



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

Sandra Willkommen^{a,*}, Jens Lange^b, Uta Ulrich^a, Matthias Pfannerstill^c, Nicola Fohrer^a

^a Institute of Natural Resource Conservation, Department of Hydrology and Water Resource Management, Christian-Albrechts-University of Kiel, Germany

^b Hydrology, Faculty of Environment and Natural Resources, University Freiburg, Germany

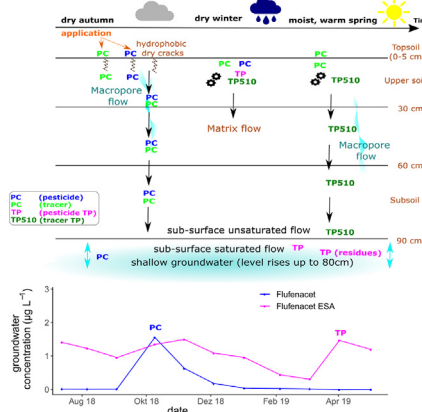
^c State Agency for Agriculture, Environment and Rural Areas Schleswig-Holstein (LLUR), Hamburger Chaussee 25, 24220 Flintbek, Germany

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.

GRAPHICAL ABSTRACT

Temporal occurrence of pesticides and fluorescent tracers in antecedent dry soil.



ARTICLE INFO

Article history:

Received 28 May 2020

Received in revised form 30 July 2020

Accepted 10 August 2020

Available online 13 August 2020

Editor: Jay Gan

Keywords:

Flufenacet

Flufenacet ESA

Fluorescent tracer

Uranine

Sulforhodamine - B

Shallow groundwater

Preferential flow

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 10 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

* Corresponding author.

E-mail address: swillkommen@hydrology.uni-kiel.de (S. Willkommen).

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.

© 2020 Elsevier B.V. All rights reserved.

1. 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 Papadopoulou-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?

2. Methods and materials

2.1. 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. 1).

In the area of the Colluvic Gleysol, groundwater could reach up to 0.8 m below surface and loamy colluvial sediments were situated

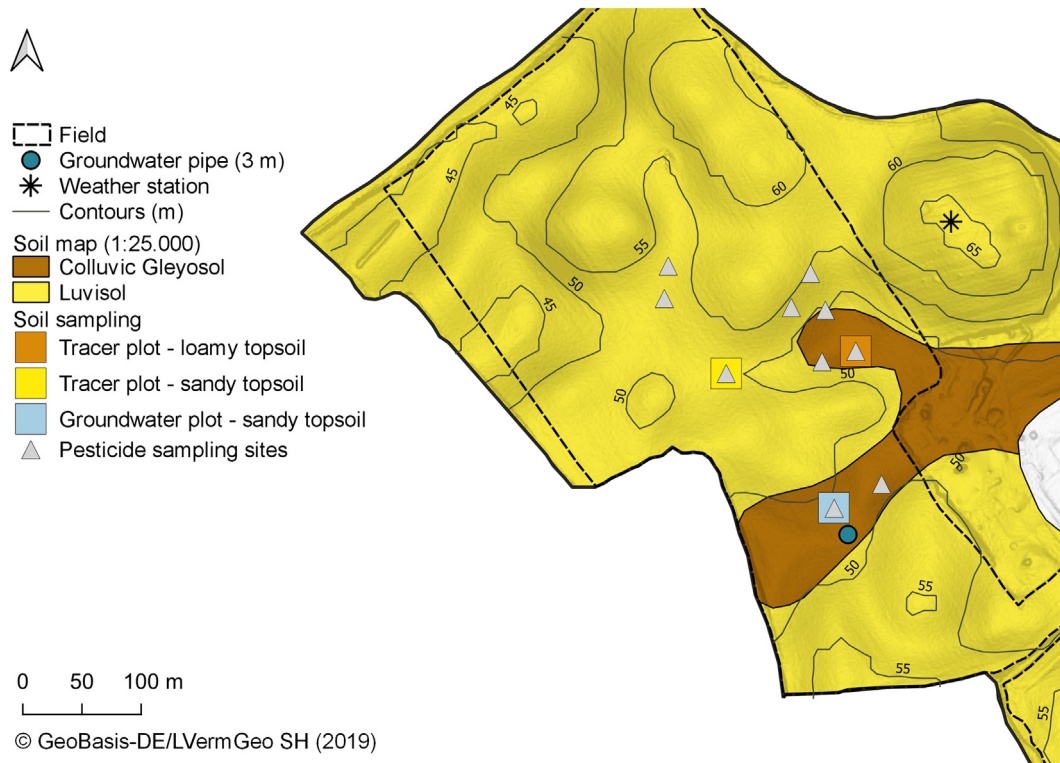


Fig. 1. Location of investigated field with 10 soil sampling sites for mixed pesticide samples in 0–30, 31–60, 61–90 cm (grey triangles). Additionally, two 4 m² large tracer plots and a groundwater plot (squares) are tagged.

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).

2.2. 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) (Table 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 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 (Table 1). The tracer experiment was carried out in the second year during the dry period and lasted until 06th of June 2019 (Table 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 (Table 1). The farmer continued crop rotation and pesticide application according to local practice.

2.3. 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

Table 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.

Sampling design		Wet period	Dry period
Application date	Pesticide	30/10/2017	28/09/2018
Application rate	Tracer		01/10/2018
	Pesticide	Flufenacet: 0.21 kg ha ⁻¹	Flufenacet: 0.20 kg ha ⁻¹
Groundwater monitoring	Tracer		12.5 g m ⁻²
	Pesticide	Monthly	
Soil monitoring	Pesticide	H0: 24/09/2017	H0: 24/09/2018
		H1: 7/11/2017	H1: 16/10/2018
		H2: 19/12/2017	H2: 27/11/2018
	Tracer		T0: 24/09/2018
			T1: 16/10/2018
			T2: 27/11/2018
			T3: 10/04/2019
			T4: 02/05/2019
			T5: 16/05/2019
			T6: 06/06/2019

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 (Table 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).

