend at most of the sites. For acephate and carbofuran, the survey data was not in line with the MEC. Acephate was not detected at SC2 and SC3 though applied according to the survey. Carbofuran was detected at all sites, though according to the survey, was applied only at SC2. Given these inconsistencies, and being aware of the limits of the information provided by the survey (low and varying numbers of farmers being interviewed per site), these data were not further evaluated in this study.

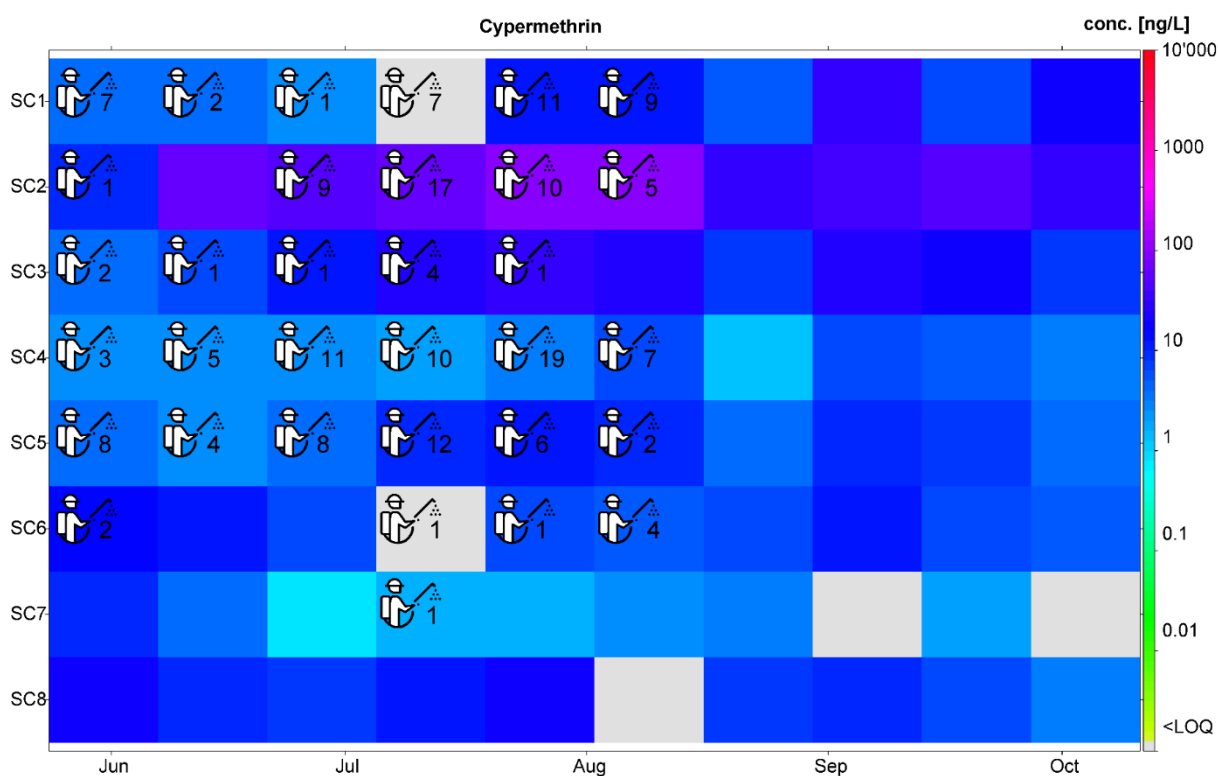


Figure 6: Overview of the spatio-temporal application and detection of cypermethrin. Icons in squares indicate application based on survey data, which referred to the period from June to mid-August ($\Delta T2b$ and first interval $\Delta T2a$). The numbers next to the icons represent how many farmers reported to have applied cypermethrin during each biweekly interval. Heatmap shows the measured environmental concentrations in ng/L.

4.4.2 Pesticide concentration peaks from handling

Pesticide inputs via handling (including inputs from cleaning as well as from direct spray drift) were identified based on visual or statistical examination as well as based on the TP/parent compound ratio of diuron. In total, 9 PPTP concentration peaks were identified to fulfil the criteria for direct inputs from handling (explained in section 4.3.4, results SI-4 A4.3; Table SI-4 A3). For three pesticides, inappropriate handling was very likely and confirmed via statistical and visual examination (dimethoate and diuron), or by showing distinct visual peaks during dry periods (thiamethoxam) as shown in Figure 7. In more detail, for thiamethoxam, inappropriate handling was very likely at SC6 during the first two sampling periods in $\Delta T1$ (Figure 7A). For dimethoate and diuron, elevated concentrations were found at SC6 in the third sampling interval of $\Delta T2b$ (Figure 7B-C). For five pesticides (bifenthrine, boscalid, deltamethrin, imidacloprid, propamocarb), the inputs from handling were thought possible but were confirmed only either visually, or statistically (SI-4 A4.3, Table SI-4 A3). With respect to the TP/parent pesticide ratios, the abrupt decreased ratio of diuron TP and its parent compound, diuron, indicated as well a direct input into the stream of diuron (Figure 7D). Water level and concentration time series of all considered PPTP are demonstrated in SI-4 B6.1 (2015) and SI-4 B7.1 (2016); water level and TP/parent compound ratio time series (diuron and carbendazim) are presented in SI-4 A5.

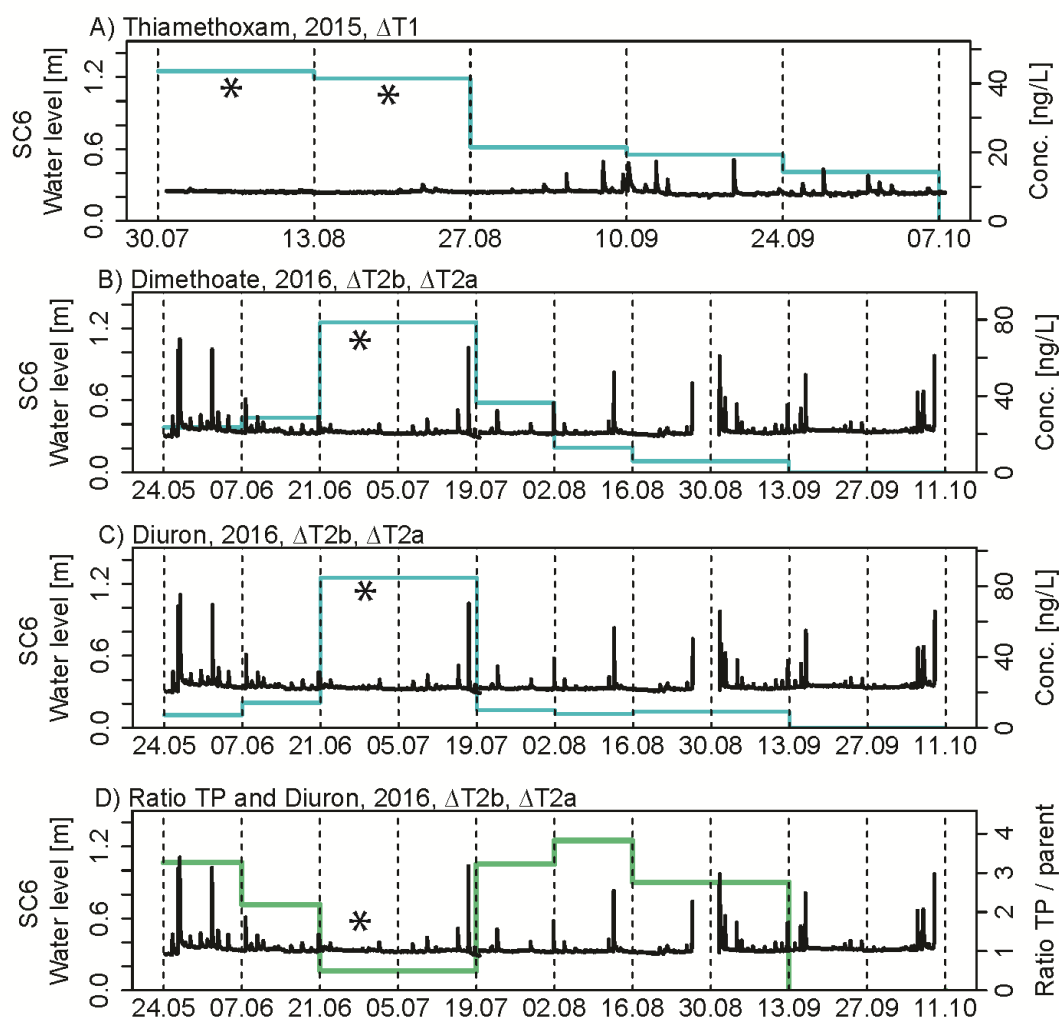


Figure 7: Identification of pesticide peaks indicative of inadequate pesticide handling using SC6 as representative example. Water levels (black lines) and biweekly concentrations (blue lines) of thiamethoxam (A), dimethoate (B), diuron (C) and the ratio of the sum of the diuron transformation products and diuron (D) are presented (green line). The left y axis present water levels and right y axis the pesticide concentrations (A-C), respectively, the ratios of the diuron TP and the parent diuron (D). Sharply decreased TP/parent pesticide ratios indicate direct inputs without long residence times of the parent compound before entering the streams (asterisk in D). Asterisks mark peaks likely originate from handling errors (A-C).

Survey data revealed that pesticide residual waters were disposed in drains adjacent to the streams or into the streams directly in three of the four headwater catchments studied here (Table 1). However, it has to be mentioned that within SC6 and SC7, only 7 and 3 farmers or field workers, respectively, were interviewed. Thus, available answers for these site may be less representative compared to the others.

Table 1: Reported disposal of water during cleaning of pesticide application equipment for farmers using synthetic pesticides in the four studied headwater SCs. The survey data (Fuhrmann et al. 2020, Fuhrmann et al. 2019, Staudacher et al. 2020) was further exploited and the answers were distributed among the individual headwater SCs.

SC	Answers (farmers and field workers)	Does not apply pesticides	In the courtyard of the house	Next to the farm	Specific place where pesticides are mixed	In the drain	in the garbage	In the river	In the biobed	Other
	Number of answering to questions about handling of pesticides	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
1	38	0.0	4.2	16.7	0.0	33.3	0.0	16.7	12.5	16.7
2	42	0.0	0.0	29.4	11.8	29.4	0.0	5.9	17.6	5.9
6	7	0.0	0.0	50.0	0.0	50.0	0.0	0.0	0.0	0.0
7	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0

4.4.3 Rain driven pesticide inputs

Catchment and hydrological explanatory variables were explored in order to delineate pesticide inputs into streams from rain driven surface run-off. In order to facilitate clear interpretation of results, those variables were selected for the weighted linear regression that were independent of each other, i.e. without showing a collinearity, which was investigated in a first step (SI-4 A6, SI-4 C4). Subsequently, the then defined explanatory variables were used within the linear regression analysis (more details, section 4.3.6) in order to investigate if these explanatory variables show effects on the percentile concentrations of the considered PPTP.

4.4.3a Variables used for modelling

Variables from catchment attributes: From the vectorized land use and digital elevation model data, nine different catchment variables were derived (Table 2) and five were tested for collinearity. The key outcome of this analysis was that among the SCs, SC1 had the highest share of horticultural land, though all SCs had a share of horticultural land exceeding ~9%; SC2 had the highest share of forest in the 100 m buffer zone radial around the streams. The longest distances between horticultural fields and streams were identified for SC1. The mean slopes of the horticultural land were lower at SC1, SC2 and SC4 as opposed to SC3, SC5, SC6, SC7 and SC8. More detailed information for each SC, about the land uses in general and in the 100 m stream buffer zone are presented in SI-4 A2, SI-4 B2 and SI4 B3.

Table 2: Variables from catchment attributes based on topographical features of the eight SCs located in the Tapezco river catchment (data from SI-4 B2 and SI-4 B3)

Sub	Horti-cultural	Horti-cultural area [#]	Weighting factor unnested area per respective total SC	Share of forest in 100 m buffer zone [#]	Distance of the horticultural fields from the river [m] with&:				Mean [#] /max [#]
Catchment	area	area [#]			10% Q* horticultural land	25% Q horticultural land	50% Q horticultural land	75% Q horticultural land	Slope horticultural land
	[ha]	[%]		[%]	[m]	[m]	[m]	[m]	[%]
SC1	17.2	55.6	1	32.3	130	235	365	460	3.3/9.5
SC2	21.9	11.8	1	79.7	45	90	155	230	7/43.2
SC3	39.1	8.9	0.58	78	50	110	200	290	8.3/59.1
SC4	236.7	30.4	0.40	54	100	190	285	410	6.1/41.5
SC5	390.4	18.2	0.64	68	90	170	260	370	9.9/65.2
SC6	144.7	36.2	1	39.1	100	180	290	400	10.2/41
SC7	106.7	17.2	1	49.6	100	170	290	425	11.8/50.1
SC8	689.4	19.2	0.12	62	95	170	270	390	10.6/65.2
Standard deviation among the sites	217.8	14.42	0.3	16.3	26.3	42.5	59.2	70	2.6

*Q = quantile.

[#] tested for collinearity; from distance of the horticultural fields from the river, only 75%Q values were selected since the 10% Q, 25% Q, 50% Q and 75% Q data was similarly distributed among the SCs (Figure SI-4 A2.1).

& Additional information about the relation between the radial distance from the streams and the cumulative horticultural land in percent are presented in SI-4 A2.

Hydrological variables from water levels: In a first analysis, biweekly periods with rain events influencing the water level (indicated as biweekly period with water level factors higher than 1.3, see section 4.3.3), were observed almost continuously at all SCs (SI-4 A3.1, SI-4 A3.2). Drier periods with biweekly water level factors < 1.3 (Eq. 4.2) were only occasionally observed. For illustration, the water level time series of SC6 from 2016 ($\Delta T2b$ and $\Delta T2a$) was selected showing such a drier period during the third biweekly sampling interval (Figure 8). From the water level data for each SC two variables were derived and tested for collinearity, namely the median water level factor exceeding minimum weekly water level and median cumulative water level per period [m] (SI-4 B2, based on the data of SI-4 A3.1, SI-4 A3.2 and equations of section 4.3.3).

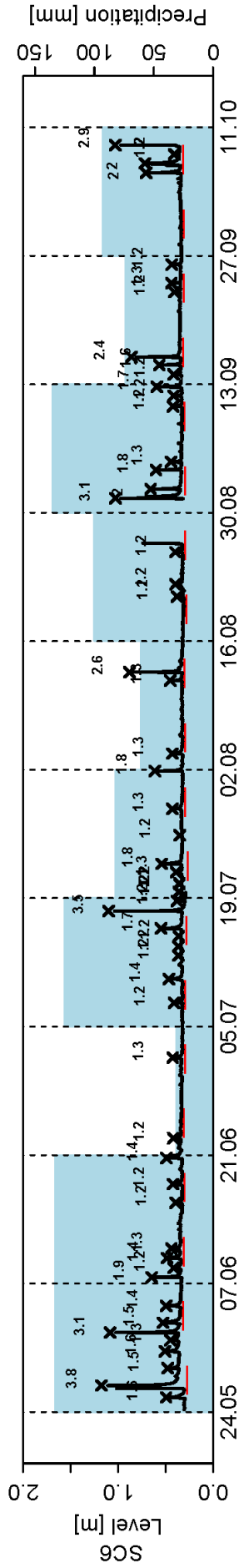


Figure 8: Water level and precipitation time series at SC6. Data from $\Delta T2b$ (24th May to 2nd of August) and $\Delta T2a$ (2nd of August to 11th October) in 2016 are presented. Water levels are presented on the left y axis (black line) and precipitations on the right y axis (blue bars). Red lines represent the minimum weekly base water levels; numbers represent the factor of water level peak maxima exceeding the weekly base water level. Water level factors above a variation of 30% (i.e. factor above 1.3) were defined as peaks from precipitations influencing the water level. X show water level factors above or equal to 1.2.

For modelling from the seven explanatory variables, two were selected, namely average slope of horticultural area and median biweekly water level factor, which showed no inter-correlation among each other as demonstrated in SI-4 A6, similar to the approach of Schreiner et al. (2021) and as described in section 4.3.6. As exception, the two explanatory variables, the share of horticultural fields and the share of forest in the 100 m river buffer area were selected even though they anti-correlated with each other (SI-4 A6, $R = -0.89$) since they were considered as important variables. The share of horticultural area was used since this variable was expected to describe the pesticide concentrations at the outflow of each SC (section 4.3.6); and share of forest in 100 m buffer zone was used as well to demonstrate if in SCs with stream buffer areas with a high share of forest, the pesticide inputs were lower than in others with low share of forest in the buffer zone. Except for the two latter variables, generally if two variables correlated with each other, only one of those variables was selected for the modelling. For example, the share of forest in the 100 m river buffer area was strongly anti-correlating with the radial distance from the streams with 75% of horticultural land. However, in the model outputs, due to the anti-correlation of these variables, it cannot be clearly distinguished if the concentrations decrease with increasing share of forest, or if concentrations decrease with decreasing radial distance from the streams with 75% of horticultural land. The share of 100 m river buffer area was then selected as variable for this study because it is not plausible that concentrations decrease with decreasing distance of the horticultural land. This triage resulted in four previously described explanatory variables that were subsequently considered as potentially important drivers of surface run-off into streams (section 4.3.6).

4.4.3b Evaluation of important drivers influencing rain driven pesticide inputs

From the 24 PPTP investigated, the linear regressions for carbendazim were explored first as this was the pesticide with the highest percentile concentration among all SCs (see Figure 5). The weighted linear regressions for carbendazim are presented in Figure 9, residual and Q-Q plots are presented in SI-4 A7 (created as described in SI-4 C6). Within this study, correlations between the explanatory and dependent variable were considered reliable if 50% of the variations of the percentiles were explained by the explanatory variables ($R^2 \geq 0.5$) and, at the same time, p values were < 0.05 . If p values fall below 0.05, the null hypothesis was rejected, meaning that the slope was not equal to zero and the explanatory variable significantly affected the percentile concentration.

The results show that for carbendazim during the 20-percentile and the 50-percentile concentration scenarios the explanatory variables could not explain the variation of the percentile concentrations (Figure 9) as presented by the low R^2 values (< 0.5) and p values above 0.05. In the 80-percentile scenario, the explanatory variable mean slope horticulture could explain 60% of the variations ($R^2 = 0.6$) and was significant ($p < 0.05$). In this case, the higher the mean slope, the lower were the carbendazim percentile concentrations, a finding which was unexpected.

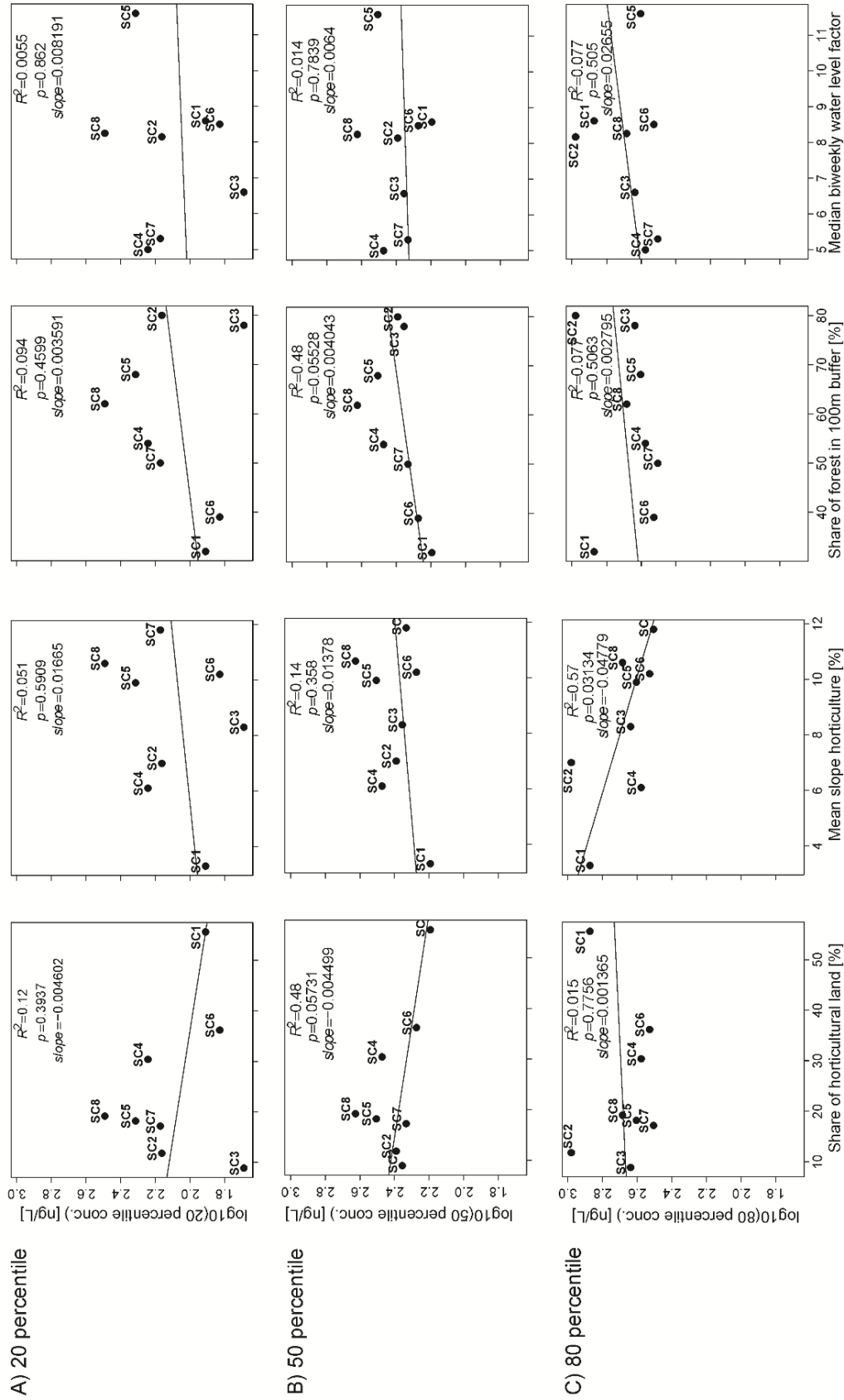


Figure 9: Influences of the explanatory variables on the percentile concentrations of carbendazim within the applied linear regression model. For linear correlations, the topographic and hydrological variables for each SC were used as explanatory variables and the 20-, 50- and 80-percentile concentrations were used as dependent variable. A weighting was conducted according to the ratio between the unnested area and the entire nested area per each SC (described section 4.3.6). The black lines show the linear regressions.

An overview of the linear regression data of all 24 PPTP is provided in Table 3 (individual regressions were estimated as described in SI-4 C5, and correlation scatter plots for 20-, 50- and 80-percentile concentration regressions and corresponding residual and normal-QQ plots are presented in SI-4 B8.1, SI-4 B8.2 and SI-4 B8.3, respectively). The most striking result to emerge from this analysis was that, when considering all three scenarios (20-, 50- and 80-percentiles), for most of the weighted linear regression no clear general trends and very compound specific patterns were observed. To be more precise, it was surprising that in most of the cases the percentile concentrations did not increase with the share of horticultural area. Only for 2,6-dichlorbenzamide did the concentration significantly increase with increasing share of horticultural area, observed during all three scenarios. The same was true for diazinon in the 50- and 80-percentile scenarios ($p < 0.03$). In addition, the median biweekly water level factor did not correlate significantly at all with the percentile concentrations for all three scenarios.

