
LOSS POTENTIAL AND RETENTION EFFICIENCY OF
PESTICIDES AND THEIR TRANSFORMATION PRODUCTS IN
A SMALL DRAINED AGRICULTURAL CATCHMENT

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Dedication

Für Maja und alle Kinder, für die wir unser Trinkwasser schützen müssen.

„Alles ist aus dem Wasser entsprungen!!

Alles wird durch Wasser erhalten!

Ozean, gönn uns dein ewiges Walten.

Wenn du nicht in Wolken sendetest,

Nicht reiche Bäche spendetest,

Hin und her nicht Flüsse wendetest,

Die Ströme nicht vollendetest,

Was wären Gebirge, was Ebenen und Welt?

Du bist's, der das frischeste Leben erhält.“

Johann Wolfgang von Goethe (Faust. Der Tragödie zweiter Teil, 1832. 2. Akt)

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Abstract

Studies on the reduction of diffuse agricultural inputs through pesticides and transformation products in surface waters and groundwater are currently receiving a lot of attention against the background of the European Green Deal, the European Water Framework Directive, and the Nations Action Plan on Plant Protection. In agriculturally drained areas without direct connection to surface water, pesticides and their transformation products are transported mainly via tile drainage pipes to the wider environmental compartment. The transport of pesticides and transformation products via tile drainage pipes is characterized by highly fluctuating pesticide loads, which are controlled by fast-response and precipitation-driven drainage events.

The overall main objective of this thesis is the elaboration of the negative impacts to the aquatic environment of pesticides and their transformation products in tile-drained agricultural headwater catchments. Measures will be developed to mitigate pesticide loads and, consequently, to preserve downstream water quality.

To identify targeted retention measures for impacted areas, the first step is to analyse the hydrology of a catchment and the pesticide transport pathways. In a 4-year study, the herbicides Metazachlor, Diflufenican, Flufenacet, Pendimethalin applicable against grass weeds and four transformation products were targeted in a small agricultural catchment (100 ha) in northern Germany. Pesticide loads in tile drainages were recorded over several months, each time starting after autumn application. For a spatial comparison, monitoring was carried out at the field and catchment scale in different environmental compartments, such as in soil, shallow groundwater, and in tile drainages up to a daily resolution.

Initially, environmental conditions such as soil moisture and temperature, CN - ratio, and the behaviour of fluorescent tracers in the soil were further elucidated to derive new conclusions on the transport and transformation behaviour of pesticides in soil and leaching to shallow groundwater at the field scale (Part I).

Newly applied and mobile pesticides leached into shallow groundwater under very dry soil conditions with only a minimal amount of precipitation. Formation of the transformation products required a warm and moist environment for microorganisms, which was only present in the capillary water-filled pores during dry conditions. This is because the main percolation of the transformation products was measured only after soil rewetting and warmer spring temperatures.

In a second step (Part II), field investigations at field and catchment scales were used to analyse the influence of factors such as weather conditions, discharge, application date and amount, and physico-chemical properties on pesticide transport in tile drainage over an extended period at daily resolution. Transport from field to catchment outlet was strongly dependent on subsurface hydrologic connectivity activated by adequate soil saturation. The magnitude of loads varied by a factor of 10 between field and catchment scale and between dry and wet weather conditions. A phasing system for pesticide loads at

the field and catchment scale was described to derive the timing of high and delayed loads and to provide recommendations for targeted tile drainage monitoring.

In a third step (Part III), a drainage pond system was investigated regarding its pesticide retention capacity. The hydraulic function of the 3,000 m² drainage pond system installed at the area outlet was determined using fluorescent tracers. The drainage pond system was modified to increase the flow paths and residence time of the pesticides and transformation products in the ponds. Finally, the retention efficiency was determined daily considering the interaction of pond water and shallow groundwater. The drainage pond system could serve as retention ponds to buffer high discharge and dilute peak concentrations, especially under wet conditions. Transformation processes occurred during extended residence times under moderate inflows. Pesticide retention potential by infiltration into the hyporheic zone of the pond was highest shortly after the drying period. In summary, existing drainage ponds can serve as retention measures if a) the temporal loads for pesticides and transformation products, as well as the hydrological characteristics (with tracers) are recorded and b) on this basis, pond modifications are made to improve retention.

In this dissertation, it was shown that high loads of pesticides and their transformation products occur at field and catchment scales in the short and long term under both dry and wet climatic site conditions. In particular, the permanent detection of mobile and persistent transformation products poses a risk. Future efforts should focus on improving regulatory monitoring strategies, such as monitoring of tile drainages and setting limits for transformation products in the Surface Water Regulation. In addition, this thesis demonstrates the need to promote small-scale agricultural retention measures close to field to directly mitigate pesticides and transformation products loads and to improve downstream water quality.

Zusammenfassung

Untersuchungen zur Reduzierung diffuser landwirtschaftlicher Einträge durch Pestizide und Transformationsprodukte in Oberflächengewässer und Grundwasser bekommen vor dem Hintergrund des Europäischen Grünen Deals, der Europäischen Wasserrahmenrichtlinie und des Nationalen Aktionsplans Pflanzenschutz gegenwärtig eine große Aufmerksamkeit. In landwirtschaftlich drainierten Gebieten ohne direkte Anbindung an Oberflächenwasser werden Pestizide und ihre Transformationsprodukte hauptsächlich über Drainagerohre in weitere Umweltkompartimente transportiert. Der Transport von Pestiziden und Transformationsprodukten über Drainagerohre ist durch stark schwankende Pestizidbelastungen charakterisiert, welche durch schnell reagierende und niederschlagsbedingte Drainageereignisse gesteuert werden.

Das Hauptziel dieser Arbeit besteht darin, die negativen Auswirkungen von Pestiziden und ihren Transformationsprodukten in drainierten landwirtschaftlichen Wassereinzugsgebieten auf die aquatische Umwelt aufzuzeigen. Es sollen Maßnahmen erarbeitet werden, wie der Pestizideintrag und damit einhergehend die Belastung der Gewässer in drainierten Einzugsgebieten verringert werden kann.

Um gezielt Rückhaltemaßnahmen für belastete Gebiete identifizieren zu können, müssen in einem ersten Schritt die Hydrologie eines Wassereinzugsgebiets und die Pestizidtransportwege analysiert werden. Im Rahmen einer vierjährigen Studie wurden gezielt die Herbizide Metazachlor, Diflufenican, Flufenacet, Pendimethalin und vier Transformationsprodukte in einem landwirtschaftlich geprägten Oberflächenwasserkleineinzugsgebiet (100 ha) in Norddeutschland untersucht. Die Erfassung der Pestizidfrachten in Drainagen erfolgte über mehrere Monate jeweils beginnend mit der Herbstapplikation. Für einen räumlichen Vergleich wurde das Monitoring auf Feld- und Einzugsgebietsebene in verschiedenen Medien wie im Boden, oberflächennahen Grundwasser und in den Drainagen bis hin zu täglichen Intervallen durchgeführt.

Zunächst wurden die Umweltbedingungen wie Bodenfeuchte und -temperatur, CN - Verhältnis sowie das Verhalten von Fluoreszenztracern im Boden näher beleuchtet, um neue Aussagen zum Transport- und Transformationsverhalten von Pestiziden im Boden und zur Versickerung in oberflächennahe Grundwasser auf der Feldskala abzuleiten (Part I). Neu applizierte und mobile Pestizide wurden bei sehr trockenen Bodenverhältnissen mit nur einer minimalen Menge an Niederschlag in das oberflächennahe Grundwasser ausgewaschen. Die Bildung der Transformationsprodukte erforderte ein warmes und feuchtes Milieu für Mikroorganismen, welches bei Trockenheit nur in den kapillarwassergefüllten Poren vorhanden war. Denn die hauptsächliche Versickerung der Transformationsprodukte wurde erst nach Wiederbefeuchtung des Bodens und wärmeren Frühlingstemperaturen gemessen.

In einem zweiten Schritt (Part II) wurde auf der Feld- und Einzugsgebietsskala, über einen längeren Zeitraum in täglicher Auflösung, der Einfluss von Faktoren wie Witterungsbedingungen, Abfluss, Applikationsdatum und -menge sowie physikalisch-chemische Eigenschaften auf den Pestizidtransport in der Drainageentwässerung analysiert. Der Transport vom Feld- zum Einzugsgebietsauslass hing stark

von der unterirdischen hydrologischen Konnektivität ab, welche durch eine ausreichende Bodensättigung aktiviert wurde. Das Ausmaß der Belastung variierte um das 10-Fache zwischen Feld- und Einzugsgebietsebene sowie zwischen trockenen und nassen Wetterbedingungen. Es wurde ein Phasensystem für Pestizidfrachten auf Feld- und Einzugsgebietsskala beschrieben, um den Zeitpunkt hoher und verzögerter Belastungen abzuleiten und Empfehlungen für das Drainagemonitoring zu geben.

In einem dritten Schritt (Part III) wurde ein Drainageteichsystem auf sein Rückhaltevermögen für Pestizide untersucht. Die hydraulische Funktion des am Gebietsauslass installierten 3,000 m² Drainageteichsystems wurde unter Verwendung von Fluoreszenztracern ermittelt. Um die Fließwege und die Aufenthaltszeit der Stoffe in den Teichen zu verlängern, wurde das Drainageteichsystem modifiziert. Abschließend wurde die Retentionseffizienz, auf täglicher Basis, unter Berücksichtigung der Interaktion von Teichwasser und oberflächennahem Grundwasser ermittelt. Das Drainageteichsystem konnte besonders unter nassen Bedingungen als Rückhaltebecken dienen und hohe Abflüsse puffern und Spitzenkonzentrationen verdünnen. Umwandlungsprozesse fanden bei längeren Verweilzeiten unter moderaten Zuflüssen statt. Das Rückhaltepotenzial für Pestizide durch Infiltration in die hyporheische Zone des Teichs war kurz nach der Trockenperiode am höchsten. Zusammenfassend lässt sich übertragen, dass bestehende Drainageteiche als Retentionsmaßnahme dienen können, wenn a) die zeitlichen Belastungssituationen für Pestizide und Transformationsprodukte sowie die hydrologischen Eigenschaften (mit Tracern) erfasst werden und b) auf dieser Basis Teichmodifikationen vorgenommen werden, um den Rückhalt zu verbessern.

In der vorliegenden Arbeit konnte gezeigt werden, dass Pestizide und deren Transformationsprodukte sowohl unter trockenen als auch unter feuchten klimatischen Standortbedingungen kurz- und langfristig zu erhöhten Konzentrationen auf Feld- und Einzugsgebietsskala führen können. Insbesondere der dauerhafte Nachweis von mobilen und persistenten Transformationsprodukten stellt ein Risiko dar. Zukünftig sollte sich auf die Verbesserung der behördlichen Überwachungsstrategien, wie das überblicksmäßige Monitoring von Drainagen und die Festlegung von Grenzwerten für Transformationsprodukte in der Oberflächengewässerverordnung konzentriert werden. Darüber hinaus wird die Notwendigkeit aufgezeigt, kleinräumige Rückhaltemaßnahmen in Ackernähe zu fördern, um Pestizidfrachten direkt zu vermindern und um flussabwärts die Gewässerqualität zu verbessern.

1. Introduction

For increased crop yields and a stable food supply, prevailing agricultural practices rely on the use of pesticides against pests, weeds, and diseases (Mohaupt et al., 2020). However, the benefit to the agricultural sector adversely affects other parts of our environment. Pesticides can severely harm environmental compartments (Ulrich et al., 2018; García-Delgado et al., 2019) and human health (Swartjes and Van der Aa, 2020).

Within an EU-wide project launched by the European Environment Agency, 180 pesticides have been monitored from 2007 to 2017 (Mohaupt et al., 2020). This collective European database was a first attempt at assessing pesticide risks at the European level. As an example, the measured herbicide values showed exceedances at 5 to 15 % of the surface water and 7 % of the groundwater monitoring stations. This statistical and monitored evidence justifies the need for the measures currently adopted in the European Green Deal to significantly reduce the application of pesticides by 50 % by 2030 to shape a sustainable future and pollution-free environment (EC, 2019). Different regulatory instruments are used in Germany to assess pesticide and transformation product (TP) detections in water bodies (Tab 1-1). In Germany, the total consumption of pesticides in 2018 was 44,948 tonnes, including a herbicide consumption of 14,544 tons (FAO, 2020). The offered spectrum of active ingredients approved in Germany was 288 in 2019 and increased by 39 since 2010 (BVL, 2020). This increase was mainly caused by fungicides and herbicides.

Tab 1-1: Legal regulations in Germany to assess pesticide and transformation product concentrations in water bodies.

Parameter	Source	Unit	Explanation
UQN	OGewV (2016)	$\mu\text{g L}^{-1}$ pesticide-specific	environmental quality standard for surface waters (ZHK = max concentration, JD = annual average concentration)
RAK	UBA (2020)	$\mu\text{g L}^{-1}$ pesticide-specific	regulatory acceptable concentration for selected pesticide active ingredients in surface water
GW-QN	GrwV (2010)	$0.1 \mu\text{g L}^{-1}$	regulatory threshold for pesticides and relevant transformation products in groundwater
GOW	UBA (2019)	1 or $3 \mu\text{g L}^{-1}$	health related guide values for non-relevant transformation products in drinking water
precautionary value	TrinkwV (2016)	$0.1 \mu\text{g L}^{-1}$ single, $0.5 \mu\text{g L}^{-1}$ sum of compounds	threshold for pesticides and relevant transformation products in drinking water

It can be assumed that pesticides will still be approved in the next years and negative effects on water bodies cannot be completely prevented. To counteract this trend, the current German National Action Plan (BMELV and BMU, 2013) was initiated to increase the sustainable use of pesticides and to mitigate

negative impacts to the environment. It addresses the need for targeted water protection measures to prevent pesticides from entering surface waters and groundwater.

1.1. Pesticides and transformation products in agricultural landscapes

The hydrology of a watershed and the pesticide transport pathways need to be analysed to identify targeted measures for a specific area of interest. In general, pesticide transport in agricultural landscapes encompasses spray drift, volatilization, runoff, leaching, and tile drainage. Soils are the main environmental compartment where transporting, transforming, and storing pesticides and TPs takes place (Vryzas, 2018). Factors affecting their behaviour in soil are the sorption potential, depending on their physico-chemical properties, and their affinity to degradation processes such as photolysis, hydrolysis, and biodegradation (Fenner et al., 2013). After degradation, the resulting TPs are often more persistent in the environment (Schuhmann et al., 2019). They are often detected in higher frequencies and higher concentrations in comparison to parent compounds in surface water and groundwater bodies (e.g., Reemtsma et al., 2013; Rosenbom et al., 2015; Ulrich et al., 2019). Especially in lowlands with strong surface water - shallow groundwater interaction (Sophocleous, 2002), the transport of pesticides (McKnight et al., 2015) and the even more mobile TPs can interact in both directions, i.e., exfiltration and infiltration to groundwater (Hintze et al., 2020). The occurrence, fate, and behaviour of TPs are rarely monitored (Rousis et al., 2017) and field data are especially scarce (Fonseca et al., 2019).

The mobility and persistence of pesticides within soils is determined by their physico-chemical properties (Barriuso et al., 2008). Soil properties e.g., organic matter, clay type and content, soil pH, and soil temperature determine whether pesticides are adsorbed to soil particles or leached (Vryzas and Papadopoulou-Mourkidou, 2007). Leaching of pesticides in soil also depends on the amount and the distribution of precipitation events (Huseth and Groves, 2014) as well as on antecedent soil moisture conditions. Higher soil moisture content and a low adsorption capacity of soil (low clay content or low organic matter content) (Gupta and Gajbhiye, 2002) trigger compound availability for microbial transformation and an increased leaching rate (Pallud et al., 2004). Soil moisture and temperature are the main controls of transformation by microbial communities (Fenner et al., 2013; Vryzas, 2018).

Roughly 73 % of the soils in agricultural landscapes in the German federal state of Schleswig-Holstein are drained (Tetzlaff and Kuhr, 2011). Tile drainage systems shorten flow paths considerably (Holsten et al., 2012), and reduce the baseflow between 40 to 60 % (Schilling et al., 2010). Tournebize et al. (2017) presented an annual pattern for tile drainage pipes in Northern Europe with summer drought and highest flows in late fall and winter. The drainage discharge can vary seasonally and interannually depend on prevailing weather conditions (Pfannerstill et al., 2015; Willkommen et al., 2018; Guse et al., 2019). In highly tile-drained areas, pesticides are mainly transported from soil to surface water bodies by tile drainages (Kreuger, 1998; Holvoet et al., 2007). Kreuger (1998) observed an annual cycle of pesticide loss with maximum concentrations during or right after application. The first flush effect is followed by several load peaks during events of tile drainage discharge (Kreuger, 1998; Brown and van

Beinum, 2009). Common characteristics for pesticide transport via agricultural tile drainage pipes are highly variable pesticide loads controlled by fast reacting and precipitation-induced tile drainage discharge events (Schottler et al., 1994; Brown and van Beinum, 2009; Sandin et al., 2018). Preferential flow is an important transport pathway for pesticides in soil to tile drainages. Preferential flow occurs in macropores, like earthworm borrows, cracks or root channels (Jarvis, 2007), especially in anaerobic fractures of clay soils (Brüsch et al., 2016) but was also observed in loamy soils (Zehe and Flühler, 2001a, b). The fast transport is expected to depend on the prevailing subsurface connectivity of macropores and tile drainages in the soil profiles (Shipitalo et al., 1990). During wet hydrological conditions, in areas where surface runoff cannot reach receiving waters and infiltrates into depressions, macropore transport to tile drainage pipes was shown as a dominant pesticide loss pathway (Leu et al., 2004).

1.2. Pesticide retention strategies

The most important measure to mitigate pesticide entries in surface and groundwater is to minimize the applied pesticide amounts directly on the field. Areas with a high contribution to pesticide loss into surface water can be identified with the concept of critical source areas (i.e., Doppler et al., 2014). The location and size of high-risk areas vary with antecedent and prevailing weather conditions and impact the extent of pesticide loads strongly (Doppler et al., 2014). These results demand temporally and dynamically adapted retention solutions. Strong efforts are being made to develop new application techniques like spot farming (Wegener et al., 2019) with the aim of using less pesticides in agriculture. A variety of other future smart farming methods are being tested in many European research projects (reviewed in Moysiadis et al., 2021) to help facilitate the work and optimise pesticide management decisions for farmers.

Currently, for lowland drained agricultural catchments, several measures integrated between the drained field and receiving waters already exist to improve water quality and support the achievement of water quality goals of the European Water Framework Directive (EC, 2000). Those measures encompass reactive ditches (Pfannerstill et al., 2016), riparian buffer zones (Mander et al., 2017), constructed wetlands (Mander et al., 2017; Dollinger et al., 2018), vegetated buffer stripes (Prosser et al., 2020), and drainage ponds (Ulrich et al., 2019; Gaullier et al., 2020). These measures are essential elements of the European Green Infrastructure plan (EC, 2013) in rural landscapes and offer ecosystem services such as water purification and climate change mitigation (Mander et al., 2017). Depending on the heterogeneous regional conditions in terms of soil type and hydrology, these mitigation measures have to be selected and adapted according to the catchment specifications. For example, in drained agricultural areas with a surface water connection, the legally regulated width of riparian buffer stripes alone is often not sufficient to achieve optimal pesticide retention (Prosser et al., 2020). Riparian buffer zones cannot be applied in drained agricultural catchments without surface water connections. In those regions, the focus

is shifted to locally adapted and dynamic mitigation systems like drainage ponds (Ulrich et al., 2019; Gaullier et al., 2020).

Drainage ponds can be classified as natural landscape elements (Oertli et al., 2009) and are often connected to shallow groundwater. If they are of anthropogenic origin, they can be classified as free surface constructed wetlands (FSCW) (Vymazal, 2007) and they can be grouped based on their groundwater interaction as infiltration and non-infiltration ponds (Baird et al., 2020). Most natural ponds are in contact with shallow groundwater. So far, the existing knowledge about the effects of surface-groundwater interactions on budgets of pesticides and TPs is limited. Common processes within the drainage ponds include physical and biological degradation as well as sorption to sediment or plants (Imfeld et al., 2009). The degradation or retention rate is highly variable and depends further on the vegetation type (Vymazal and Březinová, 2015) and vegetation density (Mohr et al., 2007), which act as barriers to decelerate the flow velocity in the pond to support retention processes. The variety of applied and studied pesticides hampers the identification of single processes which effectively degrades the pesticide within the pond system. Since the physico-chemical properties of pesticides vary greatly (Maillard et al., 2011; Vymazal and Březinová, 2015), they react differently to the processes in their environment. Vymazal and Březinová (2015) discussed the coincident demand of anaerobic and aerobic degradation conditions for different pesticides. The key function of the drainage ponds is the prolongation of hydraulic detention time (Bundschuh et al., 2016) to facilitate retention or even degradation processes of target substances in the ponds (Brown and van Beinum, 2009; Sandin et al., 2018, Ulrich et al., 2019). Hydraulic conditions such as shallow water levels and reduced flow velocities (Gaullier et al., 2017; Tournebize et al., 2017) as well as an elongated pond shape (Persson and Wittgren, 2003; Gaullier et al., 2020) contribute to the efficiency of the pond system. In the retention system, the pollutant retention is most efficient for peaky chemographs (Greiwe et al., 2021), a common characteristic for agricultural tile drainage pipes, which are fast reacting, non-steady in discharge, and contain highly variable pesticide concentrations (Ulrich et al., 2012; Sandin et al., 2018). The retention efficiency depends on the properties of the pollutant and the wetland system and may reach up to 100 % (Gregoire et al., 2009). Pesticide retention reached 50 % in a pond with ten days residence time (Tournebize et al., 2017). In contrast, no or even negative retention (this is the case when output loads exceed input loads) was occasionally reported in small systems and explained by hydrological short-cuts or additional input from groundwater (Gaullier et al., 2019; Ulrich et al., 2019). Tournebize et al. (2017) stated design guidelines for optimum pesticide retention in new wetlands, which can be taken into account to optimise existing constructed or natural drainage ponds: (1) maximum distance of 100 ha between retention system and pesticide source, (2) a ratio > 1 % of pond surface area to drained catchment, (3) a 76 m³ pond volume per ha drained field area, (4) an average level of pond water at 0.8 m water, (5) implementation of barriers to increase water pathways through system, (6) avoidance of hydraulic dead zones by placing the inlet and outlet diagonally shifted from each other.

1.3. In-situ proxy for pesticide pathways in different environmental compartments

Pesticide concentrations in heterogeneous soil are very difficult to measure and the measurement process is very costly, time-consuming, and laborious. It follows, then, that data about the biochemical transformation of pesticides in the soil are scarce. Therefore, further techniques were sought out to reduce the effort. In soil, fluorescent tracers have traditionally been regarded as largely resistant to degradation, (Flury and Wai, 2003). However, in soil, the TP TP510 (Lange et al., 2018) of the fluorescent tracer Uranine was newly detected. It still needs to be investigated whether Uranine and its TP, TP510, can describe transformation processes of pesticides with similar characteristics to the fluorescent tracers and whether it can be used as an in-situ proxy.

In ponds, fluorescent tracers can be used as a tool to characterize solute transport (Stern et al., 2001; Leibundgut et al., 2009; Schuetz et al., 2012). Tracer breakthrough curves (TBC) illustrate the combined effect of conservative solute transport (i.e., advection, dispersion, mixing) and non-conservative solute retention (i.e., sorption, biochemical or photolytic decay). TBC parameters like mean residence time, hydraulic efficiency, and tracer mass recovery serve to characterize FSCW (free surface constructed wetlands) mitigation performance (Thackston et al., 1987; Kadlec, 1994; Lange et al., 2011). When applying the residence time approach (Kadlec, 1994), parameters of the TBC serve to assess hydraulic performance of the pond before and after modification. The residence time distribution (RTD) may be regarded as a probability density function for residence times inside the pond. The effective volume ratio (ϵ) (Thackston et al., 1987) characterizes the degree of mixing inside ponds, where small ϵ -values are an indicator for dead zones or short-circuiting. For more details, the interested reader is referred to Kadlec (1994) or Lange et al. (2011).

1.4. Research deficits

Pesticides and TP monitoring studies in soil and groundwater with a higher spatial and temporal resolution are highly sought after (Vryzas, 2018). The environmental behaviour and pathways of pesticide TPs under field conditions has not yet been fully analysed. Headwater catchments in agricultural lowlands with shallow groundwater are often tile-drained. It is expected that concentrations of pesticides are subject to very strong dynamic fluctuations based on the dynamic water flows (Rabiet et al., 2010). Rasmussen et al. (2013) highlights the need to investigate multiple anthropogenic stressors (e.g., pesticides) to delineate key contamination areas (Doppler et al., 2014) in headwater catchments. This knowledge could serve for the improvement of downstream water quality and the selection of suitable mitigation measures (Rasmussen et al., 2013). Field approaches with a higher temporal resolution and long-time tile drainage monitoring are still rare (Leu et al., 2004a; Freitas et al., 2008; Ulrich et al., 2012; Sandin et al., 2018). Hence, the research gap elaborated was the unclear impact of varying and closely intertwined control factors (antecedent and prevailing weather conditions, discharge, application amount and date, and physico-chemical properties) on the drainage transport pathways of pesticides at the field- and catchment scale in daily intervals. An important, long discussed, and current topic is the analysis of the

various conditions for compound transport via preferential flow (Jarvis et al., 2016; Sternagel et al., 2021). Pesticide transport via preferential flow pathways during low-intensity precipitation periods has not been explicitly studied in the field so far (Demand et al., 2019). An adjusted monitoring strategy according to hydrological conditions within a tile-drained landscape would need to be applied to identify both times and areas of special interest.

There is a choice of in situ retention measures depending on local conditions in the headwater catchment. Nevertheless, field data of pesticide mitigation measures in high temporal resolution are scarce and even scarcer for TPs (Ulrich et al., 2019). A continuously high temporal resolution would be necessary to assess retention effectiveness without loss of information. Concerning the calculation of the retention efficiency, existing knowledge about the effects of surface-groundwater interactions on budgets of pesticides and TPs in ponds is limited and surface-groundwater interaction is often neglected (Kadlec, 2010; Tournebize et al., 2013) or approximated as infiltration loss by water balance data (Baird et al., 2020).

1.5. Research questions

The overall main objective of this thesis is the elaboration of the negative impacts to the aquatic environment of pesticides and their transformation products in tile-drained headwater catchments and how pesticide inputs can be mitigated to preserve downstream water quality. This main objective can be put into a broader context and the approach of this thesis is transferable to other small-scale drained agricultural lowland areas. Three research questions can be derived from the identified research deficits:

- **How do variable hydrological conditions affect the soil transport of pesticides and their transformation products and how does the soil interaction respond to shallow groundwater?**
- **Which factors control the temporal dynamics of pesticide loads from tile drainages at field and catchment scales?**
- **What conditions allow drainage ponds to be a suitable agricultural management measure to effectively retain pesticides and their transformation products?**

The research questions were assigned to three thematic research parts (Fig 1-1). These interlinked parts frame this thesis and analyse in three steps the procedure on how to develop a suitable mitigation measure for pesticide and TP loads in a previously unknown catchment area.

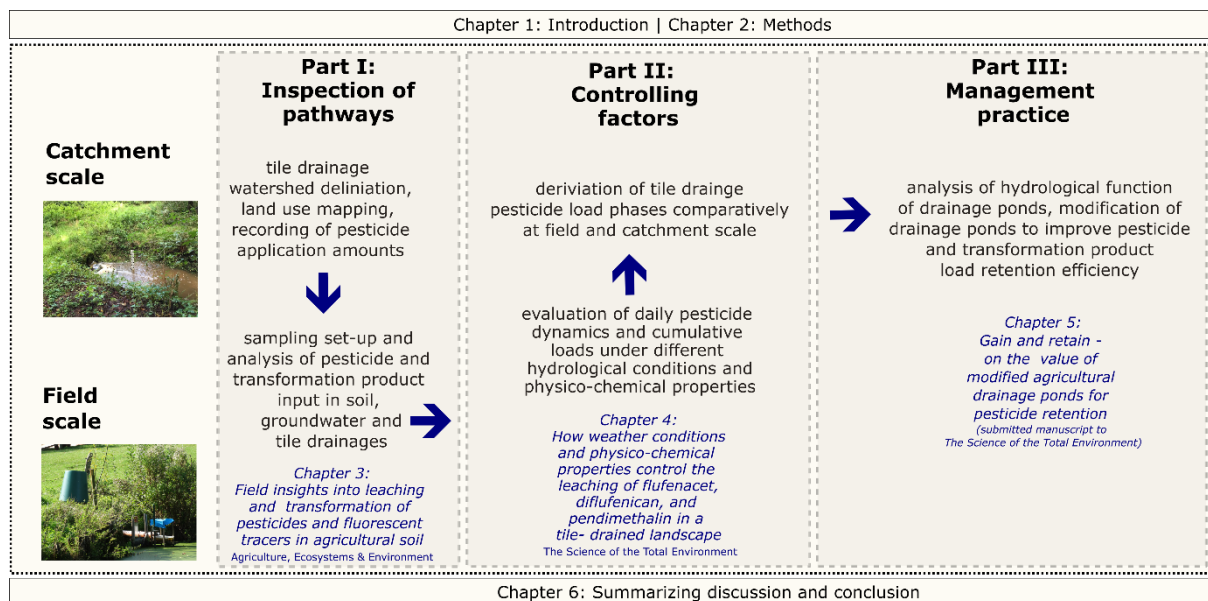


Fig 1-1: Structure of the thesis (Chapter 1 to 6) and thematically superordinate classification (Part I to III).

2. Methods

2.1. Study site

An exemplary study site, representative of the aforementioned steps (Fig 1-1) for implementing suitable retention measures, is presented here. In this hydrologically well-defined small agricultural headwater catchment area, the pesticide transport, transformation, and drainage pond retention under field conditions and conventional agricultural practice could be studied. The farm is located in the eastern hillside region of Schleswig-Holstein in Northern Germany. On 40 ha of cultivated fields, the main crops are winter wheat, winter barley, winter oilseed rape, and corn. Shallow groundwater levels in sandy depressions and surface water in loamy hilly terrains require an intensive use of tile drainage pipes with a total length of 6.3 km. Dominating soil types in the catchment are Colluvic Gleysol, Luvisol and peat soil. At the field scale, a 15-ha large agricultural field with the dominating soil types Colluvic Gleysol and Luvisol and the shallow groundwater underneath was investigated (Fig 2-1, Part I). In the area of the Colluvic Gleysol, groundwater levels reach up to 0.8 m below surface and loamy colluvial sediments are situated above sandy solifluction deposits and deeper glacial loam. The Luvisol area is characterized by glacial loamy subsoil with sandy topsoil in depressions and loamy topsoil on hilltops. There, the groundwater level is deeper, up to 2 m below the surface. The topsoil of the sandy depressions is characterized by sand contents of 60-70 %, silt contents of 20-30 %, pH 6.3, and C_{org} 1.5 %. The clay content of the loamy topsoil is 20-30 %, the silt content 50-60 %, pH 7.0, and C_{org} 1.4 %. This field outlet drains a 10-ha area including one part of a field (Fig 2-1, Part II).

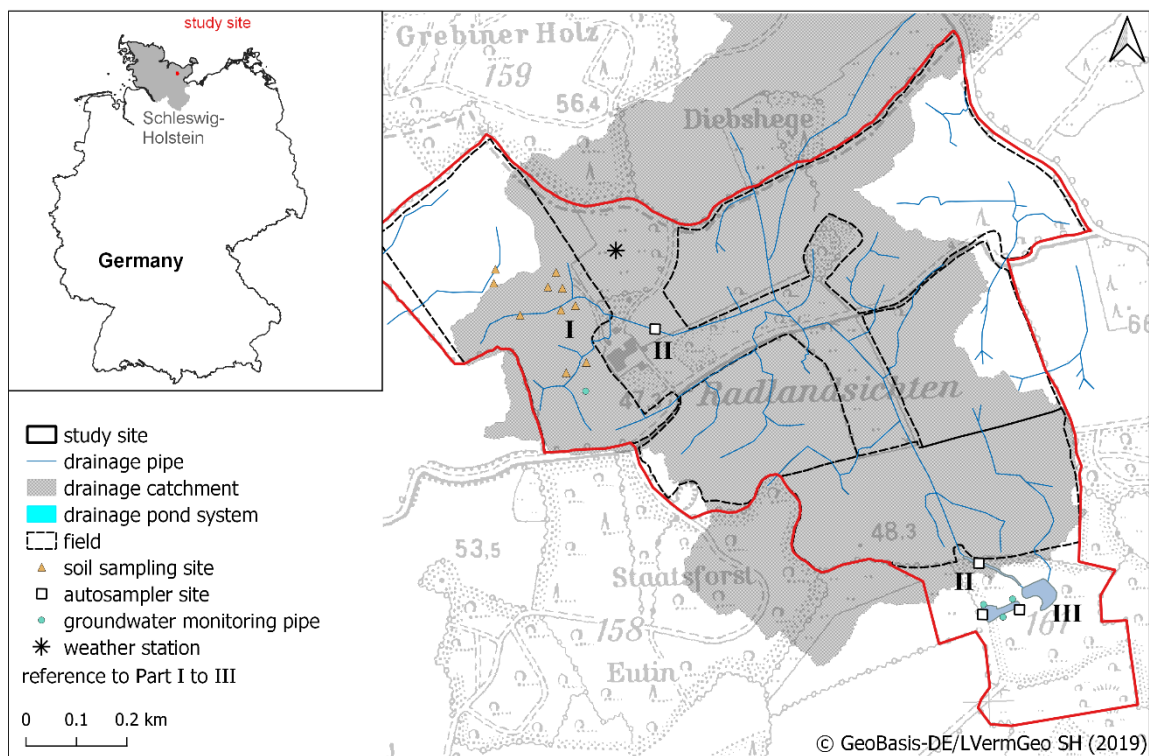


Fig 2-1: Map of the 100-ha investigation area including the drainage pond system with contributing catchment. The markings in the graphic refer to the structure of the thesis parts I to III.

The outlet of the 100-ha catchment (Fig 2-1, Part II) represents the catchment scale. This area includes the smaller area of 10-ha, which represents the field scale. Two drainage ponds (Fig 2-2) with a total size of 3,000 m² receive the outflow of the tile drainage system from the contributing catchment (Fig 2-1, Part III).