2.4. Field data and sampling

2.4.1. Precipitation measurements

Precipitation was measured by a tipping bucket rain gauge (Campbell Scientific) in 10-minute resolution located within the catchment (Fig. 1). 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 September 2017 to 23rd September 2018 was labeled as "winter wheat", the second period from 24th of September 2018 to 23rd September 2019 as "winter barley".

2.4.2. Groundwater sampling

A groundwater pipe was installed on the investigated field (Fig. 1), 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.

2.4.3. Sampling in soil

For the pesticide soil sampling, ten soil sites were determined and tagged via coordinates (Fig. 1). 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

Table 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 Gleysol		Luvisol			Colluvic Gleysol		
Layer (cm)	0–30	31–90	0–30	31–60	60–90	0–30	31–60	60–90
<2 μ m clay (%)	3	4	3	3	3	20	10	40
<2–63 μ m silt (%)	23	41	23	23	23	60	20	60
<63–2000 μ m 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

representative average soil samples were obtained by mixing the sub-samples 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 September 2018 to 27th 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 (Table 3). The first soil profile was located at the groundwater plot (Fig. 1) and consisted of a Colluvic Gleysol 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, 30–60 and 60–90 cm were taken at the groundwater plot. The mean saturated hydraulic conductivity was 55.66 ± 40.74 cm d⁻¹ in upper soil, 168 ± 99.57 cm d⁻¹ between 30 and 60 cm and in bottom soil 41 ± 99.57 cm d⁻¹. The soil porosity and bulk density in the upper soil were 46% and 1.56 g cm⁻³, in 30–90 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. 1) had a mild slope of <2%. The soil profile was homogenous with silty sand from 0 cm to 90 cm (Table 3). The tracer plot in Colluvic Gleysol with loamy topsoil (Fig. 1) 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. 2). During the first three sampling dates (Table 3), three soil samples were taken from each tracer plot at 0–30 cm, 30–60 cm, and 60–90 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

Table 2

Properties for pesticides by Lewis et al. (2016), Gupta and Gajbihiye (2002)^a, for tracers by Leibundgut et al. (2009)^b, and Bork et al. (2020)^c.

Properties	Flufenacet	Flufenacet ESA	UR	SRB
Chemical structure	$C_{14}H_{13}F_4N_3O_2S$	$C_{11}H_{14}FNO_4S$	$C_{20}H_{12}O_5$	$C_{27}H_{30}N_2O_7S_2$
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	–		



Fig. 2. Left: Set up of tracer experiment at 4 m² plot equipped with six soil moisture sensors directly after pesticide and tracer application (01/10/2018) and right: winter barley at tracer site (06/06/2019).

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.

2.5. Laboratory methods

2.5.1. 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 ISO 10694:1995, 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. 1), the soil size distribution for 0–30 cm and 31–90 cm was measured using a Mastersizer (Hydro 2000G, 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, −1500, −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).

2.5.2. 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 µg L^{−1} for Flufenacet and 0.025 µg 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 µg 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.

2.5.3. 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. Results and discussion

3.1. 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 Dörnack (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). In the wet period, a high precipitation sum (97 mm) occurred in autumn between 28/09/2017 and 07/10/2017, including a daily maximum of 45 mm at 05/10/2017. 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.

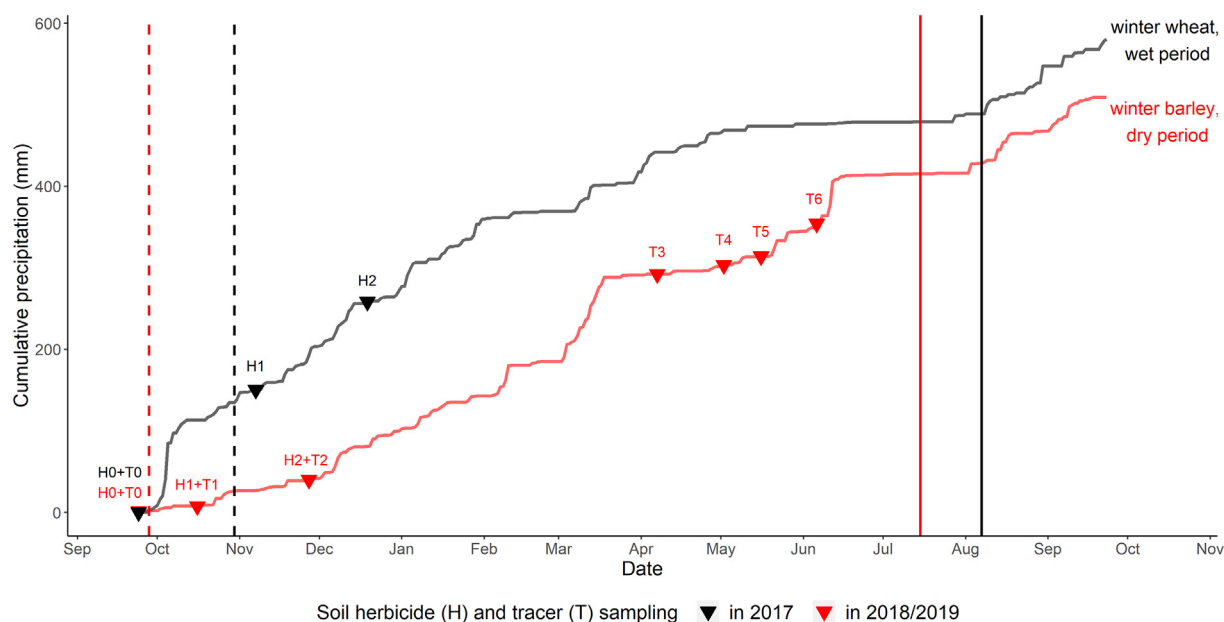


Fig. 3. Dashed black line marks pesticide application dates in 2017 and dashed red line in 2018. The harvest dates are given as a solid black line for winter wheat in 2018 and a solid red line for winter barley in 2019. The soil pesticide (H) and tracer (T) sampling dates are numbered and are also used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

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 18/03/2019 with continuous precipitation not exceeding 16 mm.