Only the two remaining explanatory variables, the share of forest in 100 m river buffer, and the mean slope of the horticultural fields, showed influences on the inputs for some PPTP.

With respect to the share of forest in the 100 m buffer zone, the influence on the percentile concentrations was the highest. For example for five PPTP, boscalid, diazinon, diuron-desdimethyl, linuron and prometryn + terbutryn, the percentile concentrations decreased significantly with increasing share of forest in 100 m river buffer zone ($p < 0.05$) for all three scenarios. For 2,6-dichlorbenzamide, carbfouran, deltamethrin and diuron-desmonomethyl, this latter relationship was observed at least for the 50- or the 80-percentile scenario, or for even both of these scenarios. Based on the medium and higher input scenario (50- and 80-percentile, respectively), the share of forest in the 100 m buffer zone correlated negatively for a broader variety of PPTP than during the low input scenario. Even though the share of forest in 100 m stream buffer zone was anti-correlating with the share of horticultural land, the correlations between the share of forest in 100 m river buffer and concentration percentiles seemed more pronounced, leading to significant effects for a higher number of PPTP as with the share of horticultural land.

Regarding the horticultural mean slope, for cyhalothrin and thiamethoxam, the percentile concentrations increased with increasing mean slopes of the horticultural areas for all three scenarios. For acephate, the concentrations increased with mean slopes of horticultural areas during the 50- and 80-percentile scenarios. For the remaining compounds, the pattern was more different and for deltamethrin and fipronil, the 20-percentile increased significantly with increasing slopes of horticultural areas, and diuron during the 20- and 50-percentile scenario. For the remaining compounds, no clear trend was observed for the discussed explanatory variable.

Generally, it was observed that a natural riparian area with a 100 m natural buffer zone led to decreased inputs; and in some cases, increased mean slopes led to higher inputs. However, this trend was not observed for all PPTP. For example for tebuconazole, the inputs increased with increasing share of forest in the 100 m stream buffer area considering all three scenarios, and for chlorpyrifos, the inputs increased with increasing share of forest in the 100 m buffer area during the 20- and 50-percentile scenario. For carbendazim, the 80-percentile concentrations decreased with increasing mean slope of horticultural area (as demonstrated as well in Figure 9).

Table 3: Statistics of the linear regressions between the explanatory variables and the different percentile concentrations for 24 PPTP. For correlations with $R^2 \geq 0.5$ and p values < 0.05 , the slope is indicated in blue or red. Red = significant positive correlation, blue = significant negative correlation.

Correlation statistics		2,6-dichlorobenzamide												Prometryn + Terbutryn												Thiamethoxam		
		Acaphate	Bifenthrine	Bocallid	Carbendazim	Carbofuran	Chlorpyrifos	Cyhalothrin	Cypermethrin	Deltamethrin	Diazinon	Dimethoate	Duron	Duron-desdimethyl	Duron-desmonomethyl	Fipronil	Imidacloprid	Linuron	Metribuzin	Permethrin								
A) 20 percentile																												
	Horticultural land	R^2	0.6	0.07	0.1	0.4	0.1	0.1	0.1	0.001	0.5	0.00007	0.0009	0.4	0.07	0.004	0.03	0.5	0.04	0.05	0.5	0.004	0.5	0.004	0.6	0.0006	0.6	0.0006
	[%]	p	0.029*	0.52	0.43	0.087	0.39	0.38	0.37	0.45	0.93	0.98	0.94	0.13	0.54	0.88	0.71	0.066	0.65	0.58	0.051	0.89	0.051	0.89	0.02*	0.95	0.02*	0.95
	Mean slope	R^2	0.5	0.3	0.003	0.002	0.05	0.1	0.002	0.7	0.09	0.6	0.5	0.04	0.3	0.5	0.2	0.006	0.2	0.2	0.03	0.0003	0.02	0.03	0.0003	0.02	0.6	0.036*
	horticulture [%]	p	0.065	0.13	0.91	0.93	0.59	0.43	0.91	0.014*	0.48	0.017*	0.045*	0.65	0.16	0.042*	0.32	0.86	0.34	0.26	0.69	0.97	0.78	0.97	0.78	0.036*	0.036*	
	Share of forest	R^2	0.4	0.02	0.2	0.7	0.09	0.4	0.9	0.005	0.4	0.2	0.6	0.8	0.4	0.3	0.2	0.8	0.3	0.0006	0.6	0.02	0.7	0.2	0.7	0.2	0.2	
	in 100m buffer [%]	p	0.081	0.74	0.25	0.0092*	0.46	0.09	0.00008*	0.87	0.11	0.32	0.026*	0.5	0.25	0.003*	0.077	0.055*	0.18	0.95	0.02*	0.76	0.01*	0.76	0.01*	0.26	0.26	
	Median biweekly	R^2	0.04	0.4	0.06	0.002	0.006	0.008	0.02	0.2	0.1	0.04	0.003	0.3	0.09	0.1	0.1	0.04	0.08	0.08	0.002	0.08	0.03	0.09	0.03	0.09	0.09	
	water level factor	p	0.63	0.11	0.57	0.91	0.86	0.84	0.77	0.3	0.43	0.62	0.97	0.19	0.47	0.41	0.43	0.44	0.51	0.58	0.91	0.5	0.67	0.48	0.48	0.48	0.48	
B) 50 percentile																												
	Horticultural land	R^2	0.9	0.005	0.2	0.4	0.5	0.2	0.5	0.06	0.08	0.07	0.6	0.01	0.002	0.4	0.2	0.05	0.08	0.5	0.03	0.1	0.5	0.0004	0.8	3E-06	0.8	3E-06
	[%]	p	0.00029*	0.86	0.24	0.071	0.057	0.29	0.0503	0.55	0.51	0.52	0.03*	0.81	0.92	0.087	0.22	0.6	0.51	0.064	0.71	0.42	0.052	0.96	0.0035*	0.96	0.997	
	Mean slope	R^2	0.2	0.6	0.004	0.007	0.1	0.2	0.009	0.6	0.1	0.4	0.006	0.4	0.5	0.05	0.1	0.4	0.1	0.02	0.3	0.4	0.006	0.004	0.1	0.6	0.6	
	horticulture [%]	p	0.23	0.017*	0.88	0.84	0.36	0.3	0.82	0.02*	0.37	0.12	0.85	0.075	0.049*	0.59	0.42	0.11	0.4	0.77	0.16	0.1	0.86	0.88	0.36	0.36	0.36	
	Share of forest	R^2	0.9	0.2	0.5	0.8	0.5	0.6	0.9	0.04	0.4	0.4	0.7	0.05	0.2	0.8	0.7	0.4	0.3	0.8	0.3	0.003	0.7	0.02	0.7	0.2	0.2	
	in 100m buffer [%]	p	0.001*	0.33	0.06	0.004*	0.055	0.034*	0.00003*	0.62	0.12	0.083	0.006*	0.59	0.25	0.0024*	0.013*	0.097	0.14	0.0028*	0.15	0.9	0.015*	0.74	0.0096*	0.74	0.0096*	
	Median biweekly	R^2	0.0002	0.1	0.03	0.0006	0.01	0.005	0.03	0.2	0.07	0.002	0.01	0.02	0.07	0.0001	0.09	0.06	0.02	0.0002	0.07	0.08	0.01	0.004	0.05	0.09	0.09	
	water level factor	p	0.97	0.44	0.68	0.95	0.78	0.86	0.72	0.27	0.52	0.92	0.79	0.74	0.51	0.98	0.48	0.55	0.74	0.97	0.54	0.49	0.79	0.88	0.59	0.48	0.48	
C) 80 percentile																												
	Horticultural land	R^2	0.8	0.001	0.2	0.4	0.02	0.2	0.09	0.08	0.04	0.3	0.6	0.2	0.001	0.4	0.3	0.08	0.002	0.5	0.3	0.03	0.5	0.07	0.7	0.00004	0.7	0.00004
	[%]	p	0.0045*	0.94	0.26	0.087	0.78	0.31	0.48	0.51	0.64	0.16	0.028*	0.31	0.94	0.088	0.18	0.5	0.92	0.06	0.15	0.71	0.06	0.53	0.0067*	0.99	0.99	
	Mean slope	R^2	0.08	0.6	0.006	0.009	0.6	0.2	0.3	0.7	0.2	0.05	0.00005	0.7	0.5	0.05	0.1	0.3	0.3	0.007	0.3	0.05	0.0002	0.0006	0.1	0.6	0.6	
	horticulture [%]	p	0.51	0.023*	0.85	0.82	0.031*	0.26	0.15	0.01*	0.25	0.59	0.99	0.011*	0.059	0.59	0.42	0.17	0.21	0.85	0.16	0.6	0.98	0.96	0.36	0.36	0.36	
	Share of forest	R^2	0.9	0.2	0.4	0.8	0.08	0.5	0.4	0.03	0.3	0.7	0.9	0.002	0.2	0.8	0.7	0.4	0.1	0.8	0.07	0.2	0.7	0.2	0.6	0.2	0.2	
	in 100m buffer [%]	p	0.00054*	0.24	0.073	0.0055*	0.51	0.039*	0.073	0.66	0.15	0.0084*	0.0012*	0.92	0.25	0.0028*	0.0088*	0.082	0.41	0.005*	0.52	0.35	0.0096*	0.29	0.02*	0.29	0.29	
	Median biweekly	R^2	0.0003	0.03	0.04	0.005	0.08	0.001	0.03	0.2	0.1	0.05	0.004	0.07	0.2	0.0004	0.03	0.01	0.0001	0.0005	0.3	0.1	0.005	0.1	0.03	0.08	0.08	
	water level factor	p	0.97	0.7	0.64	0.87	0.51	0.94	0.69	0.31	0.37	0.6	0.88	0.53	0.29	0.96	0.67	0.78	0.98	0.96	0.2	0.37	0.87	0.45	0.69	0.51	0.51	
			Positive correlation/slope												p<0.05 = *													
			Negative correlation/slope																									

As explained in section 4.2.5, a comparison of observed data with predicted modelled data was conducted as well by using the determined correlation parameters of the weighted linear model. These comparison plots were created as described in SI-4 C7 for the 20-, 50- and 80-percentile concentrations. The plots are shown in SI-4 B9.1, SI-4 B9.2 and SI-4 B9.3. These analyses comprise a base to investigate if it is possible to predict the percentile concentrations of these PPTP per each site with the weighted linear regression and one of the available explanatory variables. The better the predicted and the observed values were located on or close to the 1:1 line between the observed and predicted data the better was the fit of the applied weighted linear model. If the fitting between the predicted and the observed values was poor, this indicates that further improvements of the modelling could be conducted in the future.

4.4.4 Exfiltration of pesticides via groundwater

In the groundwater samples from the drinking water tank in SC1, a broader spectrum of PPTP was found as opposed to the samples of the tank in SC7. Specifically for SC1, four pesticides were detected at maximum concentrations between 2 and 6 ng/L and four TP were found with maximum concentrations between 1.1 and 47 ng/L. In the drinking water from SC7, only iodopropynyl butyl-carbamate (IPBC) was detected with maximum concentrations up to 36 ng/L (Table 4).

According to the linear regression analysis, data inputs via exfiltration could not clearly be identified. The median biweekly water level factor did not show any clear negative correlations (p values below 0.05) with either the 20-, 50- and 80-percentile scenario among the sites (Table 3).

Table 4: Maximum pesticides and TP concentrations in grab samples from groundwater-fed drinking water tanks and their physicochemical characteristics. Drinking water tanks were located in the headwater catchments SC1 and SC7.

Compound	Type	Log K _{ow} *	Log KOC*	Water solubility at 25°C [mg/L]*	LOQ [ng/L]	Maximum concentration [ng/L] at SC1	Maximum concentration [ng/L] at SC7
Acetochlor-ESA + Alachlor-ESA	TP herbicide	1.82	1.07	0.25	2.4	5	< LOQ
Boscalid	Fungicide	2.96	3.98	4.60	2	2.4	< LOQ
Bromoxynil	Herbicide	2.70	2.52	130	0.2	< LOQ	< LOQ
Carbendazim	Fungicide	1.52	2.58	29	4	6	< LOQ
Chloridazon-desphenyl	TP herbicide	-1.59	1.56	87'820	6	15	< LOQ
Chlorothalonil-4-hydroxy-carbonacid amide	TP fungicide	3.09	2.92	115.70	1	47	< LOQ
Cyromazin	Insecticide	0.96	1.46	13'000	0.4	< LOQ	< LOQ
Dimethomorph	Fungicide	2.36	3.76	49.20	0.6	2	< LOQ
Imidacloprid	Insecticide	-1.45	3.69	369'200	0.9	< LOQ	< LOQ
Metribuzin	Herbicide	1.49	1.73	1'304	1	9.9	< LOQ
Metribuzin-Desamino (DA)	TP herbicide	2.51	2.46	318	0.4	1.1	< LOQ
IPBC	Fungicide	2.45	2.46	126.60	9	< LOQ	36

* taken from [EPISuite4.L.](#)

The TP/parent ratios can provide as well information about possible inputs via exfiltration (section 4.3.7). The water level and 2,6-dichlorobenzamide/carbendazim ratio time series in streams of SC1 and SC7 are presented in Figure 11. For carbendazim, the highest TP/carbendazim ratio at SC1 was five times higher than the highest ratio at SC7 (0.1 vs 0.02, Figure 10). At SC1, the ratios were higher as opposed to SC7. For diuron, at SC1 only for one biweekly period a TP diuron/diuron ratio could be determined (section SI-4 A8, Figure SI-4 A12), therefore a comparison of the ratios among both sites was not possible.

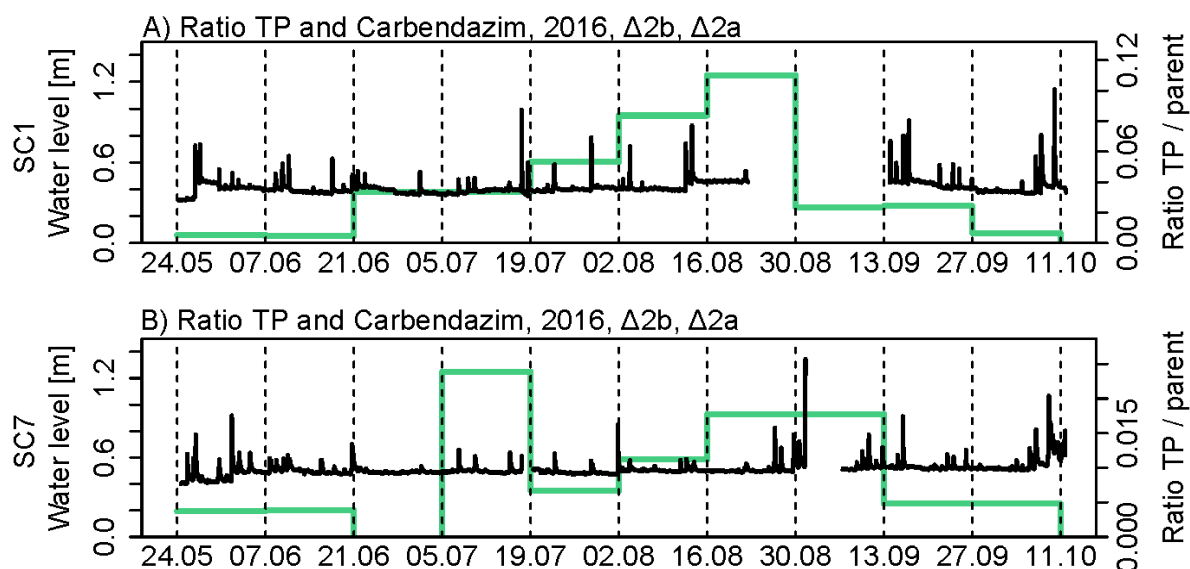


Figure 10: Identification of highest carbendazim TP/carbendazim ratio at SC1 (A) and SC7 (B). Water levels (black lines) and the ratios of the carbendazim TP and the parent carbendazim (blue lines) are presented. The left y axis present water levels and right y axis the ratios of the carbendazim TP and the parent carbendazim. Elevated ratios among the SCs are used to indicate inputs with long residence times and advanced transformation of the parent compound before entering the streams.

4.5 Discussion

4.5.1 Spatio-temporal pesticide distribution

The concentrations of the PPTP considered in this study were generally comparable between the sampling periods. This was true despite the fact that the time intervals included periods with below average ($\Delta T1$) and with average precipitation ($\Delta T2a$, $\Delta T2b$) as shown in Figure 4. Accordingly, it can be concluded that for these PPTP within the studied catchment, precipitation seemed not to be the only main driver for pesticide inputs into streams, a finding that is similar to that described by Leu et al. (2004a) for herbicides. Handling, application practices and disposal of leftovers could lead to a significant pesticide input within the Tapezco river catchment also during dryer periods, as also previously reported for atrazine and diazinon in Switzerland (Wittmer et al. 2010). The fact that for two PPTP (diuron and propamocarb) the concentrations were higher in the dryer period, $\Delta T1$, than in one of the periods with usual precipitation ($\Delta T2b$, $\Delta T2a$) further confirms that PPTP inputs can be influenced by variables other than precipitation.

For a smaller selection of PPTP (carbendazim, linuron, metribuzin, cypermethrin, diuron-desdimethyl, thiamethoxam and fipronil, Figure 4), the concentrations were higher during the periods with more precipitation, indicating the possibility of precipitation-related surface run-off. However, it was observed that for these PPTP, physicochemical characteristics typically associated with mobility (such as water solubility, low log K_{ow} , log K_{oc}) varied widely (SI-4 A8). Accordingly, even PPTP with a low water solubility and high log K_{ow} and log K_{oc} reached highest concentration levels during $\Delta T2a$ and $\Delta T2b$. This observation is in line with the results of prior studies (Leu et al. 2004b, Schriever et al. 2007), showing that in some cases, the impact of environmental factors may override the influence of physicochemical characteristics. It might be that, due to the fact that crops are cultivated on steep slopes and due to strong hydrological dynamics in the Tapezco catchment, even compounds with high log K_{ow} and log K_{oc} and low water solubility enter the streams after strong rain events. It has to be noted that, for pesticides entering the streams directly via inappropriate handling, their inputs are expected to be independent of their physicochemical characteristics as well. However, for the leaching of PPTP into the ground and inputs via exfiltration, the physicochemical characteristics play an important role (Mechelke et al. 2019, Romero et al. 2010, Verstraeten et al. 2003) and were taken into account (section 4.5.4).

The PPTP were spatially distributed throughout the catchment though SC2 and SC3 stood out considering all three scenarios. They were distinct by having several PPTP that were below the level of detection ($\leq LOQ/2$) and others that were detectable but at levels below those found in other SCs (Figure 5). It is plausible that the percentile concentrations are similar in SC2 and SC3 since SC2 flows into SC3. The low inputs might be explained by the share of agricultural area, which was the lowest for SC2 and SC3. As demonstrated in a prior study (Szöcs et al. 2017), the percent of agricultural land within a catchment on pesticide concentrations is more important than the catchment size. Nevertheless, at the 80-percentile scenario, some chemicals were found at high levels in SC2 and/or SC3, especially carbendazim, chlorpyrifos, cypermethrin and tebuconazole. For these PPTP and SCs, direct inputs from handling could not be confirmed. Spatially distinct crop patterns might instead lead to high inputs of these pesticides. Potatoes, for example, require intensive treatment with fungicides, such as carbendazim and tebuconazole. However, due to a lack of detailed crop data this assumption could not be tested. Available survey data (Staudacher et al. 2020) did not reveal differences in pesticide application patterns among SC1-SC5, at least for seven PPTP (SI-4 A4.2, Figure SI-4 A7). The site-dependent distribution of PPTP seemed very similar using the 50- and the 80-percentile scenarios, shown due to the identical site specific cluster formation.

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Of the 21 parent pesticides considered here, 19 had been confirmed within the Tapezco river catchment in a prior study (Ramírez et al. 2016). In their study, only the application of cyhalothrin and diuron could not be confirmed. The other set of recent survey data from the Tapezco river catchment confirmed as well the application of seven (acephate, boscalid, carbendazim, carbofuran, chlorpyrifos, cypermethrin and propamocarb) of the 21 parent pesticides (Staudacher et al. 2020). Their survey-based application data provided relevant insights about the spatio-temporal application of these pesticides, showing that six pesticides were applied with high spatio-temporal frequencies. This was as well reflected in the MEC for chlorpyrifos, boscalid, carbendazim, cypermethrin and propamocarb. For carbofuran and acephate, the MEC patterns are not in line with the application survey data (SI-4 A4.2, Figure SI-4 A7) (Staudacher et al. 2020). Therefore, it has to be noted that the survey data is limited. A specific selection of farmers were asked sporadically and not all farmers were surveyed during each biweekly interval and at all sampling sites. This made it impossible to precisely correlate stated applications with MEC.

4.5.2 Pesticide inputs from handling

Inputs from inappropriate handling were very likely for three pesticides (thiamethoxam, dimethoate and diuron, Figure 7) and possible for five pesticides (bifenthrine, boscalid, deltamethrin, imidacloprid and propamocarb, SI-4 A4.3) according to the analysis of the time series of the concentrations and water levels. Thus, inputs from handling comprised pesticides from all pesticide types studied (herbicides, insecticides and fungicides). Available survey data (Staudacher et al. 2020) also confirmed that a direct input of pesticides into streams from inappropriate handling practices is possible within the Tapezco river catchment. While presence of pesticides in Costa Rican streams has been shown in several studies (Carazo-Rojas et al. 2018, Echeverría-Sáenz et al. 2018, Echeverría-Saenz et al. 2012, Rämö et al. 2018), none have attempted to relate the observed pesticide concentrations to direct inputs from handling.

Therefore, this study revealed that the education of farmers and field workers in sound handling of pesticides needs to be improved. Particularly, the washing of the pesticide equipment near streams and the disposal of leftovers, including washing water, into streams, seemed to be frequent practice and should be avoided. One way to achieve this would be through workshops held for local farmers and field workers. Such measures are raising awareness of risks from pesticides to humans and the environment and improve application and handling practices (Hashemi et al. 2009, Martin and Hurst 2014, Walker and Farmer 2013). Moreover, it can be recommended to implement measures that facilitate proper handling, such as specific areas with biobeds or filter stations for safe disposal (Castillo et al. 2008). In fact, introduction of biobeds within the Tapezco river catchment has been initiated by Laboratorio de Análisis de Residuos de Plaguicidas (LAREP) and the Universidad Nacional in Heredia, Costa Rica after 2016. Biobeds are simple constructions intended to collect pesticide residuals during handling and cleaning of pesticide equipment. Generally they are pits in the ground filled with three layers: a water resistant clay bottom layer to prevent leaching of pesticides into the ground, a middle layer with a mixture of straw, peat and soil (50:25:25 vol%) and a top grass layer (Castillo et al. 2008). As reported by Staudacher et al. (2020), these biobeds are being used already by at least some farmers and field workers, though their use should be further extended to protect the streams from handling-related pesticide inputs.