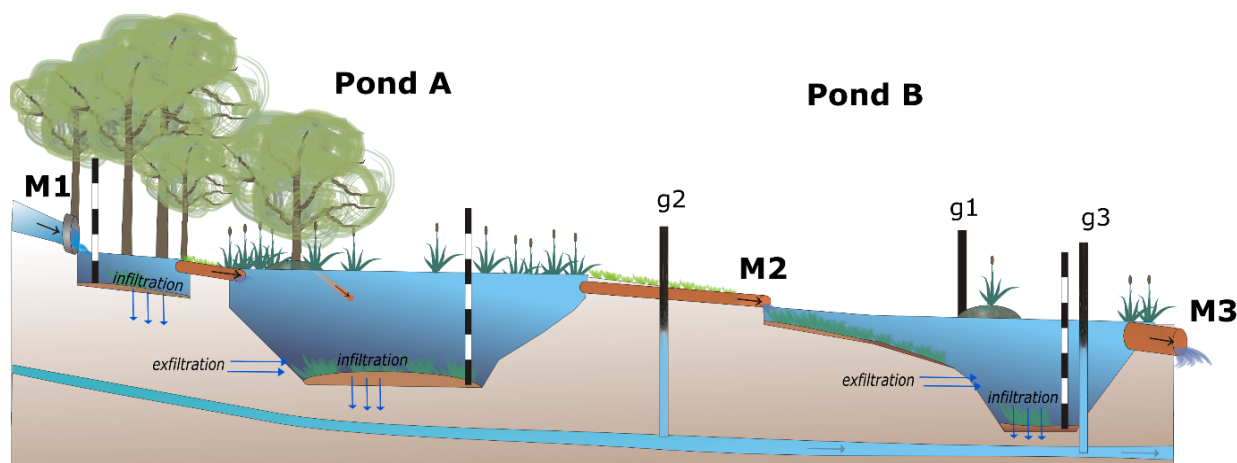


Fig 2-2: Cross-sectional view of the investigated two-part pond system with inlet structure (M1), outlet of pond A (M2) and outlet of pond B (M3). The blue arrows indicate the direction of surface-groundwater exchange. The groundwater monitoring pipes g1, g2, g3 are screened at 3 m below ground surface.

2.2. Selected pesticides/transformation products and their properties

Within this thesis, commonly used pesticides in northern Germany were selected. These pesticides are applied in the study area in autumn and have been frequently detected in surface waters (Jarosch and Brunke, 2018). In addition, they cover a wide range of physico-chemical characteristics. These are characterized by differences in adsorption, mobility, half-life, and persistence in the soil and water phases. The pesticides Diflufenican, Flufenacet, Pendimethalin, and Metazachlor were studied. These pesticides differ mainly in their sorption capacities and half-lives and can be divided into more mobile substances with high leaching potential and less mobile substances that prefer sorption to the soil. Flufenacet and Metazachlor have a low sorption coefficient to soil organic matter (k_{foc}) and are moderately mobile and mobile with leachate. Diflufenican and Pendimethalin have high k_{foc} values and sorb better to soil particles and desorb more heavily for transport with pore water. Pendimethalin (non-mobile) and Diflufenican (low mobility) are persistent in soil because they have a long half-life (dt_{50}), meaning they degrade slowly. Flufenacet degrades faster in soil than Diflufenican and Pendimethalin. All pesticide properties are listed in the Pesticide Properties Database (PPDB, Lewis et al., 2016) and can be found in Tab 2-1.

Tab 2-1: Properties of investigated pesticides and transformation products (TPs) from PPDB (Lewis et al., 2016).

Substance	Metaza-chlor	Flufe-nacet	Pendi-methalin	Diflufen-ican	Metaza-chlor ESA	Flufen-acet ESA
Group	Chloro-acetamide	Oxyacet-amide	Dinitro-aniline	Carboxa-mide	TP	TP
LogP at pH 7, 20°C	2.49	3.5	5.4	4.2		
K _{foc} , mL g ⁻¹	79.6	273.3	13,792	2,215	5	12.5
Aquatic photolysis in water Dt ₅₀ at pH 7, days	stable	stable	21 days (7 June, 94 Dec)	stable, pH 5 to pH 9 for 30 days		
Hydrolysis in water Dt ₅₀ at pH 7, 20°C, days	stable, pH 7	stable, pH 5-9	stable, pH 4-9	133		
Dt ₅₀ in water, days	216	54	4	-	1,000	1,000
Dt ₅₀ in soil, days	6.8	39	100.6	64.6	96.3	11.1
Dt ₅₀ in water-sedi-ment phase, days	20.6	81	16	175	1,000	1,000

2.3. Data collection

The overall study is based on a daily-based and multiple-year tile drainage pipe monitoring under field conditions and monthly measurements of the groundwater, as well as soil sampling at selected points in time (Tab 2-2). Within the three thesis parts (Fig 1-1), evaluations for selected pesticides and TPs in the different environmental compartments were presented (Tab 2-2).

Tab 2-2: Date of pesticide and transformation product monitoring campaigns and environmental compartments processed in the Parts I, II, III of the present work. MC = Monitoring campaign. Number of sampled days is displayed in brackets.

Pesticide / transformation products	Soil	Shallow ground-water	Tile drainage pipe	Pond water
Part I				
Flufenacet, Flufenacet ESA	MCI = 09/24/2017 to 12/19/2017 (3) MCII = 09/24/2018 to 11/27/2018 (3)	09/24/2017 to 05/02/2019 (21)		
Part II				
Flufenacet, Diflufenican, Pendimethalin			MCI = 09/27/2016 to 02/27/2017 (154) MCII = 10/03/2017 to 01/21/2018 (111)	
Part III				
Flufenacet, Flufenacet ESA, Metazachlor, Metazachlor ESA, Pendimethalin		MCI = 10/03/2018 to 01/08/2018 (4) MCII = 10/03/2019 to 01/08/2019 (4)		MCI = 10/03/2018 to 01/08/2018 (98) MCII = 10/03/2019 to 01/08/2019 (98)

The data compilation of the analysed pesticide samples in the different environmental compartments enables a comprehensive and complex evaluation of the different pesticide and TP transport processes between the individual media, as well as the description of selected controlling parameters (Fig 2-3). The work results in an overall investigation of a small-scale agricultural headwater catchment: a sequence is monitored and investigated from the application of pesticides to the individual field, via the pathways soil, groundwater, tile drainage to the outlet of the drainage pond system (Fig 2-3).

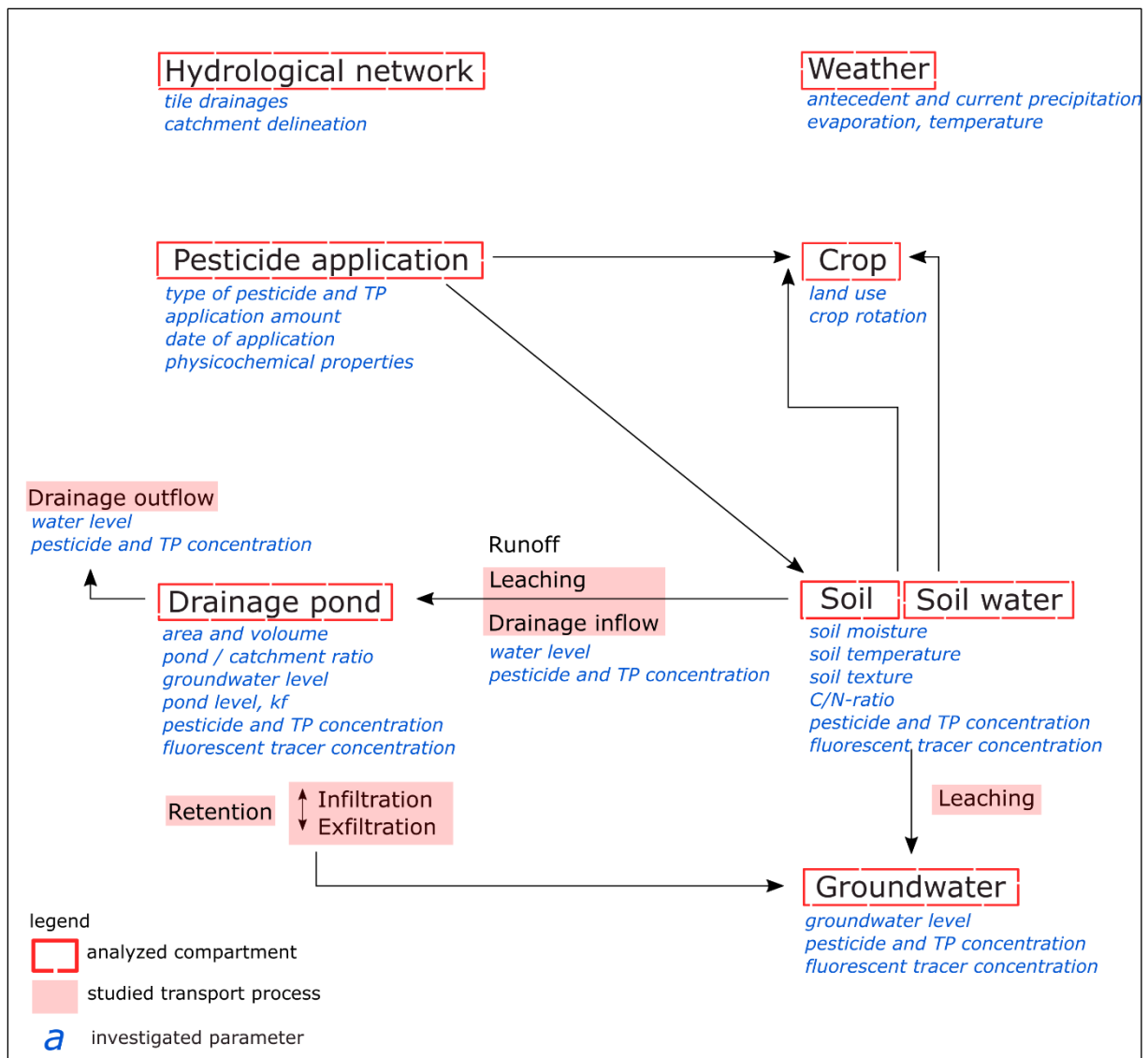


Fig 2-3: Pathways of pesticides and transformation products - from field to surface water in drained agricultural lowland catchments, edited according to Arias-Estévez et al. (2008). The red squares mark the environmental compartments and the red shades the transport processes examined in this work.

3. Field insights into leaching and transformation of pesticides and fluorescent tracers in agricultural soil

Willkommen S., Lange J., Ulrich U., Pfannerstill M., Fohrer N., 2021. Field insights into leaching and transformation of pesticides and fluorescent tracers in agricultural soil. *Science of the Total Environment*. 751, 141658. 10.1016/j.scitotenv.2020.141658.

Received: 28.05.2020 - Accepted: 10.08.2020

3.1. Highlights

- Leaching of pesticides to shallow groundwater poses a risk for drinking water.
- Pesticides were measured in agricultural soil and in shallow groundwater.
- Transport and transformation of pesticides and fluorescent tracers were similar.
- During dry conditions transformation was limited but preferential flow significant.
- During wet conditions Flufenacet ESA constantly developed and reached groundwater.

3.2. Abstract

The frequent detection of residues from pesticides in various natural water types has raised public awareness. This study investigated the pesticide transformation in soil and their loss to shallow groundwater in a small agricultural catchment in Northern Germany. The pesticide Flufenacet and its transformation product Flufenacet ESA were examined in Luvisol and Colluvic Gleysol under field conditions during two consecutive years. In the second year, a fluorescent tracer experiment applying Uranine and Sulforhodamine - B was carried out to gain additional insights into leaching and formation of transformation products in soil during and after a drought. We found preferential flow in response to low precipitation as an important transport pathway for Flufenacet in dry soil, as a Flufenacet concentration ($1.57 \mu\text{g L}^{-1}$) was detected in shallow groundwater within ten days after application. Leaching of Flufenacet to shallow groundwater by preferential flow posed greater risks during the dry than during the wet period. In contrast, Flufenacet ESA was detected in all groundwater samples. During the dry period, we detected no formation of TP510 (tracer transformation product) in the immediate topsoil. A fraction of both tracers remained there, suggesting also long-term residues of pesticides in the topsoil caused by limited living conditions for microorganisms under dry conditions. Newly formed transformation products of Uranine and Flufenacet were mainly trapped in upper soil if capillary flow was marginal. Formation of TP510 could be related to a soil water optimum and a soil temperature threshold. The occurrence of increased TP510 amounts in soil after drought was concurrent with the main peak of Flufenacet ESA in

shallow groundwater. This suggested similar retention and transformation processes of fluorescent tracers and organic pesticides inside the soil. This study contributed to an extended understanding of the leaching and transformation of organic pollutants in agricultural soil under real field conditions.

Keywords: Flufenacet, Flufenacet ESA, Fluorescent tracer, Uranine, Sulforhodamine – B, Shallow groundwater, Preferential flow

3.3. Graphical abstract

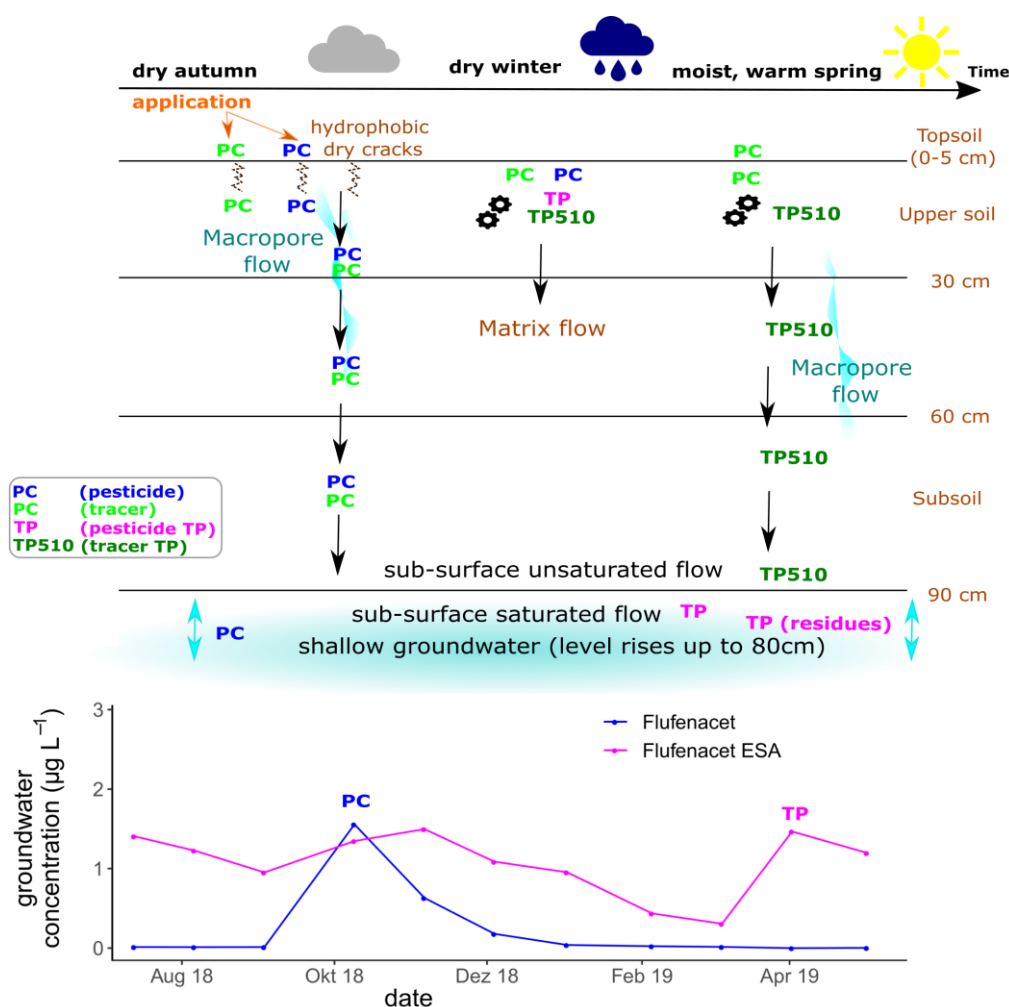


Fig 3-1: Temporal occurrence of pesticides and fluorescent tracers in antecedent dry soil.

3.4. Introduction

The use of pesticides in agriculture adds to increased crop yields and food security. However, the current political debate concerning worldwide biodiversity loss and detection of residues from pesticides has raised public awareness (Goulson et al., 2015; Dudley et al., 2017). Pesticides and their transformation products pose risks for soil microbiology (García-Delgado et al., 2019) and water bodies (Ulrich et al., 2018) but are also hazards for humans in terms of drinking water pollution (Swartjes and Van der Aa,

2020). The frequent detection of pesticides in standardized European groundwater monitoring studies is a highly discussed topic (Gimsing et al., 2019). Nevertheless, holistic field studies about pesticide leaching (e.g., Klaus et al., 2014; Carpio et al., 2020), transformation (e.g., García-Delgado et al., 2019), and formation of transformation products in soil and shallow groundwater are rare. The leaching of pesticides and their transformation products to surface and groundwater is mainly controlled by processes within the soil. Depending on their physico-chemical properties, pesticides are affected by sorption, volatilization, plant uptake and degradation processes such as photolysis, hydrolysis, and biodegradation (Fenner et al., 2013). Whether pesticides are adsorbed to soil particles or leached depends on soil properties e.g., organic matter, clay type and content, soil pH, and soil temperature (Vryzas and Papadopoulos-Mourkidou, 2007). Soil depth has a direct influence on the half-life of pesticides (Vryzas et al., 2012). In addition, the physico-chemical properties of pesticides themselves decide about mobility and persistence within soils (Barriuso et al., 2008). Soil moisture and temperature are the main controls of transformation by microbial communities (Fenner et al., 2013; Vryzas, 2018). García-Delgado et al. (2019) have demonstrated a higher dissipation rate for Prosulfocarb and reduced half-life (dt_{50}) values for Triasulfuron in surface soil samples under irrigated field conditions in comparison to non-irrigated conditions. In a controlled field irrigation experiment, Klaus et al. (2014) illustrated the influence of connected macropores to preferential flows and the long-term remobilization of pesticides and residues from the soil matrix. Only a few field studies explicitly addressing Flufenacet in soil have been published e.g., in upper soil zone (Rouchaud et al., 1999; Rouchaud et al., 2001), a lysimeter leaching study under simulated irrigation conditions was carried out by Milan et al. (2015), and a current long-term mobility study under real conditions up to 1 m soil depth was published by Carpio et al. (2020). Leaching of pesticides in soil also depends on the distribution of precipitation events (Huseth and Groves, 2014). Thereby, antecedent soil moisture conditions and precipitation characteristics are dominant parameters for timing and degree of Flufenacet leaching (Willkommen et al., 2019). A low adsorption capacity of soil (low clay content or low organic matter content, Gupta and Gajbhiye, 2002) and a higher soil moisture content trigger compound availability for microbial transformation and the leaching rate (Pallud et al., 2004). Marín Benito et al. (2019) revealed the acceleration of microbial transformation of Flufenacet in soil under laboratory conditions by a 10°C increase of soil temperature (Q10 factor determined by EFSA, 2007). To our knowledge, there is no field study published showing the leaching of Flufenacet and its transformation product Flufenacet ESA in soil and additionally their concentrations in shallow groundwater. Several studies have demonstrated that the concentrations of transformation products may be higher than those of parent compounds (e.g. Reemtsma et al., 2013; Rosenbom et al., 2015; Ulrich et al., 2018; Ulrich et al., 2019). Therefore, more investigations of the environmental behaviour of pesticide transformation products are warranted (Vryzas, 2018). Furthermore, there is a general demand to investigate pesticide leaching and transformation with alternative techniques, because conventional pesticide analyses are expensive and elaborated, especially when the numbers of samples are high. Traditionally, conservative tracers were used to analyse the behaviour of pesticides in soil (e.g., Brown et al.,

2000; Carpio et al., 2020). Also, Fluorescent dye tracers have been used for decades to characterize transport processes in aquatic environments (Leibundgut et al., 2009). They have traditionally been regarded as largely resistant to degradation, both for the soil (Flury and Wai, 2003) and for groundwater (Käss et al., 2004). However, recent studies in experimental wetlands have suggested that for monitoring periods of several months or longer, tracer degradation by biochemical transformation may occur. This was proven for the most common fluorescent dye tracer Uranine (Maillard et al., 2016; Fernández-Pascual et al., 2019; Fernández-Pascual et al., 2020). In agricultural soil, the Uranine fluorescent signal disappeared after approximately 3 months and was gradually replaced by a new signal at 510 nm (Lange et al., 2018). This new signal was stable against acidification, appeared earlier under wet conditions and remained inside the topsoil for more than four years. The molecular structure of its source could be proposed by LC-MS/MS as a transformation product of Uranine and was termed TP510. Owing to structural similarity, TP510 was anticipated as an in-situ proxy to describe biochemical transformation of chloroacetanilide pesticides inside the soil zone (Lange et al., 2018). A novelty of this study is the comparison of the tracer transformation product TP510 with the behaviour of the pesticide transformation product Flufenacet ESA. So far, TP510 was only detected in soil (Lange et al., 2018) but a field comparison with a pesticide transformation product is missing. This study aims at contributing to an extended understanding of the leaching and transformation of organic pollutants in agricultural soil and shallow groundwater for two years under real field conditions, where the application of pesticides is managed by the farmer. To gain knowledge about transformation and leaching pathways within the soil, soil parameters were linked to the formation of transformation products of both pesticides and tracers. Doing so, this study intends to answer the following research questions:

- Do different hydrological conditions affect the groundwater leaching potential of Flufenacet and its transformation product Flufenacet ESA?
- How much precipitation is required to trigger compound transport via preferential flow and which component is mostly affected?
- Are similar environmental conditions controlling the formation of the pesticide transformation product Flufenacet ESA and the tracer transformation product TP510?

3.5. Method and materials

3.5.1. Study area and soil plot characteristics

The examined area, located in the eastern hillside region of Schleswig-Holstein in Northern Germany, was first described by Willkommen et al. (2019). We investigated a 15-ha large agricultural field with dominating soil types Colluvic Gleysol and Luvisol and the shallow groundwater underneath (Fig 3-2). In the area of the Colluvic Gleysol, groundwater could reach up to 0.8 m below surface and loamy colluvial sediments were situated above sandy solifluction deposits and deeper glacial loam. The Luvisol

area was characterized by glacial loamy subsoil with sandy topsoil in depressions and loamy topsoil on hilltops. There, groundwater was deeper, up to 2 m below surface (Willkommen et al., 2019). The soil types were determined according to the German manual of soil mapping (Ad-hoc-Arbeitsgruppe Boden, 2005).

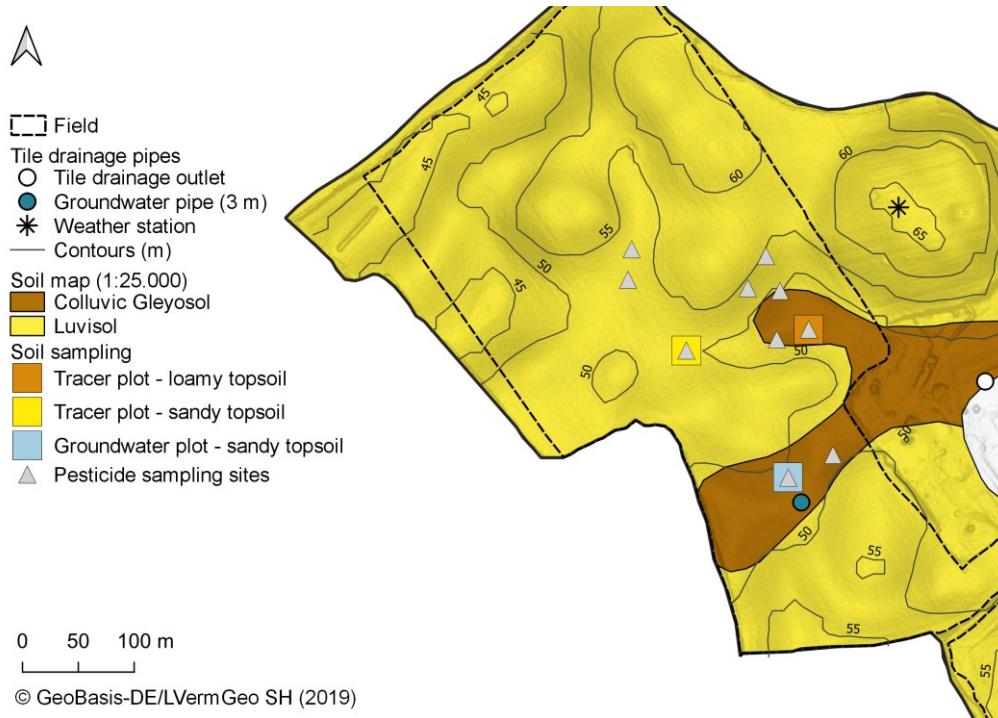


Fig 3-2: Location of investigated field with 10 soil sampling sites for mixed pesticide samples in 0-30, 31-60, 61-90 cm (grey triangles). Additionally, two 4 m² large tracer plots and a groundwater plot (squares) are tagged.

3.5.2. Study design

The investigated field belonged to a farm practicing conventional agriculture with crop rotation of winter wheat, winter barley, winter oilseed rape, and corn (Willkommen et al., 2019). Flufenacet was applied in autumn 2016 (winter wheat), 2017 (winter wheat) and 2018 (winter barley) (Tab 3-1). Pesticide soil sampling was performed during the autumn periods of two consecutive years. In the first year, pesticide application on winter wheat was delayed to 30th of October 2017 due to very wet soil conditions. After the second pesticide application on winter barley on 28th of September 2018, a long-lasting drought motivated an extended campaign for pesticide soil sampling until late spring 2019. Monthly groundwater samples were collected during both vegetation periods (Tab 3-1). The tracer experiment was carried out in the second year during the dry period and lasted until 06th of June 2019 (Tab 3-1). On the 1st of October, a mix of 50 g of Uranine and 50 g of Sulforhodamine - B diluted in 10 L water was applied on two plots using a hand-operated sprayer (Tab 3-1). The farmer continued crop rotation and pesticide application according to local practice.

Tab 3-1: Monitoring periods in groundwater and soil. Application dates and application rates of pesticide, and fluorescent tracers during the wet period (2017) and dry period (2018/2019). The pesticide soil sampling days are labeled with H and the tracer sampling days with T, which can be found in subsequent figures. HO = sampling before application. Grey gaps represent no monitoring data.

Sampling Design		Wet period	Dry period
Application Date	Pesticide	10/30/2017	09/28/2018
	Tracer		10/01/2018
Application Rate	Pesticide	Flufenacet: 0.21 kg ha ⁻¹	Flufenacet: 0.20 kg ha ⁻¹
	Tracer		12.5 g m ⁻²
Groundwater Monitoring	Pesticide	monthly	
Soil Monitoring	Pesticide	H0: 09/24/2017 H1: 11/07/2017 H2: 12/19/2017	H0: 09/24/2018 H1: 10/16/2018 H2: 11/27/2018
	Tracer		T0: 09/24/2018 T1: 10/16/2018 T2: 11/27/2018 T3: 04/10/2019 T4: 05/02/2019 T5: 05/16/2019 T6: 06/06/2019

3.5.3. Selected pesticides, tracers and their properties

The pesticide Flufenacet and its transformation product Flufenacet ESA were selected whose properties are described in more detail in Willkommen et al. (2019). In short, Flufenacet has a low organic carbon sorption coefficient (K_{oc}) and is moderately mobile (Lewis et al., 2016). The transformation product Flufenacet ESA is even more mobile than its parent compound (Tab 3-2) and largely persistent in soil (Lewis et al., 2016). Only few information is available for photochemical stability of Flufenacet ESA. In EFSA Rappateur Assessment Report (2009), it was stated, that the photolytic degradation has a minimal relevance for Flufenacet transformation in soil. Further, the probability to detect Flufenacet ESA at the soil surface is minimal, as transformation takes place in the topsoil closely below soil surface, where sun light degradation is reduced. The transformation rate of Flufenacet ESA is quite low, hence it is considered as persistent in soil and water (Lewis et al., 2016; ECHA, 2017). In general, physico-chemical soil properties (pH, organic matter, and clay content) dictate the affinity to sorption of Uranine and Sulforhodamine - B in soils and lead to large differences in K_d values (Bork et al., 2020). The affinity to sorption of both organic tracers increases with clay content and decreases with increasing pH. A high organic matter content intensifies Uranine sorption but leads to higher mobility of Sulforhodamine - B, which preferentially sorbs to mineral surfaces (Bork et al., 2020). Uranine is sensitive to photolysis at the soil surface, a process that did not affect our samples at depths until 90 cm. The anticipated formation of TP510 from Uranine by sulfonation is described in Lange et al. (2018).

Tab 3-2: Properties for pesticides by Lewis et al. (2016), Gajbhiye and Gupta (2002)^a, for tracers by Leibundgut et al. (2009)^b, and Bork et al. (2020)^c.

Properties	Flufenacet	Flufenacet ESA	UR	SRB
Chemical structure	C ₁₄ H ₁₃ F ₄ N ₃ O ₂ S	C ₁₁ H ₁₄ FNO ₄ S	C ₂₀ H ₁₂ O ₅	C ₂₇ H ₃ ON ₂ O ₇ S ₂
Aqueous solubility (g L ⁻¹)	0.051	55	300 ^b	10 ^b
Soil degradation (Dt ₅₀ field, days)	39	302		
Photolytic stability (Dt ₅₀ , hours)	stable	-	11 ^b	820 ^b
Soil adsorption coefficient (K _d , mL g ⁻¹)	0.77 to 4.52 ^a	-	0.6 - 73.2 ^c	2.7 - 19.3 ^c
Soil organic carbon sorption coefficient (K _{oc} , mL g ⁻¹)	401	-		

3.5.4. Field data and sampling

3.5.4.1. Precipitation measurements

Precipitation was measured by a tipping bucket rain gauge (Campbell Scientific) in 10-minute resolution located within the catchment (Fig 3-2). A rainy day was defined as a day with precipitation larger than or equal to 0.1 mm as recommended by the DWD Climate Data Center (2018). Annual precipitation totals were calculated according to the vegetation period of the current crop on the field. The first period, 24th of September 2017 to 23rd of September 2018 was labelled as “winter wheat”, the second period from 24th of September 2018 to 23rd of September 2019 as “winter barley”.

3.5.4.2. Groundwater sampling

A groundwater pipe was installed on the investigated field (Fig 3-2), surrounded by gravel, and screened at 3 m below surface. Groundwater levels were measured in hourly resolution by HOBO Onset data loggers, which were verified in weekly intervals by manual measurements using an electric contact gauge. A submersible pump (12 V, Premium Pump, company Whale) collected monthly 350 mL groundwater samples in glass bottles.

3.5.4.3. Sampling in soil

For the pesticide soil sampling, ten soil sites were determined and tagged via coordinates (Fig 3-2). Samples were taken by a geological Edelman-drill up to 1 m. The samples were subdivided in depth classes of 0–30 cm, 31–60 cm, and 61–90 cm. Per sampling day six representative average soil samples were obtained by mixing the subsamples with the same depth class and soil type. The soil samples were stored in glass vessels. The same herbicide soil sampling procedure was carried out from 24th of September 2017 to 19th December 2017 (three sampling dates) and from 24th of September 2018 to 27th of

November 2018 (three sampling dates). The first sample H0 was taken before herbicide application of the current year. Beside the mixed herbicide soil samples, three soil profiles were investigated in detail to link the pesticide and tracer concentrations and their transformation product concentrations with site-specific soil properties (Tab 3-3). The first soil profile was located at the groundwater plot (Fig 3-2) and consisted of a Colluvic Gleyosol containing a high fraction of sand, especially in the upper soil (0–30 cm, 74 %). Six parallel soil sampling rings (DIN 19672-1, 100 cm³) in depths 0–30 cm, 31–60 cm and 61–90 cm were taken at the groundwater plot. The mean saturated hydraulic conductivity was $55.66 \pm 40.74 \text{ cm d}^{-1}$ in upper soil, $168 \pm 99.57 \text{ cm d}^{-1}$ between 31 and 60 cm and in bottom soil $41 \pm 99.57 \text{ cm d}^{-1}$. The soil porosity and bulk density in the upper soil were 46 % and 1.56 g cm^{-3} , in 31–90 cm, they accounted for 33 % and 1.79 g cm^{-3} between 30 and 90 cm. The plot had a slope of 3 %. The tracers were simultaneously applied on two other plots with different soil types. The tracer plot with soil type Luvisol and sandy topsoil (Fig 3-2) had a mild slope of < 2 %.

Tab 3-3: Parameters describing soil size distribution, pH, C (Carbon) and N (Nitrogen) content in the three soil plots with layers 0-30 cm, 31-60 cm, and 61-90 cm.

Parameter	Groundwater plot – sandy topsoil		Tracer plot – sandy topsoil			Tracer plot – loamy topsoil		
Soil type	Colluvic Gleyosol		Luvisol			Colluvic Gleyosol		
Layer (cm)	0-30	31-90	0-30	31-60	61-90	0-30	31-60	61-90
< 2 μm clay (%)	3	4	3	3	3	20	10	40
> 2-63 μm silt (%)	23	41	23	23	23	60	20	60
> 63-2000 μm sand (%)	74	55	74	74	74	20	70	0
pH	6.0	6.3	5.8	6.1	6.1	5.8	5.9	5.9
C _{org} (%)	1.7	0.7	1.8	1.4	1.9	2.2	2.6	3.5
Total N (%)	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.3
Total C (%)	1.7	0.7	1.8	1.4	1.9	2.2	2.6	3.5

The soil profile was homogenous with silty sand from 0 cm to 90 cm (Tab 3-3). The tracer plot in Colluvic Gleyosol with loamy topsoil (Fig 3-2) had a slope of 10 %, the soil type varied from silty loam (0–30 cm) to loamy sand (31–60 cm), and silt-clayey loam (61–90 cm). For the tracer experiment, two plots (of the 10 existing herbicide sampling sites) with 4 m² size each were selected and permanently tagged (Fig 3-3). During the first three sampling dates (Tab 3-3), three soil samples were taken from each tracer plot at 0–30 cm, 31–60 cm, and 61–90 cm depth. During the sampling dates T4-T6 monitoring was carried out in a higher resolution with samples from layers 0–1 cm, 2–5 cm, 6–15 cm, 16–30 cm, 31–60 cm, and 61–90 cm. In the second year, each plot was equipped with six SM300 sensors (Delta T Devices) at 15 cm, 45 cm, and 75 cm depth. Two SM300 sensors measured in parallel soil moisture content (Vol-%) and soil temperature (°C) in 10-minute resolution.