3.2. Temporal occurrence in shallow groundwater

The groundwater level was higher before and after pesticide application in the wet than in the dry period ($\phi_{\text{wet}} = 1.36 \pm 0.34$ m, $\phi_{\text{dry}} = 1.8 \pm 0.34$ m below surface, respectively, Fig. 4). 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 (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 3 months after application, with concentrations of $2.92 \mu\text{g L}^{-1}$ in February 2018 (Fig. 4). The slight but constant precipitation from application in October 2017 (Fig. 3) 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. 4). A concentration peak ($1.57 \mu\text{g L}^{-1}$) in shallow groundwater occurred only within 10 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 (Section 2.4.3), 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. 4). Under these conditions, preferential transport of Flufenacet in existing macropores is most likely, since also Zehe and Flüßler (2001) 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 $1.48 \mu\text{g L}^{-1}$.

3.3. Transport pathways in soil

During both seasons, Flufenacet was used at similar application rates which allowed for direct comparisons (Table 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

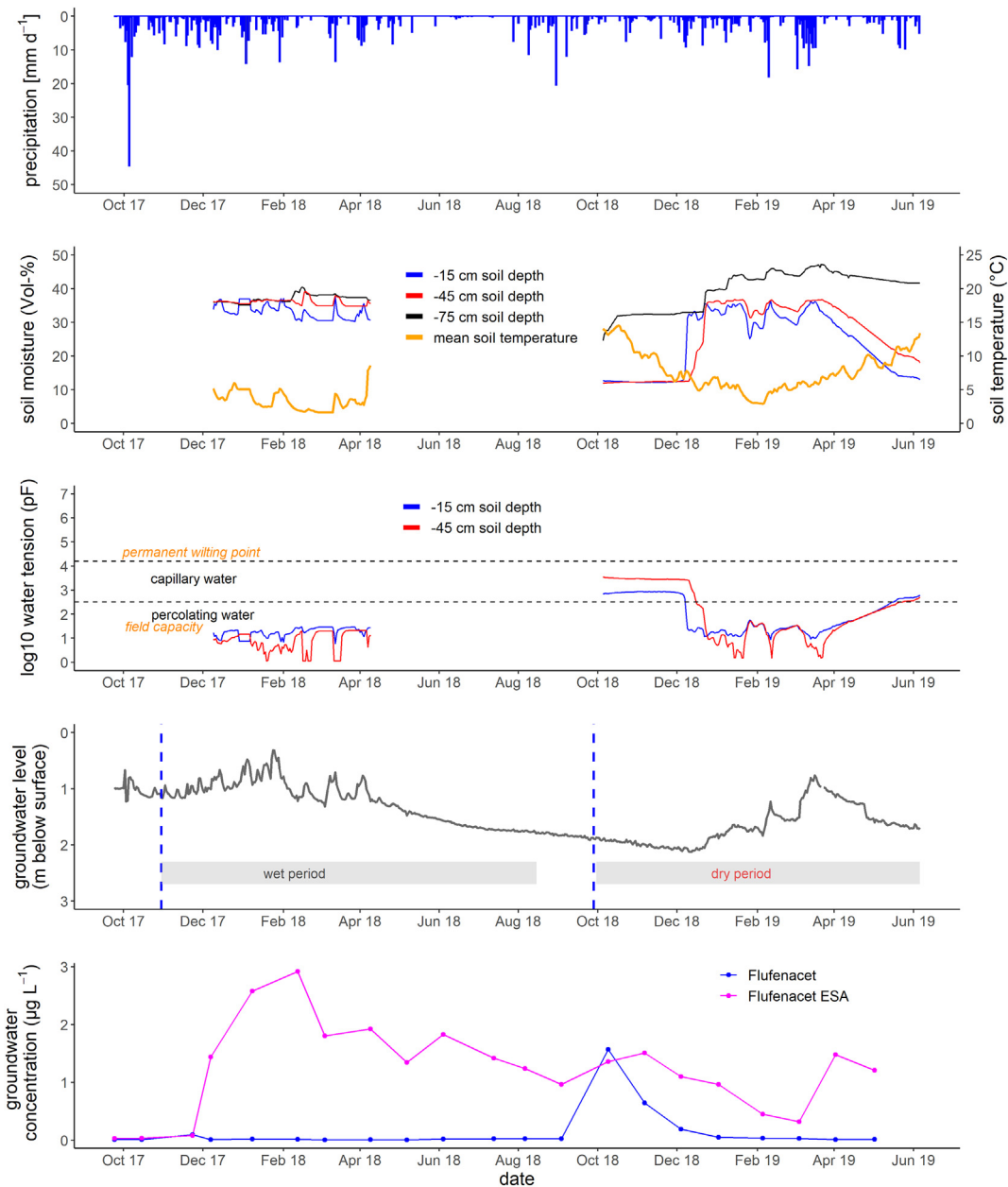


Fig. 4. Monthly groundwater levels, soil moisture, soil temperature, pF value for soil depths at groundwater plot in Colluvic Gleysol with sandy topsoil. Pesticide concentrations in shallow groundwater for wet period and dry period. Flufenacet application dates are marked by dashed blue lines.

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 8 days after application, assuming preferential flow transport with rising soil saturation (Jarvis, 2007). However, the majority of Flufenacet remained in upper soil (Fig. 5b) 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. 5f), which was closely connected to the low groundwater level at that time (Fig. 4). The detection of a single, low Flufenacet concentration in shallow groundwater (Fig. 4) 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 to the observations of Flufenacet in 60 cm soil depth under similar weather conditions by Carpio et al. (2020).

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. 5b,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. wormholes (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).