4.5.3 Pesticide inputs from surface run-off discharges

Indeed, in discussion with scientists from the Universidad Nacional, Heredia, topography and hydrology were empirically seen as very important drivers to explain pesticide inputs into streams. Based on the weighted linear model, it was difficult to find relations between the topographic and hydrological explanatory variables and the percentile concentrations from eight SCs. Only the two explanatory variables, the share of forest in the 100 m stream buffer area, and the average slopes of the horticultural areas per SC stood out and showed highest effects on the percentile concentrations ($R^2 \geq 0.5$ and $p < 0.05$) for several PPTP.

In more detail, with respect to the medium and higher input scenario, the share of forest in the 100 m stream buffer zone correlated negatively for a variety of PPTP (eight or nine, respectively), more so than during the low input scenario (five PPTP). This indicates that for these PPTP a 100 m river buffer zone with a high share of forest seemed to be a potential barrier to attenuate discharges from run-off. This finding is consistent with Reichenberger et al. (2007) and Parkyn (2004) who showed that, at sites with stream buffers containing a high share of forest, pesticide concentrations in the streams were lower than in areas without such buffer zones. However, this relationship did not hold true for all pesticides. For example, for the fungicide, tebuconazole, and the insecticide, chlorpyrifos, the input into the streams was not reduced but even increased for at least one of the scenarios, in areas with natural riparian stream buffers containing a high share of forest. The remaining PPTP did not show significant correlations at all between the share of forest in the 100 m buffer area and the MEC percentiles. This discrepancies could be attributed to the presence of critical source areas (explained section 4.2.3) occurring at specific fields in the SCs. As demonstrated in previous studies (Doppler et al. 2014, Pionke et al. 2000), it is possible that even small parts of a catchment (even individual fields) can represent critical source areas and contribute to a significant transport of agricultural pollutants from the fields into the streams. In these cases, the fields might be well connected to the streams via ditches, streets or other hydrologically connecting pathways. Detailed information to explore the role of such hydrology-based connectivity, however, was not available for this study, clearly a limitation of the output of the weighted linear regression model.

The only consideration of connectivity within this study was the radial distance in meters from the streams containing 75% of the horticultural land (section 4.3.2). Due to the strong anti-correlation between the radial distance containing 75% horticultural land and the share of forest in 100 m river buffer zone (SI-4 A6), it is important to bear in mind that the use of the radial distance containing 75% as explanatory variable would lead to correlations with inverse plus/minus sign. Accordingly, using the radial distance instead of the share of forest would lead to inverse variable and concentration relations. This would mean that for some pesticides, the concentrations are increasing with increasing radial distance with 75% horticultural fields. Such trends can only be further explored based on detailed knowledge of critical source areas within the SCs. However, critical source areas are not mapped yet within the Tapezco river catchment. Hence, for the evaluation of the variables for modelling, it was assumed that the fields were more or less well connected to the streams due to the slope-directed pathways on the fields as illustrated in Figure 2, and that, therefore, the share of forest is the better suited variable explaining the estimated effects. It can, nevertheless, not be excluded that the variables, share of forest in the 100 m river buffer and the radial distance with 75% horticultural area, are influencing each other. To more thoroughly understand the transport behavior of these pesticides with regard to forested buffer zones and general connectivity, further studies need to be undertaken. One potential avenue for investigation is the role of the flow directed paths on the fields as critical source areas or other topographical features, such as ditches and streets. Such features can be recorded by field visits.

One of the other findings, namely that for several pesticides (e.g. cyhalothrin and thiamethoxam), increased average slope of horticultural fields lead to increased inputs is in line with a previous study conducted on fields with different slopes in the Waikato Region, New Zealand (Müller et al. 2004). There, the slope of the fields affected cumulative runoff, and the losses of applied herbicides significantly. At areas with 30% slopes, maximum losses of 65% were reached, whereas at fields with 20% slope, the herbicide losses were $\leq 1\%$. Considering the 50- and 80-percentile regressions it seems that particularly for the insecticides, acephate, cyhalothrin and thiamethoxam, increased inputs are found at SCs that are characterized by horticultural areas with an elevated average slope, such as SC6, SC7 and/or SC8 (Table 3, SI-4 B8.2 and SI-4 B8.3). Indeed, for several insecticides, the highest concentrations were found in the areas with the highest mean average slopes, though this did not hold true for all pesticides. For instance in the 80-percentile concentration scenario for carbendazim, the average slope showed a significant negative relationship with its percentile MEC.

Considering these findings, a shift of crops requiring a high demand of the insecticides, acephate, cyhalothrin and thiamethoxam, from fields with steep slopes to areas with gentle slopes might help to reduce the input of these types of pesticides into streams. Alternative pesticide application practices should also be considered and applied more broadly. For example, the spread of insects could be controlled by use of insect pheromones, insect growth regulators or application of natural enemies including parasitoids and predators (Perveen 2012). As alternative practice to herbicides, it needs to be investigated if the removal of weeds by tillage with tractors is possible for fields on such steep slopes. Another option is controlling weeds by mulching (Bond and Grundy 2001). Manual cutting at the soil surface would be another possible alternative to the conventional herbicide-based weed control practice (Bond and Grundy 2001). Since the Tapezco river catchment is a relatively new study area it is difficult to evaluate how the local farmers accept the use of alternative approaches to pesticides. However, according to recent survey data, 10% of the farmers within the Tapezco river catchment conducted organic farming practices (Staudacher et al. 2020). The previously described alternative pest control practices are proposed by local researchers (Ramírez et al. 2016). For several of the organic farmers, such alternative pest control practices are already accepted, feasible and applied. By providing attractive incentives e.g. that farmers receive state subsidies for organic pest treatment products, the share of organic cultivation practices could be increased in the future. Nevertheless, the results indicate as well that the input patterns varied in a compound-specific manner and that the relocation of pesticide-intensive crops from fields with steep slopes may not be an all-encompassing solution to reduce insecticide inputs. This was illustrated by carbendazim for which highest inputs were observed in areas with low average slopes as well (Table 3, Figure 9, SI-4 B8.3). Based on the weighted linear regression analysis, the median water level factors did not explain the variety of the percentile concentrations. Therefore, the effect of the median biweekly water level factors on the percentile concentrations was less pronounced than expected from the results of other studies (Leu et al. 2004a, Wittmer et al. 2010). An implication of this is that there might be an overlay of concentration peaks from direct inputs from handling and surface run-off. Particularly due to the biweekly sampling, exposure signals could be superimposed, making the identification of specific exposure patterns more difficult. Another point valuable for discussion is that the biweekly water level factors were selected for trying to compare water level dynamics among the SCs and explaining relations between these hydrological dynamics and concentrations. However, the intensity of the water level peaks defining the water level factors are dependent as well on the topography at the specific sampling site where the water level data was collected. Using discharges for showing the latter described relationships would be more elegant though such data was not available.

Application of weighted linear regression revealed valuable information about the pesticide input pathways. In particular the share of forest in the 100 m buffer and the mean slope of the horticultural area emerged as important explanatory variables. In addition, the data showed that effects of the explanatory variables on the PPTP concentration were compound specific and that the influence of these variables and the pesticide application practices seemed to be stronger than effects due to physicochemical properties. Further investigation of the data by more sophisticated models, such as multivariate linear mixed models, may shed further light onto pesticide input and explanatory variables. With such an approach, particularly for the PPTP of which concentrations could not clearly be explained by one explanatory variable, improvement of the modelling could be obtained. Interactions between different explanatory variables could then be taken into account, enabling a better prediction of the pesticide data and helping to further improve the robustness of the conclusions drawn from the modelling results. Inclusion of categorical variables, such as sites and periods, for determination of random effects would be possible as well. Due to the relatively few SCs and the limited hydrological and topographical data sets, a further description of such possible variables having systematic influence could not be confidently conducted and therefore, this was out of the scope of this thesis.

Overall, despite being able to associate transport via surface run-off for several PPTP with the approaches applied in this study, sampling of more than eight sampling sites (e.g. about twenty, Schreiner et al. (2021)) would be recommended for a more comprehensive analysis. By doing so, inter-correlation of catchment variables could be prevented and more variables could be included into the modelling. Another option would be to focus on two sites with different catchment characteristics, e.g. two with starkly contrasting slopes (such as SC7 vs. SC1) and conduct sampling of PPTP with a higher temporal resolution (several minutes) as reported previously (Doppler et al. 2012, Leu et al. 2004a). With a higher temporal resolution, it would be easier to distinguish pesticide peaks from handling and from surface run-off. The resolution of water level data of 5 to 15 minutes was sufficient to capture water level peaks accurately. However, additional measurements of the discharges within the streams at the individual sampling sites would be helpful to determine loads and with these better understand the transport of the pesticides and dilution effects within the catchment.

4.5.4 Pesticide exfiltration into the groundwater

This study confirmed that at least at SC1, PPTP reached groundwater aquifers while within the headwater SC7, pesticides concentrations in the groundwater were negligible (Table 4). Compared to SC7, SC1 is characterized by horticultural fields with shallow average slopes which implies a higher residual times of the pesticides on the fields or in the ground before reaching the streams, compared to SC7. The higher residence time and slower transport into streams can be assumed to facilitate biotransformation reactions, which was confirmed for carbendazim by the highest TP/parent ratios found in the streams in SC1 as opposed to SC7 (Figure 10). However, other explanations could be advanced to account for the transport of PPTP into groundwater at SC1. At SC1, the requirement of the 100 m radial natural forest area around the groundwater source was not met, whereas at SC7, the drinking water tank was surrounded by 100 m of forest. As well, there was a lower share of horticultural land in SC7 as opposed to SC1. Additional differences, such as in soil compositions, or groundwater flow direction, could play a role but could not be covered in this study due to lack of data. Notwithstanding, the data showed that a potential infiltration of river water into the aquifer could be possible as well. Theoretically, such a transport process seemed reasonable since: i) all PPTP had a certain water solubility (above 0.25 mg/L), ii) they were classified as polar and semi-polar compounds according to their log K_{ow} values (below 3), and iii) they had relatively low soil adsorption coefficients (log K_{oc} values below 4). However, additional studies should be performed to help better understand the bank filtration processes involved. Further analysis

of the pore water of the river banks or the hyporheic zone by passive sampling for semi-polar and polar compounds (Mechelke et al. 2019) and for freely dissolved non-polar compounds (Bartolomé et al. 2018, Xu et al. 2018) would be interesting lines of investigation in this regard.

Overall, the inputs of PPTP via bank filtration seemed to be negligible and a much less dominant transportation process than surface run-off or the inputs from handling. Nevertheless, monitoring the quality of the groundwater is highly recommended, particularly at the tank in SC1, since it is a source of drinking water for the local community.

4.6 Conclusion

This study aimed at linking elevated pesticide concentrations in streams to pathways of transport from the site of application. Inappropriate handling of pesticides and the slopes of the horticultural land, leading to transfer of PPTP to streams via surface run-off, were identified as main drivers. Having a high share of forest in the 100 m buffer zone adjacent to the streams seemed to help to reduce the inputs of several of the detected PPTP from surface run-off into the streams but further investigations about the effectiveness of stream buffers for different types of pesticides would be advisable. The inputs of the fungicide, carbendazim, could not at all be explained by the considered variables. A reasonable explanation is that carbendazim and some insecticides might enter the streams via critical source areas, or overlay of inputs from handling and surface run-off prevented identification of distinct input paths. Thus, the aspect of carbendazim transport especially warrants further investigation also because carbendazim concentrations in the streams were high at all investigated sites (Chapter 2).

While, this study was able to elucidate several trends to start clarifying pesticide input pathways, the data of this study showed as well that, for a more detailed analysis, event-driven concentration data or data with a higher spatio-temporal resolution are needed. Having such comprehensive pesticide monitoring data in combination with geo-referenced, time-resolved pesticide application data, more detailed than those of Staudacher et al. (2020), would have helped to elucidate pesticide inputs even more precisely. Moreover, detailed topographical and hydrological knowledge needs to be obtained to identify critical source areas. Nevertheless, several mitigation measures to at least partly reduce the input of pesticides that dominate the aquatic ecotoxicological risk can be suggested: i) training of farmers in pesticide handling and provision of sites for proper disposal, ii) alternatives to conventional pesticide use in fields with steep slopes and iii) emphasize on proper buffer zones.

The focus of this study was on the input mechanisms of compounds dominating the risk to aquatic organisms (Chapter 3). In a next step, to obtain an even more comprehensive picture of the input pathways of pesticides into streams, a further exploitation of the effects of the catchment variables on the complete pesticide concentration data set (all compounds and individual MEC instead of percentile concentration) would need to be performed. This step could build on the modelling strategy established here but would require inclusion of additional multiple or multivariate regression models and maybe additional information, such as soil types and the soil properties, estimated discharges of the streams and groundwater flow direction. Such a more detailed model may be applicable to predicting pesticide concentrations in the streams where predictions could then be verified by using the observed pesticide concentration data and taking the biases of concentration inputs and water levels changings among the individual SC into account.

4.7 Literature

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Chapter 4

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SI-4 A

Supporting information 4. Chapter

Identification of pesticide input pathways in tropical streams as a basis to propose potential mitigation options

SI-4 A1 PPTP selected for this study

Table SI-4 A1: Confirmed pesticide applications by surveys conducted in the Tapezco river catchment and pesticides dominating environmental risks in Chapter 3. Within the study of Ramirez et al. 2016, the farmers and field workers were generally asked which pesticides were applied. Within the study of Staudacher et al. 2020, Fuhrmann et al. 2019 and Fuhrmann et al. 2020, the farmers and field workers were explicitly asked if carbendazim, carbofuran, chlorpyrifos, cypermethrin, Prometryn + Terbutryn, acephate, propamocarb and boscalid were applied or not.

Compound	Type	Environmental risk (Chapter 3)	Applied in the Tapezco river catchment (Ramirez et al. 2016)	Applied in the Tapezco river catchment (Staudacher et al. 2020) (Fuhrmann et al. 2019 and 2020)
2,6-Dichlorbenzamide	TP H			
Acephate	I		✓	✓
Bifenthrine	I	✓	✓	
Boscalid	F		✓	✓
Carbendazim	F	✓	✓	✓
Carbofuran	I	✓	✓	✓
Chlorpyrifos	I	✓	✓	✓
Cyhalothrin	I	✓		
Cypermethrin	I	✓	✓	✓
Deltamethrin	I	✓	✓	
Diazinon	I	✓	✓	
Dimethoate	I	✓	✓	
Diuron	H	✓		
Diuron-desdimethyl	TP H			
Diuron-desmonomethyl	TP H			
Fipronil	I	✓	✓	
Imidacloprid	I	✓	✓	
Linuron	H	✓	✓	
Metribuzin	H	✓	✓	
Permethrin	I	✓	✓	

Compound	Type	Environmental risk (Chapter 3)	Applied in the Tapezco river catchment (Ramirez et al. 2016)	Applied in the Tapezco river catchment (Staudacher et al. 2020) (Fuhriemann et al. 2019 and 2020)
Prometryn + Terbutryn	H	✓	✓	
Propamocarb	F		✓	✓
Tebuconazole	F	✓	✓	
Thiamethoxam	I	✓	✓	

TP = transformation product; I = insecticide; F = fungicide; H = herbicide.

SI-4 A2 Catchment attributed of the SCs within the river Tapezco catchment

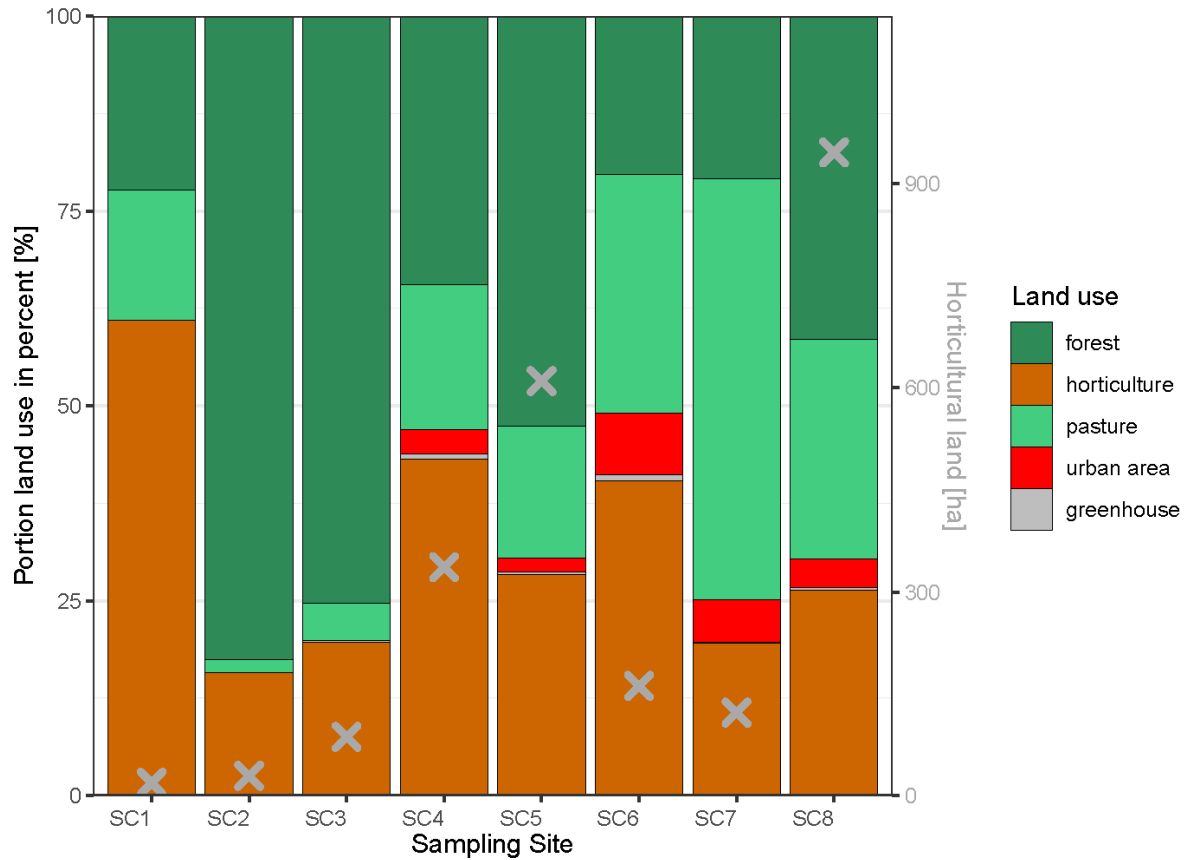


Figure SI-4 A1.1: Individual land uses within the different SCs of the Tapezco river catchments. Portion of land use in percent on the left y axis and absolute horticultural land per SC on the right y axis. Headwater sub-catchments: SC1, SC2, SC6, SC7; nested sub-catchments: SC3, SC4, SC5, SC8.

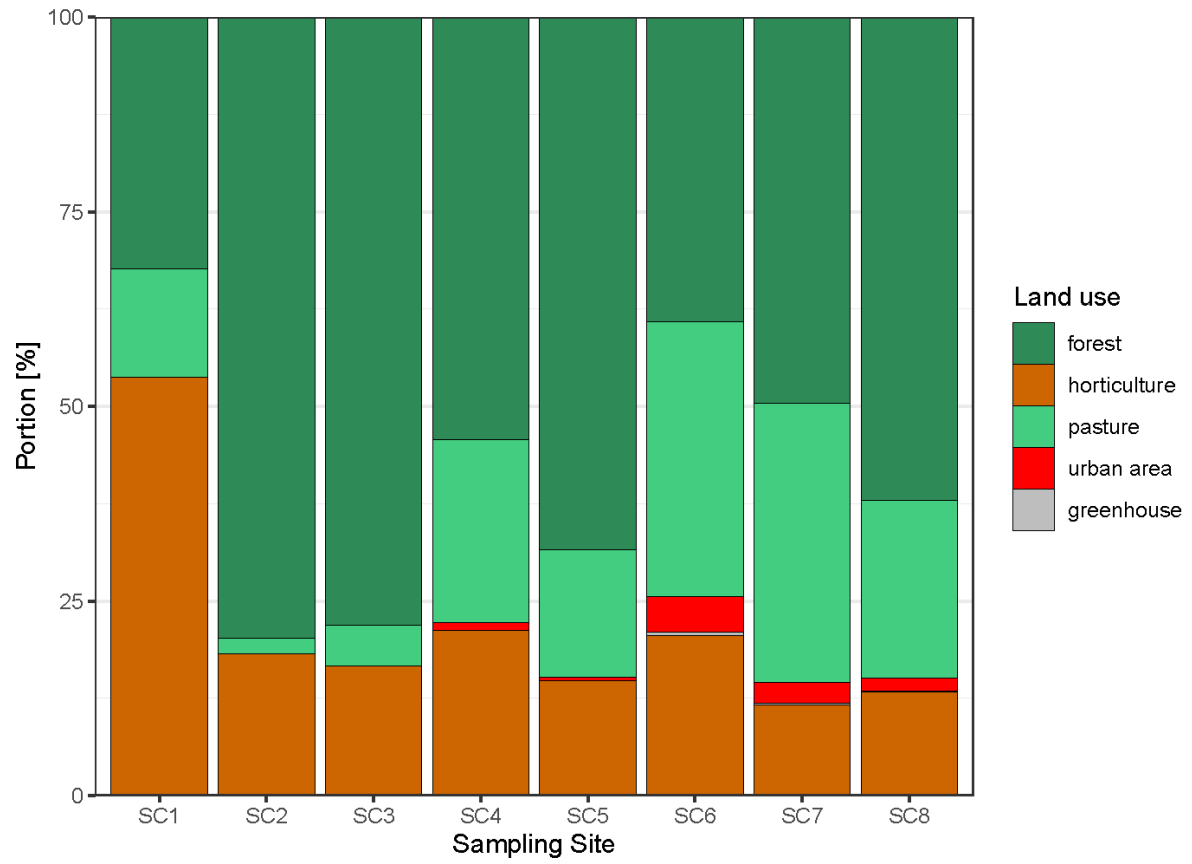


Figure SI-4 A1.2: Share of Individual land uses in the 100 m stream buffer zone, within the different SCs of the Tapezco river catchments. Headwater sub-catchments: SC1, SC2, SC6, SC7; nested sub-catchments: SC3, SC4, SC5, SC8.