Fig 3-3: Left: Set up of tracer experiment at 4 m² plot equipped with six soil moisture sensors directly after pesticide and tracer application (10/01/2018) and right: winter barley at tracer site (06/06/2019).

3.5.5. Laboratory methods

3.5.5.1. Determination of soil parameters

For each soil depth and date 100 g of the mixed soil samples were prepared for further laboratory analyses. The pH - values in soil were determined according to DIN ISO 10390:2005 using a pH meter (Schott Instruments, Lab 860). For the calculation of total carbon (C) and total nitrogen (N), an EuroEA Elemental Analyzer was used (C: DIN ISO10694:1995; N: DIN ISO 13878:1998). Inorganic carbon was determined using an IC-Kit, an add-on module of the EuroEA Elemental Analyzer. The organic carbon content (C_{org}) was calculated by subtraction of total carbon and inorganic carbon. The CN - ratio (%) was the division of C_{org} by N. At the groundwater plot (Fig 3-2), the soil size distribution for 0–30 cm and 31–90 cm was measured using a Master sizer (Hydro2000G, Malvern). The saturated hydraulic conductivity was measured with a hood-permeameter (Hartge, 1966). Two soil water retention curves in 0–30 cm and 31–60 cm were determined for pressures -1, -30, -60, -150, -300, -500, -1,500, -15,000 hPa with pressure plates. Technical problems caused a missing soil water retention curve for 61–90 cm. The shapes of the soil water retention curves were described by the Mualem Van Genuchten model (Van Genuchten, 1980) parameterized by the non-linear pF curve optimisation program RETC with the least squares method (Van Genuchten et al., 1991). The soil water potential was then calculated by the Mualem Van Genuchten function with empirical curve-fitting parameters m and n (Van Genuchten et al., 1991).

3.5.5.2. Pesticide analysis in water and soil

In water samples, the substances Flufenacet and Flufenacet ESA were analysed with an AB Sciex 5500 Qtrap with Agilent 1260 Infinity HPLC (direct injection, no extraction or concentration procedure) by an accredited laboratory (DIN 38407-36:2014-09). The Limit of Quantification (LOQ) was 0.01 $\mu\text{g L}^{-1}$ for Flufenacet and 0.025 $\mu\text{g L}^{-1}$ for Flufenacet ESA. The uncertainty of the concentrations within a

measurement stated by the analytical laboratory was in a range of 20 %. The soil samples were first prepared in a 10:1-water eluate (DIN EN 12457-4:2002). After 24 h shaking, Flufenacet concentrations were analysed in water samples with a Sciex 5500 Qtrap with Shimadzu LC 30 HPLC by direct injection, without extraction. Flufenacet ESA concentrations were analysed in water samples with an AB Sciex 4000 QQQ with Agilent 1260 Infinity HPLC by direct injection, without extraction. The laboratory protocols followed DIN 38407-36: 2014 for Flufenacet and DIN 38407-35: 2010 for Flufenacet ESA. The LOQ was $0.025 \mu\text{g L}^{-1}$ for Flufenacet and Flufenacet ESA. The overall uncertainty of the concentrations within a measurement stated by the analytical laboratory was 15 % for Flufenacet and 20 % for Flufenacet ESA.

3.5.5.3. Tracer analysis

The analyses of fluorescent tracers in soil samples followed the methods of McMahon et al. (2003) and are described in Lange et al. (2018). Briefly, the soil samples were air-dried for 48 h and prepared for a 10:1-water eluate. After 24 h of shaking, the samples were centrifuged. The remaining aliquot was measured by a fluorescence spectrometer (LS50B, Perkin Elmer) with an excitation/emission wavelength difference of 22 nm and excitation/emission spectra of 450–600 nm. The background was corrected by reference measurements of loamy and sandy soil samples collected prior to tracer application. Uranine (UR) excitation was measured at 488 nm, Sulforhodamine- B (SRB) at 560 nm and TP510 excitation at 510 nm. Since calibration for TP510 was impossible due to the absence of an analytical standard, concentrations were given in raw intensity readings of the spectrometer. When both TP510 and UR were present, the sample was scanned twice, with and without acidification using sodium acetate. TP510 intensity was then obtained at 510 nm from the acidified sample with suppressed UR fluorescence, while UR concentration was obtained as intensity difference between original and acidified fluorimeter scans at 488 nm. By calibration using standard concentrations, UR and SRB concentrations were first calculated in mg L^{-1} in solution and then converted to mg kg^{-1} of dry soil. Detection limits were 0.1 mg kg^{-1} for UR and 0.2 mg kg^{-1} for SRB.

3.6. Results and discussion

3.6.1. Weather conditions

The winter wheat period was 11 % wetter (581 mm) than the winter barley period (509 mm). However, both years were drier than the 2002 – 2017 average value of 701 mm from the nearest weather station in Dörnick (DWD Climate Data Center, 2019). The range of annual precipitation in this 15-years period was between 497 mm and 909 mm. The temporal distribution of precipitation in both studied years was very contrasting (Fig 3-4). In the wet period, a high precipitation sum (97 mm) occurred in autumn between 09/28/2017 and 10/07/2017, including a daily maximum of 45 mm at 10/05/2017. Hence, the

wet period started with high antecedent soil moisture before pesticide application. The wet autumn/winter conditions in 2017 were followed by a long-lasting drought in spring/summer 2018.

In contrast, the dry period 2018/19 started with very low precipitation, and pesticides were applied one month earlier than in the year before. The main precipitation period of 103 mm only occurred in spring between 03/03/2019 and 03/18/2019 with continuous precipitation not exceeding 16 mm.

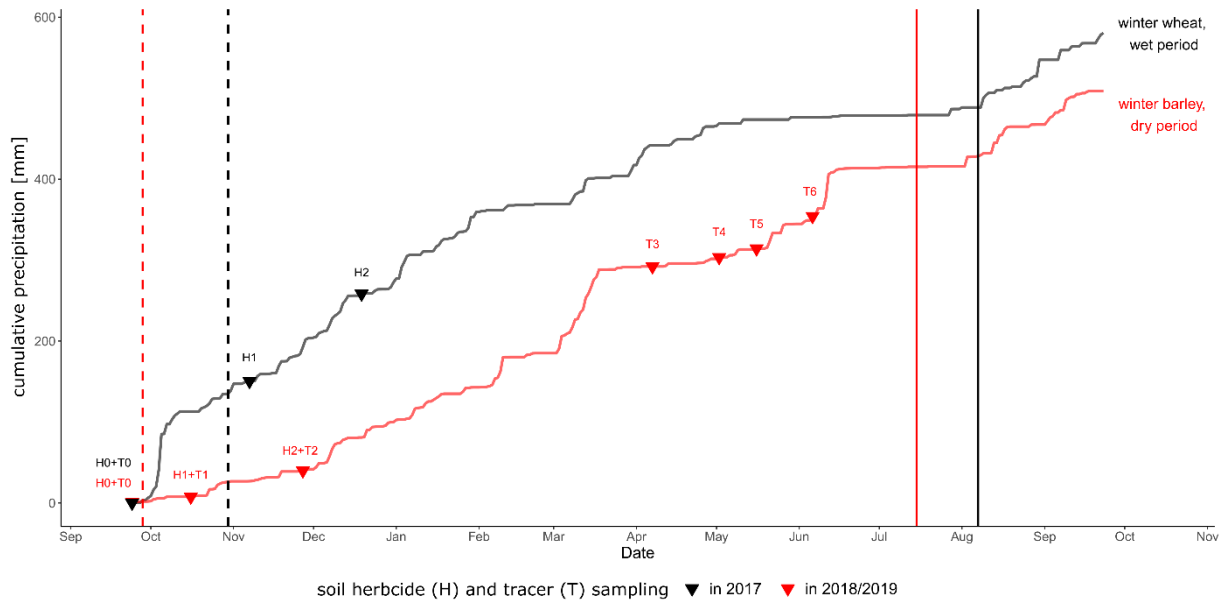


Fig 3-4: Dashed black line marks pesticide application dates in 2017 and dashed red line in 2018. The harvest dates are given as a solid black line for winter wheat in 2018 and a solid red line for winter barley in 2019. The soil pesticide (H) and tracer (T) sampling dates are numbered and are also used for the soil depth profiles. Specific dates can be found in Tab 3-1.

3.6.2. Temporal occurrence in shallow groundwater

The groundwater level was higher before and after pesticide application in the wet than in the dry period ($\bar{\varnothing}$ wet = 1.36 ± 0.34 m, $\bar{\varnothing}$ dry = 1.8 ± 0.34 m below surface, respectively, Fig 3-5). Irrespective of the groundwater level, Flufenacet ESA was detected in all groundwater samples. Two thirds of the samples exceeded the health-oriented guidance value for non-relevant transformation products in drinking water ($1 \mu\text{g L}^{-1}$) which is recommended by the German Environmental Agency (UBA, 2020). At the beginning of the wet period, before application, Flufenacet was detected at values below LOQ. Then, three weeks after application, it was measured once in low concentration ($0.093 \mu\text{g L}^{-1}$) before concentrations went down to slightly above LOQ. Contrary to its parent compound, large amounts of the transformation product Flufenacet ESA leached to shallow groundwater shortly after pesticide application. The maximum peak of Flufenacet ESA occurred three months after application, with concentrations of $2.92 \mu\text{g L}^{-1}$ in February 2018 (Fig 3-5). The slight but constant precipitation from application in October 2017 (Fig 3-4) to April 2018 prevented desiccation of the soil. Additionally, the groundwater level fluctuated between 1.3 and 0.3 m below surface between November 2017 and March 2018. Hence, it is

likely that the groundwater entered pores in shallow soil which contained high Flufenacet ESA concentrations. The highly mobile Flufenacet ESA was then transported with the fluctuating groundwater into the sampling depth of 3 m. The immediate and frequent detection of Flufenacet ESA in shallow groundwater under wet hydrological conditions until spring 2018 suggested that both the microbial transformation of the parent compound within the soil and the subsequent leaching of the transformation product occurred fast and started immediately after pesticide application. Concentrations of Flufenacet ESA decreased with decreasing groundwater tables but did not reach the initial level before application ($< \text{LOQ}$).

In the dry period, the sandy soil was below field capacity when Flufenacet was applied at the end of September 2018 (Fig 3-5). A concentration peak ($1.57 \mu\text{g L}^{-1}$) in shallow groundwater occurred only within ten days after the application. In literature, Flufenacet is generally regarded as non-leachable to groundwater (Gajbhiye and Gupta, 2002; Milan et al., 2015; Novohatska et al., 2018). With a half-life in soil of 40 days, moderate soil adsorption and low water solubility (Lewis et al., 2016), a transport of the parent compound via matrix flow rarely reaches deeper soil layers (Milan et al., 2015). However, a high risk for contamination of groundwater in soils with higher permeability was already highlighted by USEPA (1998). As the determined leaching rate of the studied Colluvic Gleysol is high (Chapter 3.5.4.), and wormholes and beetles were observed up to 90 cm in the soil sampling rings, a macropore flow to greater depths is very likely.

However, our data showed that in dry soil Flufenacet can very well be leached to shallow groundwater, in our case down to a depth of approximately 1.9 m. Directly after application, the water tension in upper soil at 15 cm and in 45 cm soil depth was high, permitting only capillary flow but no percolation within the soil matrix (Fig 3-5). Under these conditions, preferential transport of Flufenacet in existing macropores is most likely, since also Zehe and Flüßler (2001a, b) found 50 worm burrows per m^2 in a Colluvisol soil at a depth of 90 cm. Flufenacet ESA concentrations in shallow groundwater increased simultaneously with its parent compound. We assume that first mainly residues from previous year application and only little newly transformed substance entered groundwater via preferential flow, since the intensity of biochemical transformation processes and transport was limited in dry soil. The main flux of newly formed Flufenacet ESA reached the shallow groundwater apparently only in April 2019. Then matrix flow was possible through the entire soil profile, the groundwater table rose to 1 m below surface suggesting ongoing recharge, and Flufenacet ESA concentrations peaked at $1.48 \mu\text{g L}^{-1}$.

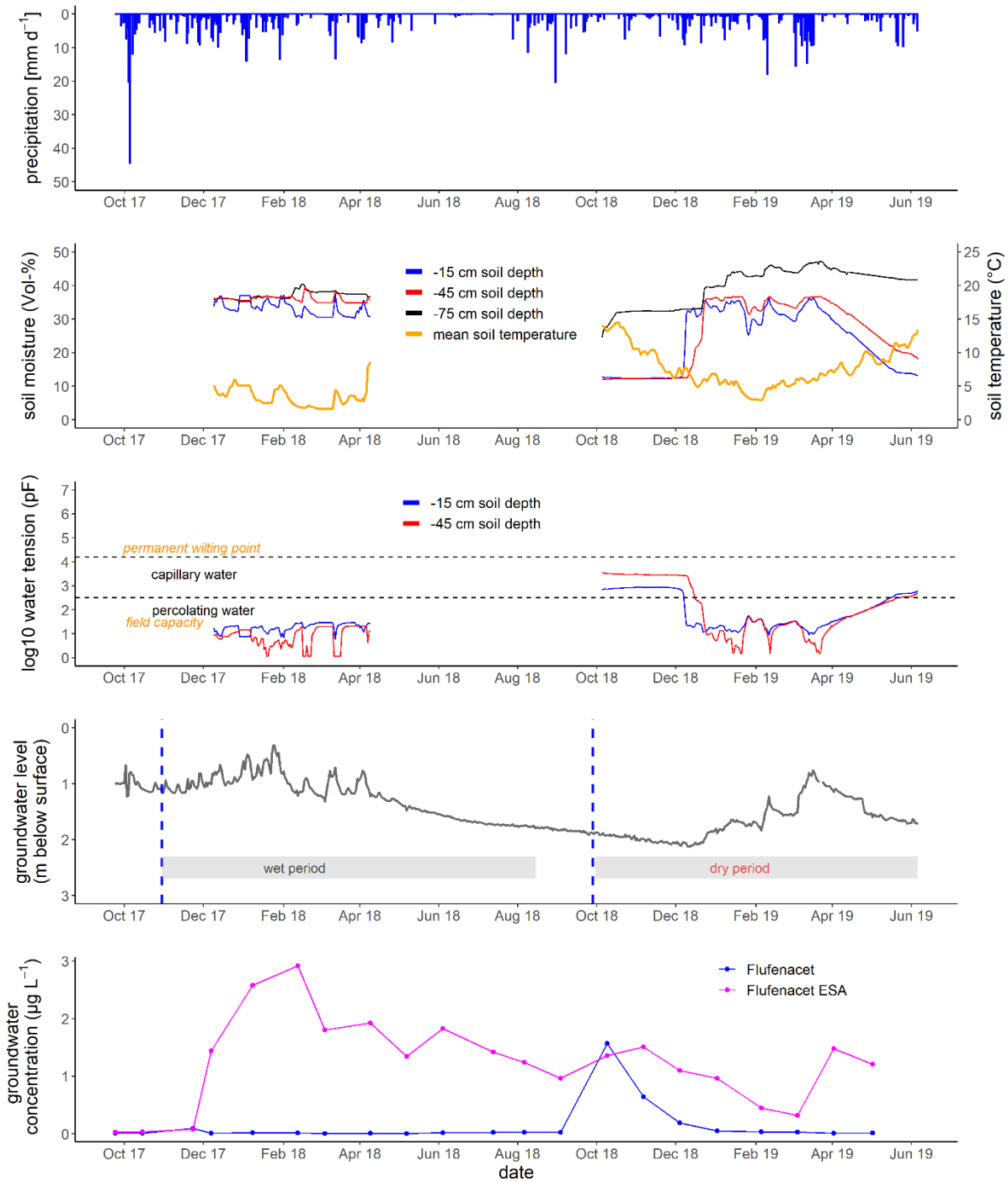


Fig 3-5: Monthly groundwater levels, soil moisture, soil temperature, pF value for soil depths at groundwater plot in Colluvic Gleysol with sandy topsoil. Pesticide concentrations in shallow groundwater for wet period and dry period. Flufenacet application dates are marked by dashed blue lines.

3.6.3. Transport pathways in soil

During both seasons, Flufenacet was used at similar application rates which allowed for direct comparisons (Tab 3-1). Our sampling strategy of mixing samples from ten different locations permitted insights into the general behaviour of a heterogenic field site with a variety of different slope angles and soil types, while the real range of absolute concentrations were not displayed. During the wet period, a minor

part of Flufenacet was quickly transported to the subsoil within eight days after application, assuming preferential flow transport with rising soil saturation (Jarvis, 2007). However, the majority of Flufenacet remained in upper soil (Fig 3-6b) and there a large fraction was transformed into Flufenacet ESA. The evenly distributed high soil moisture content indicated a hydrologically active soil matrix. The transformation product percolates then continuously to subsoil (Fig 3-6f), which was closely connected to the low groundwater level at that time (Fig 3-5). The detection of a single, low Flufenacet concentration in shallow groundwater (Fig 3-5) showed the reduced significance of preferential flow under wet soil conditions (Demand et al., 2019) and thereby a reduced leaching risk for Flufenacet, which was also in accordance with the observations of Flufenacet in 60 cm soil depth under similar weather conditions by Carpio et al. (2020).

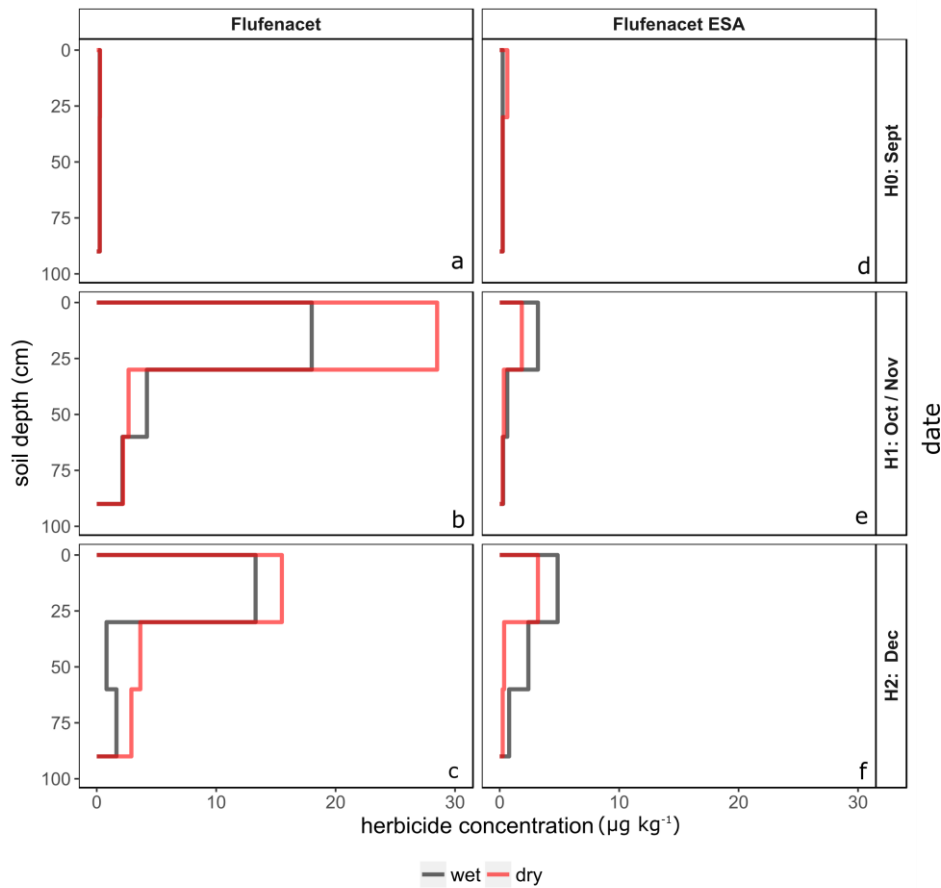


Fig 3-6: Comparison of pesticide samples in soil during wet (black line) and dry (red line) period; depth plot of pesticides Flufenacet (a-c) and Flufenacet ESA (d-f) at sampling dates H. Sampling dates are displayed on the 2nd y axis in chronological order.

During the dry period, the majority of Flufenacet remained in upper soil. Nevertheless, it was also transported to the subsoil within 18 days after application (Fig 3-6b, c). Also, Carpio et al. (2020) detected Flufenacet in the subsoil at a depth of 1 m under dry conditions. This increased mobility might be explained by the occurrence of features with a potential for preferential flow within the soil, e.g., worm-holes (Kjær et al., 2011) or dry cracks (Demand et al., 2019). Pesticide transport in preferential flow

pathways in response to low-intensity precipitation events was not explicitly studied in field so far (Demand et al., 2019). We measured only 6 mm precipitation between the application and detection of Flufenacet in shallow groundwater which apparently triggered the leaching of Flufenacet through the entire soil column. This was in the range of other studies e.g., Renshaw et al., 2003 (2 mm); Demand et al., 2019 (3 mm); and Willkommen et al., 2019 (9 mm), who assessed a minimum precipitation threshold to initiate preferential flow with high velocities in agricultural soils (Demand et al., 2019). Under water stress in soil, microbial organisms can exude hydrophobic compounds and reduce soil pore water connectivity between preferential flow paths and soil matrix (e.g., Morales et al., 2010; Vogel et al., 2015). Hence, in absence of active microorganisms within the preferential flow paths (Rosenbom et al., 2014), mobile and hydrophobic pesticides like Flufenacet (Lewis et al., 2016) may quickly leach with very low amounts of free moving precipitation water - bypassing the remaining water in soil matrix and enter to deep soil layers (Renshaw et al., 2003; Gazis and Feng, 2004; Klaus et al., 2013). The behaviour of the strongly mobile transformation products Flufenacet ESA in soil under dry conditions was very contrasting to its parent compound, as it mainly remained in the plough layer at 0–30 cm depth until the end of the monitoring period in December (Fig 3-6e, f). It can therefore be assumed, that under dry conditions, the formation of Flufenacet ESA only occurred in medium to small soil pores filled with capillary water ($pF \sim 3$, Fig 3-5). Only there, Flufenacet was bioavailable for microorganisms under stress conditions which was also found by Barriuso et al. (2004) and Babey et al. (2017). Low aerobic microbial activity and therefore reduced Flufenacet mineralization at soil matrix potential ranges of pF 3–5 were found by Schroll et al. (2006), too. Furthermore, transport of Flufenacet ESA to subsoil was restricted as matrix flow in topsoil was virtually absent in winter 2018 (Fig 3-5). The low precipitation sum of only 32 mm between sampling in October and December 2018 probably sustained a low soil pore water connectivity between preferential flow paths and soil matrix (Vogel et al., 2015). As a result and following the observations of Klaus et al. (2013), only a small peak of Flufenacet ESA reached shallow groundwater via preferential flow. This peak presumably consisted of a mixed signal of old Flufenacet ESA residues stored in pre-event water and a minor fraction of newly formed transformation products. The extrapolation of the long-term behaviour of Flufenacet and Flufenacet ESA could be delineated by means of the monitored samples (H0), which were taken before the winter wheat application (Tab 3-1, Fig 3-6a, d). Due to the wet summer 2017, no concentrations for Flufenacet and Flufenacet ESA were detected in soil before latest application in autumn 2017. All molecules seemed to be transformed and/or leached. Flufenacet ESA has a half-life time of 302 days in soil (Tab 3-2). Due to the dry spring/summer 2018, residues of Flufenacet ESA (Fig 3-6d, $0.64 \mu\text{g kg}^{-1}$) were found in upper soil before winter barley application. Flufenacet, which has a half-life time in soil of 39 days (Tab 3-2), was monitored in upper soil with concentrations slightly above LOQ (Fig 3-6d, $0.28 \mu\text{g kg}^{-1}$). The results indicated a continuous transformation and leaching rate during both periods. However, residual concentrations of Flufenacet and Flufenacet ESA were trapped above plough layer over 1-year in absence of a hydrological active soil matrix. Compared to the results of Carpio et al. (2020), also Flufenacet concentrations were detected

Field insights into leaching and transformation of pesticides and fluorescent tracers in agricultural soil in upper soil after 339 days. A future field study, investigating the pesticides and transformation products in soil and groundwater for a complete year would be useful for e.g., modelling the long-term interaction of pesticide transformation in soil under real conditions.

3.6.4. Influence of drought on fluorescent tracer transport and comparison of tracer and pesticide transformation

The tracer experiment was carried out simultaneously on two plots with different soil types and compared with mixed pesticide concentrations of the same soil types (Fig 3-2, Tab 3-3). Immediately after tracer application at dry conditions (14 % soil moisture, Fig 3-5), the parent compound retention of fluorescent tracer Uranine (UR) and Sulforhodamine - B (SRB) in topsoil was similar in terms of substances but not in terms of soil types. It was expected that the loamy topsoil of the Colluvic Gleyosol with higher contents of clay and C_{org} would have had a higher adsorption potential for Flufenacet and for the tracers than the sandy Luvisol (Gupta and Gajbhiye, 2002). However, the data showed the opposite, since in sandy topsoil (Fig 3-7i, 0–30 cm) a much higher share of substances was retained than in loamy topsoil (Fig 3-7b, 0–30 cm). The applied water eluate analysis method may have generally led to higher concentrations in sandy soil than in loamy soil, because due to lower clay and C_{org} contents in sandy soil, the desorption of pesticides was presumably favoured in this soil type (Tab 3-3). Moreover, we attribute this contradictory pattern to topography with substance losses and reduced adsorption at the steeper loamy plot. On both plots, UR and SRB were quickly leached down to 61–90 cm (Fig 3-7b, i). Apparently, leaching of the tracers was triggered by low precipitation as observed for the fast-preferential leaching of Flufenacet (Chapter 3.6.2.). Yet, a fraction of both tracers remained in the upper soil (0–15 cm) of both plots until the end of monitoring (Fig 3-7g, n). Levy et al. (2007) explained this phenomenon with a limited degradation capability of microbial communities under dry and hot summer conditions due to reversible or irreversible impacts on the bacterial composition in topsoil. The more detailed sampling (Fig 3-7, T4-T6) made the remaining concentrations of UR and SRB in the very topsoil layer (0–5 cm) apparent, for this the resolution of the mixed 0–30 cm samples (Fig 3-7, T1-T3) was too low. Flufenacet, UR and SRB have different sorption properties, which additionally depend on pH, C_{org} and clay content (Bork et al., 2020; Carpio et al., 2020). However, the different compound properties and soil type characteristics did not show distinct effects on the leaching behaviour among the parent compounds and compared to their transformation products. This suggests that preferential flow paths like macropores i.e., wormholes, root zones, fractures and dry cracks depending on the prevailing hydrological conditions seemed to be dominant for transport behaviour rather than matrix flow. Low intensities/concentrations were detected for both transformation products in the plough layer (Fig 3-7q, x, 0–30 cm) starting 57 days after application until spring 2019. The dry topsoil directly after application (14 % soil moisture and $pF \sim 3$, Fig 3-5) limited the formation of Flufenacet ESA and TP510, because of low aerobic microbial activity and mineralization in small capillary pores (Schroll et al., 2006). Also, the transport of the transformation products to subsoil was restricted due to diminished matrix flow in

topsoil (Fig 3-5). The maximum TP510 intensities in deeper soil were first detected at the beginning of May 2019 (Fig 3-7s, z). By then, an intense precipitation period in March (Fig 3-4) had increased moisture content and hydrological connectivity in the soil matrix, which facilitated downward percolation (Fig 3-5). Pallud et al. (2004) established a relationship between a higher microbial mobility and an increased access to the target substances at higher soil moisture.

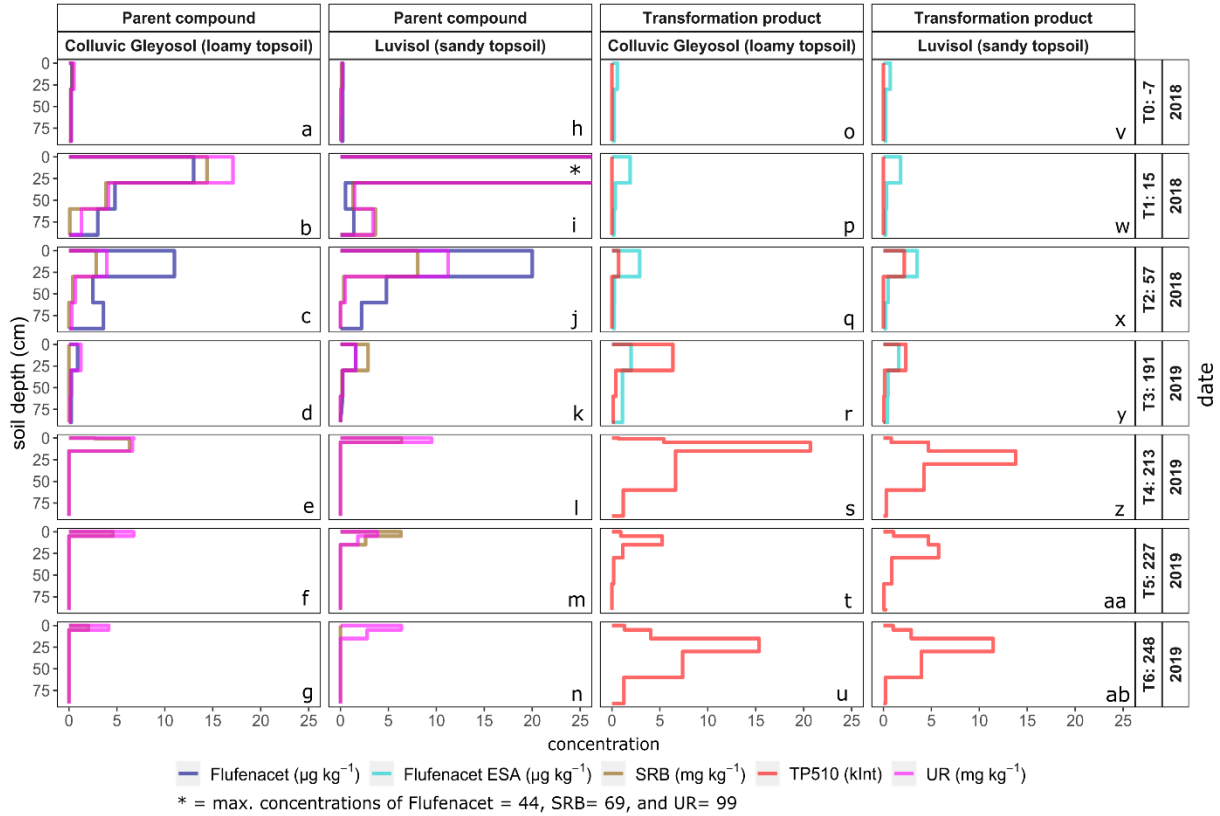


Fig 3-7: Comparison of pesticide and tracer parent compounds (a-n), Flufenacet, SRB, UR and transformation products (o-ab) Flufenacet ESA, TP510 in two soil types; sampling dates T1-T6: with number of days after application (see Tab 3-1) are displayed on the 2nd y axis in chronological order.

The main formation of TP510 occurred under wet soil conditions (pF value ~ 2), which is in accordance with the pesticide mineralization optimum at a soil matrix potential of -0.015 MPa in upper soil samples examined by Schroll et al. (2006). Hence, soil moisture content controlled both the amount of transformation and the mobility of TP510. Low soil moisture (capillary flow, Fig 3-5) impeded leaching into deeper layers. Towards the end of monitoring in June 2019, high intensities of leached TP510 were still measured in the subsoil since decreasing soil moisture hampered further leaching to deeper layers (Fig 3-5, Fig 3-7u, ab). Within the monitoring period, the main formation of TP510 occurred 213 days after application (April/May 2019) and was accompanied by a temperature increase of almost 10°C (Barriuso et al., 2008; Marín-Benito et al., 2019) and increased microbial activity. A close carbon-to-nitrogen ratio (CN - ratio < 15 , Fig 3-8) suggested accelerated microbial transformation rates (Gisi, 1997). While Lange et al. (2018) detected the main intensities of TP510 in 0–5 cm soil depth, the main layer for tracer

transformation was at depths of 6–15 cm in this study (Fig 3-8). We explain the observed shift of these organic molecules by hampered microbial degradation of the fluorescent tracers in the dried-out topsoil (0–5 cm), that also left measurable parent compound concentrations in shallow topsoil 0–5 cm below surface (Fig 3-8).

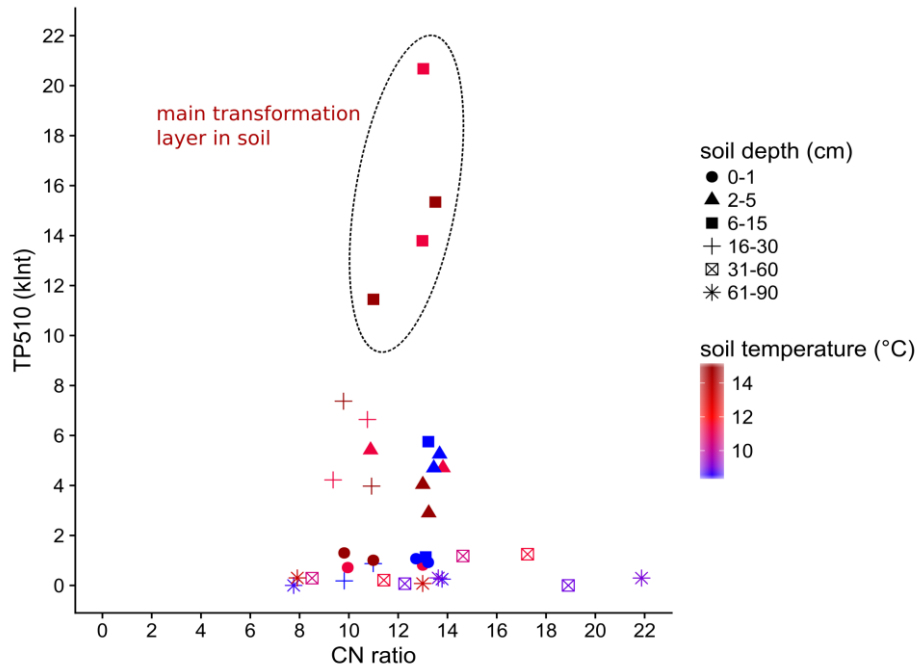


Fig 3-8: CN - ratio in relation to TP510 intensity, soil depth and soil temperature for sampling dates T4-T6. The black dashed circle marks the main transformation layer in soil.