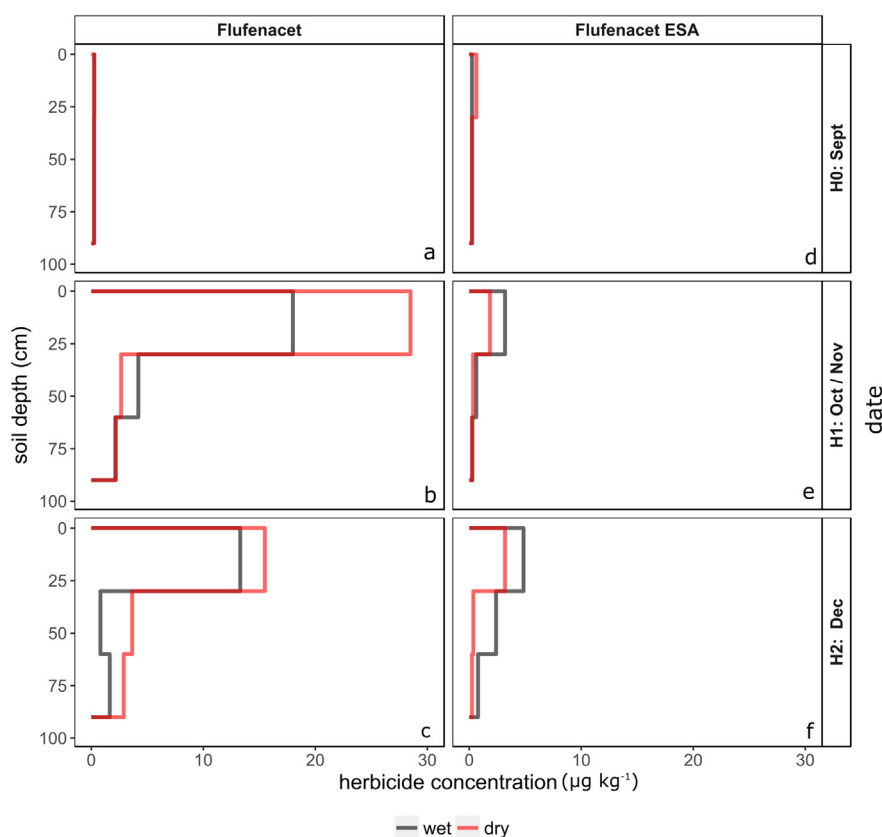


Fig. 5. Comparison of pesticide samples in soil during wet (black line) and dry (red line) period; depth plot of pesticides Flufenacet (a–c) and Flufenacet ESA (d–f) at sampling dates H. Sampling dates are displayed on the 2nd y axis in chronological order.

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. 5e,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. 4). 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. 4). 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 (Table 1, Fig. 5a, 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 (Table 2). Due to the dry spring/summer 2018, residues of Flufenacet ESA (Fig. 5d, $0.64 \mu\text{g L}^{-1}$) were found in upper soil before winter barley application. Flufenacet, which has a half-life time in soil of 39 days (Table 2), was monitored in upper soil with concentrations slightly above LOQ (Fig. 5d, $0.28 \mu\text{g L}^{-1}$). 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 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.

3.4. 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. 1, Table 3). Immediately after tracer application at dry conditions (14% soil moisture, Fig. 4), 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 Gleysol 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 Gajbiye, 2002). However, the data showed the opposite, since in sandy topsoil (Fig. 6i, 0–30 cm) a much higher share of substances was retained than in loamy topsoil (Fig. 6b, 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 (Table 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. 6b, i). Apparently, leaching of the tracers was triggered by low precipitation as observed for the fast-preferential leaching of Flufenacet (Section 3.3). Yet, a fraction of both tracers remained in the upper soil (0–15 cm) of both plots until the end of monitoring (Fig. 6g, 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. 6, 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. 6, 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. 6q, x, 0–30 cm) starting 57 days after application until spring 2019. The dry topsoil directly after application (14% soil moisture and $pH \sim 3$, Fig. 4) 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. 4).

The maximum TP510 intensities in deeper soil were first detected at the beginning of May (Fig. 6s, z). By then, an intense precipitation period in March (Fig. 3) had increased moisture content and hydrological connectivity in the soil matrix, which facilitated downward percolation (Fig. 4). Pallud et al. (2004) established a relationship between a higher microbial mobility and an increased access to the target substances at higher soil moisture. 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. 4) 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 (Figs. 4, 6u, 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 $10^\circ C$ (Barriuso et al., 2008; Marín-Benito et al., 2019) and increased microbial activity. A close carbon-to-nitrogen ratio ($CN < 15$, Fig. 7) 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. 7). 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. 7). Hence, the tracers demonstrated that living

