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Pesticide contamination of the upper Elbe River and an adjacent floodplain area

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Abstract

Purpose Pesticide contamination of river waters is a global problem, and therefore, authorities regularly monitor the water quality status. Especially, flood events might transport large pesticide loads downstream and impact adjacent areas such as sensible floodplain environments by deposing particle bound pesticides or by contaminating the environments by dissolved substances directly. Unfortunately, only little attempts were made to quantify the pesticide pollution of such environments, as the monitoring of soil and sediment contamination is by far more time consuming and complicated compared to the analysis of water samples.

Materials and methods In the study presented, we therefore used a holistic approach starting with the reconstruction of the inundation characteristics of a floodplain located in the upper part of the river Elbe, Germany, by using nearby gauging data, screened databases for pesticide concentrations and calculated pesticide loads, and finally, sampled the floodplain soils along an elevation (inundation) gradient.

Results As expected, the reconstructed inundation characteristics showed that the low-lying areas of the backwater inflow of the floodplain were flooded more frequently compared to the areas at higher elevation, whereby even the highest elevations sampled were at least flooded during each decade. Furthermore, pesticide concentrations of the river waters and calculated pesticide loads revealed that 13 pesticides can be found regularly, whereby atrazine, terbuthylazine, metazachlor, metolachlor, isoproturon, and chlorotoluron are the main contaminants.

Conclusion Concluding, a spatial pattern in the contamination could be detected. High residues of simazine and ethofumesate were associated with areas of less and more frequent inundations, respectively. The transformation products of atrazine and terbuthylazine (2-hydroxy-atrazine and 2-hydroxy-terbuthylazine) were detected, whereby the quantity could be well explained by the inundation characteristics and pesticide loads of the river water.

Keywords Floodplain soil · Pesticide · Contamination · Simazine · Ethofumesate · 2-Hydroxy-atrazine · 2-Hydroxy-terbuthylazine · Metazachlor · Metolachlor · Isoproturon · Chlorotoluron

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1 Introduction

The use of pesticides revolutionized the global crop production for a growing world population substantially (Liu et al. 2015). In Germany, the amount of active ingredients of the pesticides applied totaled 31,200 tons in 2016, of which 57% were herbicides, 40% fungicides and bactericides, and only 3% insecticides (FAOSTAT 2017). Nowadays, a wide range of pesticides can be found not only in the areas of use, such as agricultural sites and urban areas, but ubiquitously in all environmental compartments such as soils (e.g., Scherr et al. 2017), surface, and ground waters (e.g., Moschet et al. 2014).

Pesticides enter the riverine system either as particle bound, if the substances are sorbed to the topsoil and eroded and transported via surface-runoff, dissolved via drainage and the groundwater, or directly via spray-drift (Schulz 2004; Topaz et al. 2018). The transport pathways for the particle bound or dissolved transport depend on the physico-chemical properties of the substances, time of pesticide application, and the characteristics of the catchment (e.g., soils, land management) (Larson et al. 1995; Pérez et al. 2017). Once, entered the stream, the pesticide load dynamics is affected by the partitioning between the dissolved and the adsorbed phases, whereby some pesticides tend to bind to the suspended sediments and are transported as particulate-bound pollutants, whereas others are more stable in their dissolved phase (Chapman et al. 2013; Birch et al. 2015; Carpenter et al. 2016). Unfortunately, the portion and fate of sediment bound pesticides transported in river systems, especially during flood events, have not been studied well in the past, as chemical analysis of the liquid phase is much simpler especially for monitoring purposes (e.g., Topaz et al. 2018). Finally, the particle-bound (attached or absorbed) pesticides can be sedimented in floodplains, where they can remain during normal discharge conditions until the next flood event or even stored over decades (Gasith and Resh 1999).

Field pesticide inventory studies in arable soils are reported for various areas worldwide such as Spain (e.g., Plaza-Bolanos et al. 2012), Korea (e.g., Park et al. 2013), India (Sharma et al. 2014), or Kenya (Ndunda et al. 2018). For floodplain soil on the other hand, data are scarce (Witter et al. 2003; Fikarova et al. 2018; Skála et al. 2018).