Hence, the tracers demonstrated that living conditions for microbial communities were most favourable at soil depths of 6–15 cm with access to capillary water in small and medium pores.

It cannot be distinguished whether TP510 detections in 31–90 cm (Fig 3-7s, z) occurred by leaching of TP510 with increased soil moisture or by leaching of the parent compounds and transformation within a deeper layer. The intensities of TP510 evenly decreased in both soils and in all layers 227 d after application (Fig 3-7t, aa). Then soil temperatures were low (Fig 3-5) and apparently retarded transformation processes. With higher soil temperatures in June, TP510 intensities increased again (Fig 3-7u, ab).

Combining the observed tracer and Flufenacet behaviour we propose a conceptual model of substance behaviour in our agricultural fields during the dry season (Fig 3-9). In case of the water repellency phenomena during dry conditions (e.g., Ritsema and Dekker, 2000) intensified by hydrophobic compounds in preferential flow paths, small precipitation events shortly after pesticide/tracer application were sufficient to quickly transport a fraction of the mobile parent compounds into deeper soil layers or even shallow groundwater. Another fraction of the parent compound remained at the topsoil and was

excluded from transformation by adverse microbial degradation conditions. Low amounts of transformation products leached to the subsoil until spring 2019 because of low soil matrix flow. The period of main substance transformation was in April/May when highest amounts of TP510 were recorded in soil and Flufenacet ESA peaked in shallow groundwater. Since both transformation products contain sulfonated groups, their similar behaviour supports the hypothesis of Lange et al. (2018), who assumed that TP510 formation might be used as an insitu proxy for the intensity of the biochemical transformation of acetamide herbicides.

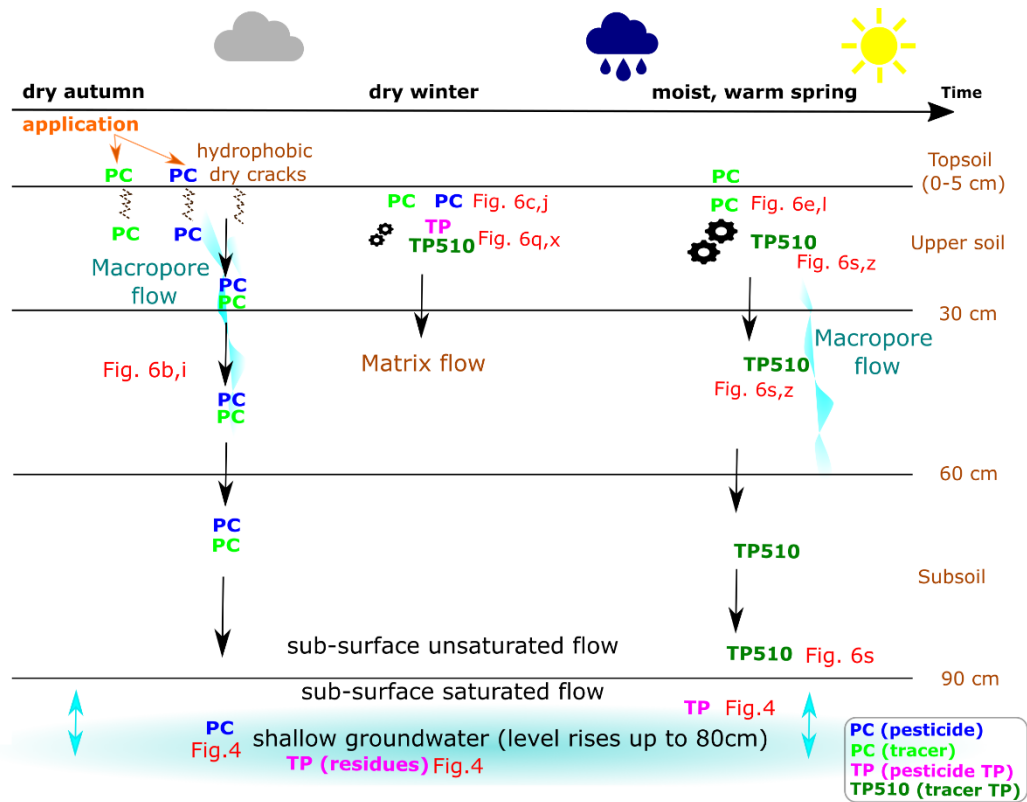


Fig 3-9: Conceptual model for the behaviour of parent compounds (PC) and transformation products (TP) in soil during a dry period followed by a wet spring. Red labels are explicit references to other figures.

Toxicity tests of Uranine photo transformation products found no indications for toxicity (Gutowski et al., 2015), however more investigations are necessary to characterize TP510 and highlight the potential and limits of using fluorescent tracers as in-situ proxy to infer information of pesticides in the fields. The results of our pilot study considering the common evaluation of TP510 and Flufenacet ESA occurrence are valid for the presented study area. The soils are typical in an agricultural landscape and the applied pesticides are common farming practice. For more general statements, further field studies on other soil types should be investigated. Additional column experiments could be helpful for calculating a mass balance of pesticides and tracers in soil. Field results may be coupled to laboratory experiments (e.g. degradation tests, photolytic stability of Flufenacet ESA) to retrieve characteristic patterns about the formation of transformation products in soil. Additionally, a physical-based model would promote

the understanding of the interconnected processes between parent compounds and transformation products in soil and shallow groundwater. However, further field measurements e.g. parameters like soil surface (cracks, porosity, etc.), biotic and abiotic degradation and leaching rates, microbial turnover/activity (by e.g. enzyme activity or biomass measurements) would be necessary to set up a realistic model.

3.7. Conclusion

This study examined the behaviour of Flufenacet and its transformation product Flufenacet ESA from agricultural soil to shallow groundwater during wet and dry weather conditions and additionally used fluorescent tracers to investigate processes within the soil. It was found that leaching of Flufenacet to shallow groundwater by preferential pathways posed a greater risk during the dry than during the wet period. Preferential flow triggered by low precipitation events had an important influence on the transport behaviour and created short concentration peaks in shallow groundwater. In contrast, Flufenacet ESA was continuously detected in shallow groundwater. Within the soil, Flufenacet and Flufenacet ESA showed contrary behaviour under different hydrological conditions. Under wet conditions, the significance of preferential transport was apparently reduced and a large fraction of Flufenacet was transformed into Flufenacet ESA. During dry conditions and triggered by minimal precipitation (6 mm), a fraction of Flufenacet quickly reached deeper soil layers presumably following hydrophobic preferential flow paths. Transformation was reduced and probably only occurred in medium to small soil pores filled with capillary water. As a result, leaching of newly formed Flufenacet ESA was firstly limited and then mainly occurred after soil rewetting and during warmer temperatures in spring. Since up to now these findings are limited to our field site, we call for more systematic monitoring approaches in soil and groundwater to understand longer term transformation product exposures in relation to water flows and soil temperatures also in other areas. A field experiment with monthly or rainfall-event based monitoring of pesticide and tracers and their transformation products in soil for at least 1-year would be useful for gathering an extended data set and gain further evidences for the detection of characteristic leaching and transformation patterns. Additional field measurements should be carried out to finally set up a physically based model, which may confirm our identified environmental behaviour of Flufenacet. In our case, the cost-efficient fluorescent tracers permitted a higher spatial resolution and a longer sampling period than the pesticide monitoring. Thereby, the formation of the tracer transformation product TP510 could be related to suitable living conditions for soil microorganisms, in terms of the soil water potential ($pF \leq 2$) and soil temperature ($> 9^{\circ}\text{C}$) in 0–30 cm depth. A fraction of UR and SRB remained in the topsoil until the end of sampling without further vertical transport, which was explained by the dysfunctional degradation capability of microbial communities under dry and hot summer conditions in topsoil. The occurrence of increased TP510 amounts in the soil after drought was temporally consistent with the main peak of Flufenacet ESA ($1.48 \mu\text{g L}^{-1}$) in shallow groundwater. This accordance and the similar dependence on retention and transformation processes within the soil corroborated the finding that fluorescent tracers are adequate tools to support process research on leaching and transformation of

Field insights into leaching and transformation of pesticides and fluorescent tracers in agricultural soil pesticides. In general, the transport of mobile pesticides and transformation products to shallow groundwater and hence, in the long-term also to deeper groundwater, poses risks for the drinking water supply by private or public wells. Therefore, our results once again emphasize that the investigation of pesticides transformation and leaching of transformation products should be mandatory for the approval procedure of agricultural pesticides.

3.8. CRediT authorship contribution statement

Sandra Willkommen: Conceptualization, Methodology, Formal analysis, Writing - original draft. Jens Lange: Conceptualization, Methodology, Formal analysis, Writing - review & editing. Uta Ulrich: Methodology, Writing - review & editing. Matthias Pfannerstill: Writing - review & editing. Nicola Fohrer: Project administration, Writing - review & editing

3.9. Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

3.10. Acknowledgments

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4. How weather conditions and physico-chemical properties control the leaching of Flufenacet, Diflufenican, and Pendimethalin in a tile-drained landscape

Willkommen, S., Pfannerstill, M., Ulrich, U., Guse, B., Fohrer, N., 2019. How weather conditions and physico-chemical properties control the leaching of flufenacet, diflufenican, and pendimethalin in a tile-drained landscape. *Agriculture, Ecosystems & Environment*. 278, 107–116. 10.1016/j.agee.2019.03.017.

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4.1. Highlights

- Hydrological conditions are key factor for total drainage loads.
- Wet weather conditions lead to 10-fold increase in drainage loss.
- Timing and frequency of pesticide peaks are controlled by sorption properties.
- Leaching of Flufenacet is not only controlled by high amounts of precipitation.
- Highest loss of Pendimethalin and Diflufenican during high discharges in winter.

4.2. Abstract

The input of harmful substances into surface waters are of major concern since their side effects may negatively affect the chemical state of surface waters. This study investigated the drainage loss of pesticides into surface waters in a small agricultural catchment in Northern Germany. The pesticides Flufenacet, Diflufenican, and Pendimethalin were monitored at a daily resolution for 154 days in 2016 (dry period) and 111 days in 2017 (wet period) for two consecutive years at both field- (10 ha) and catchment scale (100 ha). Highly contrasting weather conditions led to extremely high differences in loads between both monitoring periods. Regarding both scales and campaigns, Flufenacet was released often in considerably higher amounts and faster than Diflufenican and Pendimethalin. The very mobile pesticide, Flufenacet, is not exclusively leached during high precipitation events but also continuously discharged from soils to the drainage system during low precipitation. Pendimethalin had the lowest recovery rate in comparison to its application amount and showed a lower total loss rate than the less sorptive pesticide Diflufenican. Pendimethalin and Diflufenican showed high retarded loads caused by increased drainage discharge and sediment transport during late winter induced by freezing and thawing processes in the upper soil. Hence, leaching of the pesticides was controlled by the sorption properties of the investigated compounds and, to a large extent, by hydrological boundary conditions, which were highly variable from an (inter-) annual perspective. Our study identified antecedent and prevailing precipitation and soil moisture conditions as the key impact of pesticide leaching to the drainage system in the long-term.

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Keywords: Tile drainage, Pesticide leaching, Flufenacet, Diflufenican, Pendimethalin, Weather conditions

4.3. Graphical abstract

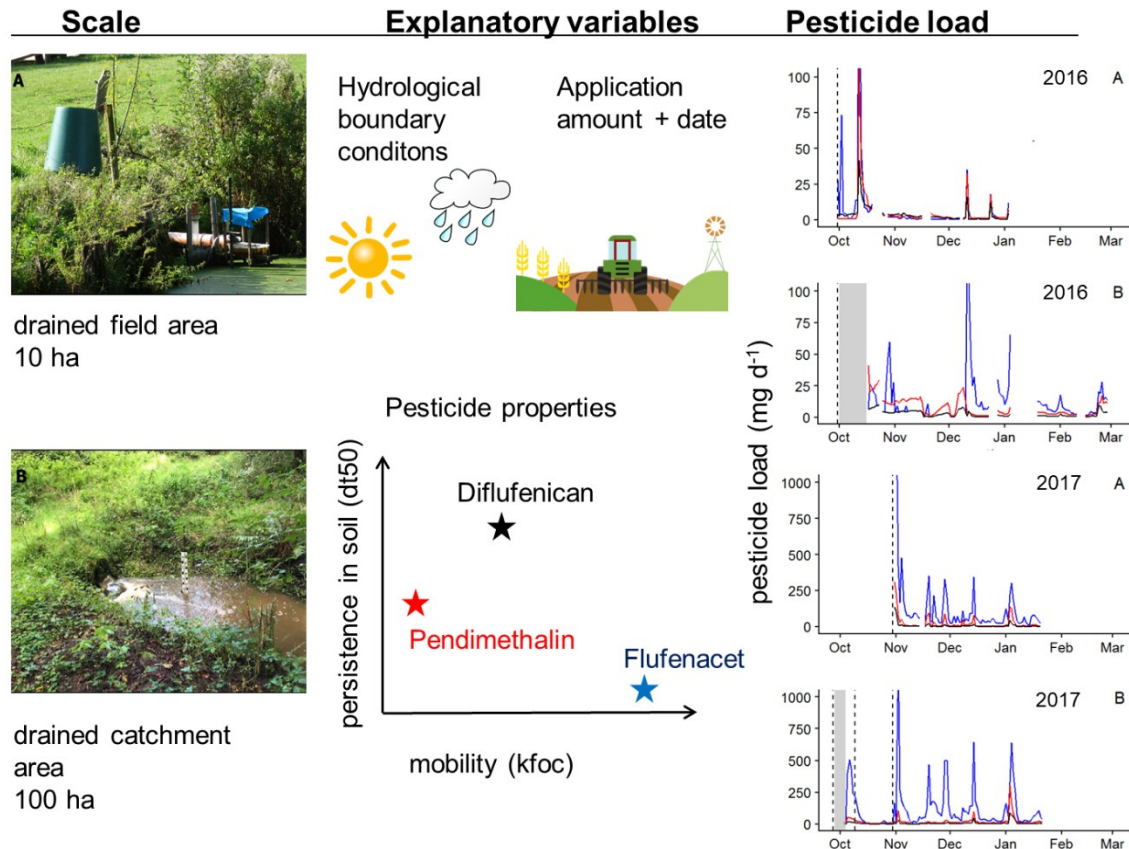


Fig 4-1: Pesticides in a tile-drained landscape.

4.4. Introduction

Diffuse sources of pesticides and their potential threat to the environment are of great general interest world-wide. This has been demonstrated by the European Union's recent decisions to prohibit three neonicotinoids imidacloprid, clothianidin, and thiamethoxam on open land (EU 2018/783–785) and the intense public debate about harmful side effects of the most commonly used pesticide glyphosate (e.g. Van Bruggen et al., 2018). Pesticide losses from cultivated fields to surface waters are investigated with diverse monitoring strategies varying in frequency, technical effort, and length (Gaynor et al., 1992; Brown et al., 1995; Kreuger, 1998; Müller et al., 2003; Holvoet et al., 2007; Rabiet et al., 2010; Ulrich et al., 2012; Ulén et al., 2014; Potter et al., 2015; Sandin et al., 2018). Depending on the specific research approach, the temporal resolution of current pesticide monitoring spreads from hourly (Wittmer et al., 2010; Chrétien et al., 2017), to daily (Müller et al., 2003; Doppler et al., 2012; Ulrich et al., 2012; Potter

et al., 2015), and to low (weekly) temporal resolution (Ulén et al., 2014; Sandin et al., 2018). Due to high technical effort and costly analysis, the monitoring covers either short discharge events in high-frequency (e.g. Chrétien et al., 2017) or long-term measurement periods in a lower sampling interval (Sandin et al., 2018) as e.g. for an operational monitoring program (Rabiet et al., 2010). The monitoring can be carried out by grab sampling (Sandin et al., 2018; Potter et al., 2015), automated time- and/or flow-proportional (Müller et al., 2003; Leu et al., 2004a; Rabiet et al., 2010; Ulrich et al., 2012; Ulén et al., 2014), or event-based with very high temporal resolution (Wittmer et al., 2010; Chrétien et al., 2017). Also common is a combined approach using automated sampling with high temporal resolution during high flows and grab sampling with low temporal resolution during base flows (Freitas et al., 2008; Doppler et al., 2012, 2014; Potter et al., 2015). Furthermore, cost-saving computer-based approaches are used to model pesticide transport and estimate pesticide loads (i.e. Ghafoor et al., 2011; Payraudeau and Gregoire, 2012; Bertuzzo et al., 2013; Fohrer et al., 2014; Novic et al., 2018). However, this data provides a rough overview for water quality assessment but still needs appropriate field sampling for model validation. All mentioned monitoring and modelling approaches help to understand the behaviour of pesticides in the environment. However, due to coarse temporal resolution of sampling or short sampling periods, these studies are limited in describing all aspects of leaching of pesticides and in providing comprehensive knowledge about the absence or presence of pesticides in aquatic environments. Although field approaches with higher temporal resolution and long-time monitoring would provide more profound insight into pesticide leaching behaviour, such studies are rare. As requested by Holvoet et al. (2007), more field experiments with continuous and extended monitoring periods should be carried out to improve this knowledge. To the best of our knowledge, it is not entirely clear how loads of known pesticides behave spatially temporally over longer time periods. Especially in headwater catchments, it is expected that concentrations of substances are subject to very strong dynamical fluctuations based on the dynamic water flows (Rabiet et al., 2010). High-resolution and ongoing measurements are important to gain this expanded understanding for the load transport of pesticides in the environment. To these ends, monitoring should encompass both the peak concentration during precipitation events and the total loss in the long-term perspective. Considering an appropriate monitoring strategy according to hydrological conditions, tile-drained landscapes are of special interest. In north-western Europe, tile drainage flow underlies an annual cycle with dry tile drainages in summer and increasing discharge in autumn. In winter, maximum discharges occur and in spring the discharge lowers again (Tournebize et al., 2017). Despite recurring cyclical patterns, the height of drainage discharge can vary to a large extent interannually depending on prevailing weather conditions (Pfannerstill et al., 2015; Willkommen et al., 2018; Guse et al., 2019). Regarding pesticide leaching, this dynamic of tile drainage discharge needs to be considered because in highly tile-drained areas pesticides are mainly transported by tile drainages (Kreuger, 1998; Holvoet et al., 2007). Since tile drainages lead to fast and shortened flow paths, they are highly relevant for these precipitation-induced discharge events (Schottler et al., 1994; Doppler et al., 2014). Accompanied with quick responses of precipitation events, pesticides are transported via tile

drainages rapidly and in high pulse-like signals with short retention time to surface waters (Kung et al., 2000). Hence, Kreuger (1998) derives an annual cycle of pesticide loss, with maximum concentrations occurring during or right after application (Capel et al., 2001). The first flush effect is followed by several load peaks during events of tile drainage discharge (Kreuger, 1998; Brown and Van Beinum, 2009). However, studies show that pesticide leaching behaviour can vary in time under specific weather conditions (Brown and Van Beinum, 2009). Since tile drainage systems may significantly impact pesticide transport and are very sensitive to antecedent and prevailing weather conditions, an interest in further investigations of drainage transport pathways of pesticides on the field- and catchment scale was claimed by Leu et al. (2004a), Freitas et al. (2008), Ulrich et al. (2012), and Sandin et al. (2018). These studies revealed that total loss rates of pesticides can vary by an order of magnitude within the catchment (Leu et al., 2004a). Ulrich et al. (2012) recommended further research on pesticide loss at different spatial scales to improve understanding of pesticide transfer processes. Doppler et al. (2014) pointed out the importance of a high-frequency monitoring in time and scale to detect controlling factors for the temporally variable spatial patterns in pesticide loss. Besides antecedent and prevailing weather conditions, additional controlling factors may play an important role for pesticide leaching. For this, the time of application and physicochemical properties of pesticides need to be linked to weather conditions to explain pesticide leaching via tile drainages. The complex interplay of many factors influencing the transport of pesticides in tile drainages is not entirely clear (Doppler et al., 2014; Sandin et al., 2018). This deficit of knowledge about temporal dynamics and patterns of pesticide outputs of tile drainages motivates a continuous daily pesticide load monitoring of agricultural tile drainage outputs at different spatial scales. Our study contributes to an improved understanding about leaching behaviour of pesticides considering Diflufenican, Flufenacet, and Pendimethalin. At different spatial scales, we investigate the impact of (i) contrasting weather conditions during two monitoring periods, (ii) physico-chemical properties, (iii) application amounts and application area on leaching of selected pesticides for a tile-drained landscape.

4.5. Methods and material

4.5.1. Study area

The catchment is located in the eastern hillside region of Schleswig Holstein in Northern Germany and has a size of 100 ha with a share of agricultural area of 71 %. The investigation area belongs to a farm which uses conventional agriculture practice. The main crops are winter wheat, winter barley, winter oilseed rape, and corn. Shallow groundwater levels in sandy depressions and surface water in loamy hilly terrains demand an intensive use of tile drainages with a total length of 6.3 km. The main soil types are sandy-loamy luvisols and peat soils. In this study, the monitoring aims to investigate two different spatial scales. The sampling point (A) represents the field scale. This field outlet drains an 8-ha area including one part of a field. The topsoil of the sandy depressions in field A are characterized by sand

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contents of 60–70 % and silt contents of 20–30 %, pH 6.3 and C_{org} 1.5 %. The clay content of the loamy topsoil is 20–30 % and the silt content 50–60 %, pH 7.0 and C_{org} 1.4 %. Sampling point (B, Fig 4-2) describes the outlet of the whole catchment (100 ha), also including the smaller area of 10 ha representing the field scale (A, Fig 4-2).

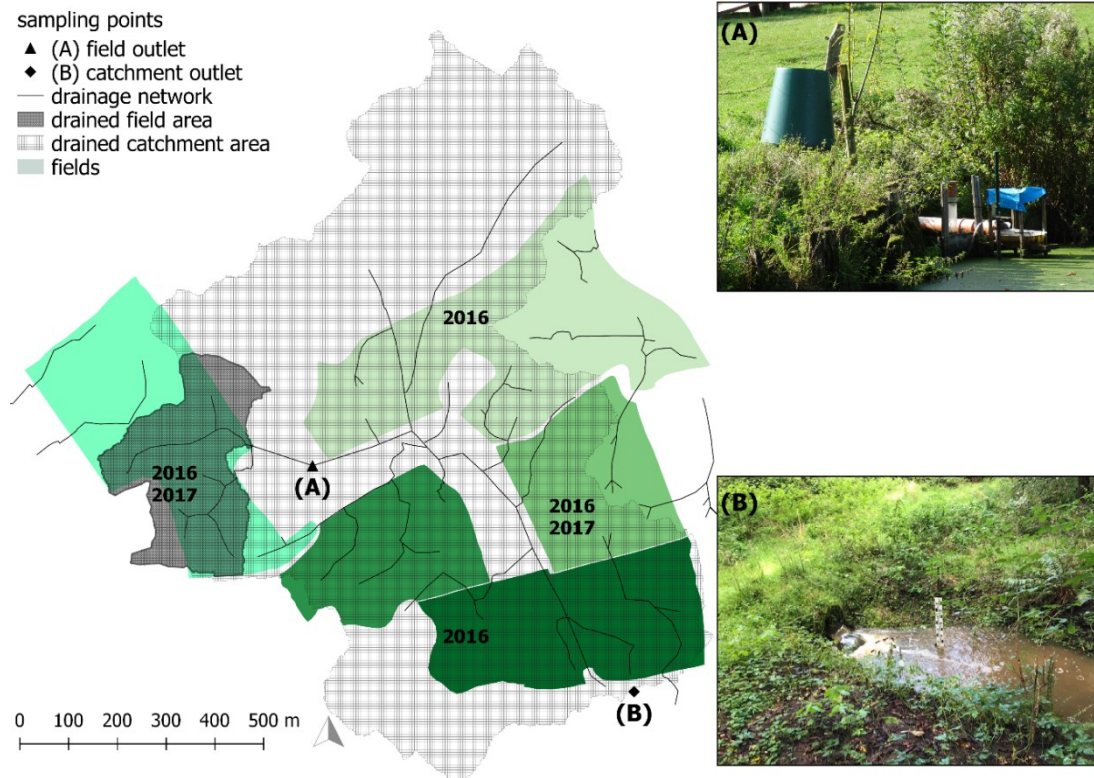


Fig 4-2: The study area shows arable fields (green coloured) and the tile drainage network. The pesticide load at field scale is measured at the field outlet (A). The pesticide load of the whole drained catchment is measured at the catchment outlet (B).

The first measurement campaign lasted from 27th of September 2016 to 27th of February 2017 (length = 154 days, campaign 1) and the second measurement campaign lasted from 03rd of October 2017 to 21st of January 2018 (length = 111 days, campaign 2). The pesticides were applied in late summer and autumn (Tab 4-1). The maximum effective application area of the 100-ha drained water catchment (B) is 50 ha. The calculated amount of cumulative pesticide load refers to the effective application area (Tab 4-1).

4.5.2. Selected pesticides and their properties

In this study, the farmer continued the crop rotation and pesticide application according to local practice. Three different pesticides (Pendimethalin, Diflufenican, and Flufenacet) were investigated. The pesticides were chosen because of their wide use in Northern Germany, common detection in surface waters

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(State Laboratory Schleswig-Holstein, 2015), and their contrasting physico-chemical properties. Furthermore, the three substances are often used in the same pesticide formulation. The properties are listed in a pesticide properties data base (PPDB: Lewis et al., 2016). The pesticides vary mainly in their sorption capacities and half-life times. The chosen pesticides can be grouped into more mobile substances with high leaching potential and less mobile substances preferring sorption to soil. Flufenacet has a low organic carbon sorption coefficient (k_{foc}) and is moderately mobile (Lewis et al., 2016) with the percolating water. Diflufenican and Pendimethalin have a high k_{foc} value, can sorb better to soil particles, and do not desorb easily for transport with pore water. The pesticides differ in their half-life times. Pendimethalin (non-mobile) and Diflufenican (slightly mobile) are persistent in soil as they have a high half-life period (dt_{50}) and degrade slowly. Flufenacet degrades faster than Diflufenican and Pendimethalin (Tab 4-2).

Tab 4-1: Total applied amount of pesticides is listed for two areas: field and catchment. The size of the effective application area (area B) depends on the number of cultivated fields. The fields are cultivated with wb = winter barley, wr = winter oilseed rape, ww = winter wheat, and x = no application.

Scale		Field		Catchment	
Outlet		A		B	
Year		2016	2017	2016	2017
Application date		09/30	10/30	09/30	09/27,10/09
Crop		ww	ww	wr, ww	ww
Effective application area (ha)		7.2	7.2	36.2	23.7
<i>Effective application area (ha)</i> <i>Drained water catchment (ha)</i>		0.72	0.72	0.72	0.47
Application rate (g ha ⁻¹)	Flufenacet	170	210	150	330
	Diflufenican	50	60	40	130
	Pendimethalin	380	450	460	480
Effective application amount (kg)	Flufenacet	1.2	1.5	8.2	13.1
	Diflufenican	0.3	0.4	2.4	4.8
	Pendimethalin	2.7	3.3	19.5	17.8

4.5.3. Field data and sampling

Hydrological data were measured continuously over the year. Precipitation data were taken from a tipping bucket rain gauge by Campbell Scientific in 10-minute (min) resolution located within the catchment. A rainy day was defined as a day with precipitation larger or equal than 0.1 mm as recommended by the DWD Weather Glossary (2018). At the field outlet, the discharge of the 150 DN tile drainage pipe was measured manually by collecting water with bucket and stopwatch. Water levels were meas-

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ured in 10 min resolution by HOBO Oneset data loggers in a connected U-junction following the principle of communication vessels. The rating curve was based on 38 measurements. At the catchment outlet, the flow velocity was measured by doppler sensor and a pressure transducer (ISCO 750 area velocity flow module). The discharge is then calculated automatically by multiplying the area of the outlet with the average velocity. A threshold of 4 mm water level for flow velocity measurements was chosen for the installed doppler sensor. The soil moisture was measured in 10 min resolution in 30 cm, 60 cm, and 90 cm depth by SM300 Delta-T sensors during the monitoring periods. For the collection of the pesticide samples, two measurement campaigns in the year 2016 and 2017 were carried out from autumn after pesticide application until the end of February. Automatic water samplers (Teledyne ISCO 6712) were installed at each outlet to collect 50 mL of water volume every 70 min in 350 mL glass bottles. Three 350 mL glass bottles covered one day.

Tab 4-2: Properties of the monitored pesticides obtained by the PPDB (Lewis et al., 2016). The half-life time is described by the degradation time in days (dt_{50}) in soil, water, and sediment. The specific dt_{50} values refer to available field studies in the PPDB. Table gaps with no available date from PPDB are expressed by x.

Pesticide CAS no.	K_{foc} (mL g ⁻¹)	Soil dt_{50} (d)	Water dt_{50} (d)	Sediment dt_{50} (d)	Kow (pH 7, 20°C)	Photo- lysis water dt_{50} (d)	Vapour pressure (25°C, mPa)	Solubility (20°C, mg L ⁻¹)
Flufenacet 142459-58-3	273.3	39	54.0	81	3.5	x	0.1	51
Pendimethalin 40487-42-1	13,792	100.6	4.0	16	5.4	21	3.3	0.3
Diflufenican 83164-33-4	1,996	315	x	175	4.2	133	0.004	0.1

4.5.4. Laboratory analysis

The physico-chemical water parameters pH, oxygen content, electrical conductivity, temperature, and redox potential were determined in-situ according to the existing norms (DIN 384044: 1976; DIN 384046: 1984; ISO 5814: 2012; ISO 7888: 1993; ISO 10523:2008) with WTW 3540. The water samples were stored at 8°C within one day after sampling if air temperature was > 8°C. The samples of one day were combined to a daily mixed sample and were sent cooled to the laboratory. The substances Pendimethalin, Diflufenican, and Flufenacet were analysed with an AB Sciex 5500 Qtrap by an accredited laboratory according to the Germany Industry Norm (DIN 38407-36:2014-09). The Limit of Quantification (LOQ) was 0.01 µg L⁻¹ for Flufenacet and Diflufenican and 0.025 µg L⁻¹ for Pendimethalin. The uncertainty of the pesticide concentrations within a measurement stated by the analytical laboratory is in a range of 20 %.

4.5.5. Calculations

For pesticide load calculation, concentration values detected below LOQ were set to 0.5 LOQ. The daily loads were calculated multiplying daily concentration ($\mu\text{g L}^{-1}$) of mixed water samples with daily averaged discharge ($\text{m}^3 \text{d}^{-1}$). In this study, we distinguished between the terms daily pesticide load (mg d^{-1}), cumulative pesticide load (mg) for the different monitoring periods, specific cumulative load (g ha^{-1}) and normalized specific cumulative pesticide loads (g ha^{-1}), and the total pesticide loss rate (%). The daily tile drainage output and discharge averaged concentration were described as load (mg d^{-1}). Cumulative pesticide loads were calculated as the sum over the monitoring period (mg). The specific cumulative load (g ha^{-1}) is the average area related cumulative load of the monitoring periods. Normalized specific cumulative loads are a measure to compare the specific cumulative loads of the three pesticides under varying application conditions (Brown and Van Beinum, 2009). The cumulative loads were standardised to the equivalent average application amount of 100 g ha^{-1} to gain a normalized ratio between the three substances (Eq 4-1).

$$\text{normalized specific cumulative load} = \frac{\text{equivalent application amount } (\text{g ha}^{-1})}{\text{average application amount } (\text{g ha}^{-1})} \quad (4-1)$$

Afterwards, the normalized specific cumulative loads were compared for both monitoring periods in 2016 and 2017. Factors of change between the two years were delineated. The share of the cumulative load to the average applied amount was calculated for each monitoring period according to Eq 4-2.

$$\text{total loss rate } (\%) = \frac{\text{specific cumulative load } (\text{g ha}^{-1})}{\text{average application amount } (\text{g ha}^{-1})} * 100 \quad (4-2)$$

4.6. Results

4.6.1. Hydrological boundary conditions

During both measurement campaigns in the years 2016 and 2017, the weather conditions varied strongly (Tab 4-3). Campaign 1 was relatively dry with only 49 % of rainy days (maximum with 17 mm d^{-1}). However, seven days exceeded 10 mm d^{-1} . To the contrary, during campaign 2 the precipitation increased and 65 % of days were rainy. The maximum peak reached 45 mm d^{-1} . Excluding this heavy precipitation event early in the monitoring, the precipitation in campaign 2 was evenly distributed with only four days exceeding 10 mm d^{-1} .

Tab 4-3: Precipitation and discharge distribution from both the field- and catchment scale during both measurement campaigns.

Scale	Field	Catchment	Field	Catchment
Outlet, year	A, 2016	B, 2016	A, 2017	B, 2017
Precipitation sum	153 mm in 154 monitoring days		158 mm in 111 monitoring days	
Precipitation max	17 mm at 22 nd of February		45 mm at 05 th of October	
Nr. of rainy days > 0.1 mm	75		72	
Nr. of rainy days > 10 mm	7		4	
Nr. of dry days	79		39	
Precipitation median	1.6 mm		3.1 mm	
Discharge mean (m ³ d ⁻¹)	83.2	487.7	240.6	955.9
Discharge median (m ³ d ⁻¹)	77.4	279.9	164.6	732.6

Comparing the last 10 years of data (2007–2017) from the nearest weather station in Dörnack (DWD Climate Data Center, 2018), the year 2016 was 11 % drier (with 650 mm) and 2017 was 22 % wetter (with 885 mm) than the average value of 728 mm per year (the range of annual precipitation in this period was between 628 mm and 885 mm). The year 2016 showed the lowest variability with a deviation of ± 21 mm in 2016. In 2017, the standard deviation of ± 36 mm represented an average variable year.