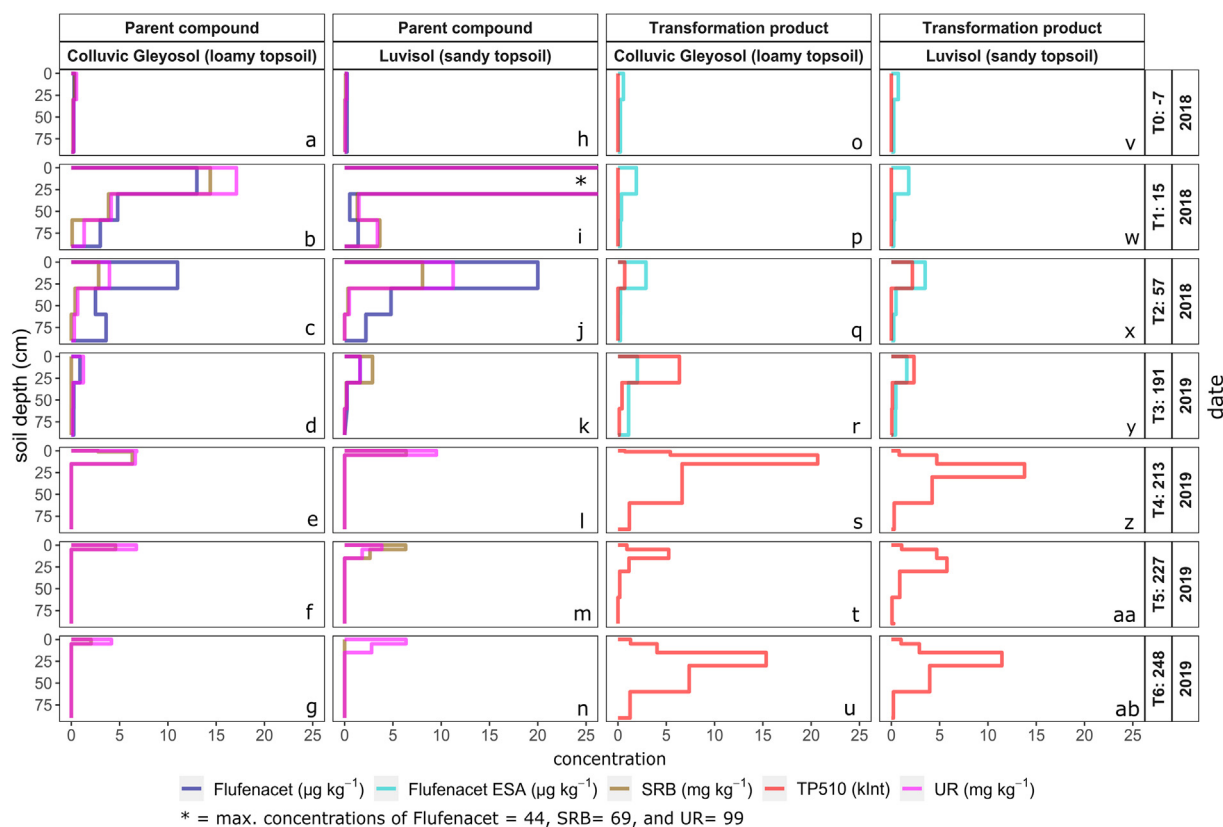


Fig. 6. Comparison of pesticide and tracer parent compounds (a–n), Flufenacet, SRB, UR and transformation products (o–ab) Flufenacet ESA, TP510 in two soil types; sampling dates T1–T6: with number of days after application (see Table 1) are displayed on the 2nd y axis in chronological order.

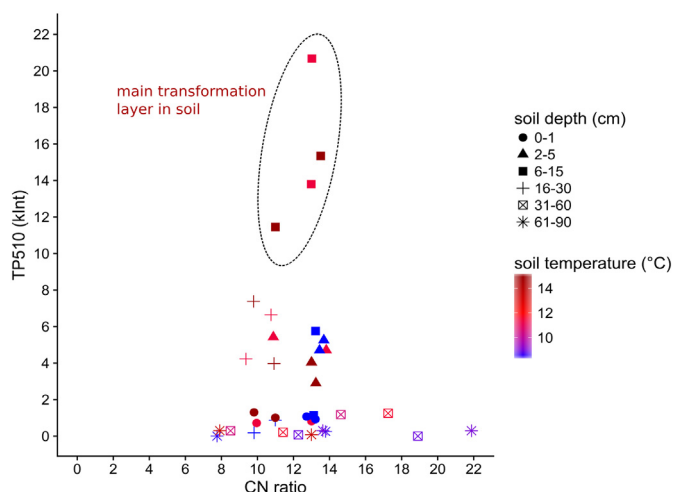


Fig. 7. CN-ratio in relation to TP510 intensity, soil depth and soil temperature for sampling dates T4-T6. The black dashed circle marks the main transformation layer in soil.

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. 6s, 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. 6t, aa). Then soil temperatures were low (Fig. 4) and apparently retarded transformation processes. With higher soil temperatures in June, TP510 intensities increased again (Fig. 6u, 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. 8). 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/Mai 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 in-situ proxy for the intensity of the biochemical transformation of acetamide herbicides. 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

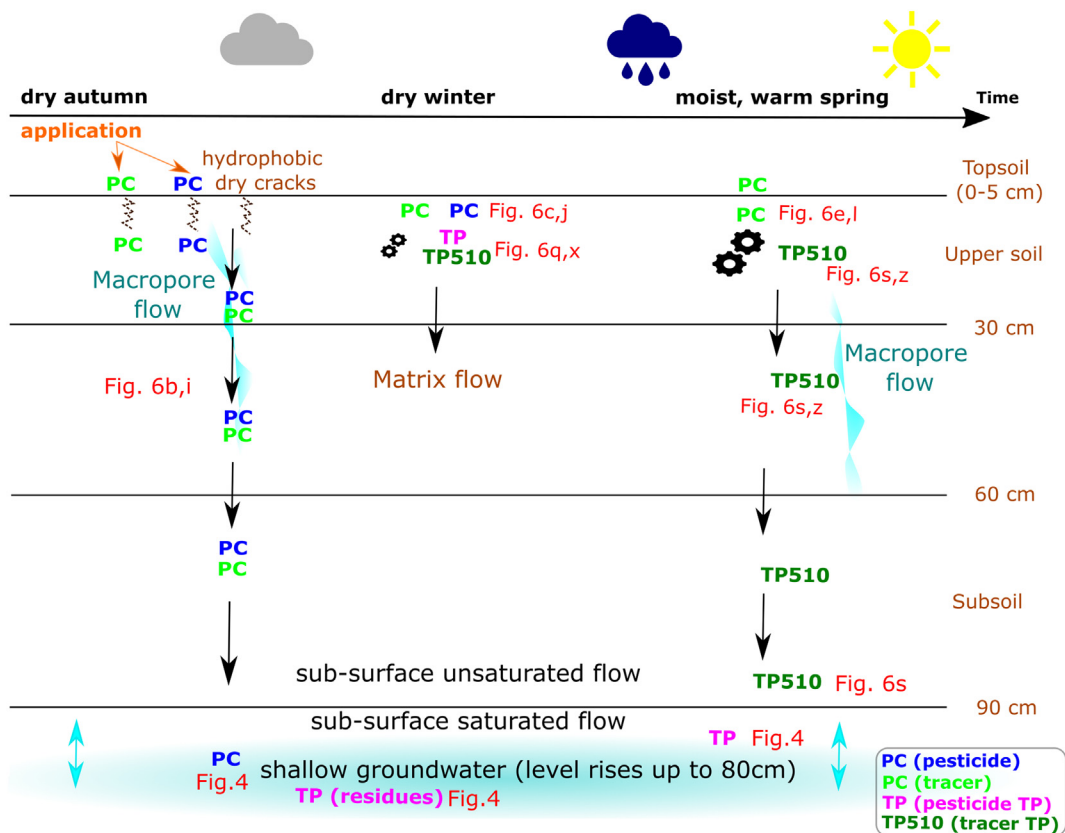


Fig. 8. Conceptual model for the behaviour of parent compounds (PC) and transformation products (TP) in soil during a dry period followed by a wet spring. Red labels are explicit references to other figures.