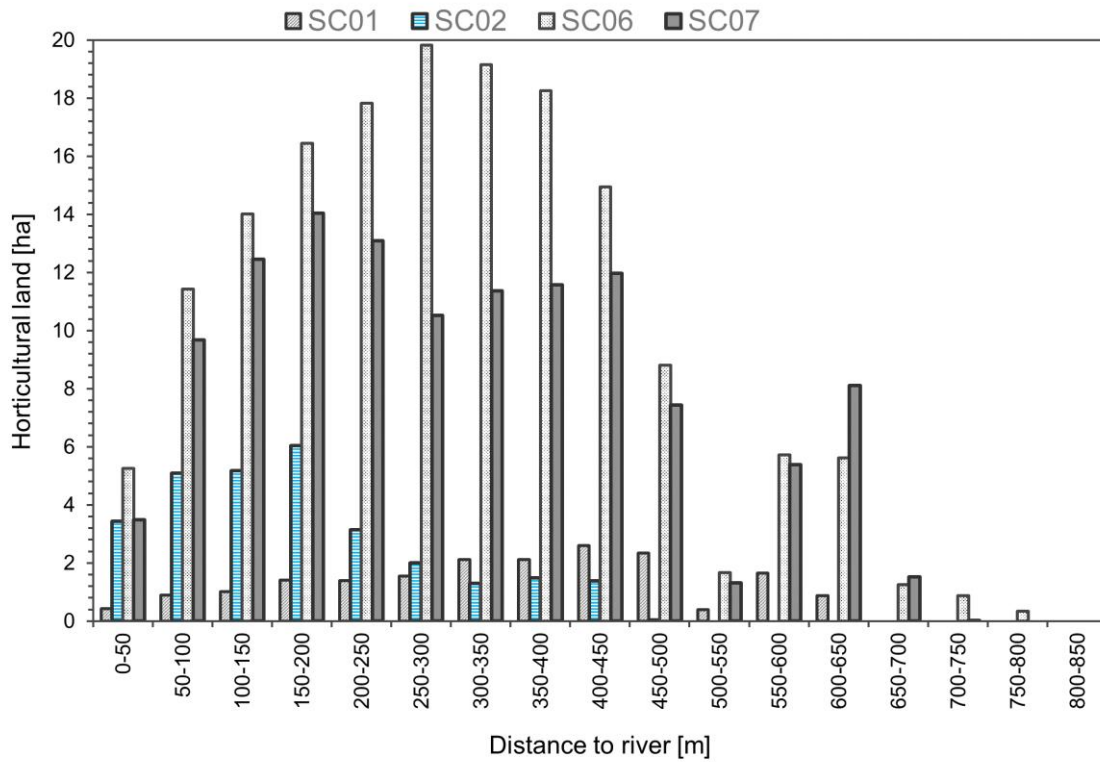


Figure SI-4 A2.1: Absolute horticultural land in ha for each 50 meter interval, radial from the stream for the headwater catchments SC1, SC2 SC6 and SC7. These data is not cumulative.

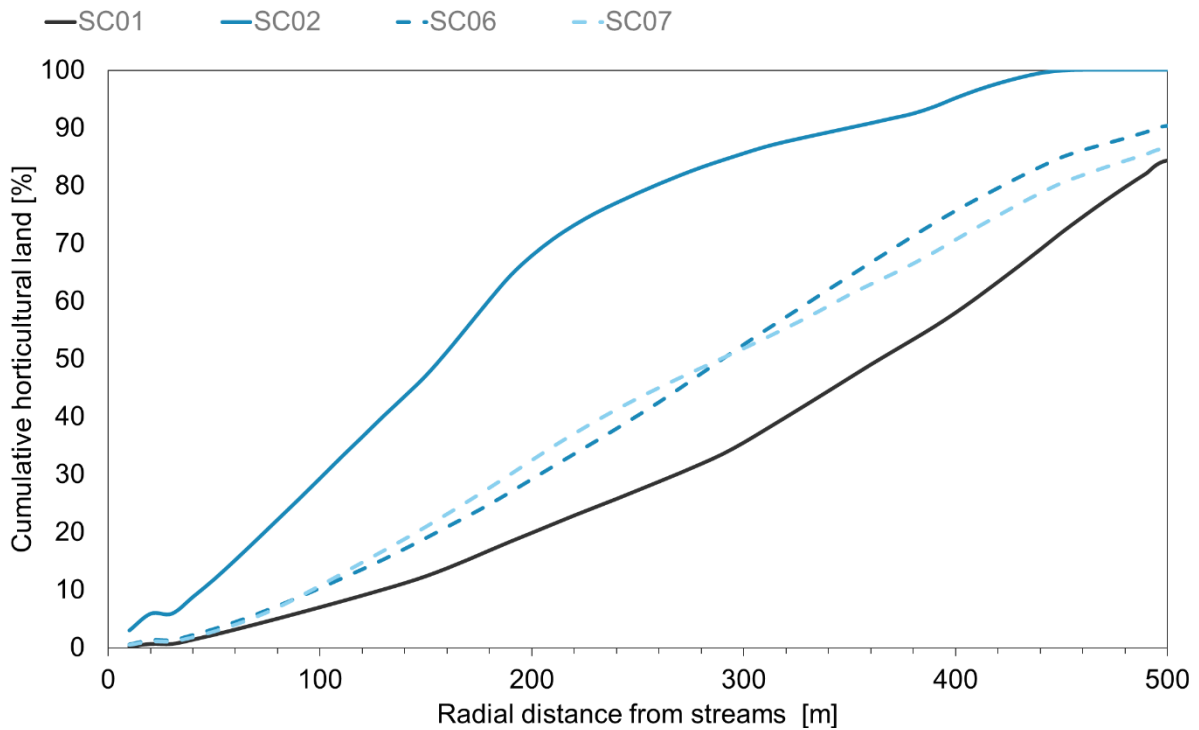


Figure SI-4 A2.2: Relation between radial distance from streams and cumulative horticultural land in percent for the headwater catchments SC1, SC2 SC6 and SC7.

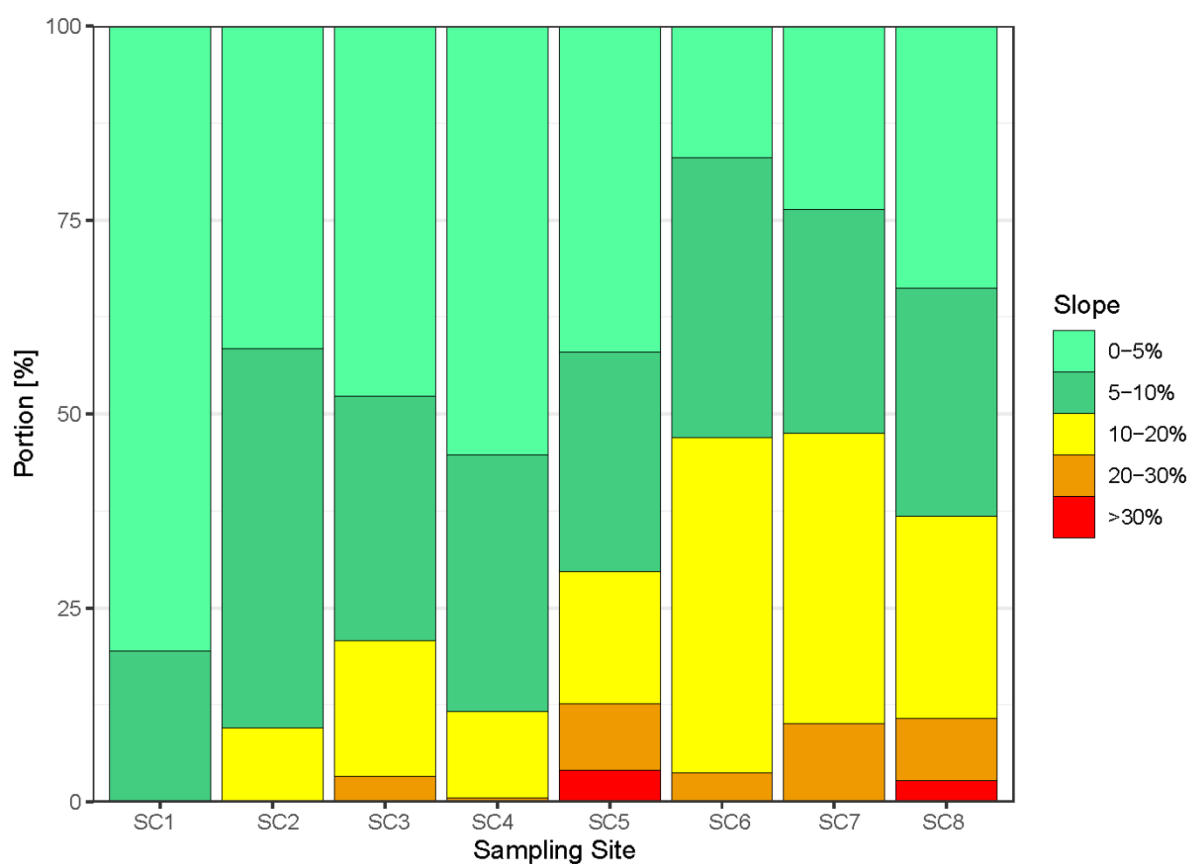


Figure SI-4 A3: Distribution of the slopes of the horticultural fields per each sub-catchment. Headwater sub-catchments: SC1, SC2, SC6, SC7; nested sub-catchments: SC3, SC4, SC5, SC8.

SI-4 A3 Hydrological information

SI-4 A3.1 Hydrographs from headwater catchments

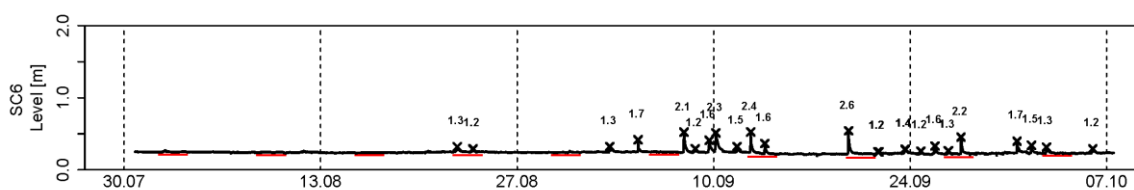


Figure SI-4 A4.1: water level and precipitation time series at headwater SC6. Data from $\Delta T1$ from 30.07 to 07.10. Water levels are presented at the y axis, black line. Red lines represent the minimum weekly base water levels. Water level peak factors above a variation of 30% (factor above 1.3) were defined as peaks from heavy rain events within this study. X show water level factors above or equal to 1.2.

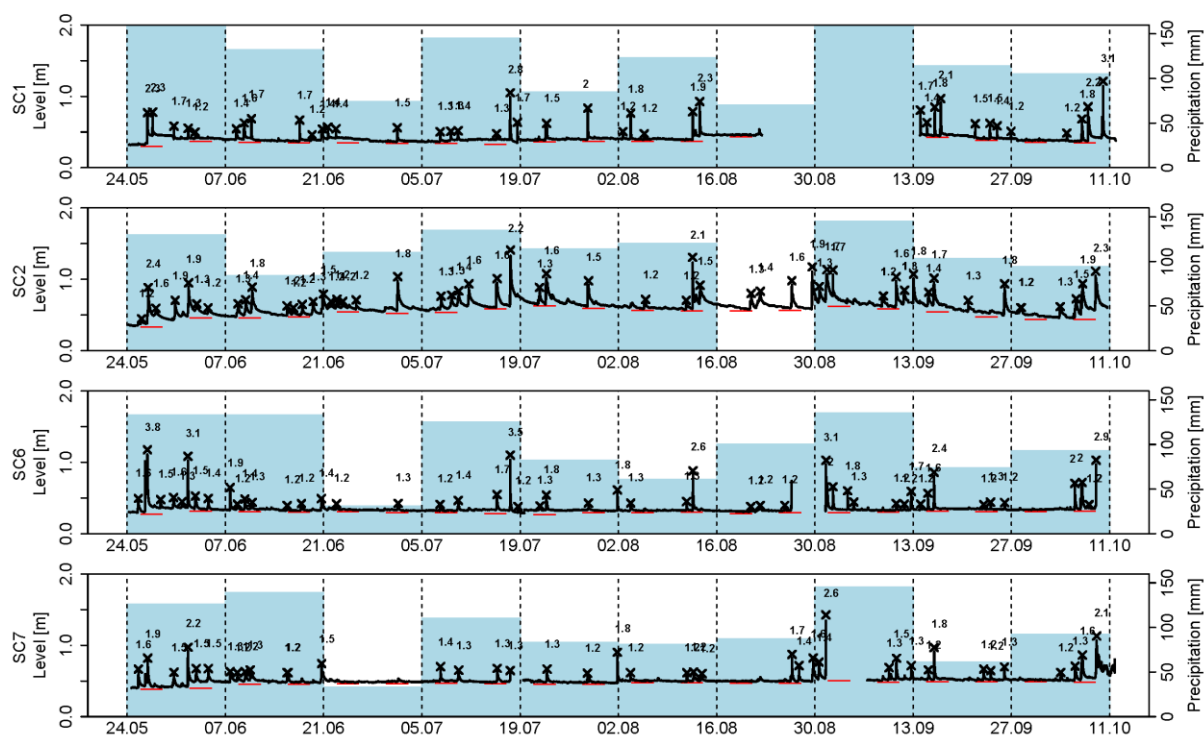


Figure SI-4 A4.2: Water level and precipitation time series at headwater SC. Data from 2016 from 24.05 to 11.10. Water levels are presented at the left y axis, black line, and precipitations at the right y axis, blue bars. Red lines represent the minimum weekly base water levels. Water level peak factors above a variation of 30% (factor above 1.3) were defined as peaks from heavy rain events within this study. Absence of water level data due to sampling issues is shown in the hydrographs by interruptions of the black water level lines. X show water level factors above or equal to 1.2.

SI-4 A3.2 Hydrographs from non-headwater catchments

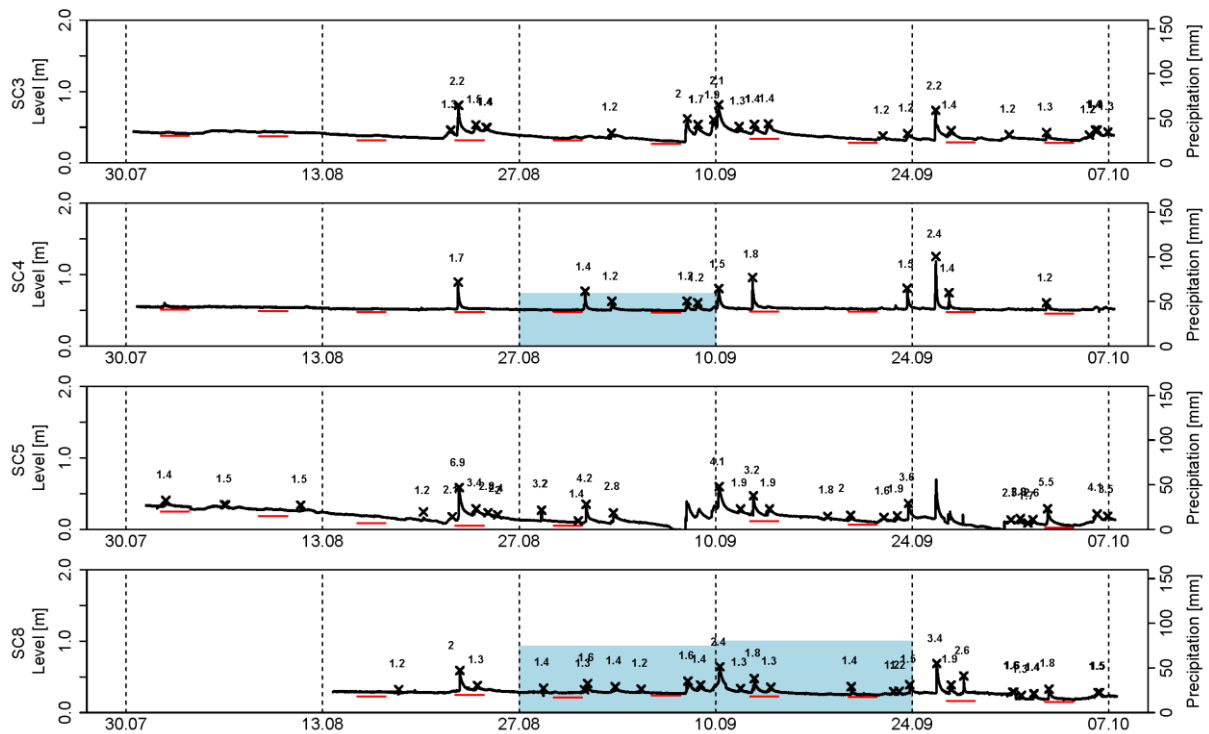


Figure SI-4 A5.1: water level and precipitation time series at non-headwater SC3, SC4, SC5 and SC8. Data from $\Delta T1$ from 30.07 to 07.10. Water levels are presented at the left y axis, black line, and precipitations if available at the right y axis, blue bars. Red lines represent the minimum weekly base water levels. Water level peak factors above a variation of 30% (factor above 1.3) were defined as peaks from heavy rain events within this study. X show water level factors above or equal to 1.2.

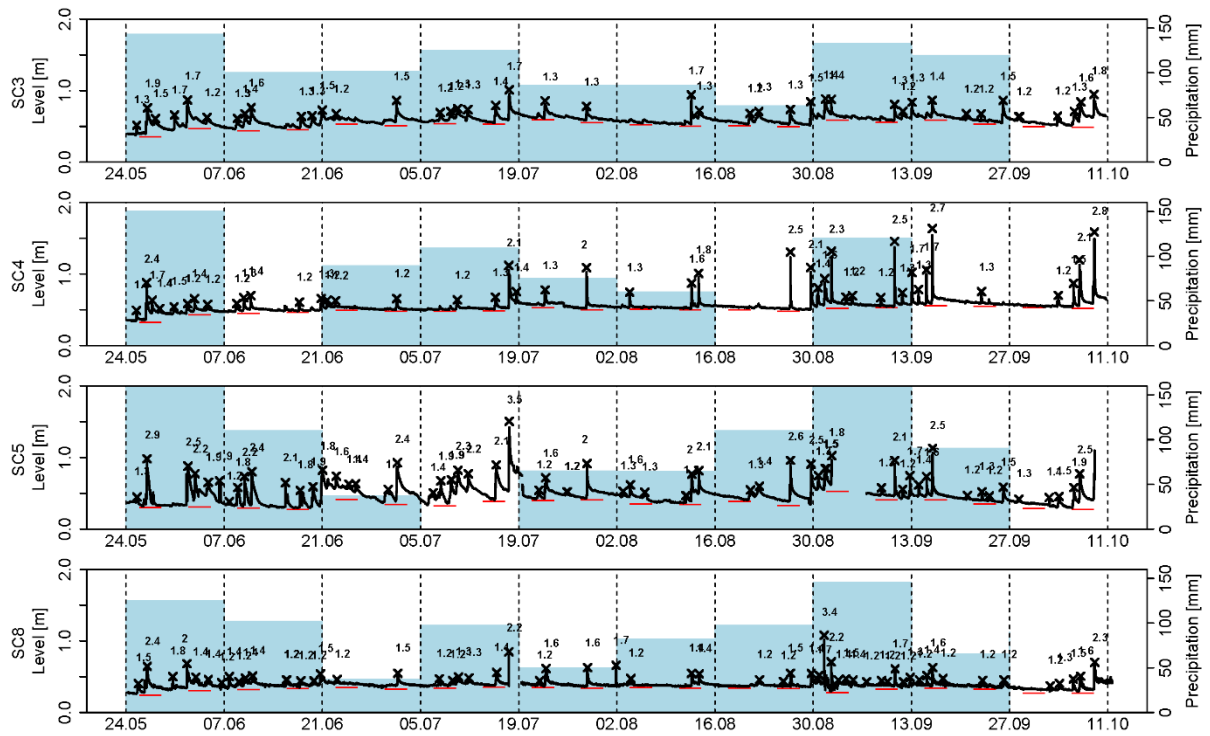


Figure SI-4 A5.2: Water level and precipitation time series at non-headwater SCs (SC3, SC4, SC5 and SC8). Data from 2016 from 24.05 to 11.10. Water levels are presented at the left y axis, black line, and precipitations at the right y axis, blue bars. Red lines represent the minimum weekly base water levels. Water level peak factors above a variation of 30% (factor above 1.3) were defined as peaks from heavy rain events within this study. Absence of water level data due to sampling issues is shown in the hydrographs by interruptions of the black water level lines. X show water level factors above or equal to 1.2.

SI-4 A3.3 Overview about biweekly hydrological data

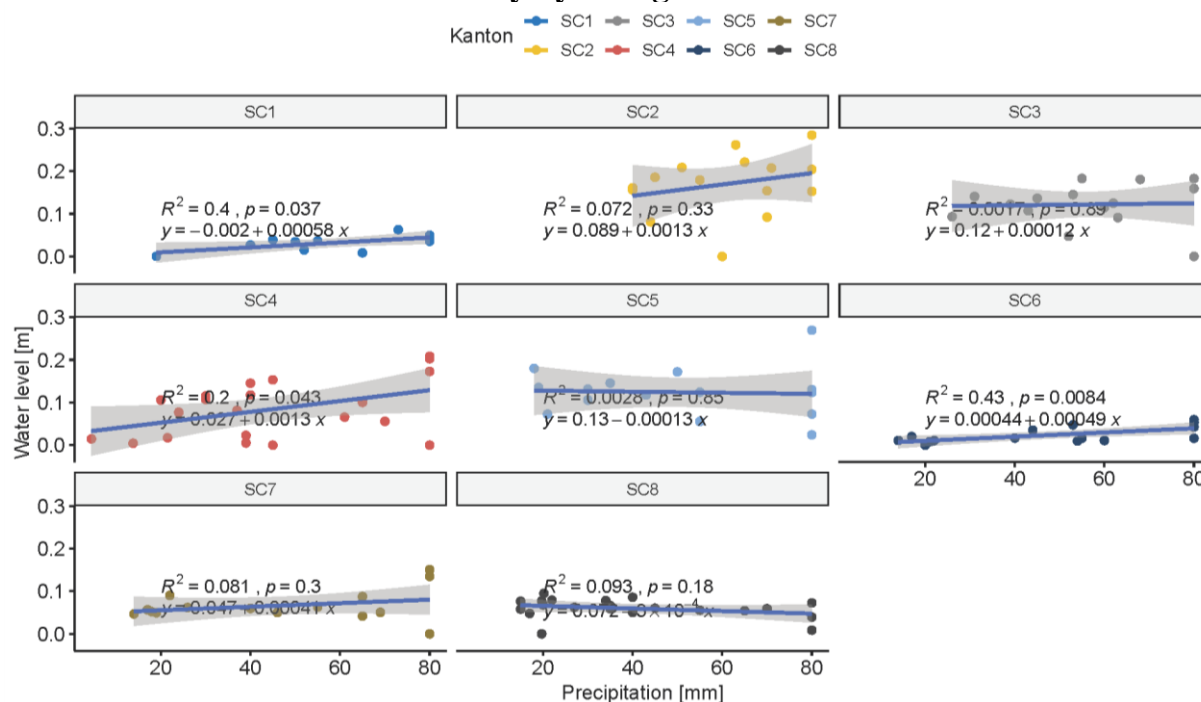


Figure SI-4 A6: Relationship between weekly precipitation and water level data. Correlations of precipitation and water levels for each sampling site.

SI-4 A4 Physicochemical characteristics of the PPTP considered in this study, pesticide application data and PPTP with possible direct inputs from inappropriate handling practices

SI-4 A4.1 Physicochemical characteristics of the PPTP considered in this study

Table SI-4 A2: Physicochemical characteristics of the Pesticide or pesticide transformation product considered in Chapter 4 for further analysis.