4.6.2. Spatial extent and amounts of applied pesticides

For the evaluation of the pesticide load dynamics, aspects of agricultural management were considered: the effective application area (Tab 4-3) and application amounts (Tab 4-1). The effective application area of 7.2 ha at field scale (A) was identical in both years. The effective application area of the drained catchment (B) decreased from 2016 to 2017 by 14 % (Tab 4-1). In 2016, four fields were connected to location B (Fig 4-2). In the following year only two fields were cultivated, and the catchment outlet received loads primary from the field of outlet location A (Fig 4-2). The application amount varied between the pesticides, but the order of application amount was the same for both years: Pendimethalin > Flufenacet > Diflufenican (Tab 4-4). The application amount increased for all substances between 18–25 % at the field scale for campaign 2. In 2017, the drained area decreased at the catchment (Tab 4-3), but the amount of applied pesticides for Diflufenican and Flufenacet approximately doubled yet remained the same for Pendimethalin. At both scales and during both years the order of total loads was similar (Flufenacet > Pendimethalin > Diflufenican, Tab 4-4), contrary to the order of application amounts.

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Tab 4-4: Average application amounts (g ha^{-1}) together with effective application area (ha) and specific cumulative load (g ha^{-1}). The specific cumulative load is the average area related cumulative load sampled at the field-outlet (A) and catchment-outlet (B).

Substance	Year	Location	Effective application area (ha)	Average application amount (g ha^{-1})	Specific cumulative load (g ha^{-1})	Total loss rate (%)
Pendimethalin	2016	A	9	300.0	0.05	0.02
	2017			366.7	0.21	0.06
	2016	B	32.6	598.2	0.03	0.005
	2017		29.7	599.3	0.08	0.01
Flufenacet	2016	A	9	133.3	0.07	0.05
	2017			166.7	1.15	0.69
	2016	B	32.6	251.5	0.05	0.02
	2017		29.7	441.1	0.44	0.10
Diflufenican	2016	A	9	33.3	0.04	0.11
	2017			44.4	0.07	0.15
	2016	B	32.6	73.6	0.01	0.01
	2017		29.7	161.6	0.03	0.02

4.6.3. Cumulative load, normalized specific cumulative loads, and total loss rate of selected pesticides

Regarding both scales, especially the cumulated daily load of the pesticide Flufenacet showed a stepwise major load output during campaign 1 and a continuous load output during campaign 2 (Fig 4-3). The difference in total load between the two campaigns is most apparent for Flufenacet (Fig 4-3).

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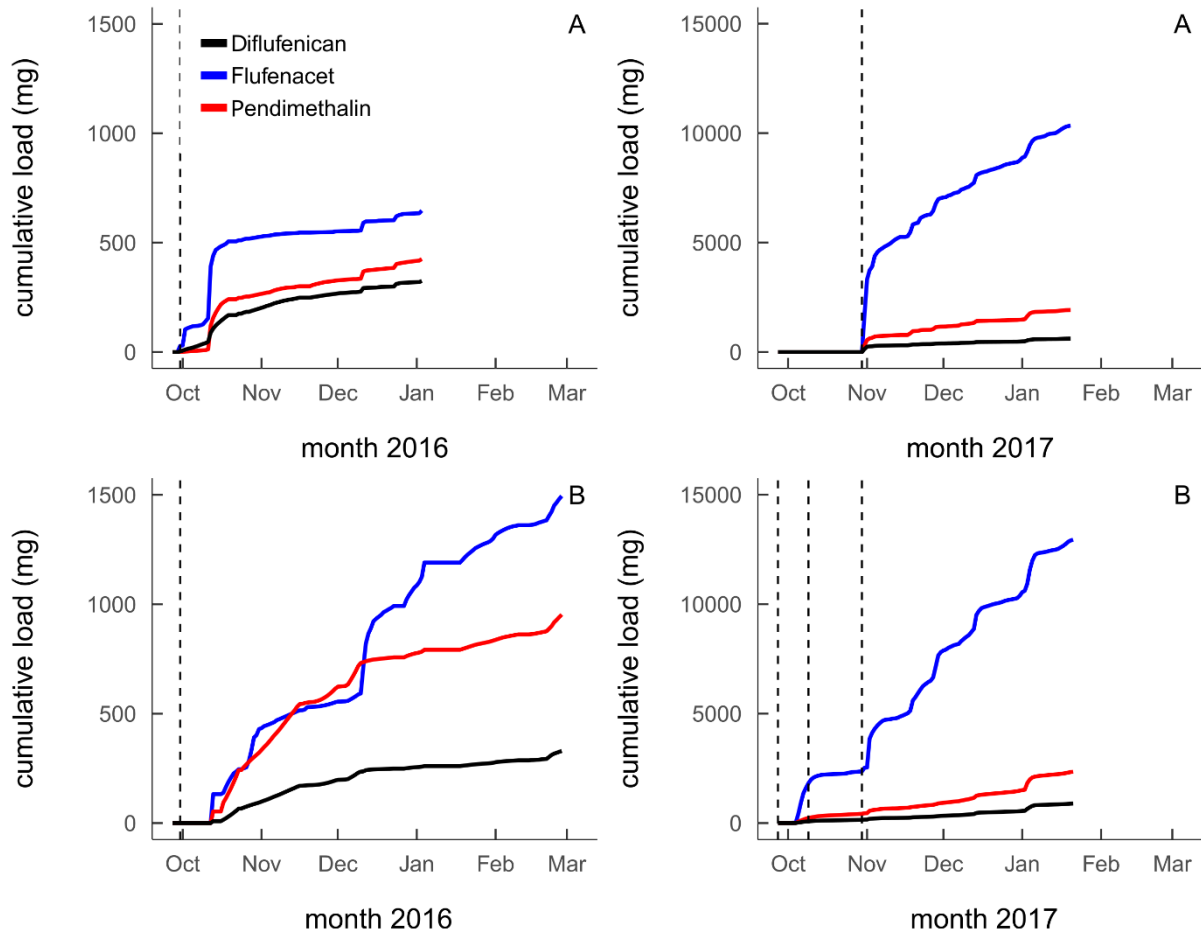


Fig 4-3: Cumulative pesticide loads (mg) for flufenacet, diflufenican, and pendimethalin in dry (2016) and wet (2017) years on two different scales: (A) outlet of field and (B) catchment outlet. The dashed line marks the application days for pesticides (one application in 2016 on 27th of September and in 2017, the 1st application was on 30th of September (B), the 2nd application on 9th of October (B), and the 3rd application on 30th of October (A)).

At the catchment scale, the total load increased for Diflufenican 3-fold, for Pendimethalin 2.6-fold, and for Flufenacet 8.8-fold. At the catchment scale, the normalized specific cumulative loads increased for the three pesticides from dry to wet conditions: for Diflufenican by a factor of 1.3, Pendimethalin by 2.7, and for Flufenacet by 5.0. At the field scale, the pattern is similar for the normalized cumulative loads: for Diflufenican by 1.4, Pendimethalin by 3.4, and for Flufenacet by 13.1. The total loss rate increased for all substances at field- and catchment scale from 2016 to 2017 (Tab 4-4). At the field scale, the total loss rate ranged between 0.02 % for Pendimethalin and 0.05 % for Flufenacet during campaign 1. Under wet conditions the total loss rate increased strongly to 0.06 % for Pendimethalin and 0.7 % for Flufenacet (Tab 4-4). At catchment scale, the total loss rate ranged between 0.005 % for Pendimethalin and 0.02 % for Flufenacet during campaign 1. For campaign 2 the total loss rate increased strongly to 0.01 % for Pendimethalin and 0.1 % for Flufenacet (Tab 4-4). To identify the impact of the sorption properties of the compounds (Tab 4-2) on the drainage output, the sorption coefficient (k_{foc}) and the total loss rate were compared (Fig 4-4). The total loss rate is higher for all substances under wet conditions. On both scales, the more mobile substance was (smallest k_{foc} value) released in a higher

amount with discharge under wet conditions. The most sorptive substance showed the lowest total loss rate. At the field scale, this relation cannot be confirmed during dry periods (Fig 4-4).

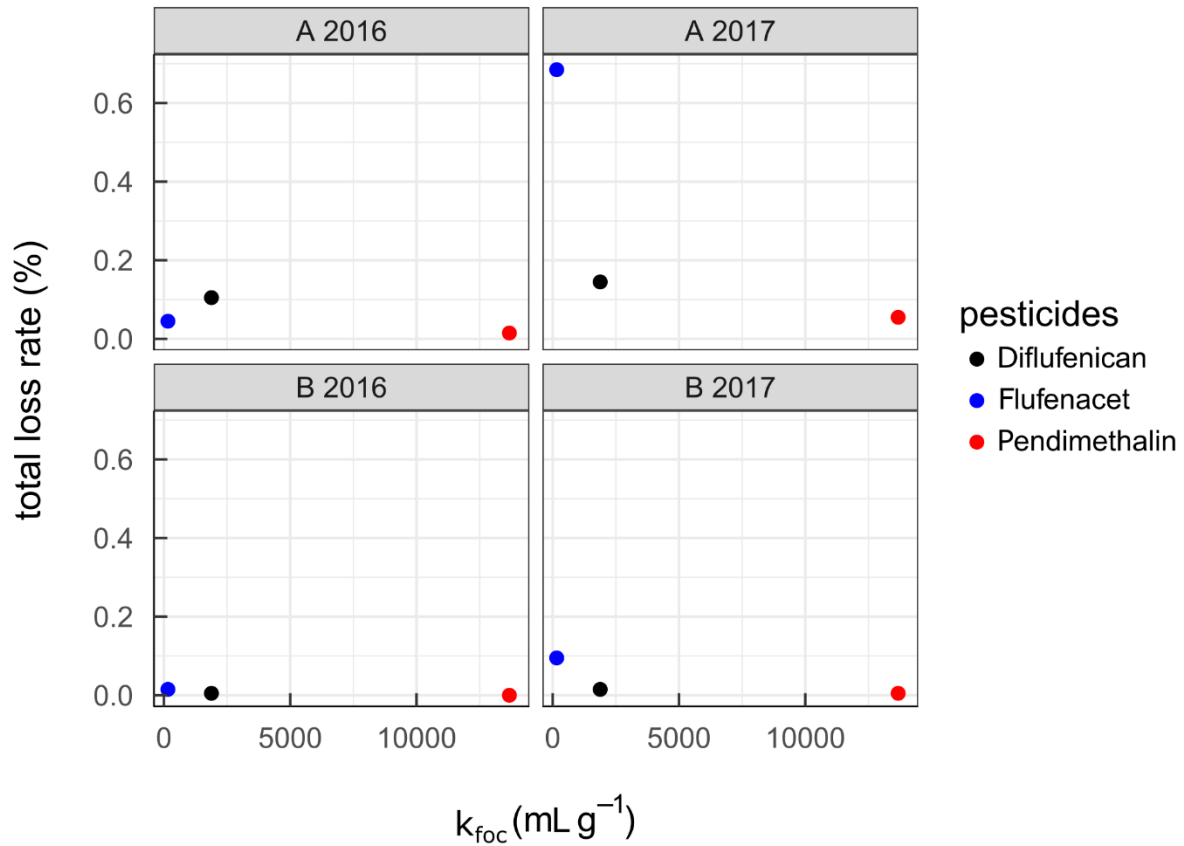


Fig 4-4: Variation of total loss rate (% share of specific cumulative load to applied pesticide amount) and sorption coefficient k_{foc} (mL g⁻¹) of the selected pesticides at the field- and catchment outlets for campaign 1 in year 2016 and campaign 2 in year 2017.

4.6.4. Pesticide load dynamics

Besides the remarkable differences in cumulative loads of the considered pesticides for the monitoring campaigns, highly variable boundary conditions and pesticide transports were observed within each monitoring campaign.

4.6.4.1. Pesticide load dynamics at field scale (outlet A)

During campaign 1, the measured soil moisture was on average around 20 % (pF value 2.5). The soils were not fully saturated. The pesticides subsequent load peaks only occurred if rainfall exceeded precipitation amounts of at least 9 mm d⁻¹ (phase 1). The peaks of all three pesticides occurred at same dates and lasted for 1–2 days (Fig 4-5). After the precipitation events the loads immediately decreased below the quantification limit. The main load peak occurred for all substances during the first precipitation event exceeding 12 mm on one day, 12 days after application. This first flush led to the highest measured load for all substances in 2016 with amounts of 236.4 mg d⁻¹ Flufenacet, 107.64 mg d⁻¹ Pendimethalin,

and 41.60 mg d⁻¹ Diflufenican. In general, the peak loads followed precipitation events. In discharge recession and background load phases, the pesticides were rarely detectable (phase 2). Remarkable is the first occurring peak concentration of 1.38 µg L⁻¹ Flufenacet immediately after application (phase 3). Pendimethalin (< LOQ) and Diflufenican (0.08 µg L⁻¹) show very low concentrations immediately after application. During campaign 2, the first flush occurred immediately after application of the pesticides within the same day (phase 1). The Flufenacet peak was measured with an amount of 1,693.8 mg d⁻¹, which was the highest monitored load in 2017. The sandy-loamy soils were almost saturated with a soil moisture of 30 % (pF value < 1) at the beginning of campaign 2. The pesticides showed more dynamics and single peaks appeared more frequently. Loads decreased later on but remained at a constant level during the following precipitation events. In recession phases, low but still traceable background loads were measured for Flufenacet (phase 2). During precipitation events the loads of Pendimethalin and Diflufenican increased slightly and could not be detected during recession phases (phase 3). However, the course of the Pendimethalin load was more dynamic than Diflufenican. The Diflufenican loads were only detectable for a short time during the highest precipitation events. After 64 days of monitoring in 2017, increased loads of the pesticides Pendimethalin and Diflufenican were monitored (phase 4).

4.6.4.2. Pesticide load dynamics at catchment scale (outlet B)

During campaign 1, the substances Pendimethalin and Diflufenican could not be detected above LOQ (Fig 4-5). Flufenacet was detected with a delay of 12 days in A (phase 1). The highest load of Flufenacet was measured 10 weeks (11th of December 2016) after application and did not occur with the first flush (phase 1). In late winter, the peaks in A and B occurred simultaneously. During campaign 2, a first flush peak occurred for all substances but especially for Flufenacet, immediately after application accompanied by a strong precipitation event exceeding 45 mm on one day (phase 1). A further high load at the catchment outlet was caused by the first flush of field outlet A and was detected for all pesticides within the same day (phase 1). This led to a main peak load of 1,313 mg d⁻¹ Flufenacet. Flufenacet responded more dynamically and with continuously increasing loads, which slowly reduced below LOQ (phase 2). Further Flufenacet loads are reduced in comparison to the main load, but the loads of all substances increased smoothly towards the end of the monitoring period. Pendimethalin and Diflufenican loads decreased after small peaks below LOQ. Their main loads were observed at the end of monitoring period (phase 4).

How weather conditions and physico-chemical properties control the leaching of Flufenacet, Diflufenican, and Pendimethalin in a tile-drained landscape

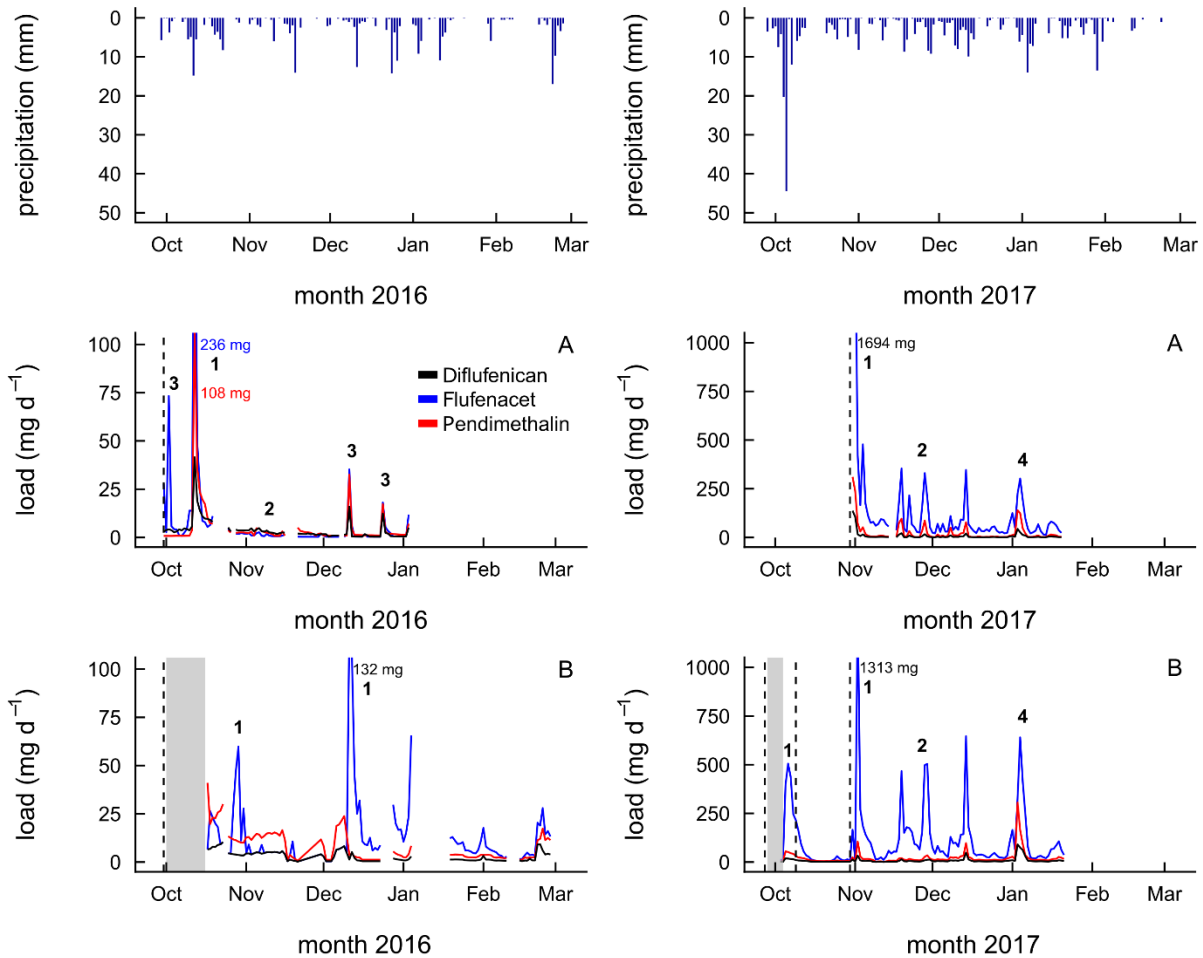


Fig 4-5: Pesticide loads of diflufenican, flufenacet, and pendimethalin during 2016 and 2017 at field scale (A) and catchment scale (B). The dashed line marks the application days (one application in 2016 on 27th of September and in 2017 the 1st application was on 30th of September (B), the 2nd application on 9th of October (B), and the 3rd application on 30th of October (A). The bold numbers label the pesticide load phases: (1) flush peak phase, (2) recession and background load phase, (3) preferential flow phase, (4) retarded pesticide load peak phase. The grey area marks the time of dry drainage pipes. Scale differs 1:10 between graphs 2016 and 2017.

4.7. Discussion

4.7.1. Cumulative loads at different spatial scales

Cumulative pesticide loads for field- and catchment scale were found to be different. The dilution effect and subsurface connectivity of tile-drained areas to the catchment outlet is a reason for higher area related cumulative loads (Tab 4-4) for all target pesticides. This difference at field scale compared to catchment scale was also found by Kreuger (1998) and Ulrich et al. (2012). Considering the tile drainage discharge as the governing transport path for pesticides, tile drainage discharge started in autumn, increased in winter, and started to minimize in late spring. During summertime, the tile drainages dried out. Our observations are in accordance with Tournebize et al. (2017). Surface runoff could only be observed in lanes on the field after a heavy precipitation event, which occurred once during the two monitoring periods (45 mm at 5th of October 2017). However, the current pesticide application at field

A was not carried out at that point in time. With less precipitation amounts, the installed surface runoff samplers located on the hillside of the field were empty. Under dry conditions, the low discharges explain similar cumulative loads per hectare at both scales between the investigated pesticides. However, the transport pattern at the catchment outlet is shifted in time in comparison to the field scale, because the tile drainage discharge of several fields started especially under dry conditions at different dates, which is also described by Bertuzzo et al. (2013). The heterogeneity of pesticide leaching at different spatial scales is assumed to be controlled rather by hydrological factors than by physico-chemical properties (Frey et al., 2009). At both spatial scales, Flufenacet was released under dry and wet conditions in considerably larger amounts than Diflufenican and Pendimethalin. The highest spatial difference for area related cumulative loads was observed for Flufenacet, which was 2.6 times higher at field scale (1.15 g ha^{-1}) under wet conditions than at catchment scale (0.44 g ha^{-1}). This can be explained by the fast transport of very high loads at field scale in comparison to the diluted, but continuously released lower loads at catchment scale. In comparison to Flufenacet, the loads of the sorptive substances (Diflufenican, Pendimethalin) are lower and less frequent at field scale. The pesticide concentrations Pendimethalin and Diflufenican were often detected below LOQ. The load relations of the two spatial scales are more similar for Pendimethalin and Diflufenican than for Flufenacet. Regarding load estimation for these two substances, it has to be mentioned that a high proportion of the values from Pendimethalin and Diflufenican detected at catchment outlet were below LOQ. Hence, the level of LOQ has significant impact on the total load estimation at the catchment outlet, especially in dry years with very slow substance transport from field to catchment outlet. The specific cumulative load estimation for field scale (0.02 to 0.12 g ha^{-1}) was comparable to results of Ulrich et al. (2012), which ranged between 0.01 to 0.05 % of applied amount for Flufenacet. The reported weather conditions of Ulrich et al. (2012) were comparable to campaign 1, where Flufenacet total loss rate accounts for 0.05 % (0.07 g ha^{-1}). In general, the studied pesticides of our study meet total loss rates of < 0.5 % and rarely < 3 % reported by other studies (Brown et al., 1995; Boithias et al., 2014).

4.7.2. Temporal dynamics of pesticide loads

4.7.2.1. Impact of weather conditions

The inter-annual variability of weather conditions showed remarkable impact on pesticide loads. The monitored periods represented the precipitation character during the year quite well. The year 2016 was a dry year with rather low variability. During the dry monitoring period in year 2016, the precipitation patterns were characterized by many days without precipitation alternating with daily precipitation events $> 9 \text{ mm}$. Due to the low initial soil moisture conditions, a low connectivity of soil matrices within the catchment can be assumed so that the potential of pesticide leaching was limited. Our findings cover with Walker et al. (2005), that leaching was reduced most, because the timespan after application was dry with only light precipitation and slow soil-wetting. However, at field scale, pesticide loads were

transported by low tile drainage discharge to field outlet A with a considerable contribution of preferential flows. At the catchment scale, the maximum pesticide peak occurred quite late. This leaching behaviour can be explained by an increased subsurface connectivity and a considerable increase in discharge after a dry period (Leu et al., 2004b). The pesticide application in the catchment in year 2017 was accompanied by a heavy precipitation event of 45 mm (except the field linked to outlet A which was sprayed later), leading to a high soil moisture content which supported pesticide leaching. After application, the wet period in year 2017 was characterized by continuous precipitation. The moderately variable annual precipitation in 2017 was represented well by the monitoring conditions. The travel times for the main peak loads from field and catchment outlet ranged between several days during dry periods and less than one day during wet periods according to the antecedent soil moisture content. Therefore, a high subsurface connectivity in the catchment with more continuous matrix flow can be assumed. The temporal variability of pesticide loss directly after application in our study demonstrates that the pesticide transport by tile drainages and height of pesticide loss depends on the current state of the functional subsurface connectivity (Blume and Van Meerveld, 2015). Hence, we highly recommend supporting the assumptions about the state of subsurface connectivity by monitoring of soil characteristics and moisture along with pesticides concentrations in the soil. In this regard, subsurface connectivity seems to be a crucial point since our study shows that the timing of leaching of very mobile pesticides itself does not depend on the time gap between application and first strong precipitation events, which is in accordance with Boithias et al. (2014).

4.7.2.2. Impact of pesticide application

The seasonally changing drainage area and application amounts are crucial variables towards the understanding of pesticide leaching. Considering the agricultural management, the fields are cultivated similarly in each year so that the same pesticides were applied over the catchment in 2016 and 2017. Due to the wet soils in 2017, which were induced by exceptional weather conditions, only parts of the fields could be cultivated. Consequently, the ratio between connected fields and catchment area decreased from campaign 1 to campaign 2. Hence, the application of pesticides was strongly localized on a smaller area due to the wet soils in 2017. Additionally, the discharges were considerably higher in that time, so a higher possibility for pesticides to be released in very high loads was given. In general, the weather conditions during application and the time span between application date and first precipitation event or appearing drainage discharge were very important for the height of the first occurring loads. We conclude that field A is a strong contributing area for pesticide leaching in the catchment, whose relevance changes depending on weather conditions. This finding is in accordance with Doppler et al. (2014). The pesticide transport time to the monitored outlets under wet conditions was less than one day. In 2016, the weather conditions were quite dry before and after pesticide application. Under these conditions a longer retention time on the topsoil was responsible for longer times of soil passage and, thus, for transformation processes to take place (Leu et al., 2004a; Lange et al., 2018). The first precipitation event

causing a hydrological response at the catchment scale occurred 12 days after application. Consequently, potential transport of pesticides and transformation products was delayed.

4.7.2.3. Environmental impact

The study area is considered as a headwater catchment where, water and pesticides are transported within a relatively short time to larger receiving waters. Along the channel pathway, the pesticide concentration peaks were attenuated. The highest contribution to receiving waters was calculated for the mobile substance Flufenacet during the main peak phase and on average. The main concentration peak contributed less than 2 %. It is recognizable during wetter periods that the peak concentration contribution is diluted (below 1 %) for all the substances in comparison to drier periods with lower discharge. The tile-drained area, which is connected to outlet A, had a remarkable impact on the water quality of the catchment outlet. To evaluate the impact of changing weather conditions on the water quality at the catchment outlet, a threshold value of $0.2 \mu\text{g L}^{-1}$ was chosen. This value is oriented to the German environmental quality standard for the maximum allowable concentration for Flufenacet in surface water (OGewV, 2016). Under dry conditions, the threshold value was only exceeded once by Flufenacet with the major peak ($0.462 \mu\text{g L}^{-1}$, 11th of December 2016). However, under wet conditions the situation changed at the catchment outlet. The threshold was exceeded by Flufenacet for four weeks beginning directly after pesticide application at field A. The study results show that high loads at field scale, especially under wet conditions, can lead to continuous exceedance of concentration thresholds at catchment scale. Hence, small headwater catchments can contribute with critical high substance loads to the receiving water bodies. Consequently, sources for environmental pollution of priority water bodies can better be located investigating upstream small head-water catchment. From the perspective of protecting the chemical status of surface waters, an additional increase in application amounts under wet and adverse farming conditions should be avoided as the pesticides have a greater chance of being released faster and in higher amounts under high-flow situations. For improved surface water protection, we support the suggestion of Lewan et al. (2009) to avoid pesticide application if significant precipitation events (our study: $> 9 \text{ mm}$) are forecasted. Hence, we share the common pesticide mitigation recommendation to avoid exceptional wet soil conditions for pesticide application in autumn (e.g., Brown and Van Beinum, 2009), as our study shows the 10-fold pesticide loss under a hydrological connected catchment area. Lewan et al. (2009) identified soil water deficit and medium-term rainfall until 90 days after application as most influencing factors for pesticide loss. This covers our findings that after the autumn application important transport processes take place until late winter, still leading to considerable pesticide amounts at the catchment outlet.

4.7.2.4. Integrated view on load phases

The results of the study indicate that inter-annual weather conditions and variabilities at both spatial scales are appropriate to derive the general leaching of pesticides within the environment. However, to explain the short-term daily variability of pesticide loads, further variables like application of pesticides and their physico-chemical properties need to be considered jointly with specific hydrological boundary conditions. Each variable contributes to a varying extent to phases of pesticides loads, which can be differentiated into (1) first flush peak, (2) recession and background load, (3) preferential flows, and (4) delayed pesticide loads.

First flush peak phase (1)

Dryer periods with low initial soil moisture content were found to be relevant for pesticide transport if a daily precipitation sum of 9 mm was determined. In that case, not all field regions are connected (Stieglitz et al., 2003) and precipitation induced vertical soil water movement triggered pesticide drainage loss after application. As soon as water is available for transport, pesticide peaks of the target substances occur largely at the same time. During our studies, a large precipitation event (5th of October 2017 with 45 mm) occurred along with application at conditions with high initial soil moisture content. Only Flufenacet was transported via the drainage system. Pendimethalin has the strongest sorption properties in soil. Hence, it is likely that the pesticides with high sorption strength are transported mainly with eroded particles in surface runoff (Müller et al., 2002; Freitas et al., 2008; Ulrich et al., 2013) or remain on the topsoil layer. Hence, the more mobile substances seem to be preferably transported by drainage.

Recession and background load phase (2)

The pesticide peaks pass during dry periods within two days without any further recession flow loads. This finding highlights the necessity of an appropriate monitoring concept to safely capture high and short-term pesticide loads, which are connected to single and short precipitation events. Under wet conditions with subsequent continuous precipitation, field capacity of the soil is quickly reached, and regions are hydrologically connected by interflow (Stieglitz et al., 2003). The interflow causes higher and continuous pesticide losses (Duffner et al., 2012). Interflows may saturate the deep soil and enrich a pesticide storage (Sandin et al., 2018), which is responsible for slow and continuous leaching processes to the drainage system (Leu et al., 2004a). These pesticide leaching phases explain the longer recession and background load phases after the high peaks, especially for Flufenacet, and highlight the necessity of long-term monitoring campaigns.

Preferential flow patterns (3)

Inter- and preferential-flows also play a dominant role under dry conditions with minimum precipitation as shown during a first Flufenacet peak at the field scale. Flufenacet might be able to “rush through” with preferential flows (Leu et al., 2004a). Due to the higher polarity and low k_{foc} value of Flufenacet, the

pesticide is infiltrated directly into the soil and can be easily desorbed from the soils (i.e. Leu et al., 2004a; Ulrich et al., 2012).

Retarded pesticide load peaks (4)

At wet conditions, the sorptive Pendimethalin and Diflufenican showed relatively high drainage loads three months after application in winter accompanied by high discharges. So far, retarded loss of pesticides, especially with low water solubility and relatively high persistence, was mainly found for long periods with no- or low-flow after application (Gaynor et al., 1992; Kreuger, 1998; Vymazal and Březinová, 2015). It is also known from semi-arid regions (Olsson et al., 2013) that pesticide release is delayed along with the first precipitation event after drought. In that case, well-sorbing substances with very high k_{foc} values can be relocated from the soil in detectable concentrations. Hence, continuous water transport through the system accompanied with long half-life times in soil may considerably impact leaching of Pendimethalin and Diflufenican. It is assumed that the delayed pesticide movement is caused by increased drainage discharge and drainage sediment transport during late winter induced by freezing and thawing processes in the upper soil (Brown et al., 1995). The sorption properties have strong influences on pesticide load patterns at different temporal phases and take effect with sufficient available water in the soil-drainage system. As the hydrological boundary conditions vary, also the impact of the sorption properties is highly variable between and during the observed monitoring periods.

4.8. Conclusion

In this study, the pesticides Diflufenican, Flufenacet, and Pendimethalin were monitored in a high temporal resolution for two consecutive years. Based on our results, we identified long-term and short-term load dynamics of pesticides at different spatial scales. To a temporally varying extent, weather conditions, pesticide application, and physico-chemical properties contribute to pesticide leaching: Weather conditions are relevant to provide a functional subsurface connectivity, which in turn are required to allow pesticide transport by tile drainages. During dry periods, the contribution of tile drainages to pesticide leaching is limited and dominated by preferential flows. During wet periods, with high subsurface connectivity in the catchment, preferential flows are less. However, the load phase assessment showed continuous soil matrix flows. Therefore, high-frequency monitoring is recommended for all phases of drainage output. The relevance of field A as a contributing area for the catchment load depends on weather conditions. During the dry period, the influence on the catchment load is rather low because of interrupted subsurface connectivity. However, under wet conditions, the impact of field A on the catchment outlet is high, as under hydrologically connected conditions the tile drainage pesticide peaks reach the catchment outlet within very short travel times. The height of first occurring loads are controlled by weather conditions during application and the time span between application and the first strong precipitation event, however, leaching of very mobile pesticides is possible by low wetting. The timing of pesticide application is a crucial factor for pesticide leaching because the wet weather conditions led to

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a 10-fold increase in daily drainage loss for all pesticides. Consequently, wet conditions with adverse farming conditions are crucial for pesticide leaching since additional increases of pesticide application amounts lead to faster and higher release of pesticides under high-flow conditions. Our study demonstrates that weather conditions linked to pesticide properties control pesticide transport processes with considerable pesticide leaching until late winter, showing the necessity of a long-term monitoring.

4.9. Role of funding source

BASF SE's Agricultural Center in Limburgerhof, Germany supported the cooperation project with funding. There's no interest or belief that the financial support could affect the objectivity. BASF SE's Agricultural Center was involved in the study design. Folkert Bauer, Bernhard Jene, and Bernhard Gottesbüren proofread the manuscript before submission.

4.10. Acknowledgments

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5. Gain and retain – on the efficiency of modified agricultural drainage ponds for pesticide retention

Willkommen S., Lange J., Pfannerstill M., Fohrer N., Ulrich U., under review since September 2021.

Gain and retain - on the efficiency of modified agricultural drainage ponds for pesticide retention. Science of the Total Environment.

5.1. Highlights

- Pesticide load balances were assessed for a drainage pond system in permeable strata.
- Tracers revealed flow shortcuts and documented the efficiency of pond modification.
- Transformation products were continuously detected in surface- and groundwater.
- During low inflows, a large fraction of incoming solutes was retained in pond bottom.
- During high inflows, a filled-up pond system attenuated load peaks.

