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Title:

How weather conditions and physico-chemical properties control the leaching of flufenacet, diflufenican, and pendimethalin in a tile-drained landscape

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Graphical abstract

Caption: Pesticides in a tile drained landscape

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.

Keywords: tile drainage; pesticide leaching; flufenacet; diflufenican; pendimethalin; weather conditions

1. 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 temporal resolution (weekly (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, Doppler et al., 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 spatial-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 physico-chemical 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.

2. *Methods and Materials*

2.1. Study area

Fig. 1: The study area shows arable fields 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 years mark the current connected cultivated fields during the monitoring campaign.

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 contents of 60-70 % and silt contents of 20-30 %, pH 6.3 and Corg 1.5 %. The clay content of the loamy topsoil is 20-30 % and the silt content 50-60 %, pH 7.0 and Corg 1.4 %. Sampling point (B) (Fig. 1) describes the outlet of the whole catchment (100 ha), also including the smaller area of 10 ha representing the field scale (A, Fig. 1).

Tab. 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.

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 03th of October 2017 to 21th of January 2018 (length = 111 days, campaign 2). The pesticides were applied in late summer and autumn (Tab 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. 1).

2.1.1. 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 (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 (kfoc) and is moderately mobile (Lewis et al., 2016) with the percolating water. Diflufenican and pendimethalin have a high kfoc 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 (dt50) and degrade slowly. Flufenacet degrades faster than diflufenican and pendimethalin (Tab. 2).

Tab. 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 (dt50) in soil, water, and sediment. The specific dt50 values refer to available field studies in the PPDB. Table gaps with no available date from PPDB are expressed by x.

2.1.2. 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 German Climate Data Center (DWD Climate Data Center, 2018). At the field outlet, the discharge of the 150 DN tile drainage pipe was measured manually by collecting water with bucket and stop watch. Water levels were measured 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.

2.1.3. 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 %.

2.1.4. Calculations

For pesticide load calculation, concentration values detected below LOQ were set to 0.5 LOQ. The daily loads were calculated multiplying daily concentration (µg L^{1}) of mixed water samples with daily averaged discharge ($m^3 d^{-1}$). 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. 1).

Eq.1 $$normalized\ specific\ cumulative\ load\ (gha^{-1}) = specific\ cumulative\ load\ (gha^{-1}) * \frac{equivalent\ application\ amount\ (gha^{-1})}{avarage\ application\ amount\ \ (gha^{-1})}$$

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.2.

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

3. Results

3.1. Hydrological boundary conditions

During both measurement campaigns in the years 2016 and 2017, the weather conditions varied strongly (Tab. 3). Campaign 1 was relatively dry with only 49 % of rainy days (maximum with 17 mm d^{-1}). However, 7 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 4 days exceeding 10 mm d^{-1}. Comparing the last 10 years of data (2007-2017) from the nearest weather station in Dörnick (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 ± 21mm in 2016. In 2017, the standard deviation of ± 36mm represented an average variable year.

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

3.2. *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. 3) and application amounts (Tab. 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. 1). In 2016, four fields were connected to location B (Fig. 1). In the following year only two fields were cultivated, and the catchment outlet received loads primary from the field of outlet location A (Fig. 2). The application amount varied between the pesticides, but the order of application amount was the same for both years: pendimethalin > flufenacet > diflufenican (Tab. 3). 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. 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), contrary to the order of application amounts.

Tab. 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).

3.3. 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.2). The difference in total load between the two campaigns is most apparent for flufenacet (Fig. 2). At the catchment scale, the total load increased for diflufenican 3-fold, for pendimethalin 2.6-fold, and for flufenacet 8.8-fold.

Fig. 2: Cumulative pesticide loads (mg) for flufenacet (blue line), diflufenican (black line), and pendimethalin (red line) 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 September and in 2017, the 1st application was on 30th September (B), the 2nd application on 9th of October (B), and the 3rd application on 30th October (A)).

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). 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). 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).

To identify the impact of the sorption properties of the compounds (Tab. 2) on the drainage output, the sorption coefficient (kfoc) and the total loss rate were compared (Fig. 2). The total loss rate is higher for all substances under wet conditions. On both scales, the more mobile substance was (smallest kfoc 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. 3: Variation of total loss rate (% share of specific cumulative load to applied pesticide amount) and sorption coefficient kfoc (ml g^{-1}) of the selected pesticides at the field- and catchment outlets for campaign 1 (2016) and campaign 2 (2017).

3.4. 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.

Fig. 4 Pesticide loads of diflufenican (black), flufenacet (blue), and pendimethalin (red) 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 September and in 201,7 the 1st application was on 30th September (B), the 2nd application on 9th of October (B), and the 3rd application on 30th 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.

3.4.1. 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). 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 1693.8 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).

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

During campaign 1, the substances pendimethalin and diflufenican could not be detected above LOQ (Fig. 4). Flufenacet was detected with a delay of 12 days in A (phase 1). The highest load of flufenacet was measured 10 weeks (11th 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 1313 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).

4. Discussion

4.1. 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) 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 05/10/2017). However, the current pesticide application on 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 on 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% (0.07g 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).

4.2. Temporal dynamics of pesticide loads

4.2.1. 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 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).

4.2.2. 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.

4.2.3. 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 µg 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 µg L^{-1}, 11/12/2016). However, under wet conditions the situation changed at the catchment outlet. The threshold was exceeded by flufenacet for 4 weeks beginning directly after pesticide application on 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 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 show 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.

4.2.4. 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 (05th 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 trough” with preferential flows (Leu et al., 2004a). Due to the higher polarity and low kfoc 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 kfoc 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. 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 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.

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