Pesticide or pesticide transformation product (PPTP)	CAS	Log K_{ow}^*	Log $K_{oc}^{\&}$	Water solubility [mg/L] at 25°C ^{\$}
2,6-Dichlorobenzamide	2008-58-4	0.9	1.1	10810
Acephate	30560-19-1	-0.9	0.6	282700
Bifenthrine	82657-04-3	8.15	5.4	0.00002407
Boscalid	188425-85-6	4	2.5	20.19
Carbendazim	10605-21-7	1.55	2.1	2441
Carbofuran	1563-66-2	2.3	2.2	353.9
Chlorpyrifos	2921-88-2	5.11	3.9	0.357
Cyhalothrin	91465-08-6	6.9	5.2	0.0008533
Cypermethrin	52315-07-8	6.38	5.2	0.002
Deltamethrin	52918-63-5	6.2	4.7	0.001827
Diazinon	333-41-5	3.9	3.3	6.456
Dimethoate	60-51-5	0.7	1.2	6626

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Pesticide or pesticide transformation product (PPTP)	CAS	<i>Log K_{ow}</i> [*]	<i>Log K_{oc}</i> ^{&}	Water solubility [mg/L] at 25°C ^{\$}
Diuron	330-54-1	2.7	2.3	150.6
Diuron-desdimethyl	2327-02-8	2	2	224.9
Diuron-desmonomethyl	3567-62-2	2.5	2.5	107.4
Fipronil	120068-37-3	4	3.8	0.37
Imidacloprid	120868-66-8	0.6	1.4	10840
Linuron	330-55-2	2.91	2.6	44.3
Metribuzin	21087-64-9	1.49	2.2	1304
Permethrin	52645-53-1	7.4	4.5	0.009747
Promethryn + Terbutryn	7287-19-6	3.7	2.7	26.55
Propamocarb	24579-73-5	1.13	2	56450
Tebuconazole	107534-96-3	3.89	3.2	7.648
Thiamethoxam	153719-23-4	0.8	2.4	17710

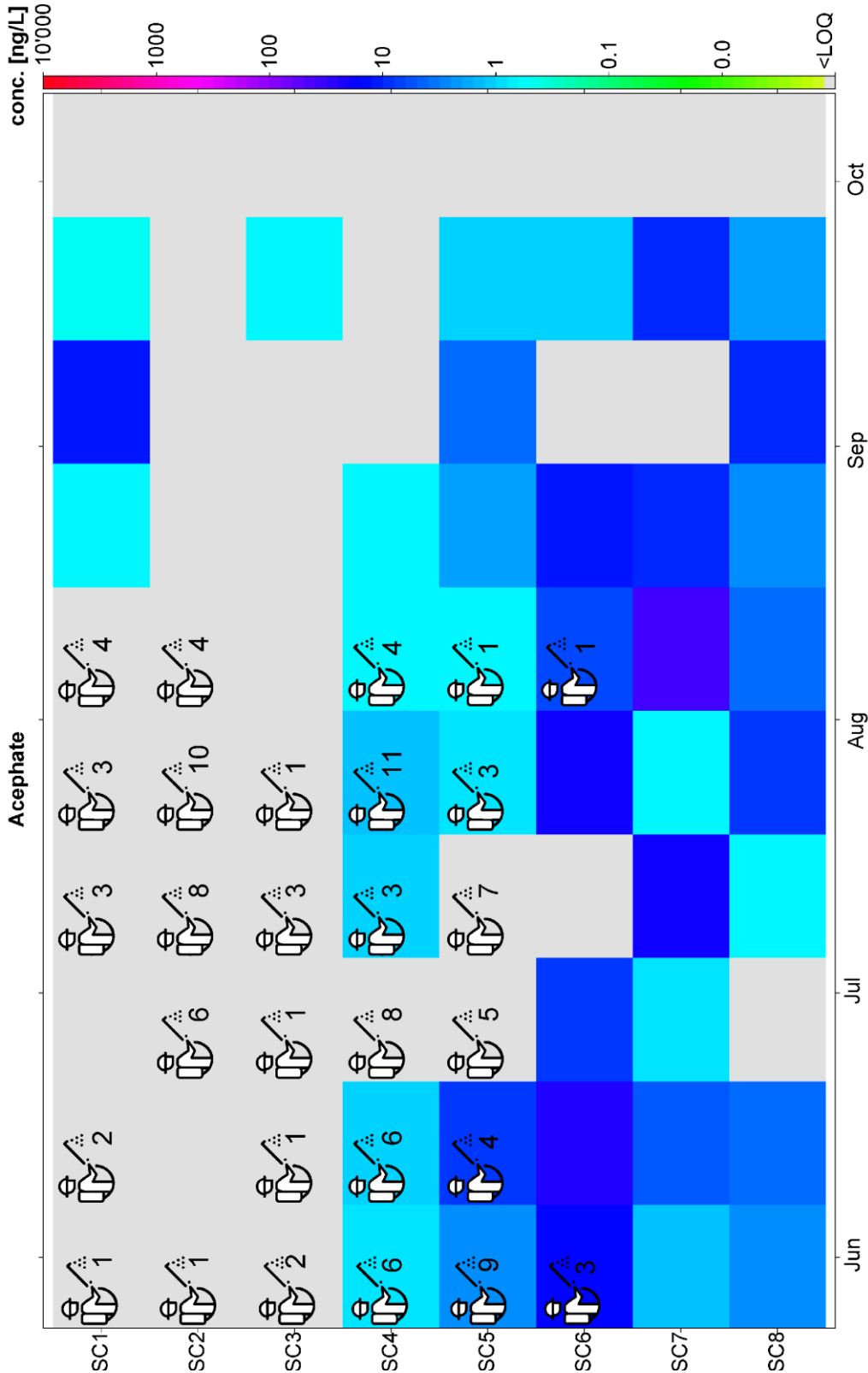
* determined with EPISuite4.1. (KOWWIN v. 1.68 estimate).

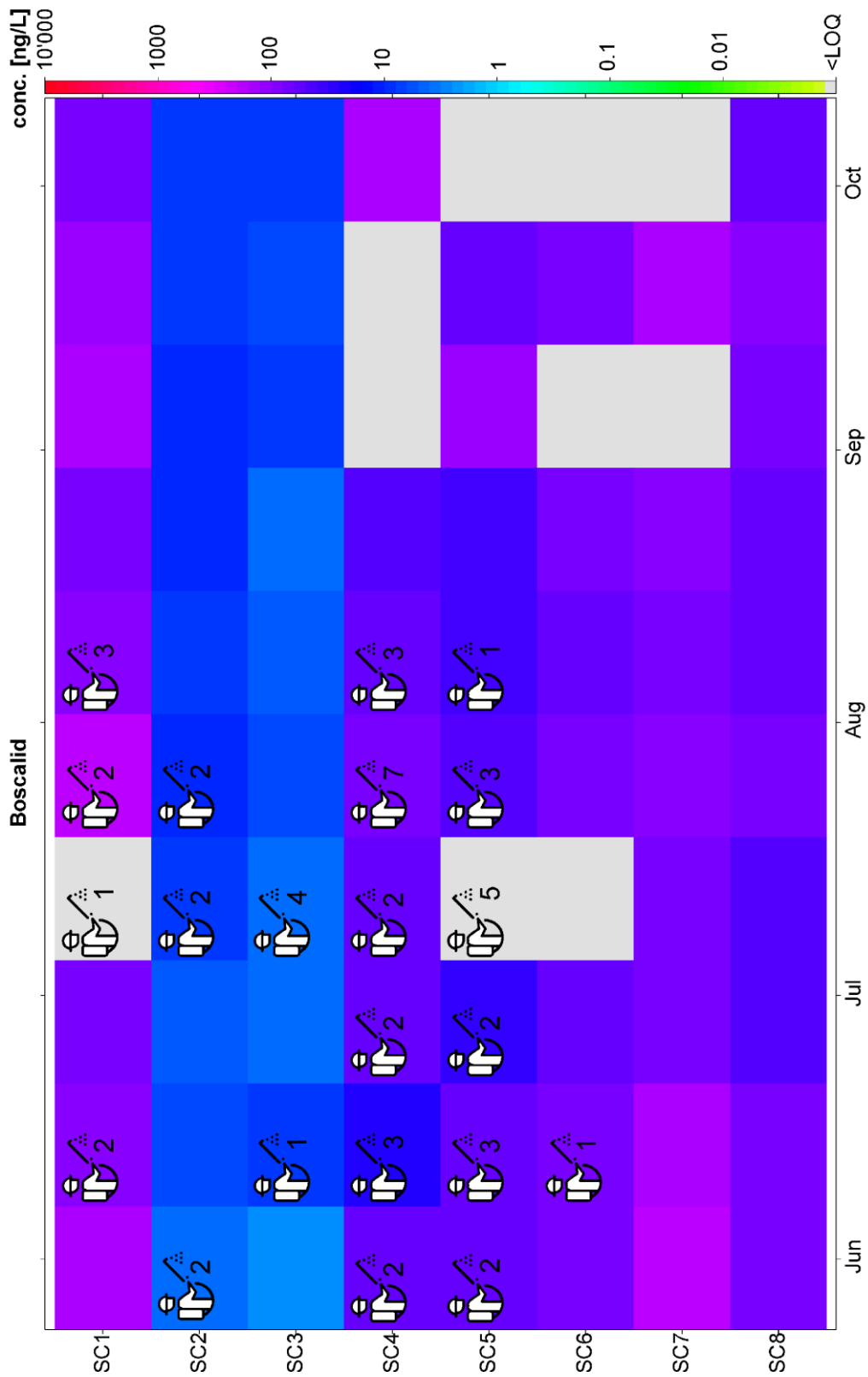
& determined with EPISuite4.1. (KOCWIN, KOW method).

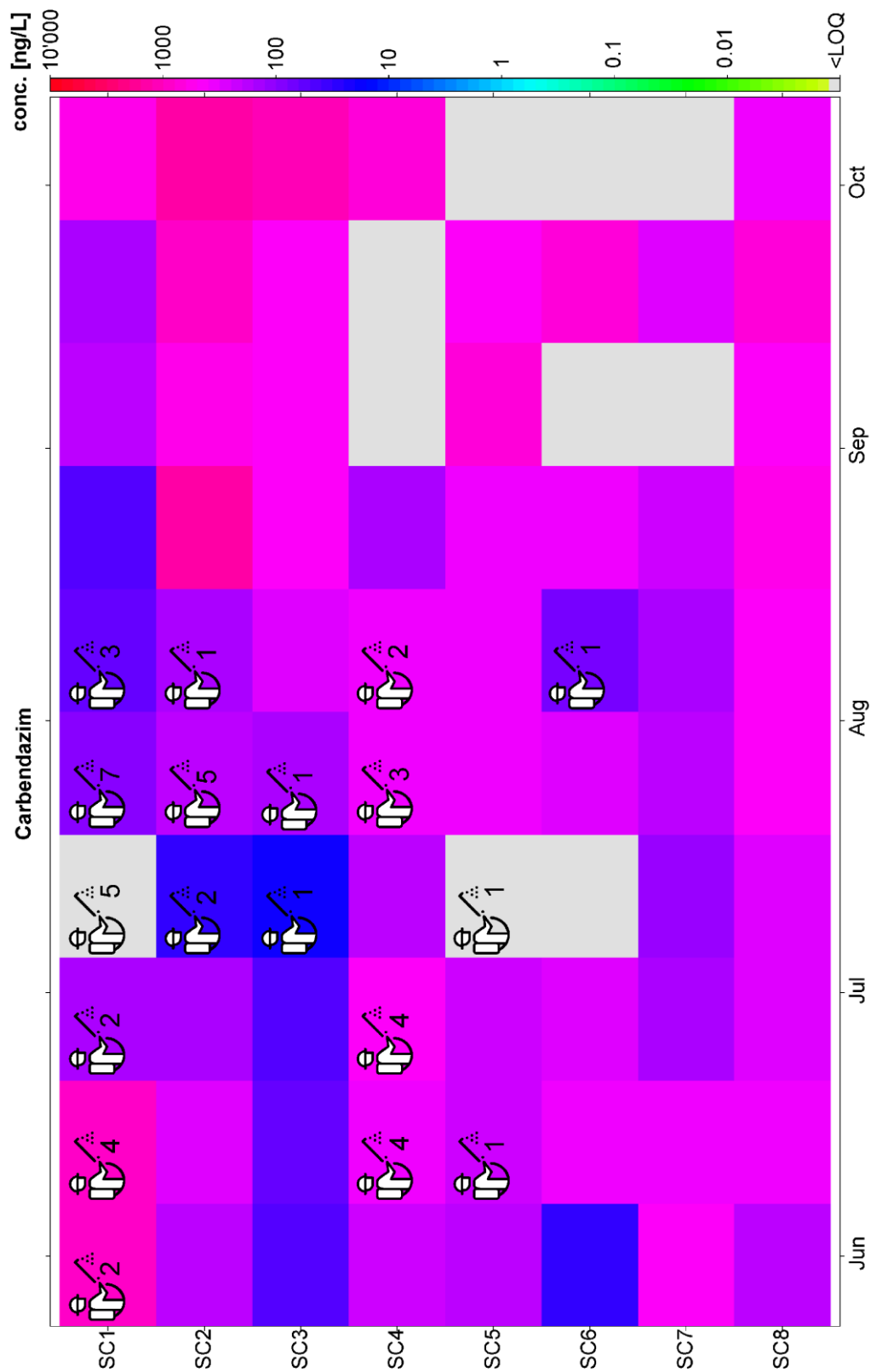
\$ determined with EPISuite4.1. (WSKOW v.1.41).

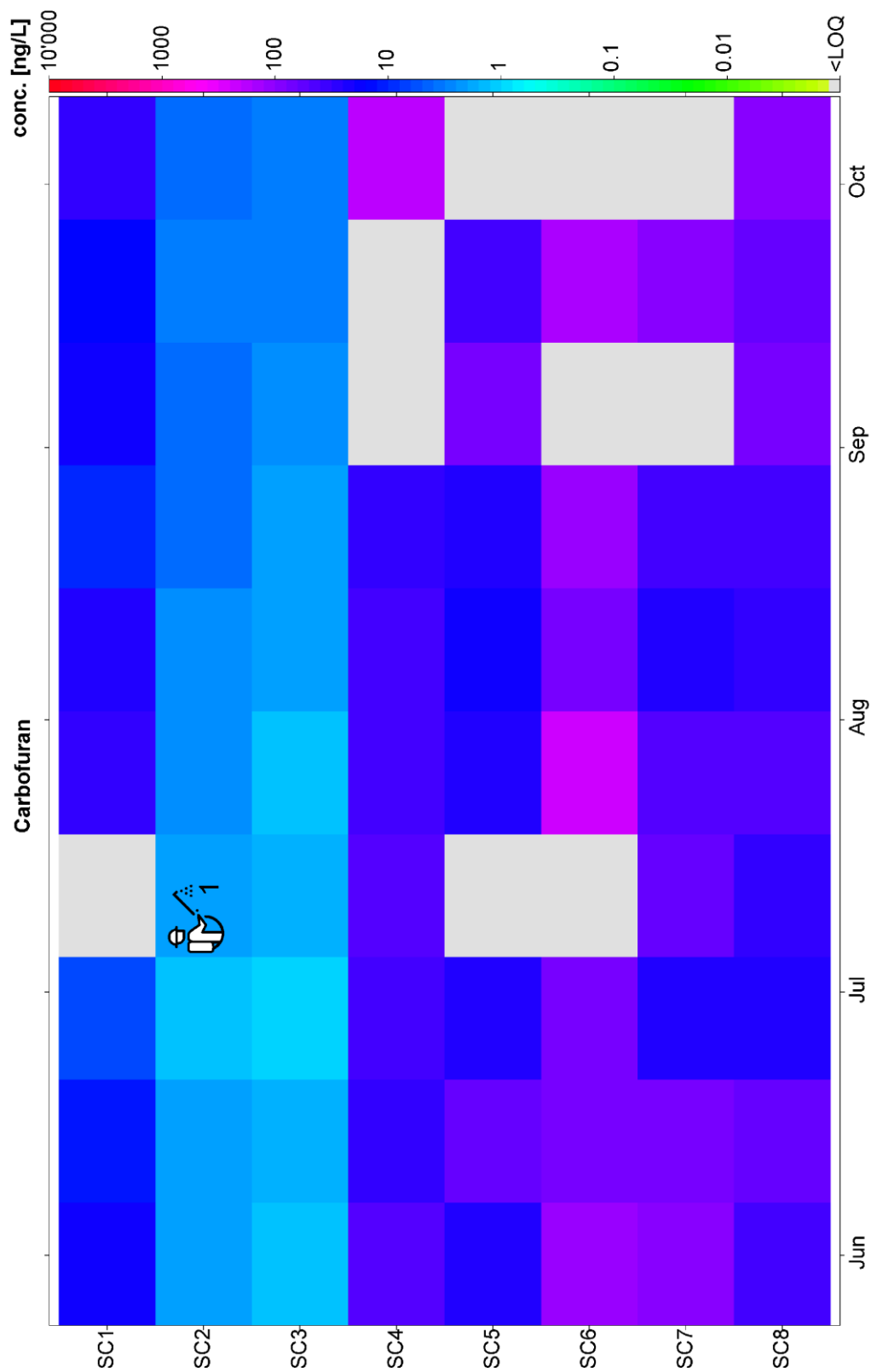
PPTP written in bold: Significant different concentrations among the sampling period with less precipitation ($\Delta T1$) and one of the period with usual precipitation ($\Delta T2a$ and $\Delta T2b$) (one-way ANOVA with Games-Howell post hoc test, significance level: * < 0.05).

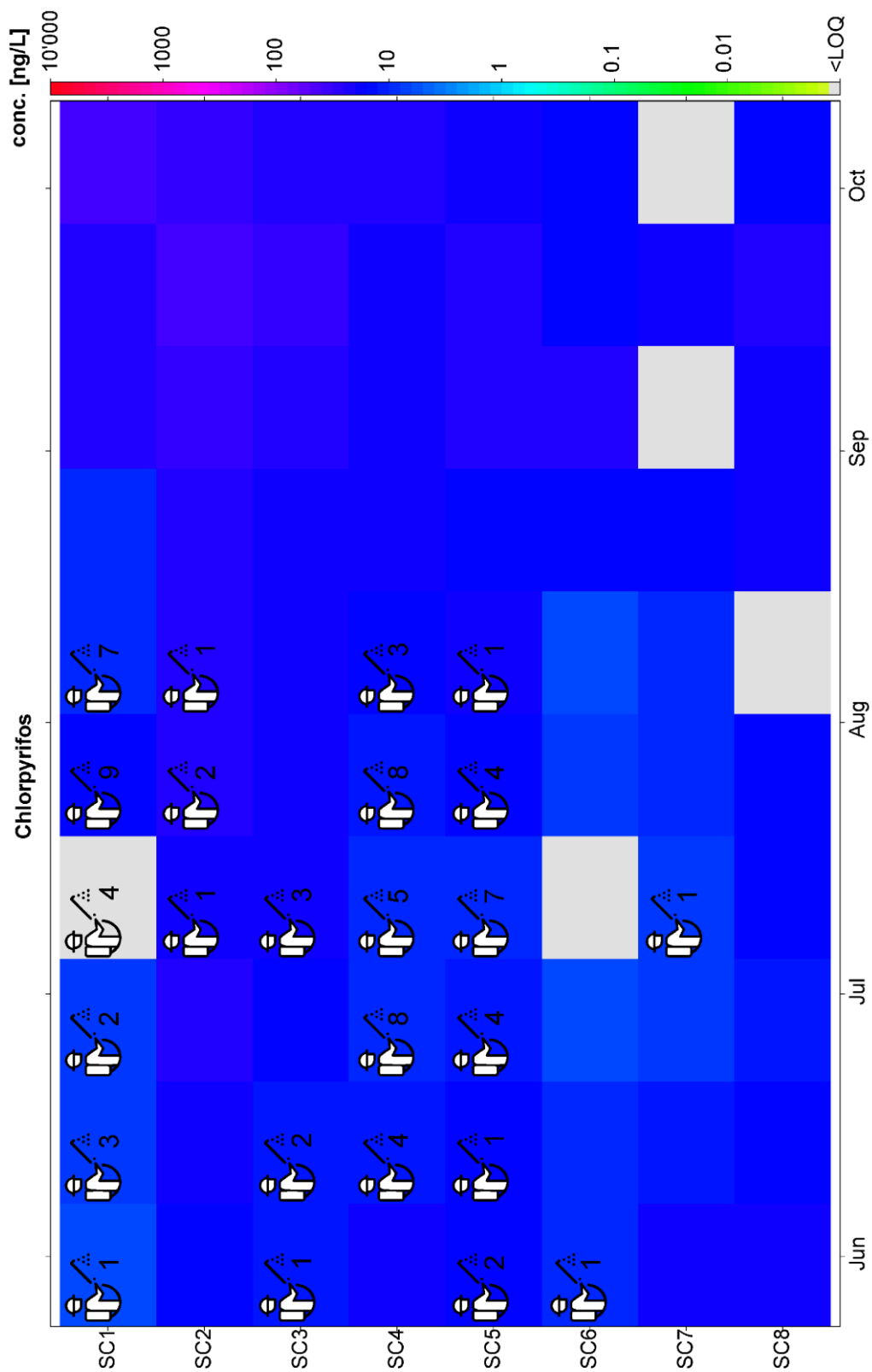
SI-4 A4.2 Pesticide concentration and application data