5.2. Abstract

Drainage ponds have the potential to serve as long-term interface measures primarily for flood control, and mass retention. They are often considered as promising supplements for the mitigation of drainage pipe loads to improve the water quality in agricultural landscapes. In this study, a highly dynamic drainage pond system with non-steady inflows and groundwater interaction was modified and investigated regarding its potential for pesticide and transformation product (TP) retention. For this purpose, two 104-day monitoring campaigns were conducted before and after pond modification. Field experiments with fluorescent tracers, Uranine and Sulforhodamine-B, proved that structural modifications improved the hydraulic functionality of the ponds. The effective volume (ϵ) increased from 20 % to almost 100 % in the modified pond and the mean hydraulic residence time (τ) was ten times longer. After a dry period, pesticide retention was high during slow refilling of the ponds, still TP loads posed a risk by infiltration into shallow groundwater due to the permeable ground. During wet periods, short nominal detention times together with high inflows led to rare high retention rates through peak attenuation. Moderate inflows resulted in extremely variable retention values, owing to the small pond storage capacity. Along with this, the average total retention efficiency after modification reached 38 % for mobile, 29 % for sorptive pesticides, and 32 % for mobile TPs. To achieve the best performances for ponds as natural landscape elements, they should be analysed for their hydrological functionality as a prerequisite and then modified for delayed pesticide and TP transport. Then, dynamic drainage ponds can utilize their full potential regarding mitigation of pesticide and TP loads in agricultural catchments.

Keywords: drainage ponds, fluorescent tracer, pesticides, retention efficiency, surface-groundwater interaction, transformation products

5.3. Graphical abstract

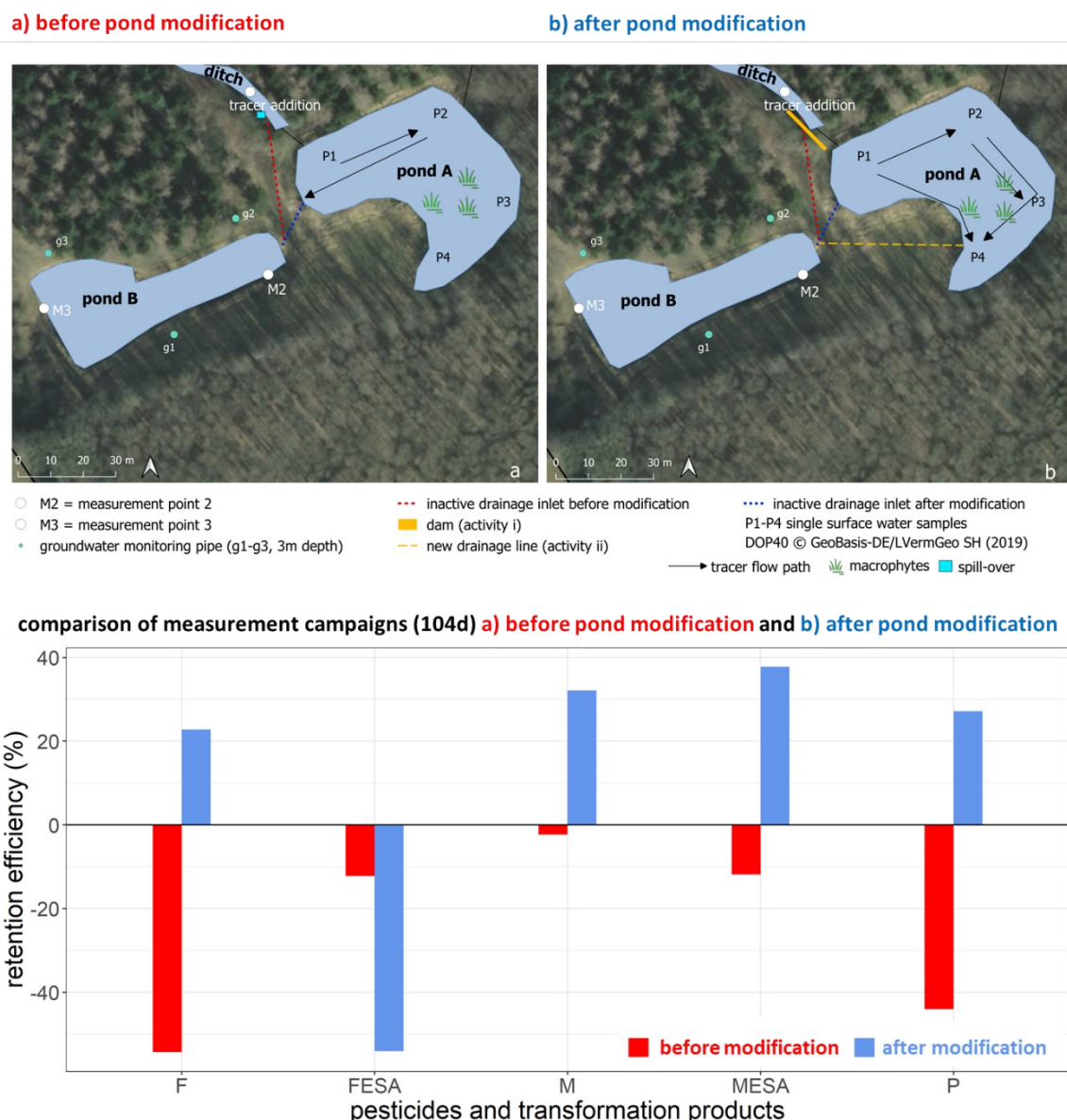


Fig 5-1: Pesticide and transformation product retention efficiency of a modified drainage pond system.

5.4. Introduction

Surface water bodies in drained agricultural landscapes are vulnerable to frequent pesticide and transformation product (TP) loads, both under wet and dry conditions (Reichenberger et al., 2007; Ulrich et al., 2019; Willkommen et al., 2019; Halbach et al., 2021). According to the European Water Framework Directive (EC, 2000), there is an increasing demand to minimize these loads to improve the chemical and ecological states of water bodies. The UN Environment Programme started a United Nations Decade of Ecosystem Restoration 2021-2030 to support nature-based solutions for a sustainable management of land, water and living resources (UNEP, 2019). In this respect, wetland systems are established mitigation techniques for flood control (Baird et al., 2020), nutrient removal (e.g., Dal Ferro et al., 2018), and

pesticide retention (Gaullier et al., 2019; Gregoire et al., 2009, Ulrich et al., 2019). If they are man-made, they can be classified as free surface constructed wetlands (FSCW) (Vymazal, 2007) and grouped based on their groundwater interaction between infiltration and non-infiltration ponds (Baird et al., 2020). In them, pollutant retention is most efficient for peaky chemographs (Greiwe et al., 2021), a common characteristic for agricultural tile drainage pipes, which are fast reacting, non-steady in discharge, and contain highly variable pesticide concentrations (Ulrich, 2012; Sandin et al., 2018; Willkommen et al., 2019).

Hydrological dye tracers are established tools to investigate solute transport in FSCW (e.g., Schuetz et al., 2012; Stern et al., 2001) to obtain insights into overall pesticide mitigation (Lange et al., 2011, Ulrich et al., 2019) or processes within wetland sediments (Fernández-Pascual et al., 2020). Thereby, tracer breakthrough curves (TBC) illustrate the combined effect of conservative solute transport (i.e., advection, dispersion, mixing) and non-conservative solute retention (i.e., sorption, biochemical or photolytic decay). TBC parameters like mean residence time, hydraulic efficiency, and tracer mass recovery serve to characterize FSCW mitigation performance (Thackston et al., 1987; Kadlec, 1994; Lange et al., 2011). FSCW retention efficiency both depends on properties of the pollutant and the wetland system and may reach up to 100 % (Gregoire et al., 2009). Thereby, FSCWs are most efficient if they have long hydraulic residence times (Bundschuh et al., 2016). Furthermore, shallow water levels, reduced flow velocities (Tournebize et al., 2017), and elongated shapes (Gaullier et al., 2020) contribute to system efficiency. In a typical example, pesticide retention reached 50 % in a pond with a 10-day residence time (Tournebize et al., 2017). In contrast, zero or even negative retention (when output loads exceed input loads) was occasionally reported in small systems, which was explained by hydrological short-cuts or additional input from groundwater (Gaullier et al., 2019; Ulrich et al., 2019).

Drainage ponds also occur as natural landscape elements (Oertli et al., 2009). Due to inherent mitigation capabilities, there is broad interest in testing their functionality and efficiency to retain water and pollutants in agricultural regions (Tournebize et al., 2017; Gaullier et al., 2020). Thereby, farmers and natural managers have promising opportunities to improve the hydrological functionality and retention efficiency through low-cost and easy-to-adapt modifications (Baird et al., 2020). Most natural ponds are in contact with shallow groundwater since bottom substrates are often permeable. However, existing knowledge about the effects of surface-groundwater interactions on budgets of pesticides and TPs is limited. Estimating fluxes and mass balances, surface-groundwater interaction is often neglected (Kadlec, 2010; Tournebize et al., 2013) or approximated as infiltration loss by water balance data (Baird et al., 2020). To close this knowledge gap, we here present a study with a semi-natural drainage pond system that is located in permeable substrate and fed by agricultural drainage pipes. We selected three pesticides and four TPs to calculate their budgets for two 104-day measurement campaigns and explicitly considered surface-groundwater interactions. Between the two campaigns, structural modifications were made to improve pond retention efficiency, which we additionally tested by fluorescent tracers. We address the following main research questions:

- To which extent does the surface-groundwater interaction affect the water balance and budgets of pesticides and TPs?
- What is the change in retention efficiency of pesticides and TPs after pond modification and was this correctly reflected by the fluorescent tracers?

5.5. Methods and Materials

5.5.1. Study area

The study area belongs to a farm which applies conventional agricultural practice and is located in the eastern hillside region of Schleswig-Holstein in Northern Germany. Shallow groundwater levels in sandy depressions and surface water in loamy hilly terrain require an intensive use of tile drainage systems with a total length of 6.3 km.

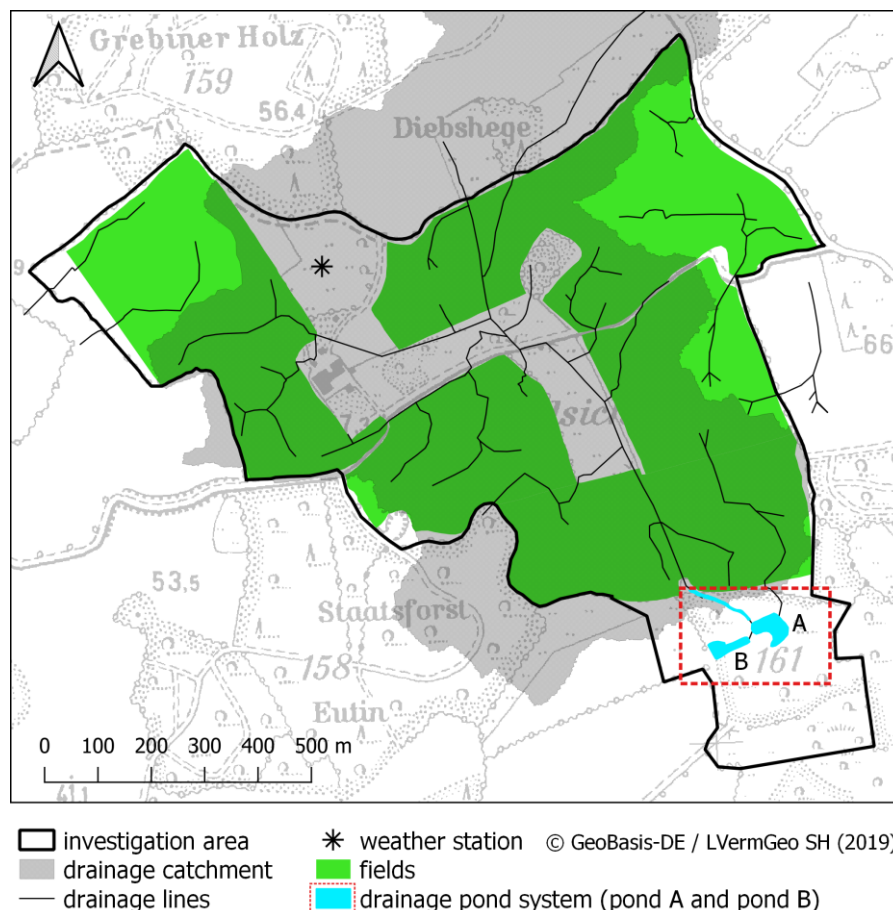


Fig 5-2: Map of the drainage pond system with contributing catchment.

Dominating soil types in the catchment are Colluvic Gleyosol, Luvisol, and Histosols (fen), which are typical for lowland regions (FAO, 2014; LLUR, 2019). Two drainage ponds in a total size of 3,000 m² receive the outflows of the tile drainage system from a 100-ha agricultural catchment (Fig 5-2). The main crops are winter wheat, winter barley, winter rape, and maize. Other land uses in the catchment

area are fallow land, forest, grassland, and farm buildings. For more details on the contributing catchment, the interested reader is referred to Willkommen et al. (2019, 2021).

5.5.2. Drainage pond system

The investigated retention system consists of two connected ponds. Pond A is kidney-shaped and has an even depth, whereas pond B has a more elongated shape including a flat and a deep water zone (Fig 5- 3, Tab 5-1). Pond A is perennial. The farmer suspects a glacial origin, while pond B was constructed as a fishpond in the 1980s.

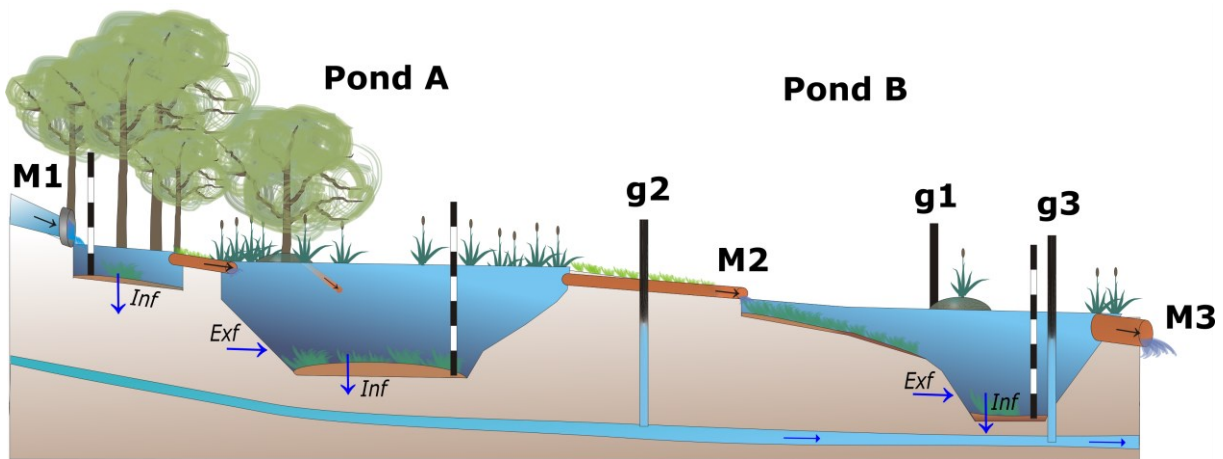


Fig 5-3: Cross-sectional view of the investigated two-part pond system with inlet structure (M1), outlet of pond A (M2), and outlet of pond B (M3). The blue arrows indicate the direction of surface-groundwater exchange (Exf = exfiltration, Inf = infiltration). The groundwater monitoring pipes (g1, g2, g3) are screened at 3m below ground surface. To represent the cumulative exfiltration and infiltration flows for each pond in the water balance plot, Inf_{g1} in pond A is expressed as Inf_A , Exf_{g2} in pond A as Exf_A , as well as Inf_{g2} as Inf_B and $Inf_{g1,g2,g3}$ as Inf_B for the cumulative infiltration flows of pond B.

Due to the permeable substrate, both ponds are affected by surface-groundwater interaction and lose water by infiltration to groundwater during times when pond water levels are higher than groundwater levels, while they receive exfiltrating groundwater when pond water levels are lower than groundwater levels. Pond B regularly dries out in summer, within monitoring between May and September in 2017 and between May and December in 2019.

Tab 5-1: Characterization of drainage pond A and drainage pond B.

Parameter	Unit	Pond A	Pond B
Average volume	m ³	1,137	683
Average water level	m	0.94	0.80
Flow length	m	115	70
Length to wide ratio		1.3 (kidney-shaped)	3.3 (elongated)
Share shallow water area (< 1 m depth)	%	32	3
Soil type		peat	loamy sand
Average thickness of organic mud layer	cm	70	30
Vegetation density	%	30	70
Vegetation type		Phalaris arundinacea	Carex acutiformis/ Lemna minor/ Phalaris arundinacea

5.5.3. Monitoring setup and pesticide sampling

Precipitation was measured in 10-minute resolution by a tipping bucket rain gauge (Campbell Scientific) located within the catchment (Fig 5-2). At M1 (Fig 5-3), discharge was determined multiplying cross-sectional area by flow velocity which was measured by a doppler sensor (ISCO 750 area velocity flow module). At M2, water levels were measured in 10-minute resolution by HOBO Onset data loggers and related to discharge by weekly volumetric flow measurements using a stopwatch and a 10-liter bucket. Automatic water samplers (Teledyne ISCO 6712) were installed at measurement points M1, M2, M3 to collect 50 mL of water every 70 min in glass bottles. Three 350 mL glass bottles covered one day. All water samples were kept cool until analysis. Three groundwater pipes (g1, g2, g3) were installed around pond B (Fig 5-4).

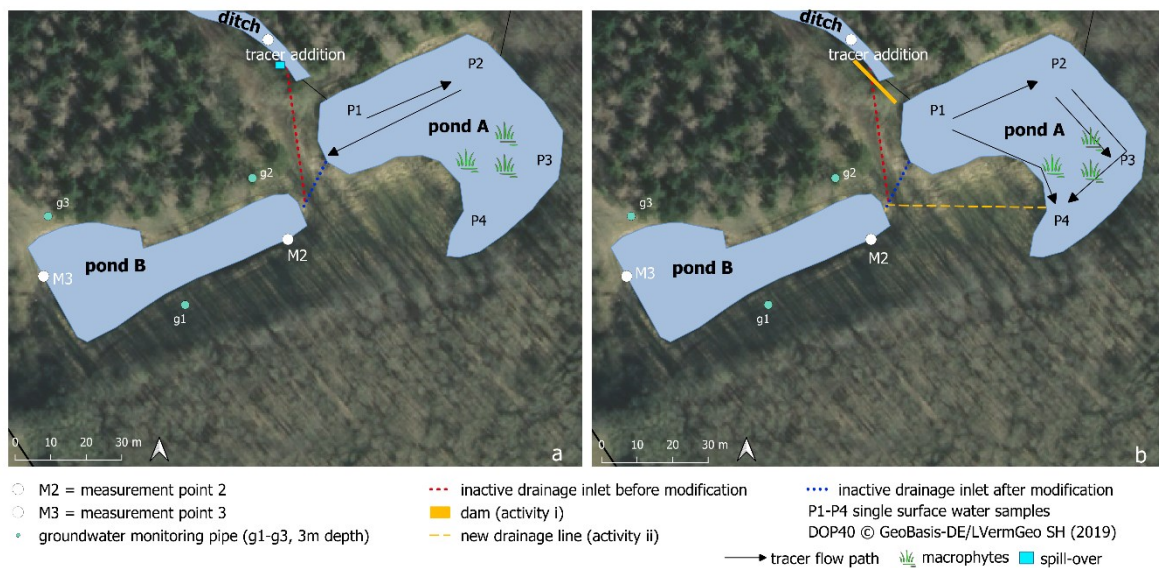


Fig 5-4: Overview of the drainage pond system a) before modification and b) after modification. The black arrows mark the tracer distribution within pond A.

The filter pipe, surrounded by gravel, collected groundwater at a depth of 3 m below surface. In all groundwater monitoring pipes, HOBO Oneset data loggers measured groundwater levels in hourly resolution and were verified by weekly measurements using an electric contact gauge. Groundwater samples in 350 mL glass bottles were taken at monthly intervals by a submersible pump (12 V, Premium Pump, company Whale).

5.5.4. Water balance

The water balance was calculated in daily steps (Eq 5-1):

$$Vol_d = Vol_{d-1} + \sum_{i=1}^n (P - E + In_{M1} + Exf_A - Inf_A - Out_{M2} + In_{M2} + Exf_B - Inf_B - Out_{M3})_i, \quad (5-1)$$

where Vol_d ($m^3 d^{-1}$) is the water volume at the end of the day and Vol_{d-1} ($m^3 d^{-1}$) at the day before, P is daily precipitation ($m^3 d^{-1}$), and E is evaporation ($m^3 d^{-1}$). Drainage pipe inflow (In_{M1-M3} , $m^3 d^{-1}$) and drainage pipe outflow (Out_{M1-M3} , $m^3 d^{-1}$) are flows measured at M1, M2, and M3 (Fig 5-3), whereas $Exf_{A,B}$ ($m^3 d^{-1}$) describes exfiltration from and $Inf_{A,B}$ describes infiltration ($m^3 d^{-1}$) into shallow groundwater of ponds A and B.

Initial volume (m^3 , Eq 5-2) and area (m^2 , Eq 5-3) for pond A (A) and pond B (B) were calculated by a regression function from the observed pond levels h (pond A = h_A , pond B = h_B , m asl.) and according to volumes/areas derived by 3D Analyst Surface Volume Tool (ArcGIS10):

$$Volume_{A,B} = \alpha_2 * (h_{A,B})^2 + \alpha_1 * h_{A,B} + \alpha_0 \quad (5-2)$$

$$Area_{A,B} = \alpha_2 * (h_{A,B})^2 + \alpha_1 * h_{A,B} + \alpha_0, \text{ where } \alpha_{0,...,n} \text{ are constants.} \quad (5-3)$$

For calculation of the total pond system water balance, the volume and the area of both ponds were merged. Precipitation data was aggregated to daily values. The amount of daily precipitation (R_d , $mm d^{-1}$) fallen onto the pond surface area was multiplied by the daily total pond surface area ($Area_{total}$, ha).

For evaporation, the pond surface area was assumed to be fully uncovered, since a forest-like tree cover started at more than 10 m around the ponds. The Penman combination method for free water surfaces (potential equals actual evaporation) was used to calculate daily volumes of water lost by evaporation E ($m^3 d^{-1}$) (Neitsch et al., 2011) and calculated by Eq 5-4.

$$E = 10 * \eta * E_w * Area_{total}, \quad (5-4)$$

where η (–) is the evaporation coefficient with a constant value of 0.6 (Neitsch et al., 2011), E_w ($mm d^{-1}$) the potential evapotranspiration for a given day, and $Area_{total}$ (ha) the total surface area of the pond system.

For each pond, exfiltration (Exf , $m^3 s^{-1}$) and infiltration (Inf , $m^3 s^{-1}$) were calculated based on the difference between the groundwater level ($groundwater_level$, m asl) and the pond level ($pond_level$, m asl). Positive values were considered as exfiltration (Eq 5-5a & b) and negative values as infiltration (Eq 5-6a & b). For the present pond system the approach of (Busch et al., 1993) was extended to each of the three groundwater monitoring pipes (g1, g2, g3, Fig 5-4).

If $pond_level_A < groundwater_level_{g2}$, then

$$Exf_{g2} = KF_{g2} \times \left(\frac{\frac{groundwater_level_{g2}^2}{2} - \frac{pond_level_A^2}{2}}{R_{g2} + CL_{g2}} \right) \times Agw_{g2} \quad (5-5a)$$

If $pond_level_B < groundwater_level_{g1,g2,g3}$, then

$$Exf_{g1,g2,g3} = KF_{g1,g2,g3} \times \left(\frac{\frac{groundwater_level_{g1,g2,g3}^2}{2} - \frac{pond_level_B^2}{2}}{R_{g1,g2,g3} + CL_{g1,g2,g3}} \right) \times Agw_{g1,g2,g3} \quad (5-5b)$$

If $pond_level_A > groundwater_level_{g2}$, then

$$Inf_{g2} = KF_{g2} \times \left(\frac{\frac{groundwater_level_{g2}^2}{2} - \frac{pond_level_A^2}{2}}{R_{g2} + CL_{g2}} \right) \times Agw_{g2} \quad (5-6a)$$

If $pond_level_B > groundwater_level_{g1,g2,g3}$, then

$$Inf_{g1,g2,g3} = KF_{g1,g2,g3} \times \left(\frac{\frac{groundwater_level_{g1,g2,g3}^2}{2} - \frac{pond_level_B^2}{2}}{R_{g1,g2,g3} + CL_{g1,g2,g3}} \right) \times Agw_{g1,g2,g3}, \quad (5-6b)$$

where KF is the coefficient of permeability ($m^3 s^{-1}$) and R (m) describes the horizontal distance between each groundwater monitoring pipe ($groundwater_level$) and water level gauge ($pond_level$). The specific area of groundwater passage (Agw , m^2) is calculated for each groundwater monitoring pipe in Eq 5 - 7).

$$Agw_{(g1-g3)} = (soil_layer_{impermeable_{pond(g1,g2,g3)}} - groundwater_{level(g1,g2,g3)}) * CL_{(g1,g2,g3)}, \quad (5-7)$$

where $soil_layer$ (m) is the height of the impermeable soil layer (m) and CL the colmation length (m) (Larson et al., 2000). The colmation length CL (m) for each pipe equals the distance between two pipes. More details on the calculation of precipitation, evaporation and surface-groundwater exchanges can be found in Willkommen et al. (2018).

The nominal detention time (Kadlec, 1994) was calculated on a daily basis (Eq 5-8):

$$T_N = \frac{Vol}{Out+Inf} \quad (5-8)$$

Measurement uncertainties were estimated for each water balance component (Tab 5-2) and combined according to ISO/IEC Guide 98-3 (2008). Total uncertainties of all inflow and outflow components were then calculated on a daily basis (Eq 5-9, Eq 5-10) and averaged over the monitored periods:

$$\delta_{incoming} = \sqrt{\delta In^2 + \delta P^2 + \delta Inf^2} \quad (5-9)$$

$$\delta_{outgoing} = \sqrt{\delta Out^2 + \delta E^2 + \delta Exf^2} \quad (5-10)$$

Tab 5-2: Estimation of measurement uncertainties.

Parameter	δ	Source
Precipitation	5 %	Sensitivity for precipitation in free water surfaces was very low in Willkommen et al. (2018)
Evaporation	5 %	Sensitivity for evaporation in free water surfaces was very low in Willkommen et al. (2018)
Discharge	M1 : 10 % M2 (2017): 25 % M2 (2019): 22 % M3 (2017): 30 % M3 (2019): 24 %	Deviation between pressure sensor measurements and in-situ field measurements during <u>peak flow conditions</u> M1: comparison measurements sensor and salt dilution method M2: if water level > 12 cm (peak flow), then 25 % sd M3: if water level > 0.9 cm (peak flow), then 30 % sd in period before modification (2017): M2: 100 % peak flow condition \rightarrow 25 % uncertainty M3: 100 % peak flow condition \rightarrow 30 % uncertainty in period after modification (2019): M2: $12 \% < 0.12 \text{ cm} \rightarrow = 0.088 * 25 \% = 22 \% \text{ uncertainty}$ M3: $21 \% < 0.9 \text{ cm} \rightarrow = 0.079 * 30 \% = 24 \% \text{ uncertainty}$
Infiltration, Exfiltration	25 %	Large variability, parameter soil conductivity and difference between pond level and groundwater level were detected as highly variable in Willkommen et al. (2018)

5.5.5. Selected pesticides and their properties

The farmer continued crop rotation and pesticide application according to local practice. We investigated the pesticides Metazachlor, Flufenacet, Pendimethalin, and their TPs Metazachlor ESA and Flufenacet ESA. The pesticides were chosen because of their wide use in Northern Germany (Jarosch and Brunke, 2018) and their contrasting physico-chemical properties. The pesticides vary mainly in their sorption capacities and half-life times. The substances vary in half-life times and tendencies to sorption and can be grouped into fairly mobile substances with high leaching potential (Flufenacet, Metazachlor) and less mobile substances that are largely sorbed to the soil (Pendimethalin). The TPs of Flufenacet and Metazachlor are even more mobile and more persistent in soil than their parent compounds (Lewis et al., 2016). A table with detailed properties of all substances is given in the supplementary material (Tab 5-7).

5.5.6. Measurement campaigns, monitoring periods, and pond modification

We carried out two 104-day measurement campaigns in the years 2017 and 2019 that both started in autumn after pesticide application and onset of tile drainage (09/27) and lasted until mid-winter (01/08). To classify hydraulic conditions, we combined the time series of calculated pond volumes and defined dry, moderate, and wet conditions according to quartiles (< 25 %, 25 – 75 %, >75 %) of 208 daily pond volumes. Then we selected four 10-day monitoring periods to investigate water, pesticide, and TP balances during different hydraulic conditions (Tab 5-3).

Tab 5-3: Selected monitoring periods to represent dry, moderate, and wet hydraulic conditions in the ponds.

Measurement campaign	State	Monitoring period	Pond volume	Hydraulic condition
2017	before modification	10/05-10/14 (1)	high (2,389-2,828 m ³ , Ø 2,599 m ³)	wet
		11/09-11/18 (2)	medium (2,162-2,233 m ³ , Ø 2,194 m ³)	moderate
2019	after modification	10/25-11/03 (3)	low (824-1,448 m ³ , Ø 1,003 m ³)	dry
		11/16-11/25 (4)	medium (2,034-2,316 m ³ , Ø 2,185 m ³)	moderate

Pond modification was performed in May 2018 between the two measurement campaigns using machinery and manpower of the farmer cultivating the investigation area. Pond B was left untouched, while pond A was modified by two activities (Fig 5-4):

- (i) an inactive drainage pipe was sealed, and the inflow was dammed, and
- (ii) the flow length inside pond A was extended by a relocation of the outlet to P4.

5.5.7. Tracer experiments

The hydraulic functionality of the drainage pond system was assessed by two fluorescent tracer experiments with Uranine (UR) and Sulforhodamine B (SRB) carried out in October 2017 (T1) before and in March 2019 (T2) after pond modification. During both experiments, 20 g of UR and 40 g of SRB were mixed with 10 L of water and instantaneously injected into the inlet channel of pond A (Fig 5-4). Water samples were taken at the pond outlets M2 and M3, stored in 100 mL brown glass bottles and kept refrigerated until laboratory analysis. UR and SRB have different characteristics (Tab 5-7, supplementary material): while UR quickly forms photolytic TPs in sun-lit surface waters (Gutowski et al., 2015), SRB has a higher tendency towards sorption on mineral substrates (Kasnavia et al., 2005). On organic material, considerable sorption losses of both tracers must be expected, particularly at low pH-values (Bork et al., 2019). The first experiment (T1) was performed before pond modification during wet conditions (average total pond volume 2,739.24 m³, T_N 2.4 days), injection was at 10/08/2017, 12 am. First samples were collected manually until 5 pm, and the automatic sampling (Teledyne ISCO 6712) lasted until 10/11/2017, 4 pm. The second experiment (T2) was a repetition of T1 and used the same tracer amounts and identical locations for injection and sampling. T2 was carried out during more moderate conditions (average total pond volume 2,476.28 m³, T_N 3.0 days) after the second measurement campaign was finished in 2019. T2 started on 03/12/2019 with tracer injection at 12 am and ended on 03/22/2019 at 12.30 pm. To investigate flow paths, daily grab samples were taken during both tests within pond A at sampling points P1 – P4 (Fig 5-4).

5.5.8. Laboratory methods

Water samples were analysed using an AB Sciex 5500 Qtrap by an accredited laboratory (DIN 38407-36:2014-09) to detect the substances Metazachlor, Flufenacet, Pendimethalin, and the TPs Metazachlor ESA and Flufenacet ESA. The Limit of quantification (LOQ) was $0.01 \mu\text{g L}^{-1}$ for Flufenacet, Metazachlor, and $0.025 \mu\text{g L}^{-1}$ for Pendimethalin, Flufenacet ESA, and Metazachlor ESA. According to the laboratory, the uncertainty of the concentrations within a measurement was in a range of 20 % (Willkommen et al., 2019).

Fluorescent tracers were analysed by fluorescence spectrometry (LS-50B, Perkin-Elmer) using a quartz cuvette (3.5 mL) which was placed in the light beam of a pulsed xenon discharge lamp and filled by a peristaltic pump. A synchronous scan method was applied with an excitation/emission wavelength difference of 22 nm and target wavelengths of 488 nm and 561 nm for UR and SRB, respectively. The instrument was calibrated using standard concentration samples. Detection limits were $0.05 \mu\text{g L}^{-1}$ (UR) and $0.1 \mu\text{g L}^{-1}$ (SRB).

5.5.9. Hydraulic performance from tracer experiments

Applying the residence time approach (Kadlec, 1994), parameters of the tracer breakthrough curves served to assess hydraulic performance of the pond before and after modification. The residence time distribution (RTD) may be regarded as the probability density function for residence times inside the pond and is given by Eq 5-11:

$$E(t) = \frac{C(t) \cdot Q(t)}{\int_0^\infty C(t) \cdot Q(t) dt}, \quad (5-11)$$

where $C(t)$ and $Q(t)$ are tracer concentrations and flow rates at time t after injection.

The first moment of the RTD is the mean hydraulic residence time τ (h) and given by Eq 5-12:

$$\tau = \int_0^\infty t \cdot E(t) dt. \quad (5-12)$$

The effective volume ratio ε (Thackston et al., 1987) characterizes the degree of mixing inside ponds and is given by Eq 5-13:

$$\varepsilon = \frac{\tau}{T_N}, \quad (5-13)$$

where small ε values are an indicator for dead zones or short circuiting. More details can be found in Kadlec (1994) or Lange et al. (2011).

5.5.10. Calculation of pesticide loads and retention efficiency

For each pond, daily retention was calculated by the difference between total inflow and outflow loads. For pond A these loads ($\text{m}^3 \text{d}^{-1}$) were calculated at M1 and M2 by Eq 5-14 and Eq 5-15:

$$\text{Total_inflow_load}_{M1} = \text{In}_{M1} \cdot \text{Cin}_{M1} + \text{Exf}_{g2} \cdot \text{C}_{g2} \quad (5-14)$$

$$\text{Total_outflow_load}_{M2} = \text{Out}_{M2} \cdot \text{Cout}_{M2} + \text{Inf}_{g2} \cdot \text{Cout}_{M2}, \quad (5-15)$$

where Cin_{M1} is the drainage pipe concentration at measurement point M1, $Cout_{M2}$ the drainage pipe concentration at M2, and C_{g2} is the concentration in the groundwater monitoring pipe g2.