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.

4. 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 ($1.48\text{ }\mu\text{g L}^{-1}$) 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 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.

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.

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.

Acknowledgments

BASF SE's Agricultural Center in Limburgerhof supported the cooperation project with funding. We are thankful to the BASF SE's Agricultural Center in Limburgerhof for the fruitful discussions, especially with Folkert Bauer, in our cooperation project. There exists no interest or belief that the financial support could affect the objectivity. BASF SE's Agricultural Center in Limburgerhof was involved in the study design. Additionally, we thank Frank Schumacher for providing his farm, Ferienhof Radlandsichten, and his active support during the investigations of the working group Hydrology and Water Resources Management of Kiel University. Furthermore, we are very grateful to Christina Radtke, Falko Torreck, Simon Pfeifer and Siri Neuner for assisting in field. We thank Birte Kretschmer and Monika Westphal for laboratory support. We thank Benjamin L. Sluckin, and Katja Mroos for proofreading and providing linguistic support.

References

- Ad-hoc-Arbeitsgruppe Boden (Hg.). 2005. Manual of Soil Mapping. Bodenkundliche Kartieranleitung (KA5). Mit 103 Tabellen und 31 Listen. Ad-hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe; Bundesanstalt für Geowissenschaften und Rohstoffe. 5. Aufl. E. Schweizerbart'sche Verlagsbuchhandlung (Nägele und Obermiller), Stuttgart.
- Babey, T., Vieublé-Gonod, L., Rapaport, A., Pinheiro, M., Garnier, P., De Dreuzy, J.-R., 2017. Spatiotemporal simulations of 2,4-D pesticide degradation by microorganisms in 3D soil-core experiments. *Ecol. Model.* 344, 48–61. <https://doi.org/10.1016/j.ecolmodel.2016.11.006>.
- Barriuso, E., Koskinen, W.C., Sadowsky, M.J., 2004. Solvent extraction characterization of bioavailability of atrazine residues in soils. *J. Agric. Food Chem.* 52 (21), 6552–6556. <https://doi.org/10.1021/jf040245l>.
- Barriuso, E., Benoit, P., Dubus, I.G., 2008. Formation of pesticide nonextractable (bound) residues in soil: magnitude, controlling factors and reversibility. *Environ. Sci. Technol.* 42 (6), 1845–1854.
- Bork, M., Lange, J., Graf-Rosenfellner, M., Lang, F., 2020. Controls of fluorescent tracer retention by soils and sediments. *Hydrol. Earth Syst. Sci. Discuss.*, 1–24 <https://doi.org/10.5194/hess-2019-229>.
- Brown, C.D., Hollis, J.M., Bettinson, R.J., Walker, A., 2000. Leaching of pesticides and a bromide tracer through lysimeters from five contrasting soils. *Pest Manag. Sci.* 56 (1), 83–93. [https://doi.org/10.1002/\(SICI\)1526-4998\(200001\)56:1<83::AID-PS98>3.0.CO;2-8](https://doi.org/10.1002/(SICI)1526-4998(200001)56:1<83::AID-PS98>3.0.CO;2-8).
- Carpio, María J., Rodríguez-Cruz, M. Sonia, García-Delgado, Carlos, Sánchez-Martín, María J., Marín-Benito, Jesús M., 2020. Mobility monitoring of two herbicides in amended soils: a field study for modeling applications. *J. Environ. Manag.* 260, 110161. <https://doi.org/10.1016/j.jenvman.2020.110161>.
- Climate Data Center, 2018. Weather Glossary. https://www.dwd.de/DE/service/lexikon/lexikon_node.html.
- Climate Data Center, 2019. Historical daily station observations (temperature, pressure, precipitation, sunshine duration, etc.) for Germany: daily precipitation data of Dörnick (station: 06163). version v006. https://opendata.dwd.de/climate_environment/CDC/observations_germany/climate/daily/kl/.
- Demand, D., Blume, T., Weiler, M., 2019. Spatio-temporal relevance and controls of preferential flow at the landscape scale. *Hydrol. Earth Syst. Sci.* 23 (11), 4869–4889.
- Dudley, N., Attwood, S.J., Goulson, D., Jarvis, D., Bharucha, Z.P., Pretty, J., 2017. How should conservationists respond to pesticides as a driver of biodiversity loss in agroecosystems? *Biol. Conserv.* 209, 449–453.
- ECHA, 2017. European Chemicals Agency. Guidance on Information Requirements and Chemical Safety Assessment, ECHA, Chapter R.11: PRT/vPvB Assessment.
- EFSA, 2007. Opinion on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil ‐2010.