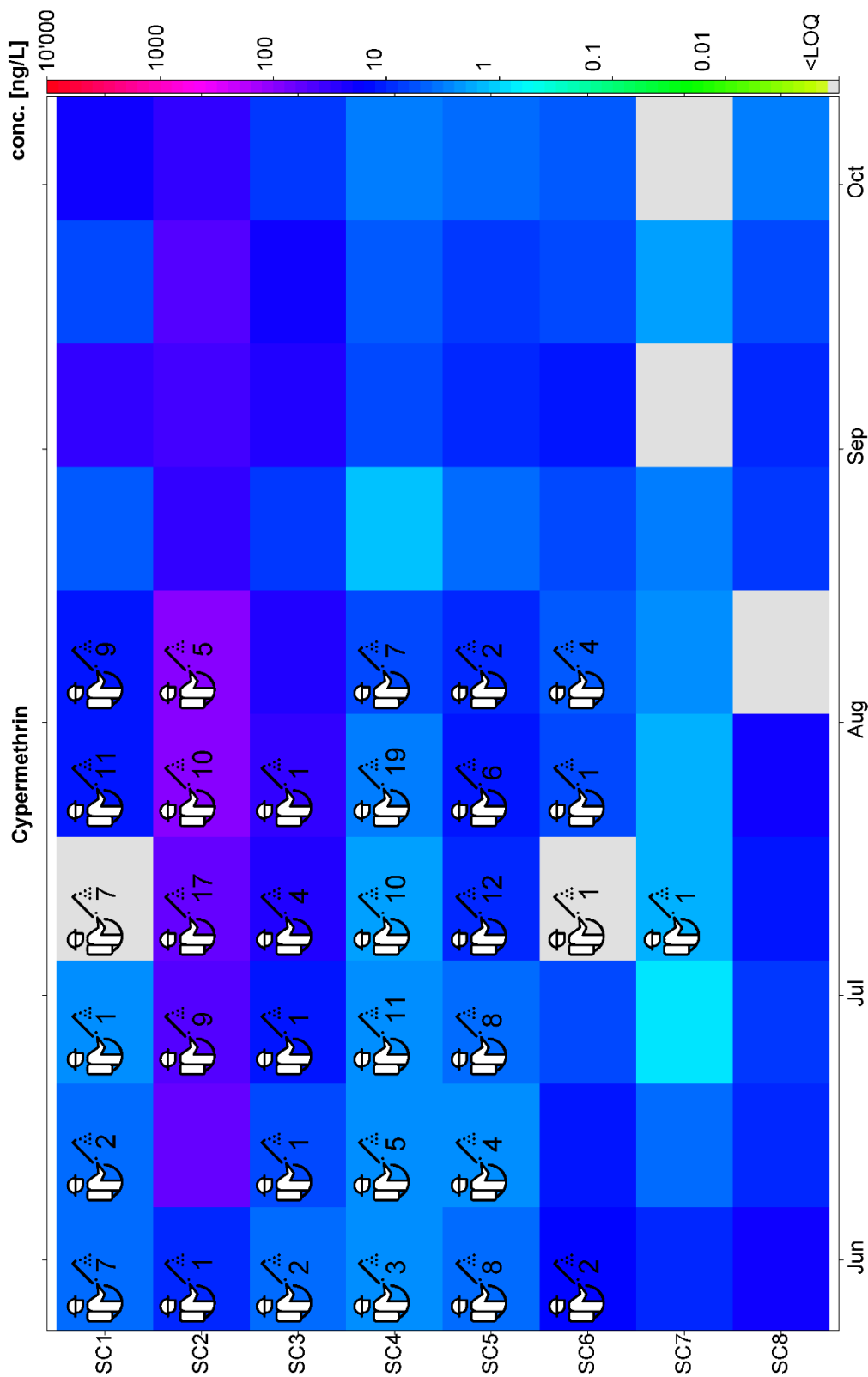












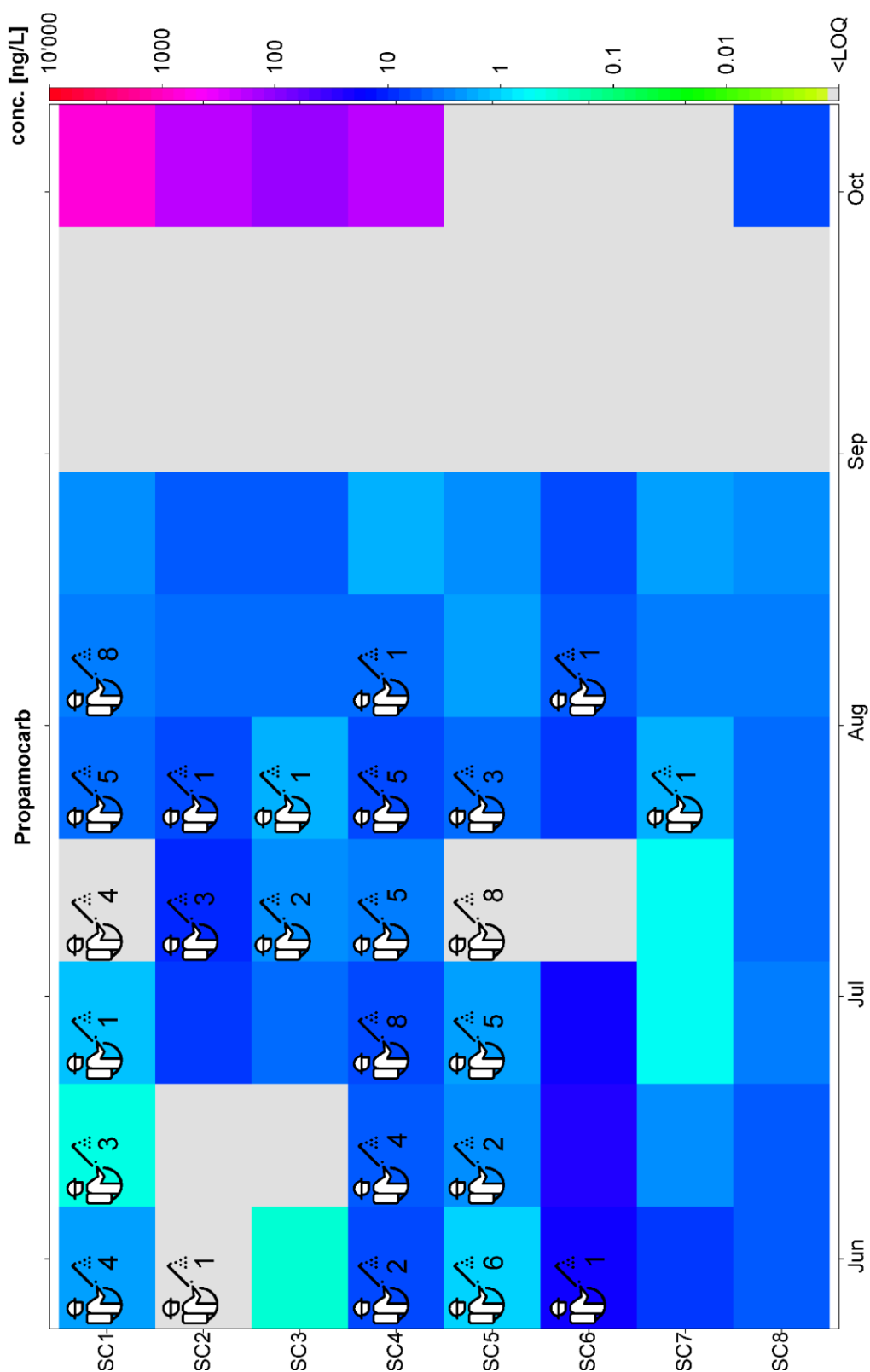


Figure SI-4 A7: Overview of the spatio-temporal application and detection of different pesticides (acephate, boscalid, carbendazim, carbofuran, chlorpyrifos, cypermethrin and propamocarb). Icons in squares indicate application based on survey data, which referred to the period from June to mid-August ($\Delta T2b$ and first interval $\Delta T2a$). The numbers next to the icons represent how many farmers reported to have applied the pesticide during each biweekly interval. Heatmap shows the measured environmental concentrations.

SI-4 A4.3 PPTP with possible direct inputs from inappropriate handling practices

Table SI-4 A3: Possible inputs of pesticides due to inappropriate handling of pesticides. Elevated concentrations observed during periods with low factors of water level (WL) peak maxima exceeding base water level (biweekly water level factors). Visually determined by investigating pesticide concentrations and hydrographs, statistically determined by looking for peaks with concentrations higher or equal than the 95% quantile (Q0.95), simultaneous at periods with biweekly water level factors below the 25% quantile (Q0.25). Categories of peaks from inappropriate handling. Likely: peaks from inappropriate handling were confirmed with both the visual and the statistical approach or visual peaks were very distinct. Possible: peaks from inappropriate handling were confirmed with either the visual or the statistical approach. Unlikely: no statistical confirmation or peaks of TP which are difficult to classify.

SC	Period	Year	Compound	Type	Visually deter- mined	Statistically deter- mined*	Possibility of direct input from inappropriate handling	Biweekly water level factors	Biweekly water level factors - Q0.25	Concen- tration [ng/L]*	Concen- tration [ng/L] Q0.95&
SC1	21 June - 05 July	2016	2,6-Dichlorbenzamide	TP herbicide	No	Yes	unlikely	4.3	4.9	5.00	5.00
SC1	19 July - 2 Aug	2016	2,6-Dichlorbenzamide	TP herbicide	No	Yes	unlikely	3.5	4.9	5.00	5.00
SC1	19 July - 2 Aug	2016	Bifenthrine	Insecticide	Not clear	Yes	possible	3.5	4.9	0.23	0.109
SC1	19 July - 2 Aug	2016	Boscalid	Fungicide	Not clear	Yes	possible	3.5	4.9	189.97	129.18
SC1	21 June - 5 July	2016	Delta-methrin	Insecticide	Not clear	Yes	possible	4.3	4.9	0.07	0.062
SC2	19 July - 2 Aug	2016	Cypermethrin	Insecticide	No	Yes	unlikely	3.5	4.9	84	43
SC6	21 June - 5 July	2016	Dimethoate	Insecticide	Yes	Yes	likely	2.5	4.9	78.57	78.57
SC6	21 June - 5 July	2016	Diuron	Herbicide	Yes	Yes	likely	2.5	4.9	84.60	28.60

SC	Period	Year	Compound	Type	Visually deter- mined	Statistically deter- mined*	Possibility of direct input from inappropriate handling	Biweekly water level factors	Biweekly water level factors - Q0.25	Concen- tration [ng/L]*	Concen- tration [ng/L] Q0.95 ^{&}
SC6	21 June - 5 July	2016	Diuron- desdimethyl	TP herbi- cide	No	Yes	unlikely	2.5	4.9	22.86	16.92
SC6	21 June - 5 July	2016	Diuron- desmono- methyl	TP herbi- cide	No	Yes	unlikely	2.5	4.9	19	18.62
SC7	02 Aug - 16 Aug	2016	Acephate	Insectici de	No	Yes	unlikely	4.8	4.9	35	18.58
SC7	16 Aug - 30 Aug	2016	Cyhalothrin	Insectici de	No	Yes	unlikely	4.7	4.9	0.47	0.264
SC7	02 Aug - 16 Aug	2016	Cyhalothrin	Insectici de	No	Yes	unlikely	4.8	4.9	0.32	0.264
SC7	16 Aug - 30 Aug	2016	Diazinon	Insectici de	No	Yes	unlikely	4.7	4.9	82	80.94
SC6	30 July - 13 Aug	2015	Imida- cloprid	Insecti- cide	Yes	No	possible	0	4.9	41.79	55.17
SC6	21 June - 5 July	2016	Propamo- carb	Fungi- cide	Yes	No	possible	2.5	4.9	19.00	60.18
SC6	30 July - 13 Aug	2015	Thia- methoxam	Insecti- cide	Yes	No	likely	0	4.9	43.57	35.7
SC6	13 Aug - 27 Aug	2015	Thia- methoxam	Insecti- cide	Yes	No	likely	1.3	4.9	41.43	35.7

* Biweekly MEC during respective period,

& 95% quantile among the concentration data from headwater catchments.

SI-4 A5 Water level and TP/parent compound ratios

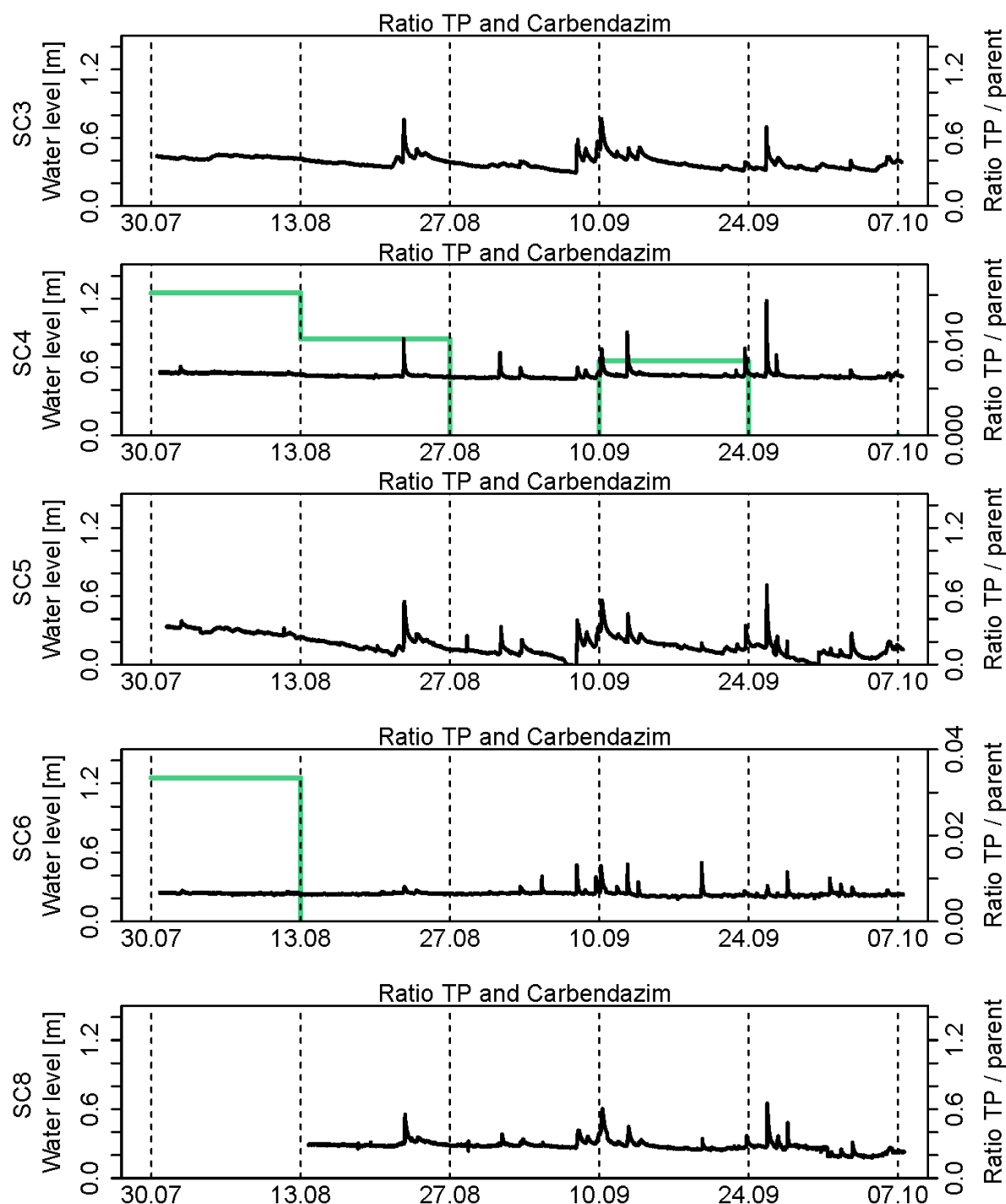


Figure SI-4 A8.1: Identification of highest carbendazim TP/carbendazim ratio at SC3, SC4, SC5, SC6 and SC8 in 2015. Water levels (black lines) and the ratios of the carbendazim TP and the parent carbendazim (green lines) are presented. The left y axis present water levels and right y axis the ratios of the carbendazim TP and the parent carbendazim. Sharply decreased ratios are used to indicate possible inputs with short residence times of the parent compound before entering the streams.

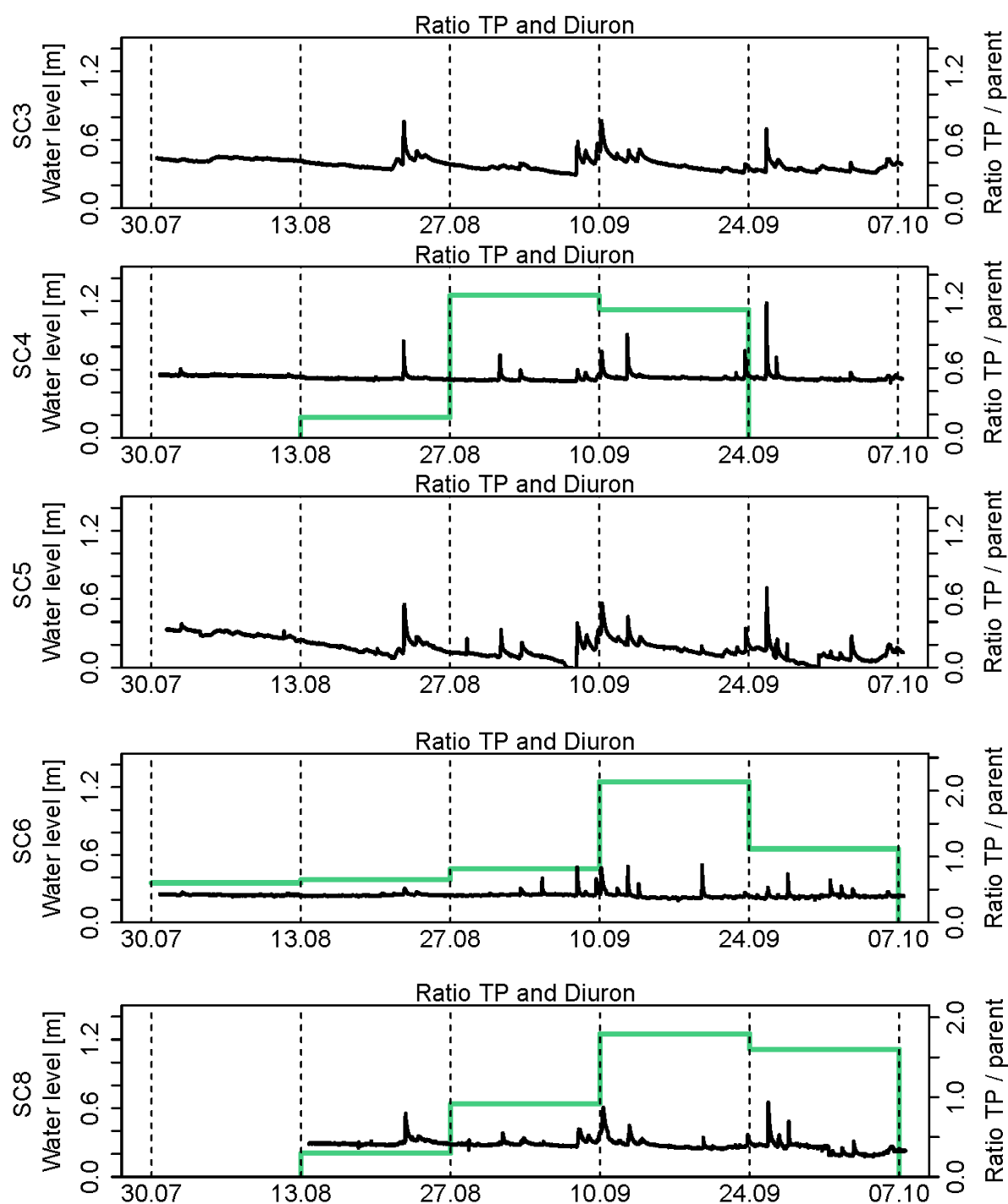
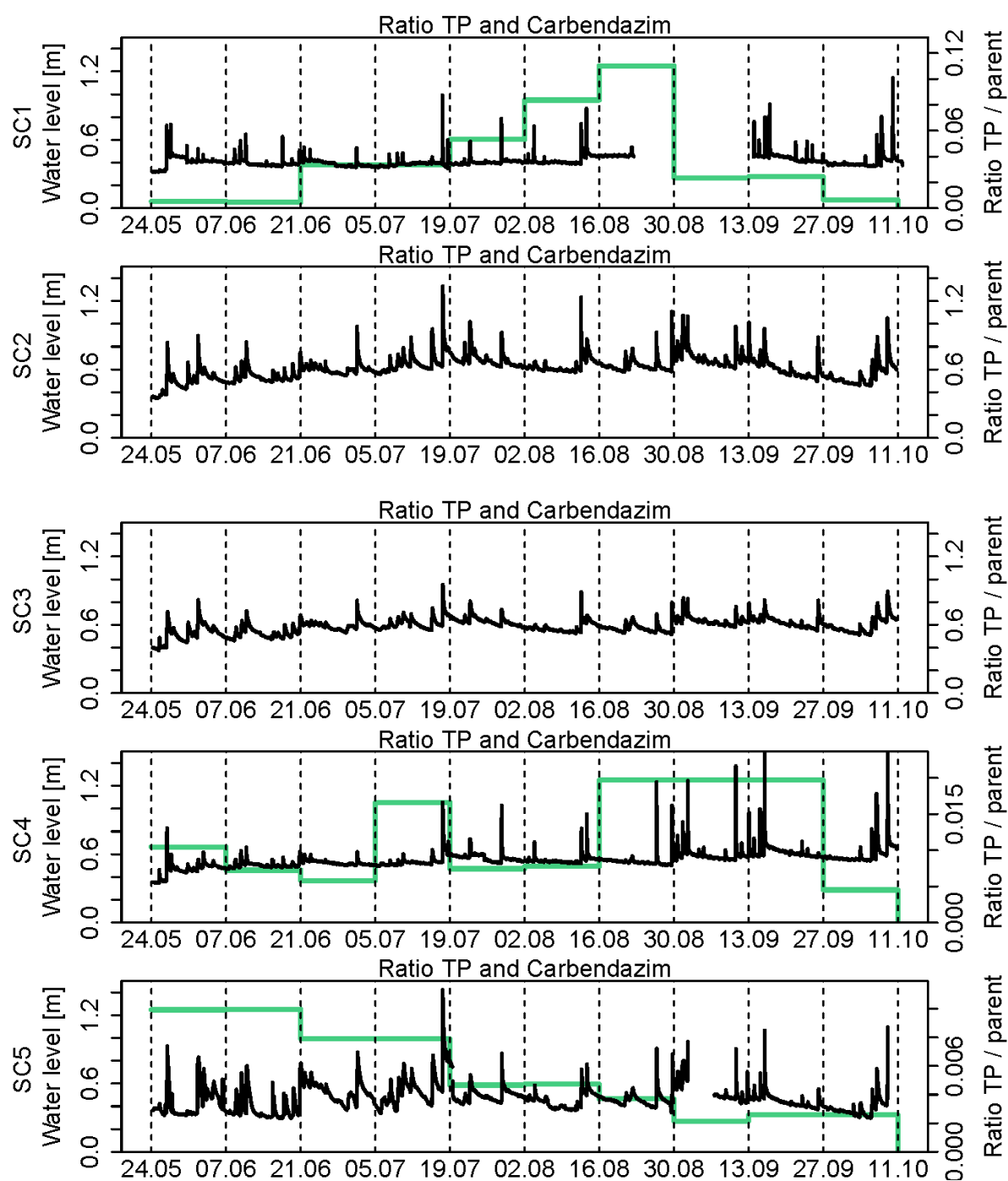


Figure SI-4 A8.2: Identification of highest diuron TP/diuron ratio at SC3, SC4, SC5, SC6 and SC8 in 2015. Water levels (black lines) and the ratios of the diuron TP and the parent diuron (green lines) are presented. The left y axis present water levels and right y axis the ratios of the diuron TP and the parent diuron. Sharply decreased ratios are used to indicate possible inputs with short residence times of the parent compound before entering the streams.