For pond B these loads were calculated at M2 and M3 by Eq 5-16 and Eq 5-17:

$$Total_inflow_load_{M2} = In_{M2} * Cin_{M2} + Exf_{g1} * C_{g1} + Exf_{g2} * C_{g2} + Exf_{g3} * C_{g3} \quad (5-16)$$

$$Total_outflow_load_{M3} = Out_{M3} * Cout_{M3} + Inf_{g1} * Cout_{M3} + Inf_{g2} * Cout_{M3} + Inf_{g3} * Cout_{M3}, \quad (5-17)$$

where Cin_{M2} describes the drainage pipe concentration at measurement point M2, $Cout_{M3}$ is the drainage pipe concentration at M3, and $C_{g1,g2,g3}$ is the concentration in each of the three groundwater monitoring pipes g1, g2, g3.

Detected pesticide concentrations in water < LOQ were set to 0.5 LOQ (Willkommen et al., 2019) and monthly groundwater concentrations in g1, g2 and g3 were linearly interpolated to obtain daily values. Daily retention was expressed in absolute or relative values ($g\ d^{-1}$ or %, see supplementary material, Eq 5-18 to Eq 5-20,) and as averages over the different monitoring periods. The cumulated sums (g) of inflow and outflow loads yielded the totally retained mass of pesticides and TPs. From these values, overall retention efficiencies for single ponds and for the entire pond system (%) were calculated as quotients of total inflow divided by total outflow mass (see supplementary material, Eq 5-21 to 5 - 23). The daily load retention ($mg\ d^{-1}$) was calculated separately for the tile drainage water (Eq 5-24) and for the shallow groundwater (Eq 5-25).

$$Retention_{tile\ drainage\ water} = (In_{M1} * Cin_{M1}) - (Out_{M3} * Cout_{M3}) \quad (5-24)$$

$$Retention_{shallow\ groundwater} = (Exf_{g1} * C_{g1} + Exf_{g2} * C_{g2} + Exf_{g3} * C_{g3}) - (Inf_{g1} * Cout_{M3} + Inf_{g2} * Cout_{M3} + Inf_{g3} * Cout_{M3}) \quad (5-25)$$

5.6. Results and discussion

5.6.1. Hydraulic pond performance by fluorescent tracer experiments

5.6.1.1. Performance before pond modification

During tracer experiment T1, the breakthrough curves of UR and SRB had similar shapes and concentrations, although twice the amount of SRB was injected (Fig 5-5). Owing to sorption losses, only 49 % of SRB was recovered at the outflow of the pond system, while the recovery of UR even exceeded 100 % indicating no measurable tracer loss (Tab 5-4). At the outlet of pond A (M2), both tracers showed a sharp first peak already 10 min after tracer application. This fast reaction was explained by a short-cut since a part of the injected tracer spilled over the ditch due to the high inflows (In_{M1}) and percolated into an inactive drainage pipe in direction of pond B (Fig 5-4a). The effect of this underground short-cut was also evident in the negative water balance of $-268.6\ m^3\ d^{-1}$ and in the fact that the recoveries of both tracers increased between M2 and M3 (Tab 5-4). The main peak was attributed to the tracer distribution in pond A. Grab samples inside pond A yielded positive tracer detections only at measurement points P1 and P2, suggesting a direct flow pathway short-circuiting most of the pond. This was reflected in

short mean residence times τ and small effective volume ratios \mathcal{E} (Tab 5-4). At the outlet of pond B (M3), both breakthrough curves were flattened and showed single peaks already after 9 h.

Tab 5-4: Hydrologic and fluorescent tracer specific values during tracer experiment T1 (10/08/2017 to 10/11/2017) and T2 (03/12/2019 to 03/22/2019). UR = Uranine and SRB = Sulforhodamine-B.

Tracer experiment (period)	T1 - 10/08/2017 to 10/11/17		T2 - 03/12/2019 to 03/22/2019	
Average inflow ($\text{m}^3 \text{d}^{-1}$)				
Pond A (In_{M1})	1,218.7		915.5	
Pond B (In_{M2})	1,383.9		770.7	
Nominal detention time T_N (d)				
Pond A	1.3		2.0	
Pond A+B	2.4		3.0	
Surface water balance ($\text{m}^3 \text{d}^{-1}$)				
Pond A ($\text{Out}_{\text{M2}} - \text{In}_{\text{M1}}$)	-268.6		171.7	
Pond A+B ($\text{Out}_{\text{M3}} - \text{In}_{\text{M1}}$)	109.1		9.3	
Tracer	UR	SRB	UR	SRB
Recovery (%)				
Pond A (Out_{M2})	78.8	36.7	44.0	39.3
Pond A+B (Out_{M3})	107.2	49.4	33.4	36.5
Mean hydraulic residence time τ (d)				
Pond A	0.2	0.2	2.5	2.3
Pond A+B	0.8	0.8	7.5	7.4
Effective volume ratio \mathcal{E}				
Pond A	0.2	0.2	1.0	1.0

5.6.1.2. Performance after pond modification

The tracer experiment T2 was carried out as a performance review. The first activity, the damming, showed a positive effect as the short-cut disappeared. During T2, tracer breakthroughs were more delayed than during T1 and tracer peaks reached the surface outlets of the ponds much later, namely 15 h (pond A) and 48 h (pond B) after injection (Fig 5-5).

While SRB showed similar recovery rates at M2, the breakthrough of UR was significantly reduced compared to T1, which was mainly due to a more intense photolytic decay during a longer residence inside pond A. In consequence of the second activity, the flow length extension by relocating the drainage outlet pipe of pond A, caused an increase in \mathcal{E} in pond A from 0.2 to more than 1. Theoretically, τ and therefore \mathcal{E} , should only be calculated for conservative tracers (Kadlec, 1994; Lange et al., 2011) and their absolute values were, in our case, affected by sorption losses (SRB) and photolytic decay (UR). Since recoveries of SRB were similar during T1 and T2, a more than fivefold increase in \mathcal{E} , nevertheless, clearly documented the efficiency of pond modification that had intensified mixing and prevented short-circuits inside pond A. Two peaks were apparent in the breakthrough curves at M2 (Fig 5-5), which were not caused by rainfall and could be observed during the experiment as two separate flow paths. Grab samples supported this observation, as a faster main transport between P1 and P4 was found and a second transport pathway from P2 to P4 followed. Two factors were responsible for the retarded T2 tracer transport: (a) smaller inflow rates reduced flow velocities inside the ponds and caused longer

nominal detention and hydraulic residence times through the pond system, and (b) modification of pond A increased mixing and prevented short circuits of flow paths. A more complete mixing inside pond A was proved both by grab samples that confirmed the arrival of both tracers at all sampling points (P1-P4, Fig 5-4), and by an effective volume ratio ε of approximately 1 (Tab 5-4). Hence, the tracers confirmed that the hydraulic performance of drainage pond A was improved.

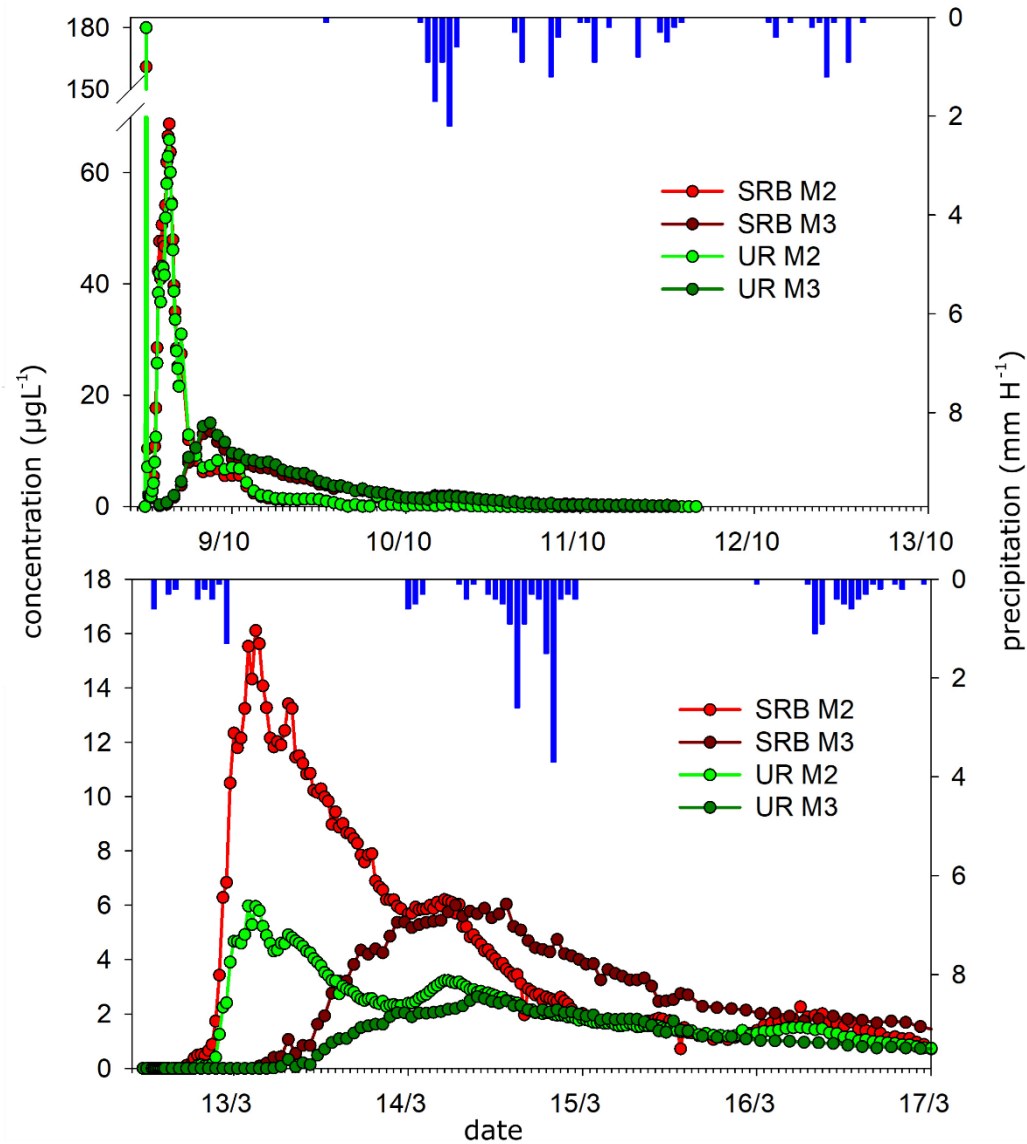


Fig 5-5: Tracer concentrations of SRB (Sulforhodamine-B) and UR (Uranine) at the drainage pipe outlet of pond A (M2) and pond B (M3) before (2017, top) and after modification (2019, bottom).

5.6.2. Hydrological conditions and water balance components

The cumulative precipitation (Fig 5-6) during the first measurement campaign (MC1) of 2017 was 306 mm and exceeded the second measurement campaign (MC2) of 2019 by 28 %, when only 220 mm of precipitation was recorded. The average water level in pond A amounted to 1 m (1 m pond B) in 2017

and 0.8 m (0.6 m pond B) in 2019. Accordingly, the average daily water volume of both ponds was higher in 2017 before pond modification ($2,196 \pm 174 \text{ m}^3$) and reached only $1,446 \pm 820 \text{ m}^3$ in 2019 (Fig 5-6).

5.6.2.1. Hydrological situation before pond modification

Considering entire MC1, the main incoming water balance component was In_{M1} (99 %) and Out_{M3} (72 %) the main outflow. The nominal detention time (T_N) was in average 2 d (median 2 d) due to the wet summer/autumn conditions in 2017 (Willkommen et al., 2019). The water masses were quite balanced with only 6 % difference.

During the first monitoring period (MP1), a major precipitation period of 94 mm occurred in the week from 09/30/2017 until 10/07/2017, with 65 mm of rain falling in two days (10/04/2017-10/05/2017) (Fig 5-6). As a result, the total pond volume increased to $2,828 \text{ m}^3$. This led to a fast transport of the water masses to the pond outlet M3.

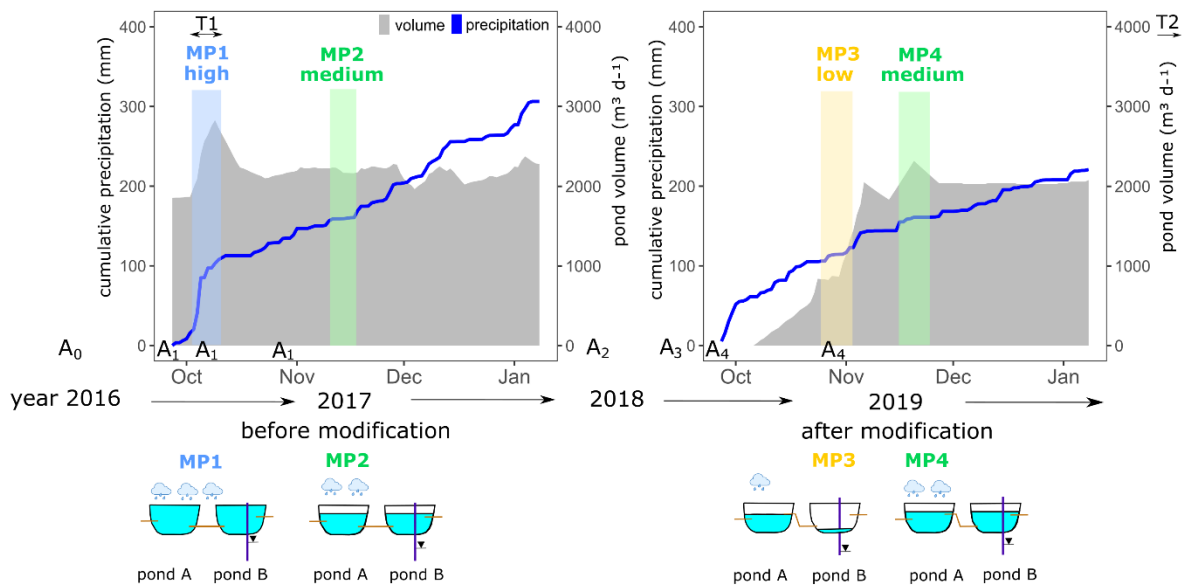


Fig 5-6: Pond A and B volume ($\text{m}^3 \text{ d}^{-1}$), cumulative precipitation (mm), and temporal placement of monitoring periods (MP1-4, Tab 5-3) and tracer experiments (T1, T2) before and after pond modification. Application dates are marked with A. Flufenacet and Pendimethalin were applied simultaneously at A_1 : at 09/27/2017, 10/09/2017, 10/30/2017, A_2 : 09/28/2018, and A_4 : 09/24/2019, 10/30/2019. Metazachlor was applied at A_0 : 08/22/2016 and A_3 : 08/23/2019. Sketches for hydrological conditions during each monitoring period (MP1-4, Tab 5-3) are shown in the lower section.

In_{M2} made up 95 % of the inflowing water of pond B, while surface outflows Out_{M3} reduced to 79 % (Fig 5-7). The remaining part (Inf_B) infiltrated to groundwater (21 %). During the second monitoring period (MP2), the water balance only had a small (5 %) difference in the entire pond system. Presumably, delayed lateral inflows due to high water saturation caused high Out_{M3} flows from pond B, which exceeded In_{M2} into pond B by 27 % during MP2 (Fig 5-7).

5.6.2.2. Hydrological situation after pond modification

During MC2, T_N increased to 7 d (median 6 d), partly explained by the reduced precipitation amounts in summer/autumn 2019 resulting in a high soil water deficit.

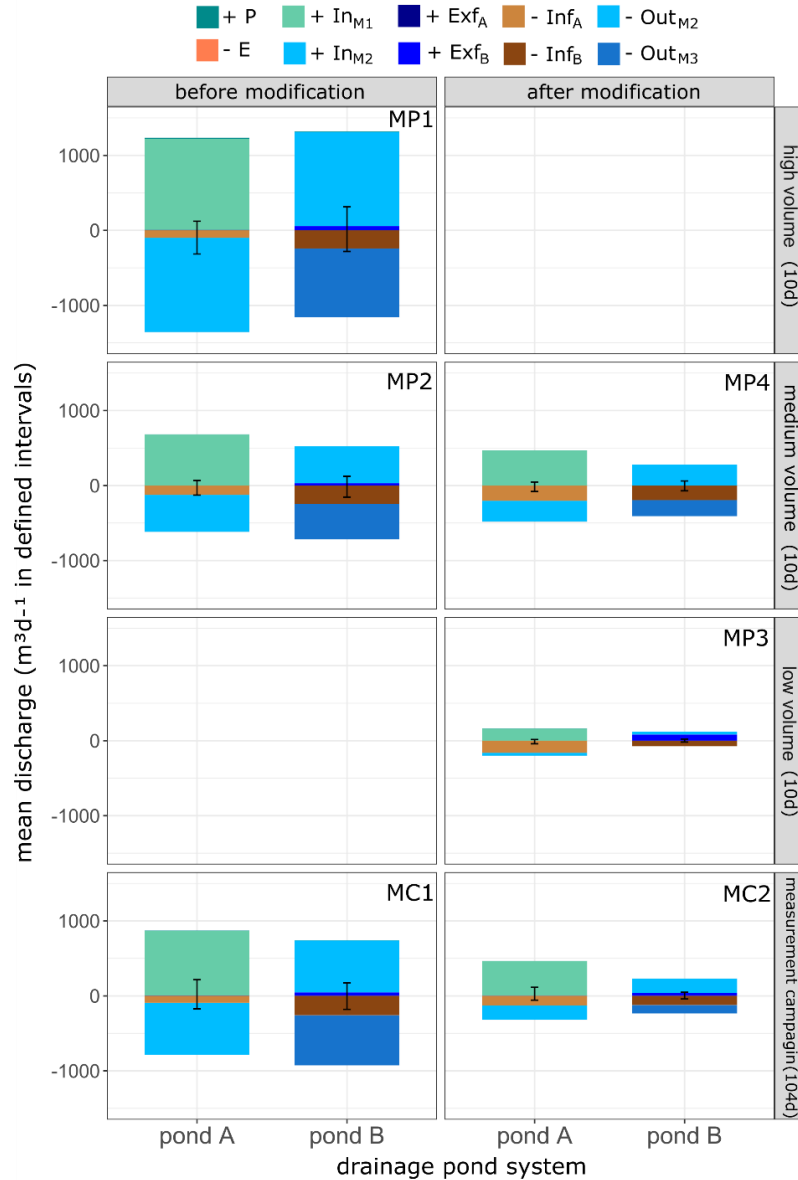


Fig 5-7: Water balance components of the pond system (pond A, pond B) during different monitoring periods (MP) and measurement campaigns (MC) representing different pond volume situations before and after pond modification. Uncertainties are marked as error bars (numeral in supplementary material). The water balance components are made of precipitation P , potential evaporation E , tile drainage inflow at $M1 = In_{M1}$, tile drainage outflow at $M2 = Out_{M2}$ = tile drainage inflow In_{M2} ($Out_{M2} = In_{M2}$ have same colour), tile drainage outflow at $M3 = Out_{M3}$, exfiltration pond A = Exf_A , infiltration pond B = Inf_B , exfiltration pond B = Exf_B , and infiltration pond B = Inf_B . All units are given in $m^3 d^{-1}$ per defined interval for MP1-4 = monitoring period 1-4 (10d) and measurement campaign before and after modification (104d), Tab 5-3.

The total exported flows were reduced by 50 % in comparison to the total inflows, due to infiltration loss of the ditch and the refilling of the ponds after a dry summer period.

Furthermore, the groundwater levels were lower in MC2 in 2019 in comparison to MC1 in 2017 and,

thus led Exf_B to increase by 11 %. The calculated uncertainties for the total inflow and total outflow sums were 14 %, on average. Due to the late onset of Out_{M3} , the component Inf_B represented the main export pathway with a share of 52 % of the total outflows. This finding raised the question of whether there is an increased potential for solute transport to groundwater after dry hydrological preconditions. During monitoring period MP3, small In_{M1} flow rates of on average $160 \text{ m}^3 \text{ d}^{-1}$ refilled pond A. T_N was on average 14 d. The refilling lasted 26 d for pond A and additional 20 d were needed for pond B. Pond B was almost dry but received small $\text{In}_{M1} + \text{Exf}_B$ rates from in average $60 \text{ m}^3 \text{ d}^{-1}$. As the outflow threshold level at M3 was not reached during MP3, the share of Inf_B to the sum of outflow in pond B was 100 % (Fig 5-7).

During monitoring period MP4, the total sum of inflows exceeded the sum of outflows by 13 %. It seems that infiltration losses (Inf_A) leached to deeper soil layers due to the drier subsoil as pond B was already filled up. In pond B, the share of Inf_B to the sum of outflows increased during MP4 to 48 %. Due to similar hydrological conditions and volumes, it is possible to compare retention efficiencies between MP2 and MP4 below.

5.6.3. Pesticide and transformation product transport pathways

During all monitoring periods and for all compounds, tile drainage pipe inflow In_{M1} made up the largest fraction of load entry into pond A (In_{M1}) and pond B (In_{M2}) and the tile drainage pipe outflow of pond A (Out_{M2}) and pond B (Out_{M3}) were the main important export pathways. Comparing averages of all compounds during MC1 in 2017 and MC2 in 2019, the share of Out_{M2} (Out_{M3}) to the total outflow loads reduced from 91 % (73 %) to 64 % (50 %), while Inf_A increased from 9 % to 36 % and Inf_B from 27 % to 50 %. In contrast, Exf_A declined from 0.5 % to 0.2 %, but Exf_B increased from 4 % to 7 %. In the years 2017, 2018 and 2019, Flufenacet and Pendimethalin were simultaneously applied in September/October, whereas Metazachlor was only applied in August 2016 and August 2019 (Fig 5-6). Nevertheless, the dominant substance for all incoming and exported load components and during all monitoring periods was the TP Metazachlor ESA. The In_{M1} total loads of Metazachlor ESA were seven times higher than the In_{M1} total load of Flufenacet ESA, which was the second highest incoming substance (Fig 5-8). Flufenacet was the main pesticide during both MCs.

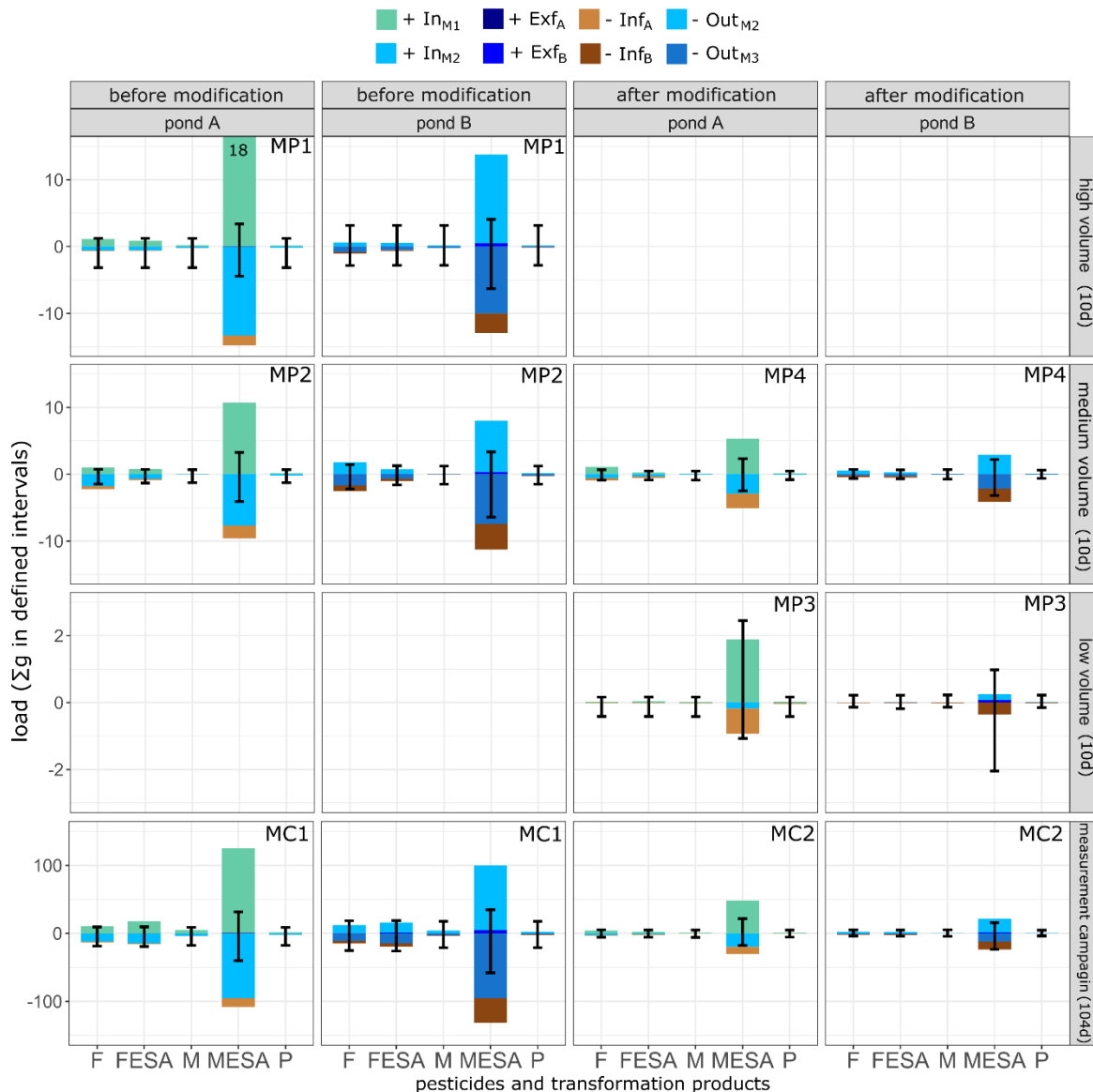


Fig 5-8: Transport pathways of pesticide loads into and out of the pond system (pond A, pond B) during different monitoring periods (MP) and measurement campaigns (MC) representing different pond volume situations before and after pond modification. Uncertainties are marked as error bars (numeral in supplementary material). F= Flufenacet, FESA=Flufenacet ESA, M= Metazachlor, MESA= Metazachlor ESA, P= Pendimethalin. The load balance components are described by tile drainage inflow load $M1 = In_{M1}$, tile drainage outflow load $M2 = Out_{M2}$ = tile drainage inflow In_{M2} ($Out_{M2} = In_{M2}$ have same colour), tile drainage outflow Out_{M3} , exfiltration load pond A = Exf_A , infiltration pond load A = Inf_A , exfiltration load pond B = Exf_B , and infiltration load pond B = Inf_B . All units are given in g per defined interval for MP1-4 = monitoring period 1-4 (10 d) and measurement campaign before and after modification (104 d), Tab 5-3.

5.6.3.1. Loads before pond modification

During the first monitoring period (MP1), the highest total loads of all investigated substances entered the pond system via tile drainage inflow In_{M1} (Fig 5-8). Exfiltration did not play a role in pond A, but was more important in pond B, since Exf_B was 4 % for Pendimethalin and 4 % for Metazachlor ESA. Both compounds left pond A and B mainly via surface flow. The small infiltration loads of all substances had an average share of only 10 % (Inf_A) and 21 % (Inf_B) to the total outflow loads. Baird et al. (2020)

observed the same effect when they compared their pond system during high flow periods, which was the case during MP1.

During MP2, all substance loads entered pond A via In_{M1} but were reduced in comparison to MP1, with the highest loads of Metazachlor ESA followed by Flufenacet and Flufenacet ESA. Metazachlor showed the lowest entry loads. The total load of Flufenacet was higher at Out_{M2} and Out_{M3} in comparison to In_{M1} , which can be explained by continuously occurring Flufenacet peaks in In_{M1} that added up in the pond and caused negative retention. Ulrich et al. (2019) observed a similar effect in their small retention pond. All other substances did not show these peaks and total loads were reduced at Out_{M2} and Out_{M3} . The incoming component Exf_B was on average 3.14 %, with the highest loads of Metazachlor ESA. The share of subsurface flow Inf_A increased for all substances to 20 %, and Inf_B to 34 %. Still the main important exporting pathways were Out_{M2} and Out_{M3} .

5.6.3.2. Loads after pond modification

Compared to MC1 in 2017, the loads at In_{M1} and Out_{M3} decreased for all pesticides and TPs during MC2 in 2019. Here, the highest load reductions were detected for Metazachlor and Pendimethalin.

During MP3, the substances transported through the drainage pond system with concentrations > LOQ were Metazachlor, which was already applied in August 2019, Flufenacet ESA, and Metazachlor ESA (Fig 5-8). The newly applied Metazachlor led to very small pesticide loads with increased inflow. Due to short degradation time in soil (Tab 5-6, supplementary material) relatively high fractions of the TP Metazachlor ESA were observed. The loads of Flufenacet ESA were quite small at that time and might be residues from the 2018-applied Flufenacet, as the parent compound did not occur in In_{M1} . Flufenacet ESA was detected in upper soil samples in the contributing catchment one year after application (Willkommen et al., 2021) due to its long dt_{50} in soil (Tab 5-6, supplementary material). Pond B was empty and as the groundwater level (g2, Fig 5-3) was higher than the water level of pond B, groundwater exfiltration filled the pond, hence, Exf_B loads increased. As the pond water level for discharging the outlet M3 in pond B was not reached, Inf_B increased to 100 %. The proportionally high infiltration loads in ponds during dry periods were also described by Baird et al. (2020). Flufenacet and Pendimethalin occurred after the second pesticide application (Fig 5-6), when both ponds were filled up. Despite losses to groundwater, total outflow loads were smaller than total inflow loads suggesting that during MP3 all substances were attenuated and mitigated in the pond system.

During MP4, the input occurred via the tile drainage (In_{M1} and In_{M2}) and mainly consisted of Metazachlor ESA, followed by Flufenacet ESA and Flufenacet to 100 % via In_{M1} and In_{M2} . These loads were lower during MP4 compared to MP2, due to lower inflows. The exported loads of Flufenacet ESA at Out_{M1} slightly exceeded those at In_{M1} . Inf_A increased for all substances to an average share of 39 % and Inf_B to 46 %, Out_{M3} decreased to 54 %, which partly was an effect of the prolonged T_N achieved by pond modification. All substances were exported via Inf_A , except for Metazachlor. However, at 3 m depth,

the groundwater samples mainly contained the TPs Flufenacet ESA and Metazachlor ESA (supplementary material, Fig 5-10). This shows that the component Inf_A should be treated as maximum estimate. It is likely that a large fraction of sorptive substances did not reach the groundwater but were retained in the hyporheic zone of the pond. Also, Hintze et al. (2020) stated that the highest risk for groundwater contamination stems from mobile and polar TP propagation.

Overall, the pesticides were mainly observed in tile drainage water (Fig 5-8). Before pond modification, during wet periods and high inflows into the ponds, the frequency of pesticides detections and concentrations in tile drainage water and shallow groundwater increased despite reduced infiltration conditions. In that time, the shallow groundwater levels favoured a fast leaching of the substances through a narrow unsaturated zone exemplified by maximum values of the pesticides and TPs in the groundwater samples of December 2017 (Fig 5-10, supplementary material). Highest concentrations were measured at Out_{M3} for several weeks in autumn 2017, when the concentrations of Flufenacet exceeded both the maximum allowable concentration of $0.2 \mu\text{g L}^{-1}$ in surface water (OGewV, 2016) (Willkommen et al., 2019) and the drinking water limits of $0.1 \mu\text{g L}^{-1}$ (TrinkwV, 2016) in the shallow groundwater (maximum Flufenacet concentration was $1 \mu\text{g L}^{-1}$). After pond modification, under low and moderate hydrological conditions, no exceedance of environmental limits occurred in Out_{M3} . Then the drainage pond system served as an effective natural retention zone. Irrespective of the pond- and groundwater levels, TPs were detected continuously in all tile drainage water and groundwater samples before and after pond modification.

5.6.4. Retention efficiency

The drainage pond system in our study was built to drain the agricultural fields belonging to the farm. The location of this drainage pond system complied with the recommendation of a maximum 100 - ha distance to the application area (Tournebize et al., 2017). However, the drainage pond system was originally not designed for pesticide retention and the wetland watershed area ratio was lower than the recommended 2 % (Tanner and Kadlec, 2013). Moreover, the potential pond storage capacity with 34 m^3 wetland per ha active catchment area was below the recommended guideline of $76 \text{ m}^3 \text{ ha}^{-1}$ (Tournebize et al., 2017). An enlargement of the ponds was not possible due to surrounding forests and would involve intensive constructions with higher expenses. As an alternative, measures concentrated on the improvement of hydraulic conditions within the pond, following the concept of Persson and Wittgren (2003) that a more elongated pond shape increases pesticide retention (Gaulhier et al., 2019). Hence, the length to width ratio of the kidney-shaped pond A was enlarged by a relocation of the outlet (Fig 5-4). During similar hydrological conditions that prevailed during MP2 and MP4, a clear improvement in retention could be recognized for the continuously detected compound Flufenacet (Tab 5-5). Apparently, prolonged residence times supported attenuation or degradation of pesticides and TPs. Flufenacet has a medium dt_{50} of 54 d in water (Tab 5-6, supplementary material). Pendimethalin concentrations were detected only $< \text{LOQ}$ at the outlet M3, generated by attenuation, sorption, or degradation (dt_{50} of 4 d,

Tab 5-6, supplementary material) in water. In contrast, Metazachlor has a dt_{50} of 216 d, and both Metazachlor ESA and Flufenacet ESA are stable in water. For these three compounds, the load retention was mainly hydrologically controlled. Particularly after high In_{M1} peaks, Out_{M3} loads exceeded those at In_{M1} both during MP2 and MP4. This behaviour caused negative retention efficiencies following phases of effective peak retention and was also described by Ulrich et al. (2019).

Tab 5-5: Comparison of total retention (mg interval⁻¹) and retention efficiency (%) of the measurement campaigns 2017 (104 d) and 2019 (104 d), and between the monitoring periods MP2 (10 d) and MP4 (10 d).