- Scientific Opinion of the Panel on Plant Protection Products and Their Residues (PPR Panel). vol. 622, pp. 1–32.
- EFSA, 2009. Draft Renewal Assessment Report Prepared According to the Commission Regulation (EU) N° 1107/2009, Volume 1, Level 3. , p. 87. <http://www.efsa.europa.eu/en/consultations/call/170920>.
- Fenner, K., Canonica, S., Wackett, L.P., Elsner, M., 2013. Evaluating pesticide degradation in the environment: blind spots and emerging opportunities. *Science* (New York, N.Y.) 341 (6147), 752–758.
- Fernández-Pascual, E., Zaman, S., Bork, M., Lang, F., Lange, J., 2019. Long-term mesocosm experiments to investigate degradation of fluorescent tracers. *Journal of Hydrology X* 2, 100014.
- Fernández-Pascual, E., Bork, M., Hensen, B., Lange, J., 2020. Hydrological tracers for assessing transport and dissipation processes of pesticides in a model constructed wetland system. *Hydrol. Earth Syst. Sci.* 24 (1), 41–60. <https://doi.org/10.5194/hess-24-41-2020>.
- Flury, M., Wai, N.N., 2003. Dyes as tracers for vadose zone hydrology. *Rev. Geophys.* 41 (1), 66.
- García-Delgado, C., Barba-Vicente, V., Marín-Benito, J.M., Mariano Igual, J., Sánchez-Martín, M.J., Sonia Rodríguez-Cruz, M., 2019. Influence of different agricultural management practices on soil microbial community over dissipation time of two herbicides. *Sci. Total Environ.* 646, 1478–1488.
- Gaziz, C., Feng, X., 2004. A stable isotope study of soil water. Evidence for mixing and preferential flow paths. *Geoderma* 119 (1–2), 97–111. [https://doi.org/10.1016/S0016-7061\(03\)00243-X](https://doi.org/10.1016/S0016-7061(03)00243-X).
- German Environmental Agency, 2020. https://www.umweltbundesamt.de/sites/default/files/medien/421/dokumente/liste_der_bewerteten_nrm_2020-05.pdf Umweltbundesamt.
- Gimsing, A.L., Agert, J., Baran, N., Boivin, A., Ferrari, F., Gibson, R., 2019. Conducting groundwater monitoring studies in Europe for pesticide active substances and their metabolites in the context of regulation (EC) 1107/2009. In: *J. Consum Prot Food Saf* 14 (S1), S. 1–93. <https://doi.org/10.1007/s00003-019-01211-x>.
- Gisi, U., 1997. *Soil Ecology. Bodenökologie*. Stuttgart. G. Thieme.
- Goulson, D., Nicholls, E., Botias, C., Rotheray, E.L., 2015. Bee declines driven by combined stress from parasites, pesticides, and lack of flowers. *Science* (New York, N.Y.) 347 (6229).
- Gupta, S., Gajbhiye, V.T., 2002. Effect of concentration, moisture and soil type on the dissipation of flufenacet from soil. *Chemosphere* 47, 901–906.
- Gutowski, L., Olsson, O., Lange, J., Kümmerer, K., 2015. Photolytic transformation products and biological stability of the hydrological tracer Uranine. *Sci. Total Environ.* 533, 446–453. <https://doi.org/10.1016/j.scitotenv.2015.07.002>.
- Hartge, K.H., 1966. Ein Haubenpermeameter zum schnellen Durchmessen zahlreicher Stechzylinderproben. A hood permeameter for fast measurement of various soil sampling rings. *Z. f. Kulturtechn. u. Flurb. vol. 7*, pp. 155–163.
- Huseth, A.S., Groves, R.L., 2014. Environmental fate of soil applied neonicotinoid insecticides in an irrigated potato agroecosystem. *PLoS One* 9 (5), e97081.
- Jarvis, N.J., 2007. A review of non-equilibrium water flow and solute transport in soil macropores. Principles, controlling factors and consequences for water quality. *Eur. J. Soil Sci.* 58 (3), 523–546. <https://doi.org/10.1111/j.1365-2389.2007.00915.x>.
- Käss, W., Behrens, H., Matthess, G., 2004. *Geohydrologische Markierungstechnik: Mit 43 Tabellen, 2., überarb. Aufl. ed. Lehrbuch der Hydrogeologie/hrs. von Georg Matthess; Bd. Borntraeger, Berlin*, p. 9.
- Kjær, J., Rosenbom, A.E., Brüsch, W., Juhler, R.K., Gudmundsson, L., Plauborg, F., Grant, R., Olsen, P., 2011. The Danish Pesticide Leaching Assessment Programme: monitoring results, May 1999–June 2010. Geological Survey of Denmark and Greenland.
- Klaus, J., Zehe, E., Elsner, M., Külls, C., McDonnell, J.J., 2013. Macropore flow of old water revisited. experimental insights from a tile-drained hillslope. *Hydrol. Earth Syst. Sci.* 17 (1), 103–118. <https://doi.org/10.5194/hess-17-103-2013>.
- Klaus, J., Zehe, E., Elsner, M., Palm, J., Schneider, D., Schröder, B., Steinbeiss, S., van Schaik, L., West, S., 2014. Controls of event-based pesticide leaching in natural soils: a systematic study based on replicated field scale irrigation experiments. *J. Hydrol.* 512, 528–539.
- Lange, J., Olsson, O., Sweeney, B., Herbstritt, B., Reich, M., Alvarez-Zaldívar, P., Payraudeau, S., Imfeld, G., 2018. Fluorescent tracers to evaluate pesticide dissipation and transformation in agricultural soils. *Sci. Total Environ.* 619–620, 1682–1689.
- Leibundgut, C., Maloszewski, P., Külls, C., Leibundgut, C., Maloszewski, P., Kils, C., 2009. *Tracers in Hydrology*. Wiley; John Wiley & Sons, Ltd, Chichester.
- Levy, W., Radl, V., Ruth, B., Schmid, M., Munch, J.C., Schroll, R., 2007. Harsh summer conditions caused structural and specific functional changes of microbial communities in an arable soil. *Eur. J. Soil Sci.* 58 (3), 736–745.
- Lewis, K.A., Tziliavakis, J., Warner, D., Green, A., 2016. An international database for pesticide risk assessments and management. *Human and Ecological Risk Assessment: An International Journal* 22 (4), 1050–1064.
- Maillard, E., Lange, J., Schreiber, S., Dollinger, J., Herbstritt, B., Millet, M., Imfeld, G., 2016. Dissipation of hydrological tracers and the herbicide S-metolachlor in batch and continuous-flow wetlands. *Chemosphere* 144, 2489–2496.
- Marín-Benito, J.M., Carpio, M.J., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2019. Previous degradation study of two herbicides to simulate their fate in a sandy loam soil: effect of the temperature and the organic amendments. *Sci. Total Environ.* 653, 1301–1310.