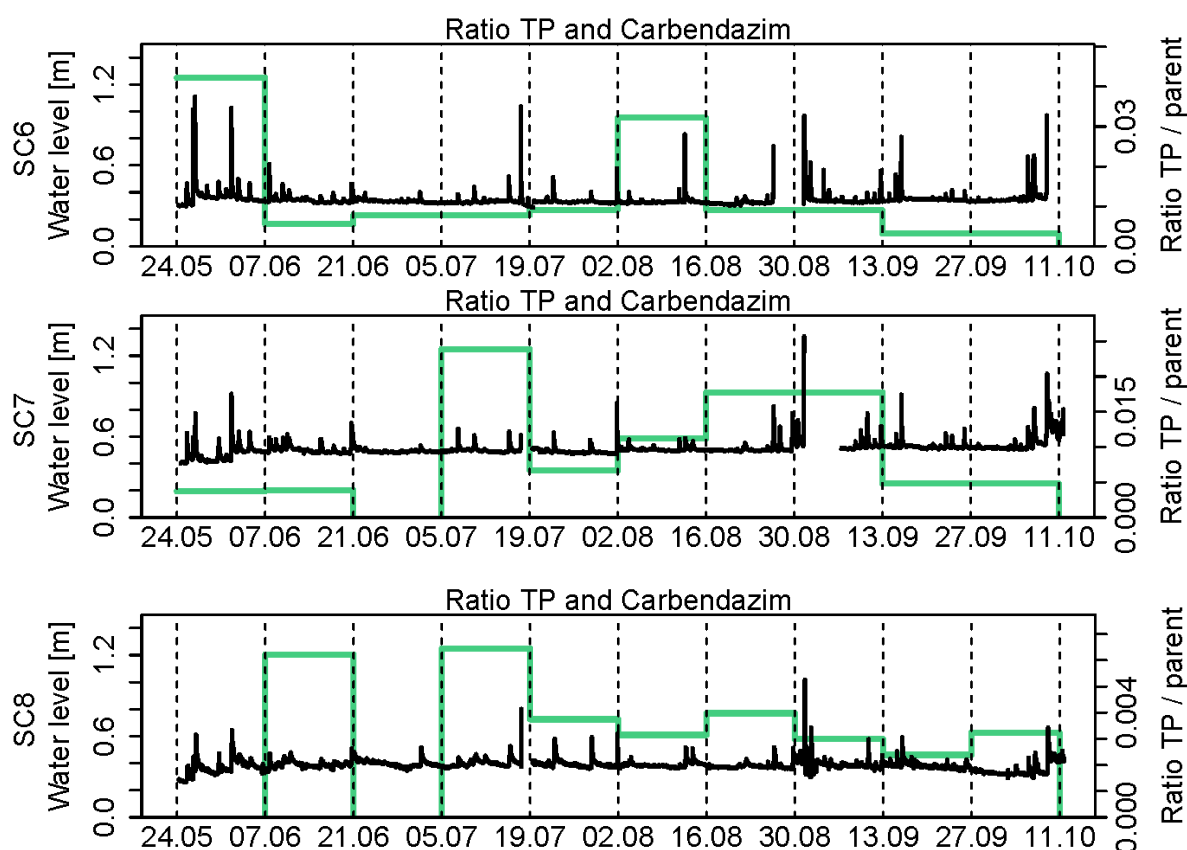
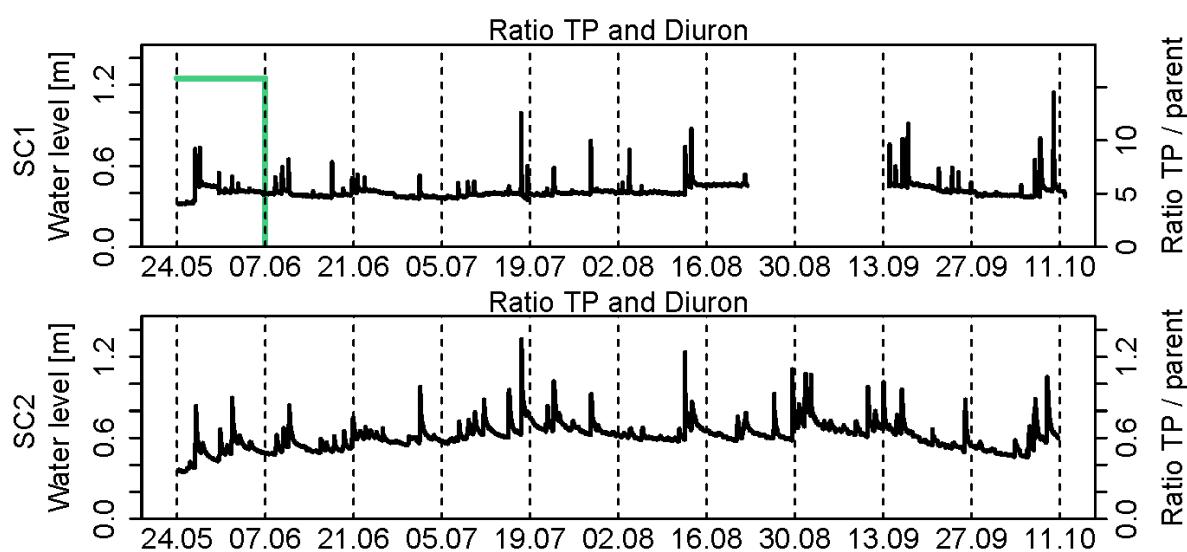


Figure SI-4 A8.3: Identification of highest carbendazim TP/carbendazim ratio at SC1, SC2, SC3, SC4, SC5, SC6, SC7 and SC8 in 2016. Water levels (black lines) and the ratios of the carbendazim TP and the parent carbendazim (green lines) are presented. The left y axis present water levels and right y axis the ratios of the carbendazim TP and the parent carbendazim. Sharply decreased ratios are used to indicate possible inputs with short residence times of the parent compound before entering the streams.



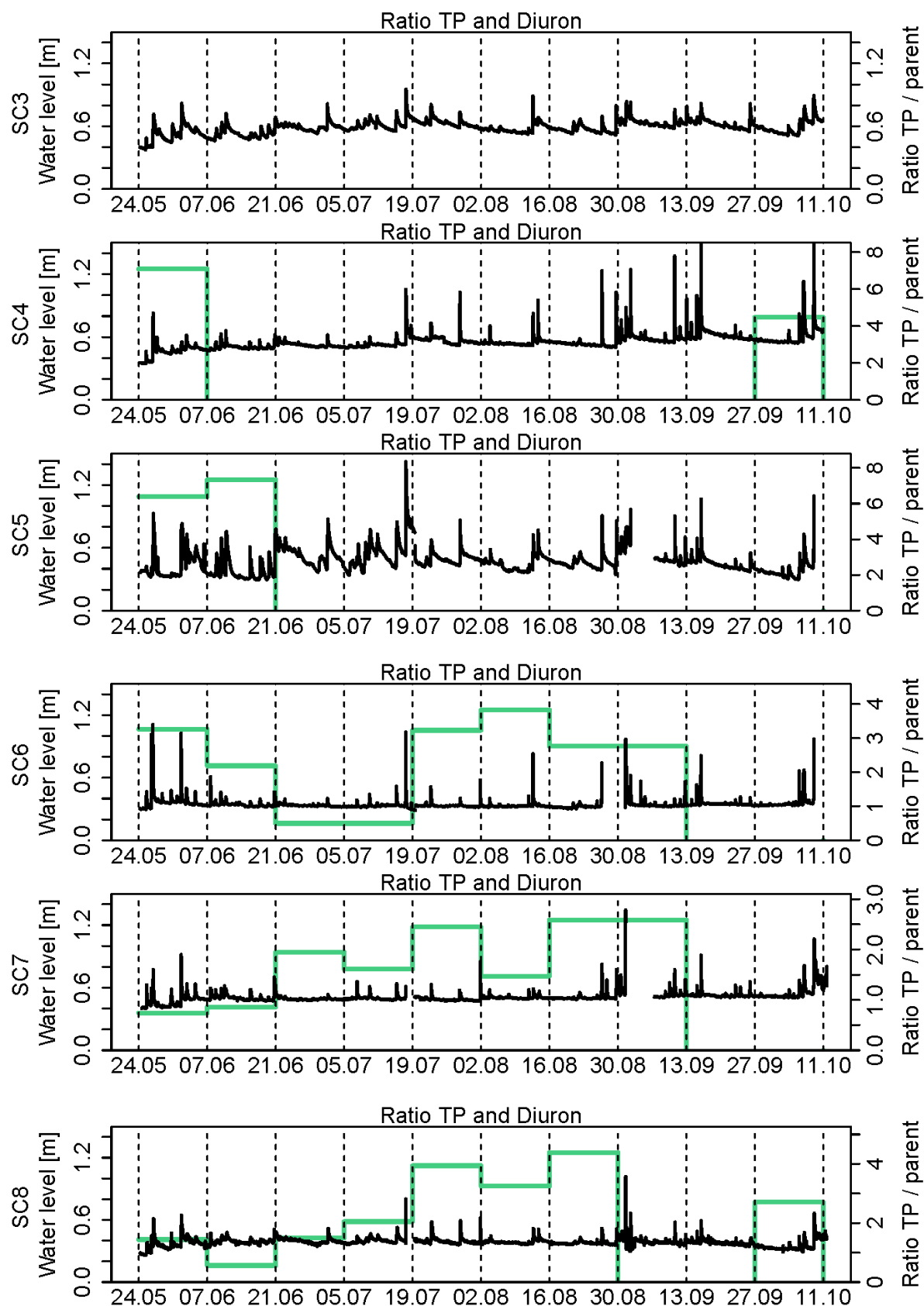


Figure SI-4 A8.4: Identification of highest diuron TP/diuron ratio at SC1, SC2, SC3, SC4, SC5, SC6, SC7 and SC8 in 2016. Water levels (black lines) and the ratios of the diuron TP and the parent diuron (green lines) are presented. The left y axis present water levels and right y axis the ratios of the diuron TP and the parent diuron. Sharply decreased ratios are used to indicate possible inputs with short residence times of the parent compound before entering the streams.

SI-4 A6 Important drivers explaining inputs from surface-runoff

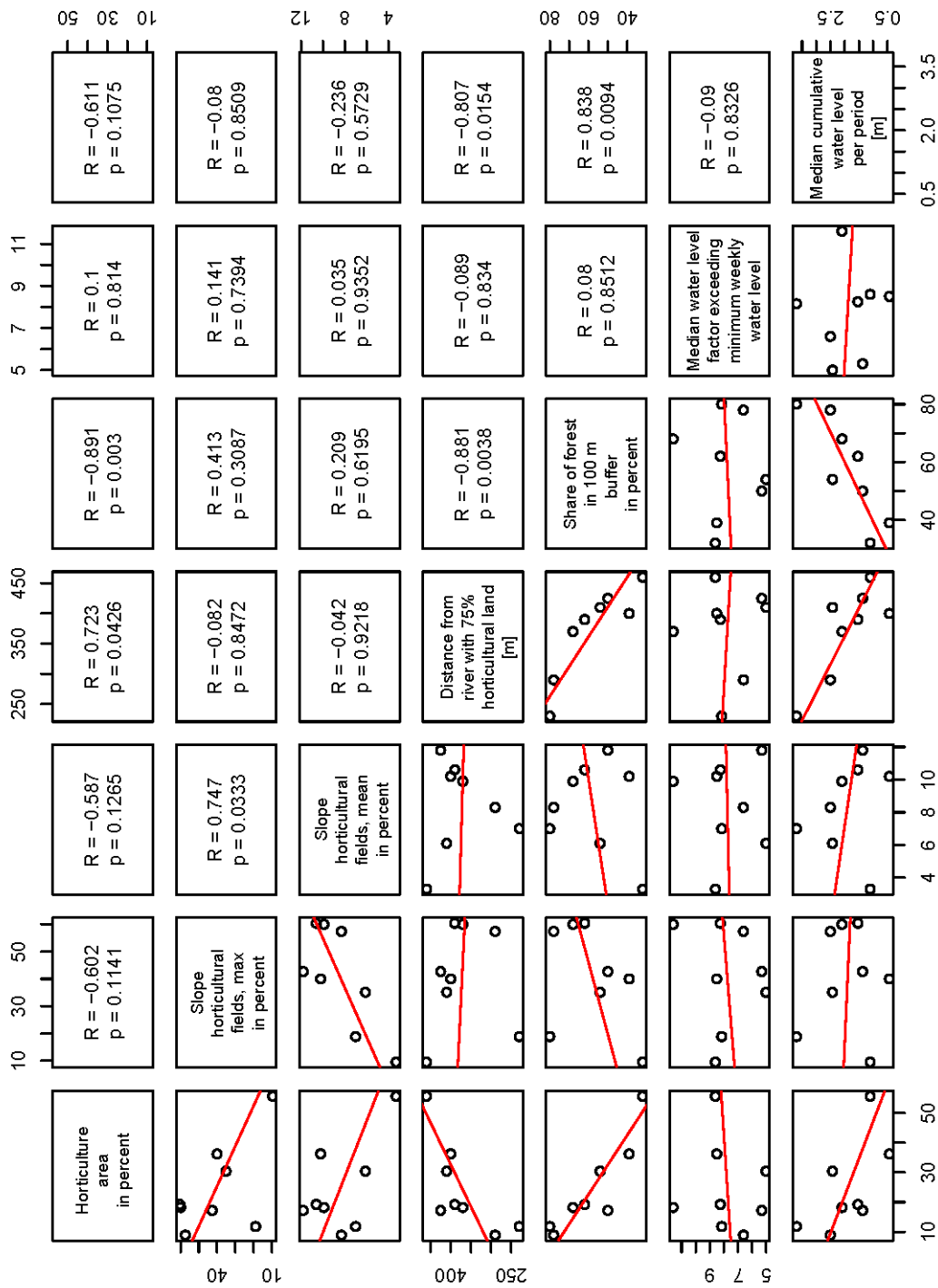
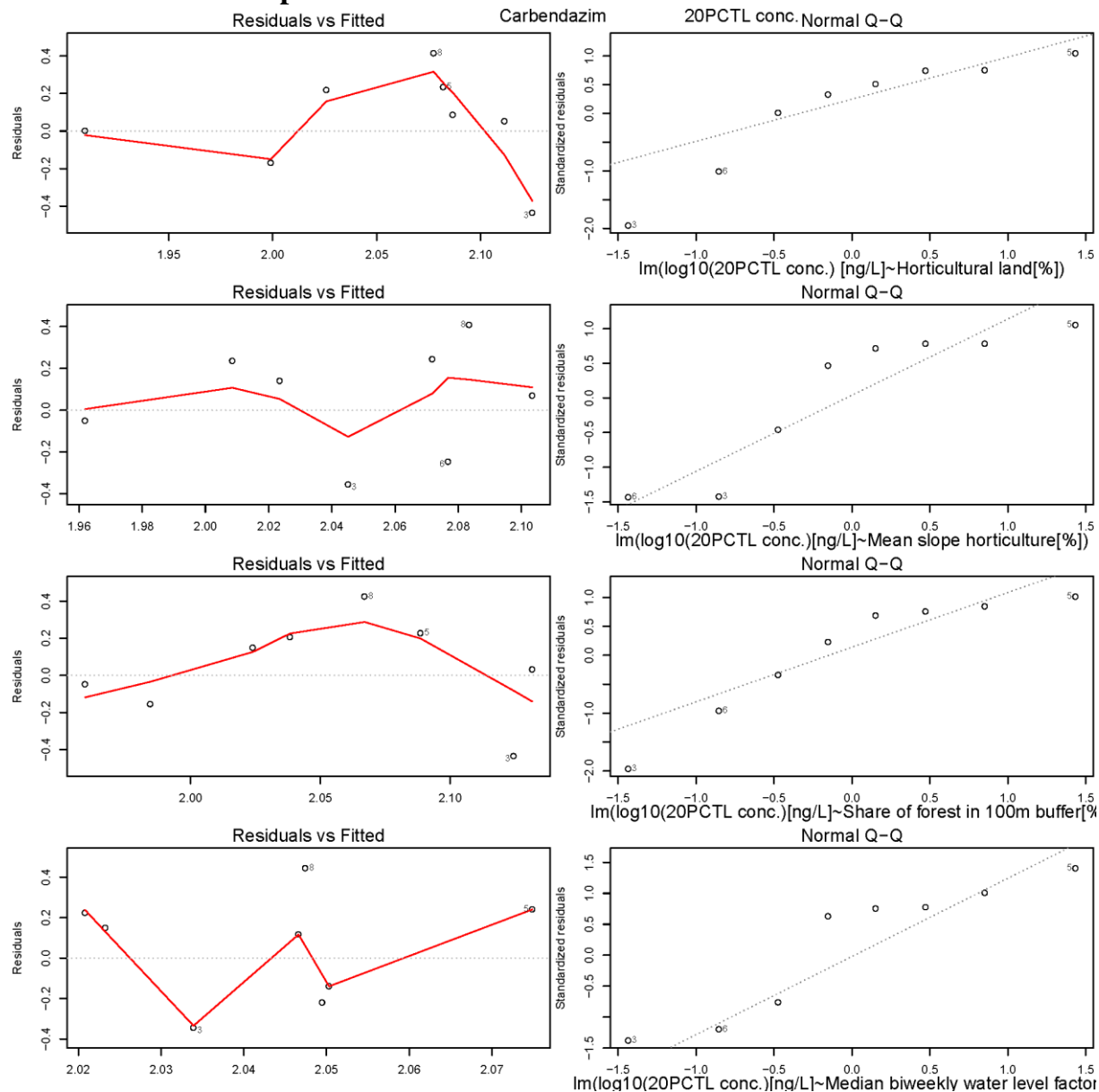


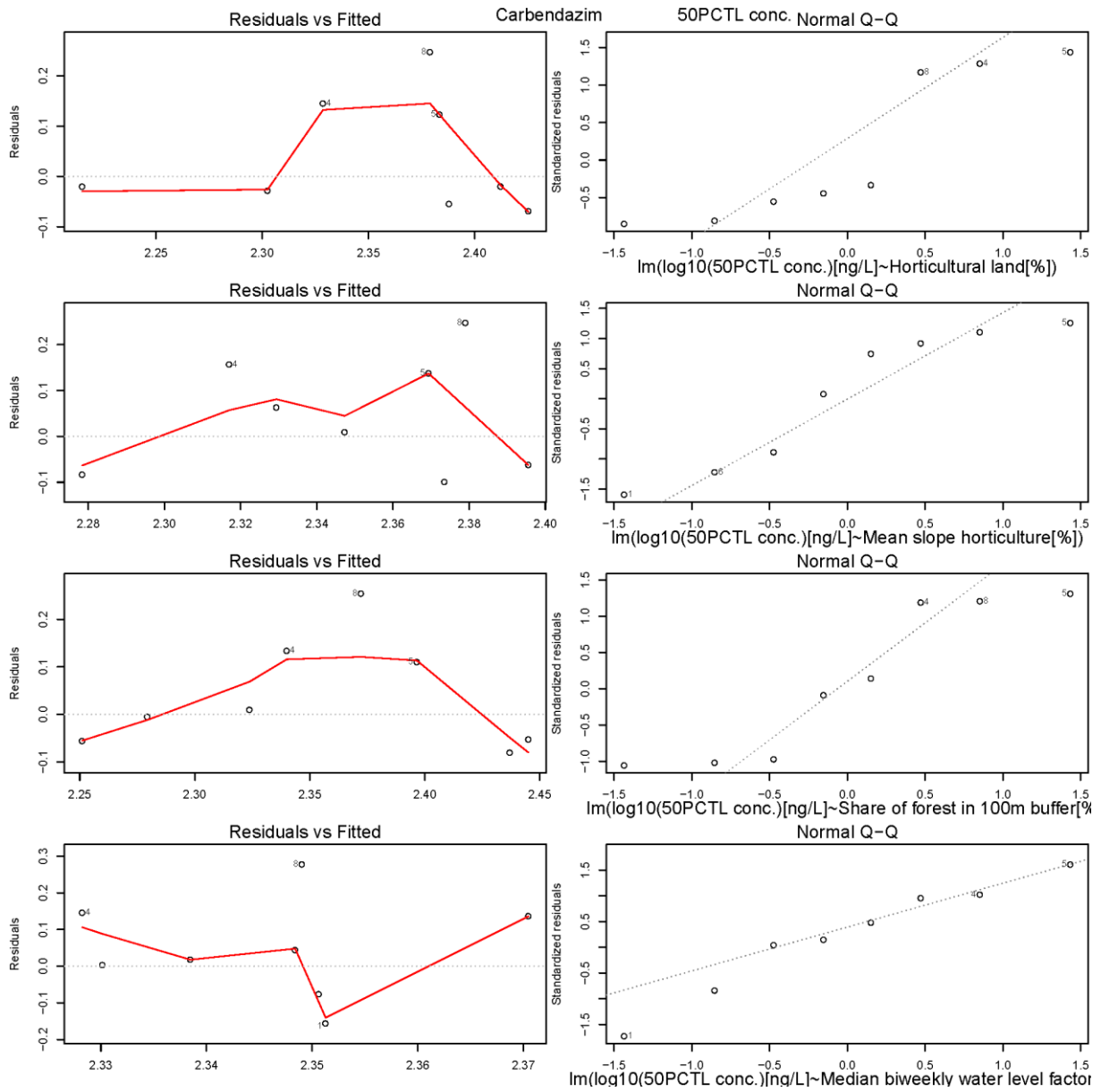
Figure SI-4 A9: Comparison of the explanatory variables. Correlation plots are presented in the bottom-left part and the pearson correlation coefficient and p values are presented on the top right part. The explanatory variable are shown in a diagonal line between the correlations and the coefficients and p-values.

SI-4 A7 Linear regression model data for carbendazim

SI-4 A7.1 Linear regression model with horticultural area [%], share of forest in 100 m stream buffer zone, median biweekly water level factors and average slope of horticultural field [%] as explanatory variables, periods and percentile concentrations as dependent variables for carbendazim.



Chapter SI-4 A



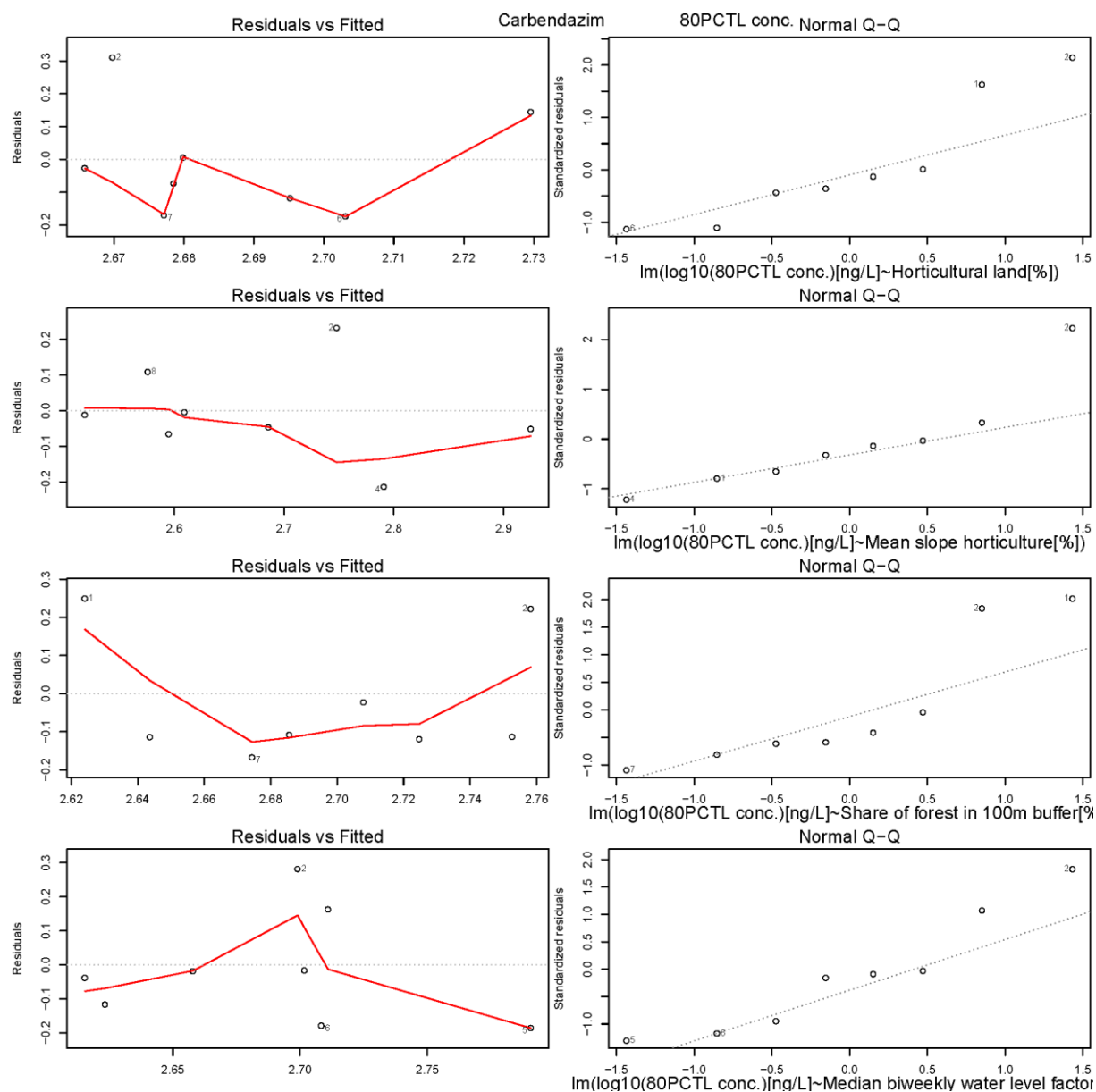


Figure SI-4 A10: Residual and Normal Q-Q plot for the weighted linear regression model for carbendazim with 20, 50 and 80 percentile concentrations, from top to bottom (left side, residual plots: x-axis: fitted value, y axis: residuals; right side normal Q-Q plots: x-axis: theoretical quantiles, y-axis sample quantiles).