Substance	Parameter	Unit	Measurement campaign 2017 (104d)	Monitoring period 2 (10d)	Measurement campaign 2019 (104d)	Monitoring period 4 (10d)
F	total retention	mg interval ⁻¹	-5,654.23	-1,960.66	922.94	277.02
	retention efficiency	%	-54.11	-196.90	22.78	25.30
FESA	total retention	mg interval ⁻¹	-2,128.06	-396.76	-1,112.00	-480.76
	retention efficiency	%	-12.10	-52.11	-54.03	-194.74
M	total retention	mg interval ⁻¹	885.37	-6.61	235.33	-35.24
	retention efficiency	%	17.56	-19.48	37.68	-45.47
MESA	total retention	mg interval ⁻¹	-14,787.16	-2,110.25	15,546.70	-1,010.05
	retention efficiency	%	-11.81	-19.63	32.12	-19.06
P	total retention	mg interval ⁻¹	-713.68	-164.17	196.57	26.59
	retention efficiency	%	-43.60	-120.07	29.20	22.12

The TP Metazachlor ESA was continuously detected in all water samples and facilitated a detailed analysis of flow-dependent retention (Fig 5-9). After pond modification, during very low flow conditions and low groundwater levels, total load retention (Eq 5-20) was positive due to the pond refill situation and long residence times (Fig 5-9a). Higher retention values occurred during higher flow, when high tile drainage inflow loads exceeded those at the outflow directly after application. Flows between 250 and 1,000 m³ d⁻¹ yielded variable retention values with partly high infiltration loads that exceeded exfiltration loads and minimized total retention in the pond (Fig 5-9a).

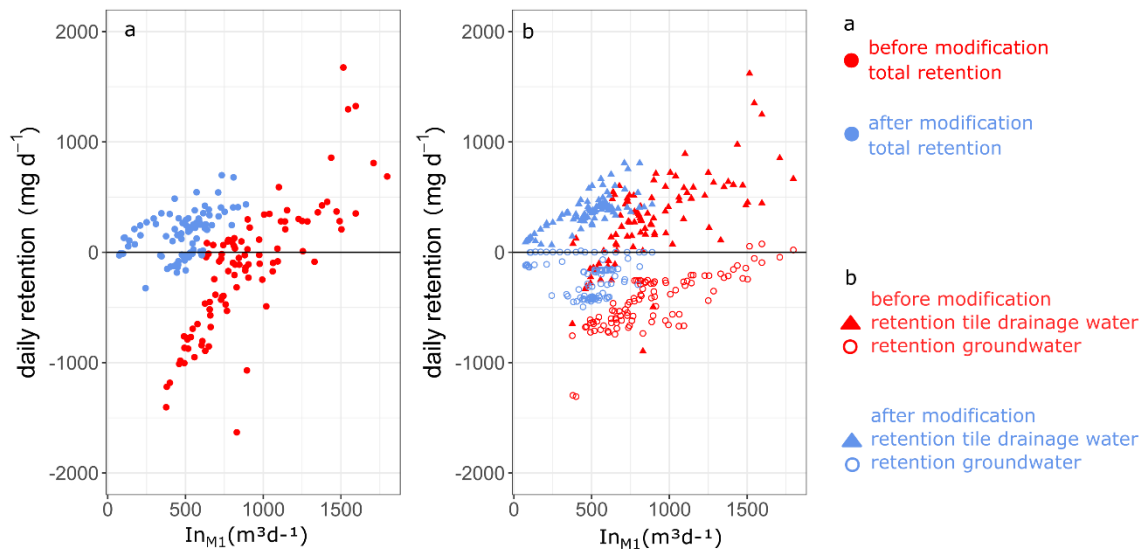


Fig 5-9: Tile drainage inflow In_{MI} ($m^3 d^{-1}$) to a) daily load retention ($mg d^{-1}$) and b) daily retention in surface water and shallow groundwater of Metazachlor ESA load ($mg d^{-1}$). For each day two retention values are plotted against one inflow value.

After pond modification, the infiltration loads to shallow groundwater (Eq 5-20) were reduced (Fig 5-9b), which also improved total retention (Fig 5-9a). The absolute load retention of Metazachlor ESA regarding shallow groundwater increased with increasing inflow amounts, which fits the findings of Baird et al. (2020) who found a minor role of infiltration during high flow periods in permeable pond substrates.

Overall, the ratio between average $Retention_{tile\ drainage\ water}$ (Eq 5-24) and $Retention_{shallow\ groundwater}$ (Eq 5-25) tile drainage water retention and average shallow groundwater retention for every substance increased (except for Flufenacet ESA). This resulted in an overall improved retention efficiency during MC2 in 2019. The average total retention efficiency for our semi-natural drainage pond system amounted to 38 % for mobile pesticides, 29 % for sorptive pesticides, and 32 % for mobile TPs (Tab 5-6). With the compliance of given hydrological design parameters for newly designed ponds, this is below the expected goal of a 50 % pesticide retention efficiency for FSCW (Gregoire et al., 2009; Tournebize et al., 2017).

In the future, a less permeable lining (i.e., loamy soil) of the permeable pond substrate could help to minimize the risk of propagation of TPs into the shallow groundwater (Hintze et al., 2020). Overall, the presented retention efficiencies for pesticides and TPs are all valid for autumn conditions, affected by different precipitation and flow conditions, but not by changes in temperature or vegetation growth. It may be expected that the macrophyte bed in pond A after pond modification will have a positive effect on retention efficiency (Vymazal and Březinová, 2015). Pesticides have different physicochemical properties (Vymazal and Březinová, 2015) why their retention is affected by different processes. In our study, compound properties seem to have affected rather the amount of retention than retention dynamics, since

the investigated pesticides and TPs are all highly stable with regard to hydrolysis and photolysis, but different regarding mobility (Lewis et al., 2016). Hence, all substances need long residence times in water to degrade, which was obvious during pond refill situations. However, the fluorescent tracer UR showed a high potential for photolytic decay, which was favoured during experiment T2 (33 % recovery) in comparison to T1 (>100 % recovery) due to the increase of τ from 0.8 d to 7.4 d (Tab 5-4). To obtain information on year-round pesticide retention efficiency, the pesticides and TPs should additionally be monitored during spring/summer at higher water temperatures and vegetation densities.

The incorporation of the farmer in the pond modification and management process was already suggested by Tournebize et al. (2013) and led to a higher awareness regarding pesticide mitigation potentials and possible pond improvements. The use of the farmer's labour, machinery, and material for pond modification kept the costs below 2,000 €. Particularly in view of future climate scenarios, agricultural areas might be exposed to more extreme precipitation and drought events, which might further amplify the variability of pesticide and TP loads entering surface water bodies. Therefore, the interest in retention ponds is rising because they contribute to goals of European Water Framework Directive (EC, 2000) in two ways by mitigating pesticide load peaks during wet and high inflow conditions in small agricultural streams (Halbach et al., 2021), while they contribute to groundwater recharge during drought periods (Baird et al., 2020).

5.7. Conclusion

In this study, the groundwater-surface water interaction of a drainage pond system was analysed to show effects on water and pesticide/transformation product (TP) load budgets. Overall, drainage inflows and outflows contained largest loads, but the permeable pond substrate favoured groundwater leaching of mobile TPs. The continuous occurrence of persistent TPs both in surface water and shallow groundwater was striking and this study once again revealed that drainage ponds constitute only a limited remediation strategy for resistant TPs. Moreover, a continuous monitoring of groundwater around ponds with permeable pond substrate and sampling of pesticide concentrations within pond substrate passage should be performed to consider all pathways and estimate robust retention efficiencies. The observed exceedance of pesticide and TP thresholds in surface water and groundwater during wet periods and high rainfall demonstrates the need for retention measures in agricultural headwater catchments. Particularly during periods of high inflows, the drainage pond system efficiently attenuated load peaks, while after drying periods pesticide retention was highest.

The fluorescent tracer experiments constituted an efficient approach to reveal flow shortcuts within the ponds and helped to document the efficiency of pond modification. Before pond modification, the overall retention efficiency in the drainage pond system was 18 % for mobile pesticides, -44 % for sorptive pesticides, and -12 % for mobile TPs. After pond modification, the hydraulic pond performance was improved and yielded an effective volume ratio of 100 % as documented by the tracers. A prolonged residence within the overall drainage pond system resulted in retention efficiencies of 38 % for mobile

substances, 29 % for sorptive pesticides, and 32 % for mobile TPs. The pond system was subject to a variable inflow and incoming pesticide and TP loads, which caused different retention efficiencies on a daily scale. Even though the system was smaller than the usual pond size recommended for planning, it represents a typical pond size occurring in agricultural land. Hence, this study provides guidance for targeted, inexpensive, and easy-to-adapt pond modification activities, which increase the retention efficiency of semi-natural drainage ponds to mitigate pesticide loads in agricultural headwater catchments.

5.8. Acknowledgments

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5.9. Supplementary material

Tab 5-6: Water balance and load uncertainties δ during the different hydraulic conditions in the drainage pond system. The blue bars mark the height of uncertainties. The numbers are illustrated as error bars in figures of the water and load balances (Fig 5-7 and Fig 5-8).

State	Hydraulic condition	Balance components	δ Water balance component (m ³ d ⁻¹) Drainage pond system	δ Load balance (mg d ⁻¹)									
				Flufenacet		Flufenacet ESA		Metazachlor		Metazachlor ESA		Pendimethalin	
				Pond A	Pond B	Pond A	Pond B	Pond A	Pond B	Pond A	Pond B	Pond A	Pond B
Before modification	wet	Incoming (+)	337	123	315	122	315	122	314	338	407	122	314
		Outgoing (-)	422	316	283	316	280	316	280	444	630	316	280
	moderate	Incoming (+)	141	74	144	72	127	68	124	325	335	68	124
		Outgoing (-)	198	147	220	132	132	127	150	409	643	128	151
After modification	moderate	Incoming (+)	77	67	72	48	66	47	70	233	221	47	61
		Outgoing (-)	106	90	65	84	68	88	72	249	318	81	61
	dry	Incoming (+)	27	16	22	17	22	16	23	245	98	16	22
		Outgoing (-)	45	41	14	41	18	42	14	107	205	41	15

Tab 5-7: Properties of selected pesticides and TPs from PPDB database (Lewis et al., 2016) and environmental quality standards.

Substance	Metaza-chlor	Metaza-chlor ESA	Flufe-nacet	Flufenacet ESA	Pendime-thalin
Group	Chloroa-cetamide	TP	Oxyacet-amide	TP	Dinitroan-iline
Log P (Octanol-water partition coefficient) at pH 7, 20°C	2.49		3.5		5.4
K _{foe} (organic-carbon sorption coefficient), mL g ⁻¹	79.6	5	273.3	12.5	13792
Aquatic Photolysis in water dt ₅₀ at pH 7, days	stable		stable		21 days
Hydrolysis in water dt ₅₀ at pH 7, 20°C, days	stable, pH 7		stable, pH 5-9		stable, pH 4-9
Dt ₅₀ in water phase, days	216	1,000	54	1,000	4
Dt ₅₀ in soil, days	6.8	115	39	302	100.6
Dt ₅₀ in water-sediment phase, days	20.6	1,000	81	1,000	16
ZHK µg L ⁻¹ (OGewV, 2016)			0.2		
RAK µg L ⁻¹ (UBA, 2020)	1.67		12		0.63
GOW nrM µg L ⁻¹ (UBA, 2019)		3		1	

Tab 5-8: Properties for tracers by Leibundgut et al. (2009) and Bork et al. (2020)***.

Properties	UR	SRB
Application amount (g)	20	40
Chemical formula	C ₂₀ H ₁₀ O ₅ Na ₂	C ₂₇ H ₂₉ O ₇ N ₂ S ₂ Na
Aqueous solubility (g L ⁻¹)	300	10
Photolytic stability (dt ₅₀ , hours)	11	820
Soil adsorption coefficient (Kd, mL g ⁻¹)	0.6 - 73.2***	2.7 - 19.3***

$$\text{Daily_load_retention_pondA} = \text{Total_inflow_load}_{M1} - \text{Total_outflow_load}_{M2} \quad (5-18)$$

$$\text{Daily_load_retention_pondB} = \text{Total_inflow_load}_{M2} - \text{Total_outflow_load}_{M3} \quad (5-19)$$

$$\text{Daily_load_retention} = \text{Total_inflow_load}_{M1} - \text{Total_outflow_load}_{M3} \quad (5-20)$$

$$\text{Retention_efficiency_pondA} = (\text{Total_outflow_load}_{M2} - \text{Total_inflow_load}_{M1}) * 100 / \text{Total_inflow_load}_{M1} \quad (5-21)$$

$$\text{Retention_efficiency_pondB} = (\text{Total_outflow_load}_{M3} - \text{Total_inflow_load}_{M2}) * 100 / \text{Total_inflow_load}_{M2} \quad (5-22)$$

$$\text{Retention_efficiency} = \frac{(\text{Total_outflow_load}_{M3} - \text{Total_inflow_load}_{M1}) * 100}{\text{Total_inflow_load}_{M1}} \quad (5-23)$$



Fig 5-10: Concentration of pesticides and transformation products sampled at the groundwater monitoring pipes g1, g2, and g3 in shallow groundwater during both measurement campaigns (MC1 in 2017, MC2 in 2019). F = Flufenacet, FESA = Flufenacet ESA, M = Metazachlor.

6. Summarizing discussion and conclusion

A cross-compartment investigation approach for pesticide and transformation product (TP) monitoring on the field and catchment scale in short- (event) and longer term (autumn season) was applied cross-year to gain an improved understanding of pesticide processes in surface water, soil, and groundwater. The major focus was on dynamic tile drainage flows and the potential retention efficiency of drainage ponds. As the main outcome of this study, a tailor-made mitigation strategy for pesticides and TPs in an agricultural headwater catchment is presented.

This goal was achieved by

- (I) the inspection of the transport pathways at the field scale in soil and shallow groundwater,
- (II) by the analysis of key factors controlling tile drainage transport comparatively at field and catchment scales, and
- (III) by analysing the hydraulic functionality of a drainage pond system using fluorescent tracers and improving pesticide and TP retention by efficient pond modification. The main findings that emerged from the three research questions presented in the introduction are summarized below. Boundary conditions and prospects for future research are also discussed.

6.1. Addressing the research questions

Studying pesticides and their transformation behaviour is very complex, as there are many kinds of pesticides that have different transport and transformation properties and depend i.e., on climatic-hydrological site factors, crop rotation, soil types and application rates. The investigation of small-scale processes needs high-resolution on-site information such as weather data, discharge data, soil properties and soil conditions, application data in addition to high-resolution sampling. The interrelated, event-based, and longer-term investigation of different environmental compartments increase the process understanding.

In the studied agricultural headwater catchment, the highly dynamic pesticide loads are mainly transported via soil directly to shallow groundwater or via tile drainage pipes to the catchment outlet. Few field studies exist about the transformation and transport of pesticide TPs in soil and their temporal occurrence in shallow groundwater. Based on this, the following research question is raised in Part I:

- How do variable hydrological conditions affect the soil transport of pesticides and their transformation products and how does the soil interaction respond to shallow groundwater?

The pesticide and TP transport from soil to shallow groundwater was highly influenced by the prevailing and antecedent climatological and hydrological conditions (Dhakal and Sullivan, 2014). Within the soil, the pesticide and TP showed contrary transport and transformation behaviour under different hydrological conditions. The microbial transformation and mobility were mainly controlled by the soil pore connectivity (Vogel et al., 2015), indirectly represented by soil matrix flow condition and water tension.

In soils with shallow groundwater levels < 1 m, especially under wet conditions, the microbial transformation of the pesticide and the subsequent leaching of the TP to shallow groundwater occurred fast and started immediately after pesticide application. During drought periods, few mm of precipitation after drying initial soil moisture conditions were sufficient (Wiekenkamp et al., 2016) for mobile pesticides to move in preferential flow paths. Hence, the dominant vertical transport (Grayson et al., 1997) created short concentration peaks of parent compounds in shallow groundwater. During wet condition, with more distributed lateral and vertical flow (Wiekenkamp et al., 2016), the risk of pesticides reaching the shallow groundwater is reduced. The TP was continuously detected in shallow groundwater independent from hydrological conditions. However, in shallow groundwater during drought conditions, occurred a mixed signal from residual TP and newly built TP, as the latter could not move from small soil pores to shallow groundwater due to absent matrix flow. The use of cost-efficient fluorescent tracers Uranine and Sulforhodamine - B for long-term process research on leaching and transformation of mobile organic pesticides can be recommended as the similar dependence on retention and transformation processes within the soil was confirmed. The occurrence of the increased tracer TP amounts in the soil after drought was temporally consistent with the main pesticide TP peak in shallow groundwater.

In small catchments (< 100 km²), Szöcs et al. (2017) presented a pollution risk from pesticides applied to agricultural fields adjacent to small streams in the downstream catchment because of the low dilution potential from field to receiving water body. The drivers for contamination were precipitation and mainly agricultural land use, as 28 % of agricultural land within the catchment exceeded regulatory acceptable concentrations (RACs). Underpinning this, the current study of Uta Ulrich et al. (2021) reported about the omnipresent distribution of pesticides in all water types in agricultural landscapes. In the study area of this thesis, all cropland areas are tile-drained and the catchment is controlled by tile drainage discharge. Inflow to the retention ponds at the catchment outlet are highly dependent on the dynamics of tile-drainage transport. Therefore, the following research question was answered in Part II:

- Which factors control the temporal dynamics of pesticide loads from tile drainages at field and catchment scales?

In headwater catchments, the control of the substance transport in agricultural fields is often discussed within the concept of hydrological connectivity (i.e. Aubert et al., 2013). This is defined as available water and, i.e., pesticides, to move from hill to slope (Blume and Van Meerveld, 2015). In dewatered agricultural headwater catchments, this travel time is reduced artificially by tile drainage pipes (Schilling et al., 2011). As the onset of tile drainages is highly dependent on the hydrological connectivity in soil, the subsurface connectivity was identified as the main controlling factor in this study. Weather conditions, subsurface hydrological connectivity, pesticide application, and physico-chemical properties contribute to pesticide leaching, but vary in their influence/effect over time.

A phasing system for field and catchment pesticide loads (Chapter 4.7.2.4) was delineated to derive the timing of high and delayed loads and make recommendations for tile drainage monitoring. Temporal patterns of tile drainage pesticide load phases can be summarized as the flush peak phase (1), the recession and background load phase (2), preferential flow patterns (3), and retarded pesticide load peaks (4). The transport by tile drainage pipes from field to catchment scale depends highly on the weather conditions, which are essential for a functional subsurface connectivity. During wet conditions, with a highly connected state, the investigated field contributed considerably to the overall catchment load. The first tile drainage pesticide peaks, so called “first flushes”, reached the catchment outlet within very short travel times (< 1 d). During dry conditions and an un- or low-connected state, the dynamic patterns were contrasting at both scales. The contribution of tile drainages to pesticide leaching was limited and dominated by preferential flows. Very mobile pesticides were not exclusively leached during high precipitation periods but also continuously discharged from soils to the drainage system during low precipitation directly after application. The influence of the dry conditions at the catchment scale was rather low because of interrupted subsurface connectivity. Those findings show that the prevailing and antecedent hydrological conditions affect the dependence of short and long-term loads at field and catchment scales. The necessity of a long-term monitoring emphasized by Pavlin et al. (2020) could be evidenced by our results regarding sorptive pesticides. They had a lower total loss rate than the mobile pesticides and peaks were considerably retarded three months after application in winter accompanied by high discharges. The timing of pesticide application was an additional crucial factor for pesticide leaching because the wet weather conditions directly after application led to a 10-fold increase in daily tile drainage loss compared to the drier period for all pesticides. Taking all these findings into account, the opinion of Szöcs et al. (2017) can be confirmed that a revision and improvement of the regulatory monitoring should be initiated. The findings from this paper lead to the conclusion that tile drainage water sampling should be considered for the monitoring strategy within the European Water Framework Directive (EC, 2000) and demand for further refinement to high-frequency monitoring (precipitation-dependent monitoring) in highly contributing areas.

The present work shows that pesticides in agricultural headwater catchments cause problems in shallow groundwater and in downstream surface water. It is recommended by Warner et al. (2021) to identify catchment hotspots, and in those, pesticides application in autumn needs to be reduced if there is a current soil water deficit and if 5-day weather forecast predicts significant precipitation amounts > 10 mm (Lewan et al., 2009). In this study, based on the monitoring observations, a precipitation threshold of 6 mm was determined to prevent “first flush” pesticide losses. Catchment-specific measures needs to be implemented and the effectiveness should be tracked (Warner et al., 2021). Measures adapted to the needs of the catchment are discussed on how to pre-clean tile drainage water by so called end-of-pipe solutions, one of which are retention ponds.

This study investigated a drainage pond system with all flow compartments to determine whether it could serve as a potential retention solution for pesticides and their TPs. Up to now the pond surface

water – shallow groundwater interaction in drainage ponds was rarely investigated. In part III, the overall research question raised was:

- What conditions allow drainage ponds to be a suitable agricultural management measure to effectively retain pesticides and their transformation products?

The priority and necessity of the subject is shown by the two recently published studies by Imfeld et al. (2021) and Le Cor (2021). Both deal with the role of ponds in terms of their retention capacity in agricultural catchments. Imfeld et al. (2021) reviewed the dissipation conditions in ponds under variable boundary conditions. A modelling framework for the role of ponds at catchment scale was designed. At the same time, a field study on the reduction of pesticide concentrations by a large pond of 4.5 ha in an agricultural headwater catchment, with special focus on TPs and a retention efficiency of 20 % to 100 % was presented for frequently detected pesticides and TPs (Le Cor et al., 2021).

Our study complements existing studies, as one outcome was a practice-relevant hydrological balance calculation for a drainage pond system in an agricultural catchment. This balance calculation is easily applicable for farmers, landscape planners and environmental agencies, as it was created in Microsoft Excel. Besides the consideration of varying tile drainage inflows and the dynamic adjustment of volume changes, the novelty was the consideration of the pond surface water - shallow groundwater interaction at several gauges (further development Willkommen et al., 2018). In addition, the load calculation of the pesticides and their TPs on a daily basis was carried out under different water level phases in ponds. To check the hydraulic functioning of the ponds, the simple use of the low-cost fluorescent tracers, Uranine and Sulforhodamine-B, has proven to be efficient. As a result, the ponds could be specifically modified. Consequently, the effective volume (ϵ) increased from 20 % to almost 100 % in the modified pond and the mean hydraulic residence time prolonged 10-fold. The tile drainage inflows and outflows contained the largest loads, but the permeable pond substrate facilitated groundwater leaching of mobile TPs. Impermeable designed ponds would prevent pesticide loads from pond water reaching groundwater. However, the highest pesticide concentrations in shallow groundwater occurred from leaching directly in the field (Chapter 3.6.2.). Careful management of pesticides, such as applying minimum necessary amounts and recognizing adverse situations for application when soils are wet in autumn (Lewan et al., 2009) and then avoiding application, can reduce loads to groundwater.

The continuous occurrence of persistent TPs in surface water and shallow groundwater was striking. Le Cor et al. (2021) and Ulrich et al. (2021) advocate the inclusion of TPs in regulatory water quality monitoring programmes and guidance values for TPs should be extended. The observed exceedance of pesticide thresholds in surface water and for pesticides and TPs in shallow groundwater during high precipitation periods demonstrated the need for retention measures in agricultural headwater catchments. Particularly during periods of high inflows, the drainage pond system efficiently attenuated load

peaks. However, the average total retention efficiency after modification reached 29 % for sorptive pesticides, 32 % for mobile TPs, and 38 % for mobile pesticides. The pond system represents a typical pond size occurring on agricultural land. This study provides guidance for targeted, inexpensive, and easy-to-adapt pond modifications, which increase the retention efficiency of semi-natural drainage ponds. After modifying the drainage pond, the system performance increased and was able to mitigate pesticide loads in agricultural headwater catchments to improve downstream water quality.

6.2. Reflections about the data situation and the monitoring design

In this work, a relatively high number of samples were taken and analysed for pesticides and TPs in soil, groundwater, and tile drainage water. Mixed soil samples were analysed for soil type and depth, nevertheless, the results capture both hotspots and less contributing sites (Chapter 3). The selection of a suitable analytical method for pesticides in soil samples led to limitations due to topography of the sampling sites and the properties of soil type and pesticides. The applied water eluate analysis method had generally led to higher concentrations in sandy soil than in loamy soil. Due to lower clay and C_{org} contents in sandy soil, the desorption of pesticides was presumably favoured in this soil type. This pattern is attributed to topography with substance losses and reduced adsorption at the steeper loamy plot. The water eluate method produced reliable desorption amounts for pesticides and TPs. For the analysis of the solid with acetone as a separating agent the limit of quantification was defined as 0.05 mg kg^{-1} . All measured values were below this limit and further conclusions could not be drawn. This problem was also stated by Tournebize et al. (2013). For this reason, in Chapter 3, results about pesticide and TP leaching in the soil were presented for mobile pesticides. A monitoring of pesticides and TPs in soil with a joined analysis of water eluate and solid extraction methods with a quantification limit in $\mu\text{g kg}^{-1}$ -range would provide important transport and transformation information about substances that sorb stronger to the soil matrix.

In this study (Chapter 3), the generalised assumption was made that only vertical pesticide and TP transport can be assumed in small areas, since especially under dry conditions the leaching is controlled by local site conditions and soil characteristics (Grayson et al., 1997). Of course, transport to groundwater can also occur laterally, especially under wet conditions (Grayson et al., 1997). There can also be a temporal and spatial shift between concentrations in the soil and groundwater beyond groundwater catchment boundaries, especially in the presence of tile drainage pipes. This migration and re-entry from groundwater to surface water occurs especially for mobile and persistent TPs (Hintze et al., 2020). The results can be justified because shallow groundwater was sampled, the investigated field was surrounded by grassland and fields of other crops, and the investigation area was completely in the same groundwater catchment “Schwentine-Oberlauf” (Landwirtschafts- und Umweltatlas, 2021). More systematic monitoring approaches in soil and groundwater are needed to understand longer term TP exposures in relation to water flows and soil temperatures also in other areas. Additional field measurements should

be carried out to finally set up a physically based model, which may confirm the identified environmental behaviour of Flufenacet. In the case of this study, the cost-efficient fluorescent tracers permitted a higher spatial resolution and a longer sampling period than the pesticide monitoring.

In the area studied here, the location of the tile drainage pipes could be successfully reconstructed (Chapter 4) through expert knowledge of the farmer, aerial photograph interpretation, and derivation via depth contours in the digital elevation model. Transferred to the large scale, this is an enormous knowledge deficit throughout Germany. The location of tile drainage pipes is known in only a few cases and often estimated by modelling. There are new large-scale approaches such as Song et al. (2021), but these are not yet transferable into practice. This lack of knowledge makes it difficult to make accurate statements about contributing areas in drained catchments. An area-wide measurement of soil moisture can, at least on a small scale, advance knowledge on subsurface connectivity (Pavlin et al., 2021), and may improve the delimitation of drained areas. In this study soil moisture measurements were carried out at selected locations, to make verifiable statements about the transport of pesticides in drained soils (Chapter 3). The elaborately measured soil water retention curves and adaptation to the Van Genuchten model (Van Genuchten, 1980) by the non-linear pF curve optimisation program RETC (Van Genuchten et al., 1991) have significantly advanced the knowledge about the subsurface connectivity conditions in the investigated soil sites. Thus, it was possible to separate topsoil, matrix, and macropore flow, at least exploratory for the investigated field site (Chapter 3).

Within this study, the monitoring design offered a traditional “input-output” mass balance (Imfeld et al., 2021) of pond water to describe the pesticide and TP retention within the drainage ponds (Chapter 5). In addition, the common methodological approach of fluorescent tracer application in wetlands (i.e., Lange et al., 2011; Ulrich et al., 2019) was used to analyse the degradation potential. By carrying out this method, the non-degradation potential by sorption and the degradation potential by photolysis could be demonstrated. A ground-breaking methodological compilation was recently published by Imfeld et al. (2021) for the detection of dissipation processes within ponds, which can be given more attention in future research.

6.3. Recommendations for future research

From the preceding results, discussions, and reflections, recommendations for future research can be derived. The results of the study on leaching and transformation of pesticides in soil to shallow groundwater (Part 1, Chapter 3) show promise for using the cost-effective and environmentally compatible fluorescent tracers in soil as a proxy for pesticide transformation. Up to now, these findings are limited to the presented field site. Hence, this approach, which follows the methods of Lange et. al (2018), should be pursued further to obtain more long-term systematic monitoring observations in high spatial resolution. Those values can be used for validation of soil leaching and transformation models. A field

experiment with monthly or precipitation-event based monitoring of pesticide and tracers and their transformation products in soil for at least 1-year would be useful for gathering an extended data set and gain further evidence for the detection of characteristic leaching and transformation patterns.

The comparative analysis of the key factors controlling tile drainage transport at the field and catchment scale (Part II, Chapter 4) revealed that, pesticide loads from tile drainages are relevant shortly after application, as well as during high discharges in winter. Therefore, a high-frequency monitoring is recommended for all phases of tile drainage output in highly contributing areas. According to Leu et al. (2004a), pesticide loads from tile drainage pipes account as a dominant pesticide loss pathway. Hence, a tile drainage monitoring system regulated by European Water Framework Directive (EC, 2000) would be desirable. The research work carried out has shown that pesticide transport from field scale to catchment scale strongly depends on the subsurface connectivity in the drained catchment. Therefore, it would be necessary for future research to consider the variability in soil moisture and weather conditions, i.e., hydrological connectivity when delineating tile drainage catchment areas. For further research, the nationwide estimation of pesticide drainage loads could be interesting. This requires further field studies and the compilation of existing studies about tile drainage pipe studies. Following the approach of Motarjemi et al. (2021), applied in Denmark, these data could be used in machine learning models to predict annual drainage discharge. The nationwide estimation of tile drainage discharge and loads would be an important factor for implementing mitigation techniques on a larger scale (Motarjemi et al., 2021). The investigated and modified drainage pond system (Part III, Chapter 5) can be considered as a pilot study regarding how farmers can be involved in the water, and pesticide management of their farm through close cooperation and communication. The pesticide retention efficiency of the drainage pond system showed strongly improved results due to the easily implemented modifications. For future work, the transferability of the established retention efficiencies could be tested a) to other drainage ponds on farms and b) to a larger scale. At a small scale, it would be of great interest in the future to develop a model for pesticide transport in ponds, including selectable degradation functions, to bring it into practical application as a measuring tool for farmers and Environmental agencies. The data collected in this study could be used for calibration and validation, and the developed water balance tool for drainage ponds could be the base for model developments. At a larger scale, there are studies from Sweden that estimated nutrient retention of wetlands on a supra-regional level (i.e., Arheimer and Pers, 2017). It could be a research objective to assess the extent to which retention ponds can reduce the pesticide load in the annual cycle on a supra-regional level, which fits into the research efforts of Imfeld et al. (2021). There is a need for better data on the range of possible loads that the retention ponds can reach. This requires more knowledge about the pesticide and TP dynamics from soil to surface water to better understand the load variation of contributing field areas. Overall, modelling of pesticide transport pathways in soil, groundwater, and in the retention ponds themselves needs more monitoring data so that models can later be calibrated and validated sufficiently and robustly.

6.4. Conclusion

The results obtained from this dissertation offer an insight into the dynamics of pesticides and their transformation products (TPs) in different environmental compartments: soil, shallow groundwater, tile drainage water, and pond water. All these media were investigated up to daily resolution to better understand the interaction of these compartments in terms of pesticide transport. Various process controlling factors such as drainage network, catchment area delineation, land use, crop rotation change, application timing, application rates, weather conditions, soil moisture and temperature, soil properties, tile drainage discharges, and the dimensioning and hydraulic function of the drainage pond system were also evaluated. Four pesticides and four TPs with different physico-chemical properties were selected for this study. Multiple fluorescent tracer experiments supported the analysis and substantiated the knowledge procedure regarding pesticide transformation in soil and detection of hydraulic short-cuts in the drainage ponds. The following is a summary of the most important research findings:

- Pesticide transport is controlled by matrix flow and preferential flow in soil. Preferential flow is also active during dry soil conditions with high leaching risk especially for mobile pesticides to reach the groundwater. This is reinforced by the proven transport of very mobile pesticides with a minimum amount of precipitation. TPs were continuously detected in shallow groundwater.
- The temporal occurrence of pesticide loads from tile drainage pipes is independent from weather conditions at field scale. First flushes occur with high discharges under wet soil conditions immediately after application. However, for very mobile pesticides first flushes occur also with initial dry soil conditions and low precipitation amounts. Retarded load peaks of sorptive pesticides occur until late winter. The transfer to catchment scale highly depends on subsurface connectivity, which is activated by sufficient soil saturation. The magnitude of pesticide load varied 10-fold between field and catchment scale, and dry and wet weather conditions.
- With increased retention time and complete mixing of the pesticides and their TPs within the drainage ponds, they can serve as retention ponds especially under wet conditions to buffer high discharges and dilute high peak concentrations. Transformation processes happen with longer retention times under moderate inflow conditions. Pesticide retention potential by infiltration into the hyporheic zone of the pond was highest shortly after the drying period.

The findings of this study contribute to the analysis of pesticide behaviour in agricultural headwater catchments. In summary, existing drainage ponds can serve as retention measures if a) the temporal loads for pesticides and transformation products, as well as the hydrological characteristics (with tracers) are recorded and b) on this basis, pond modifications are made to improve retention. While investigating

the temporal load situation, the flow dynamic of tile drainage discharge played a key role. The elaboration of tile drainage load phases can potentially help to better understand pesticide and transformation pathways and may support the revision of regulative monitoring strategies in small streams in drained agricultural areas. For more accurate estimates of pesticide loads beyond case studies, e.g., at a regional level, better access to application, land use data, and new methodological approaches to identify tile-drained catchments are needed. This dissertation showed that pesticides and their TPs can lead to increased concentrations both in the short term and in the long term under dry and wet climatic site conditions. Especially the permanent detection of mobile and persistent TPs poses risks. Future efforts should focus on improving regulatory monitoring strategies, such as monitoring of tile drainages and setting limits for transformation products in the European Water Framework Directive (EC, 2000). Finally, this thesis demonstrates the need to promote small-scale agricultural retention measures close to field to directly mitigate pesticides and transformation products loads and to improve downstream water quality.

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Declaration of authorship

Hiermit erkläre ich, dass ich die vorliegende Dissertation, abgesehen von der Beratung durch meine Betreuer, selbständig verfasst habe und keine weiteren Quellen und Hilfsmittel als die hier angegebenen verwendet habe. Diese Arbeit hat weder ganz noch in Teilen bereits an anderer Stelle einer Prüfungskommission zur Erlangung des Doktorgrades vorgelegen. Ich erkläre, dass die vorliegende Arbeit gemäß den Grundsätzen zur Sicherung guter wissenschaftlicher Praxis der Deutschen Forschungsgemeinschaft erstellt wurde.

Kiel, 16.12.2021

Sandra Willkommen