- McMahon, P., Dennehy, K.F., Michel, R.L., Sophocleous, M.A., Ellett, K.M., Hurlbut, D.B., 2003. Water movement through thick unsaturated zones overlying the central highplains aquifer, southwestern Kansas, 2000–2001. *Water Resour. Invest. Rep. U.S. Geol. Surv.* (03-4171, U.S. Dept. of the Interior, USGS).
- Milan, M., Ferrero, A., Fogliatto, S., Piano, S., Vidotto, F., 2015. Leaching of S-metolachlor, terbuthylazine, desethyl-terbuthylazine, mesotrione, flufenacet, isoxaflutole, and diketonitrile in field lysimeters as affected by the time elapsed between spraying and first leaching event. *J. Environ. Sci. Health B* 50 (12), 851–861. <https://doi.org/10.1080/03601234.2015.1062650>.
- Morales, V.L., Parlange, J.-Y., Steenhuis, T.S., 2010. Are preferential flow paths perpetuated by microbial activity in the soil matrix? A review. *J. Hydrol.* 393 (1–2), 29–36. <https://doi.org/10.1016/j.jhydrol.2009.12.048>.
- Novohatska, O., Stavnichenko, P., Kondratiuk, M., Antonenko, A., Vavrinevich, O., Omelchuk, S., Bardov, V., 2018. Comparative hygienic evaluation of behavior of different pesticides groups in soil, prediction of risk of ground water contamination and its danger for human health in areas with irrigation farming. In: *Rawal Medical Journal* 43 (1), 129–136 S.
- Pallud, C., Decesne, A., Gaudet, J.P., Debouzie, D., Grundmann, G.L., 2004. Modification of spatial distribution of 2,4-dichlorophenoxyacetic acid degrader microhabitats during growth in soil columns. *Appl. Environ. Microbiol.* 70 (5), 2709–2716. <https://doi.org/10.1128/AEM.70.5.2709-2716.2004>.
- Reemtsma, T., Alder, L., Banasiak, U., 2013. Emerging pesticide metabolites in groundwater and surface water as determined by the application of a multimethod for 150 pesticide metabolites. *Water Res.* 47 (15), 5535–5545.
- Renshaw, X.F., Kelsey, J.S., Raymond, H.D., 2003. The use of stream flow routing for direct channel precipitation with isotopically-based hydrograph separations: the role of new water in stormflow generation. *J. Hydrol.* 273, 205–216.
- Ritsem, C.J., Dekker, L.W., 2000. Preferential flow in water repellent sandy soils: principles and modeling implications. In: *J. Hydrol.* 231–232, 308–319 S.
- Rosenbom, A.E., Binning, P.J., Aamand, J., Decesne, A., Smets, B.F., Johnsen, A.R., 2014. Does microbial centimeter-scale heterogeneity impact MCPA degradation in and leaching from a loamy agricultural soil? *Sci. Total Environ.* 472, 90–98. <https://doi.org/10.1016/j.scitotenv.2013.11.009>.
- Rosenbom, A.E., Olsen, P., Plauborg, F., Grant, R., Juhler, R.K., Brüsch, W., Kjær, J., 2015. Pesticide leaching through sandy and loamy fields - long-term lessons learnt from the Danish Pesticide Leaching Assessment Programme. *Environmental pollution* (Barking, Essex: 1987) 201, 75–90.
- Rouchaud, J., Neus, O., Cools, K., Bulcke, R., 1999. Flufenacet soil persistence and mobility in corn and wheat crops. *Bull. Environ. Contam. Toxicol.* 63, 460–466.
- Rouchaud, J., Neus, O., Eelen, H., Bulcke, R., 2001. Persistence, mobility, and adsorption of the herbicide flufenacet in the soil of winter wheat crops. *Bull. Environ. Contam. Toxicol.* 67 (4), 609–616. <https://doi.org/10.1007/s00128-001-0167-y>.
- Schroll, R., Becher, H.H., Dörfler, U., Gayler, S., Grundmann, S., Hartmann, H.P., Ruoss, J., 2006. Quantifying the effect of soil moisture on the aerobic microbial mineralization of selected pesticides in different soils. *Environ. Sci. Technol.* 40 (10), 3305–3312. <https://doi.org/10.1021/es052205j>.
- Swartjes, F.A., Van der Aa, M., 2020. Measures to reduce pesticides leaching into groundwater-based drinking water resources: an appeal to national and local governments, water boards and farmers. *Sci. Total Environ.* 699.
- Ulrich, U., Hörmann, G., Unger, M., Pfannerstill, M., Steinmann, F., Fohrer, N., 2018. Lentic small water bodies: variability of pesticide transport and transformation patterns. *Sci. Total Environ.* 618, 26–38.
- Ulrich, U., Lange, J., Pfannerstill, M., Loose, L., Fohrer, N., 2019. Hydrological tracers, the herbicide metazachlor and its transformation products in a retention pond during transient flow conditions. *Environ. Sci. Pollut. Res. Int.* 26 (26), 26706–26720.
- United States Environmental Protection Agency (USEPA), 1998. *Pesticide Fact Sheet – Flufenacet*. USEPA, Washington, DC.
- Van Genuchten, M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44, 892–898.
- Van Genuchten, M.Th., Leij, F.J., Yates, S.R., 1991. *The RETC Code for Quantifying the Hydraulic Functions of Unsaturated Soils*. Version. U.S. Salinity Laboratory, U.S. Department of Agriculture, Agricultural Research Service, California.
- Vogel, L.E., Makowski, D., Garnier, P., Vieublé-Gonod, L., Coquet, Y., Raynaud, X., 2015. Modeling the effect of soil meso- and macropores topology on the biodegradation of a soluble carbon substrate. *Adv. Water Resour.* 83, 123–136. <https://doi.org/10.1016/j.advwatres.2015.05.020>.
- Vryzas, Z., 2018. Pesticide fate in soil-sediment-water environment in relation to contamination preventing actions. *Current Opinion in Environmental Science & Health* 4, 5–9.
- Vryzas, Z., Papadopoulou-Mourkidou, E., 2007. Kinetics and adsorption of metolachlor and atrazine and the conversion products (deethylatrazine, deisopropylatrazine, hydroxyatrazine) in the soil profile of a river basin. *Eur. J. Soil Sci.* 58 (5), 1186–1199.
- Vryzas, Z., Papadakis, E.N., Oriakli, K., Moysiadias, T.P., Papadopoulou-Mourkidou, E., 2012. Biotransformation of atrazine and metolachlor within soil profile and changes in microbial communities. *Chemosphere* 89 (11), 1330–1338.
- 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. *Agric. Ecosyst. Environ.* 278, 107–116.
- Zehe, E., Flüher, H., 2001. Slope scale variation of flow patterns in soil profiles. *J. Hydrol.* 247 (1–2), 116–132. [https://doi.org/10.1016/S0022-1694\(01\)00371-7](https://doi.org/10.1016/S0022-1694(01)00371-7).