Regarding the number of investigated pesticides in different monitoring or screening studies, it becomes apparent that studies focusing on water contamination (e.g., Wode et al. 2012; Reemtsma et al. 2013; Moschet et al. 2014; Fairbairn et al. 2016) generally study a broader range of compounds compared to those studies focusing on soils (Lesueur et al. 2008; Schreck et al. 2008; Homazava et al. 2014) if they do not even restrict their analysis only to one substance class only (Di et al. 2015). This concentration of analyzing surface waters (stream waters) is motivated by public and political concern of the status of water bodies as well as by regulations such as the European Council Directive (98/83/EC) and the German Drinking Water Ordinance (*Trinkwasserverordnung*), which sets threshold values for pesticides. Accordingly, the compliance with these thresholds is monitored regularly. However, this process excludes the (floodplain) soil from the monitoring programs even if pesticide pollution of soils might cause serious environmental problem, as soils may act as sink or even reservoirs for pesticides and, therefore, might pose a threat to the ecosystems (Vidal et al. 2010). The water quality in the Elbe River system in Germany in the late 1980s was so poor that for the German water quality map of 1990, an additional eighth category had to be included exclusively for the Elbe River (Schwartz et al. 2015).

Sources for this pollution were the heavily industrialized as well as urbanized areas within the Elbe catchment releasing various pollutants from numerous sources into the waterbody, particularly in times before the reunification of Germany in 1990 (Heise 2015). In general, the Elbe River system is characterized by around 1000 backwaters covering an area of altogether 50 km^2, which frequently inundate during flood events. These branch structures are relicts of river training by stream straightening or were formed by historical flooding events. Whenever these structures are inundated, contaminated sediments from the river are likely to be long-term deposited. Moreover, subject to the connection to the main stream, the backwater morphology, its use, as well as the frequency of flooding, small scale variation of pollution clusters are detectable (Heise 2015).

Once the contaminated sediments are deposited in the floodplain, the polluted sediments can be immobilized as the vegetation covers the sediment layers (Witter et al. 1998). These contaminations can vary on a regional scale, depending on inundation frequencies and soil properties as well as specific pesticide loads in the water. Witter et al. (2003) analyzed various organic pollutants in floodplain soil profiles in the Elbe River system and discovered small scale depth variations between sampling points and among the regarded compounds, whereby two closely associated soil profiles show opposite concentration patterns of chlorinated hydrocarbons. Other studies also found various persistent organic pollutants (POPs) in floodplain soils of the Elbe River, whereby some of the "historical" POP contaminants were already buried deeper in the soil profile (e.g., Kiersch et al. 2010). Even if there is good knowledge about historically used pesticides and POP concentrations in the Elbe River floodplain soils, only little is known about currently used pesticides. Therefore, the aim of this study was to analyze the pesticide concentrations and loads in the Elbe River water from a historical perspective and the pesticide residues in an adjacent floodplain soil using multiple-residue pesticide screening, in order to compile an inventory of recent pesticide residues. Due to the landscape character of the sampling area, with small plateaus and depressions, further focus was directed to the flooding characteristics and the spatial pesticide residue distribution. We therefore hypothesize that the pesticides detected in the river water samples are also abundant in the floodplain soil samples and that the inundation frequencies in the area will be reflected in the spatial distribution of the pesticides residues.

2 Materials and methods

2.1 River Elbe

With a total length of 1094 km, from its source in the Sudeten Mountains or Giant Mountains, Czech Republic, to the North

Sea at Cuxhaven, Germany, the Elbe is one of Europe's major rivers. In total, the catchment covers an area of 148,268 km^2, located with 65.5% in Germany, 33.7% in the Czech Republic, and 0.2% and 0.6% in Poland and Austria, respectively. The Elbe River catchment is located in the climatic transition zone of the humid oceanic climate of Western Europe to the dry-continental climate of Eastern Europe. While 50% of the catchment area is below 200 m a.s.l. in the lowlands of Northern Germany, 30% of the catchment located in Germany exceeds elevations higher than 400 m a.s.l. Moreover, elevations > 400 m a.s.l occur for 75% of the catchment located in the Czech Republic. Especially, these parts are of uppermost importance for the development of flood events. The average precipitation in the catchment is 628 mm with more than 60% of the average annual discharge recorded during the winter. In general, there are three different flooding events characteristic for the Elbe River system: (i) winter or early spring flooding events caused by snowmelt, particularly at the low mountain range areas, whereby these events mainly cause flooding on a local scale; (ii) flood events in spring or winter when heavy precipitation accompanied by a simultaneous snowmelt event; or (iii) summer floods caused by heavy and long lasting large scale rainfall events, which are typically occur when subtropical warm and humid air masses are introduced from southwestern direction (Heise et al. 2007).