SI-4 A8 Possible pesticide inputs via infiltration into the ground

Table SI-4 A4: Maximum pesticides and TP concentrations in grab samples from drinking water tanks and their physicochemical characteristics. Drinking water tanks were located in the nested SC2 and SC4.

Compound	Type	$\log K_{ow}^*$	$\log K_{oc}^*$	Water solubility at 25°C [mg/L]*	LOQ [ng/L]	Maximum concentration [ng/L] in SC3	Maximum concentration [ng/L] in SC4
Acetochlor-ESA + Alachlor-ESA	TP herbicide	1.82	1.07	0.25	2.4	5.4	< LOQ
Boscalid	Fungicide	2.96	3.98	4.60	2	< LOQ	< LOQ
Bromoxynil	Herbicide	2.70	2.52	130	0.2	0.3	< LOQ
Carbendazim	Fungicide	1.52	2.58	29	4	28	< LOQ
Chloridazon-desphenyl	TP herbicide	-1.59	1.56	87'820	6	< LOQ	< LOQ
Chlorothalonil-4-hydroxy-carbonacid amide	TP fungicide	3.09	2.92	115.70	1	110	< LOQ
Cyromazin	Insecticide	0.96	1.46	13'000	0.4	0.8	< LOQ
Dimethomorph	Fungicide	2.36	3.76	49.20	0.6	69	< LOQ
Imidacloprid	Insecticide	-1.45	3.69	369'200	0.9	1.3	< LOQ
Metribuzin	Herbicide	1.49	1.73	1'304	1	6.5	< LOQ

Compound	Type	$\log K_{ow}^*$	$\log K_{oc}^*$	Water solubility at 25°C [mg/L]*	LOQ [ng/L]	Maximum concentration [ng/L] in SC3	Maximum concentration [ng/L] in SC4
Metribuzin-Desamino (DA)	TP herbicide	2.51	2.46	318	0.4	1.7	< LOQ
IPBC	Fungicide	2.45	2.46	126.60	9	< LOQ	< LOQ

* determined with [EPISuite4.1](#).

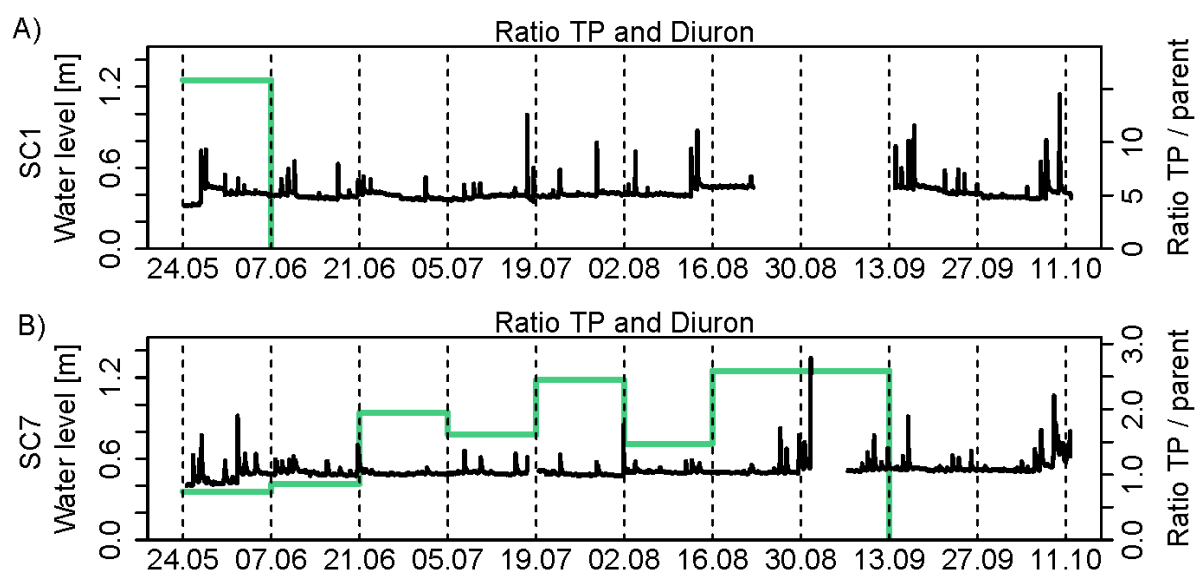


Figure SI-4 A12: Identification of highest diuron TP/diuron ratio at SC1 (A) and SC7 (B). Water levels (black lines) and the ratios of the diuron TP and the parent diuron (green lines) are presented. The left y axis present water levels and right y axis the ratios of the diuron TP and the parent diuron. Elevated ratios among the SCs are used to indicate inputs with long residence times and advanced transformation of the parent compound before entering the streams.

5. Chapter Conclusion and outlook

The aims of the presented study were to investigate the pollution of the streams in the tropical Tapezco river catchment, with a focus on pesticides and pesticide transformation products (PPTP) by using three passive sampling samplers (Chapter 2), to perform environmental monitoring and risk assessment (Chapter 3) and to suggest possible mitigation options by identifying pesticide input pathways (Chapter 4). The results of this thesis showed that the use of a multi-passive sampling approach provided a comprehensive, time-integrated picture of the PPTP pollution in all of the analyzed streams. Using this PPTP pollution data as measured environmental concentrations in combination with internationally accepted risk assessment and water quality assessment approaches revealed that particularly invertebrates suffer continuously from pesticide pollution throughout the catchment. For a selection of the most environmentally concerning pesticides, input pathways could partly be elucidated by using their pesticide concentration data, hydrological and topographical characteristics of the catchment and ground water samples. In the following part, the most important outcomes from this work will be discussed in light of perspectives for further research and possible applications.

5.1 Improvement of passive samplers and sampling strategies

By using SDB disks and the WLPSS sampler, a comprehensive spectrum of 99 semi-polar and polar PPTP were detected in the streams of the Tapezco river catchment. Using PDMS sheets as a complementary sampling method, ten further non-polar pesticides were added to the set. By this multi-sampler approach, the analyzed compound spectrum was significantly broadened compared to the single existent previous study in this catchment of Ramírez et al. (2016), which relied on grab sampling. The study presented in Chapter 2 contributes to the understanding of pesticide occurrence in little studied horticultural areas in Costa Rica and has the potential to be used as a model for studying similar tropical catchments in other Middle-Income Countries.

The SDB and the PDMS approach performed best in terms of yield in quantitative biweekly concentration data (90% sample recovery for SDB disks and 92% sample recovery for PDMS sheets) as opposed to the WLPSS sampling (15%). Previous work of e.g. Moschet et al. (2015), Schreiner et al. (2021), and Ahrens et al. (2015) has shown that in temperate regions, the applied sorbent-based passive samplers are excellent tools for monitoring a broad spectrum of emerging pollutants to yield time-integrated pesticide data. This study now demonstrated that the SDB disks and PDMS sheets are also applicable in tropical regions at difficult to reach sampling sites. Beyond that, the result of this study confirmed that these approaches can be easily applied in streams with rocky river beds and sites with strong water level fluctuations. Even though the SDB and the PDMS samplers performed well, the study was limited to material dependent (sampling rate) R_s values from the literature which is associated with an uncertainty as previously discussed (Curchod et al. 2019, Moschet et al. 2014). Uncertainty may be reduced by conducting dedicated uptake experiments for all targeted PPTP, as demonstrated by Ahrens et al. (2015), Mechelke et al. (2019) and Schreiner et al. (2020). Ideally, these uptake experiments should be performed under conditions similar to those in the concerned tropical streams, e.g., for the site studied here, in terms of temperature (17.1 ± 1.4 °C, $n = 205$), pH (7.3 ± 0.73 , $n = 173$), conductivity (105 ± 80 µS/cm, $n = 203$) and oxygen (7.8 ± 0.6 mg/l, $n = 212$). However, conducting such uptake experiments was out of the scope of this study.

Application of the WLPSS followed the hypothesis that, by sampling an increased volume of water simultaneously with increasing water levels, pesticide concentrations which increase due to heavy rain events would be captured immediately with the WLPSS in light of the absence of sorption processes as with the SDB disks and the overlayed PES membrane. Indeed, higher pesticide concentrations were confirmed for seven PPTP. Nevertheless, the WLPSS was more difficult to install in the streams and more prone to become detached and translocated by the

current than the sorbent-based samplers. Moreover, the WLPSS is still at an early stage of development and more testing and calibration of the pressure control devices (HPLC capillary and the precision valve) are required to better control the sampling volumes. Other knowledge gaps concern the dependency of the sampled volume on the immersion depth in the water over time, which should be tested in more detail both in the laboratory and under field conditions. The system should be immersed at different depths and the sampling rates determined over time.

Yet, the WLPSS sampler opens up new opportunities to tackle different research questions. In the current study, the system was applied to continuously sample pesticides from the stream. In a pending publication of a field study (Schönenberger et al. (*in preparation*)), the WLPSS system was slightly adapted and successfully applied for event-driven monitoring to record pesticide peaks in manholes next to fields right after intense precipitations. In combination with the sorbent-based passive samplers and an improved event-driven WLPSS sampling, complementary pesticide information can be obtained and allow for a more on a par comparison than was possible in this thesis. This means that continuous sorbent-based, time-integrated averaged PPTP concentrations, covering inputs during both rainy and dry periods, can be contrasted with short-term PPTP concentration peaks after rain events. The necessity to be able to distinguish short-term from time-integrating events was illustrated in this thesis where significant pesticides fluxes into the streams during both rainy and dry periods were observed.

5.2 Expansion of coverage of PPTP

The risk assessment of this study focused on quantification of 275 targeted chemicals. Of the detected PPTP, 18 pesticides reached concentrations leading to chronic pressure on aquatic organisms. Seven PPTP even reached concentrations high enough to cause acute effects. Of the different organisms groups (primary producers, vertebrates and invertebrates), invertebrates suffered the most from pesticide exposure. Negative impacts on invertebrates would be expected continuously without any phase for recovery. These results were in-line with the determined water quality status by using macroinvertebrate data, which likewise indicated adverse effects on the macroinvertebrate communities in streams of the Tapezco river catchment. These results were concordant with those of other studies in Costa Rica or other regions, showing that risks are often caused by a smaller set of pesticides (Echeverría-Sáenz et al. 2018, Munz et al. 2017, Rämö et al. 2018, Sangchan et al. 2014, Schreiner et al. 2021). In this context it is possible that the actual risk is well reflected based on a small selection of compounds. It has to be kept in mind, though, that this selection of risk-dominating compounds is very site/catchment-specific, depending on factors like land use, pesticide application practices and country-specific pesticide permits. As one example in the studied Tapezco river catchment, carbendazim posed chronic risks at all sites (chapter 3). Yet, carbendazim did not exceed its chronic Environmental Quality Standard in five medium-sized streams in Switzerland (Wittmer et al. 2014). Additionally, according to knowledge from High-Income Countries, a presence/absence control based non-target screening might be very helpful to identify unexpected though relevant pesticides, or other types of chemicals which might be present in the streams and should be added to the targeted screening (Hollender et al. 2017, Köppe et al. 2020, Ruff et al. 2015). Such compounds could include pesticides which are unregistered, prohibited or obsolete, therefore, not considered in general risk assessment approaches, such as different organochlorines (e.g. dichlorodiphenyltrichloroethane (DDT), lindane, dieldrin, endosulfan, endrin), organophosphates (for instance azinphos-ethyl, demeton, demeton, dimethoate, monocrotophos) or carbamates (such as aldicarb and aminocarb) which might be still relevant for Costa Rica (Servicio Fitosanitario del Estado Ministerio de Agricultura y Ganadería 2020). Additional chemicals from other use classes, e.g. biocides from urban areas or pharmaceuticals used in animal farming, are likely to

occur as well in the streams of the Tapzco river network, potentially causing adverse effects to the environment. Indeed, the share of urban areas in SC4, SC5, SC6, SC7 and SC8 ranges between 1.8% and 7.8% and the share of pasture (i.e. animal farming) exceeds 19% in the SC1, SC4, SC5, SC6, SC7, SC8, supporting this assumption. It is therefore likely that additional pollutants, not covered with the broad targeted analysis applied, have entered the streams.

Current analytical LC-HRMS methods allow for the application of comprehensive screening of suspect and non-target chemicals and optimized workflows for characterization, prioritization and identification of such unexpected chemicals have been implemented (Hollender et al. 2017, Hug et al. 2014, Köppe et al. 2020). Non-target screening approaches could be applied to the large MS/MS data set collected in this thesis to get a wider understanding of which other chemicals could pose risks to organisms in the streams of the Tapezco river catchment and which should be included in monitoring and risk assessment in the future.

5.3 Adaption of risk assessment and water quality approaches to tropical conditions

This study presented an environmental risk assessment based on the internationally accepted RQ and TU approaches along with the SPEAR_{pesticide}, the BMWP-CR and EPT-taxa richness indices to describe the water quality. The RQ, TU and SPEAR_{pesticide} approaches have been developed for temperate regions with a strong European focus. The EPT-taxa richness index, while focusing on enumeration of these taxa in the streams, is quite limited in terms of taxa spectrum. It would be important to adapt these approaches by using effect concentration data of species representative for tropical environments and by broadening the considered species spectrum. Indeed, a project by the eco-toxicological department of UNA, Heredia, focusing on determining EQS applicable for tropical areas based on effect data of tropical species, is in the planning stage.

A number of pesticides which were not approved in the EU for use according to EC Directive 91/414 were detected in this theses. These include, e.g., acephate, triadinemol, profenophos, butachlor thiacloprid, metolachlor, carabryl, pyrometrozin, methomyl, monolinuron, flusilazol, terbumeton, benalaxyl, hexazinon, dimefuron and empenthrin. For these compounds, no EQS values were available for risk assessment. Accordingly, it would be beneficial to derive as well EQS values for these pesticides.

In addition, even though biotransformation generally leads to the release of products which are less toxic than their respective parent pesticide, it is possible that biotransformation products exert similar or even more potent toxic effects than their parent. Three examples are 1,4-dihydroxybenzene and 5-hydroxy-,1,4-naphthoquinone, two transformation products of carbaryl, or methamidophos, the transformation product of acephate (Boxall et al. 2004, Sinclair and Boxall 2003). Effects of biotransformation products are not generally considered in current retrospective risk assessment approaches, a situation in need of change.

Another important next step to improve risk assessment would be to calibrate the SPEAR_{pesticide} index for use in tropical areas. This would require calibration for the tropics; therefore, a broad set of macroinvertebrate data should be collected from pristine reference areas without any anthropogenic influence and pollution.

5.4 Improving identification of drivers explaining pesticide fluxes into streams

Statistical evaluation of the compiled data and water level time series enabled the identification of key drivers of pesticide fluxes from the fields into the streams for the Tapezco river catchment with its distinct topographic characteristics and unconventional farming practices for example cultivating crops partly on fields with steep slopes. Direct inputs from handling were identified with confidence for thiamethoxam, dimethoate and diuron. For bifenthrine, boscalid, deltamethrin, imidacloprid and propamocarb, such inputs were considered possible but more difficult to distinguish from other routes of input. Prior survey data (Staudacher et al. 2020) as well confirmed that inputs via handling are possible within the studied area. Regular workshops for the local farmers on sound pesticide handling practices and the implementation of biobeds for disposal should significantly decrease the inputs from handling over time. However, to evaluate the content and success of these workshops, the implementation of a continuous follow-up monitoring, based on the results and approaches evaluated in this thesis, would be necessary.

From the evaluation of the spatio-temporal concentration data and water level time series with linear regression models, it was found that for three insecticides (acephate, cyhalothrin and thiamethoxam) the average slopes of horticultural areas correlated positively with concentrations in streams. Concentrations of the fungicide, carbendazim, were high at all sites without showing increased inputs at sites with high average slopes. For several PPTP (2,6-dichlorbenzamide, boscalid, carbofuran, diazinon, diuron TP, linuron and prometryn + terbutryn), a high share of forest in the stream buffer zone seemed to limit the entry of pesticides into the streams. Restrictions with regard to pesticide use on steep slopes and the implementation of a stream buffer area with a high share of natural forest are thus recommended.

However, for some pesticides (acephate, bifenthrine, carbendazim, chlorpyrifos, cyhalothrin, cypermethrin, dimethoate, diuron, fipronil, imidacloprid, metribuzin, permethrin, propamocarb, tebuconazole and thiamethoxam), the fluxes into the streams were not reduced in areas with stream buffers with a high share of forest. Hence, this research points out the need of further investigations. The application of multiple linear regressions considering each concentration data, site dependent and time dependent random effects and the incorporation of additional information would help to substantially increase the interpretability and significance of the analysis of input pathways and shed light on the fluxes of these pesticides. Additionally included data could include information about time-resolved, spatial (geo-referenced) pesticide application rates. Further, field to stream connectivity analysis should be conducted. Small geographical features in the area between the fields and the streams can have an important impact regarding favoring pesticide fluxes via surface run-off into streams. Such local details could not be captured completely within this study. Relevant geographical features in the Tapezco catchment include natural and artificial ditches or roads connecting fields with the streams. To fully understand the fluxes of pesticides via surface run-off, to explain the losses from fields and the transport through the stream buffer area, detailed information of such topographical features would need to be gathered in dedicated field visits (Schönenberger et al. (in preparation)).

Identification of input pathways was focused on the subset of pesticides provoking highest ecotoxicological risk. Clearly, the incorporation of further information, such as all measured spatio-temporal distributed pesticide data, would be a promising next step in order to further define specific pesticide fluxes from field into streams and elaborate practical mitigation options.

5.5 Closing statement

This thesis offers a thorough evaluation of pesticides in tropical streams using the Tapezco river catchment as example. It provides fundamental information about the application of different sampling techniques for environmental pesticide monitoring studies in Low- and Middle-Income Countries, such as Costa Rica. Having this environmental chemical data set at hand allowed for the evaluation of environmental risks to the aquatic freshwater system, applying internationally recognized environmental risk assessment approaches within a structured and data-based framework. This information allowed for a data-driven identification and proposition of pesticide mitigation strategies. The entire workflow, from monitoring environmental pollution, to risk assessment, with the final aim of proposing and implementing mitigation options targeted on improving environmental health, is a useful advance in the evaluation of anthropogenic input on the environment and can be applied in the future to a range of areas around the globe with similar meteorological, hydrological and topographical features.

5.6 Literature

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Glossary

Glossary

AA-EQS	Annual average Environmental Quality Standards (chronic)
AEQS	Acute Environmental Quality Standard
ARQ	Acute risk quotient
ASE	Accelerated solvent extraction
BMWP-CR	The Biological Monitoring Working Party Index adapted to Costa Rica
CAS	Chemical Abstracts Service
CEQS	Chronic Environmental Quality Standard
CRQ	Chronic risk quotient
CRQ	Chronic risk quotient
DEM	Digital elevation model
EC	Effect concentration
EC ₅₀	Median effect concentration for 50% of a reference species
EPT	Ephemeroptera, Plecoptera and Tricoptera
Eq.	Equation
EQS	Environmental Quality Standard
ESI	Electrospray ionization
F	Fungicide
GC-APCI-MS/MS	Atmospheric pressure chemical ionization gas chromatography, tandem mass spectrometry
H	Herbicide
I	Insecticide
I	Invertebrates
ILIS	Isotopically labeled internal standards
IRET	the Central American Institute for Studies on Toxic Substances, Costa Rica. In Spanish: Instituto Regional de Estudios en Sustancias Tóxicas
LAMICS	Low- and Middle-Income Countries
LAREP	Laboratorio de Análisis de Residuos de Plaguicidas
LC	Lethal concentration
LC-HR MS/MS	High resolution liquid chromatography tandem mass spectrometry
<i>Log K_{OC}</i>	Logarithmic Soil Organic Carbon-Water Partition Coefficient
<i>Log K_{OW}</i>	Logarithmic Octanol-Water Partition Coefficient
MAC-EQS	Maximum acceptable concentration Environmental Quality Standards (acute)
MEC	Measured environmental concentrations
NOEC	No observed effect concentration
NPW	Nanopure water

Glossary

P	Primary producers
PDMS	Polydimethylsiloxane
PEC	Predicted environmental concentrations
PES	Polyethersulfone
PFTE	Polytetrafluoroethylene
PNEC	Predicted non-effect concentration
PPTP	Pesticides and pesticide transformation products
PVC	Polyvinyl chloride
QM	Tapezco river site Quebrada Maquina
QS	Tapezco river site Quebrada Saino
RC	Tapezco river site Catarata
RCF	Relative centrifugal force
STDs	Reference standards
RF	Radio frequency
RJ	Tapezco river site Jilguero
rpm	Rounds per minute
RQ	Risk quotient, single compound
RQ _{mix}	Risk quotients of pesticides and pesticide transformation product mixtures
R _s	Sampling rate
RT	Retention times
RTZ	Tapezco river
RTZa	Tapezco river site Alto
RTZb	Tapezco river site Bajo
RTZm	Tapezco river site Medio
RTZn	Tapezco river site Naciente
SC	Sub-catchment
SDB	Sulfonated styrene-divinylbenzene
SPE	Solid phase extraction
SPEAR _{pesticide} index	Species at Risk index for pesticides
SSD	Species sensitivity distribution
TP	Transformation products
Tpal	Drinking water tank “Asada Palmira Laguna”
Tpap	Drinking water tank “Asada Palmira”
Tpat	Drinking water tank “Asada Palmira Tapezco”
Tpm	Drinking water tank “Municipal Palmira”

Glossary

TU	Toxic Units
TU _{estimated}	Estimated Toxic Units deviated from SPEAR _{pesticide} data according to Knillmann et al. (2018) and Liess et al. (2021) section 3.3.5 a.
TU _{mix}	Toxic Units of pesticides and pesticide transformation product mixtures
UNA	Universidad Nacional, Heredia
V	Vertebrates
WLPSS	Water level proportional sampling system
$\Delta T1$	Time period from 30-Jul to 07-Oct, 2015
$\Delta T2a$	Time period from 02-Aug to 11-Oct, 2016
$\Delta T2b$	Time period from 25-May to 02-Aug, 2016

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Curriculum Vitae

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