The floodplains or inundation areas (60,000 ha without tidal influence) along the river are part of a heterogeneous cultural landscape representing a habitat for a unique fauna and flora but also serve as important agricultural production sites (Krüger et al. 2015). A large proportion of the floodplains are located in the middle part of the Middle Elbe River (Büchele et al. 2002), where grasslands and pastures are the most common land use types.

2.1.1 Sampling site Elsnig

The floodplain sampling site *Elsnig* at river kilometer 167 is located between the *Torgau* gauge station at river kilometer 154.2 and the water quality measurement station *Dommitzsch, links* at river kilometer 172.6. The area and the surroundings belong to the community of *Elsnig*, adjacent to the small village of *Drebligar* in Saxony, about 70 km north-easterly of Leipzig in the East of Germany (LfULG Saxony 2015). As a result of straightening measures in 1850, the stream course of the Elbe at *Elsnig* was changed and shortened about 2.8 km (Simon 2010). The remains of the original course form a backwater, which is partly connected to the main course. The floodplain itself is used as grassland or arable land, whereas the backwater inflow is a designated landscape protection area.

Soil samples were collected in April 2016 within three major parts of the *Elsnig* floodplain with 4 samples per

landscape unit, (i) the inflow of the backwater (samples denoted by *BI*), (ii) small-scale depressions (samples denoted by *SD*), and (iii) the plateaus at the main floodplain area (samples denoted by *P*). Additionally, following the morphology of the inflow trench, the sampling points at the inflow were subdivided into three elevation levels. Therefore, the notation in the following is BI*x-y*, where *x* denotes the sample point and *y* the elevation (b = bottom, m = medium, and t = top). Sampling points of the small-scale depressions and plateaus were chosen after field survey, whereby apparent differences in elevation of the area guided the sampling. A schematic overview of the local conditions at the sampling site is provided in Fig. 1. At each sampling point, four undisturbed soil cores using a HUMAX auger (Martin Burch AG, Rothenburg, Switzerland) from 0 to 30 cm depth and one disturbed composite sample were collected. All samples were cooled, transported, and stored at + 4 °C in the dark before further analysis. For soil analysis, soil samples were air-dried to a water content < 10%, ground for homogenization, and finally sieved to 2 mm.

2.2 Soil physico-chemical analysis

The textures of all composite soil samples from each sampling location were determined using a combination of wet sieving and the pipette method. Note, that sand is the fraction between 2 mm and 63 μm according to the FOA classification. The soil was determined to an Arenic Fluvisol (WRB 2015). The pH-value of the soil was measured according to Thiele-Bruhn et al. (2015) in the supernatant of a settled soil suspension with a soil/solution ratio 1:2.5 (water used as solute), which was stirred two times during 1 h measurement using a WTW pH 330i probe (Weilheim, Germany). The total organic carbon content (TOC) was analyzed using a Vario Max C instrument (Elementar, Langselbold, Germany). Cation exchange capacity, CEC, was estimated based on the measured clay and silt content of the soil according to (KA5 2005):

$$CEC \ [cmol_c/kg] = 0.5 \ clay \ [\%] + 0.05 \ silt \ [\%] \tag{1}$$

2.3 Hydrological and pesticide contamination data

Hydrological data of the upstream reference gauge *Torgau* at the Elbe River were provided by the German Federal Institute for Hydrology (Bundesamt für Gewässerkunde BfG 2016). The gauge is situated at river km 154.2, roughly 12.8 km upstream of the *Elsnig* sampling site, which represents a total catchment size of 55.211 km^2 (~37% of the total Elbe catchment). A digital elevation model (DEM) was also provided by the BfG (2016). These data were used for the estimation of flooding events at the *Elsnig* site.

Fig. 1 Schematic overview of the *Elsnig* sampling area at river-km 167. A: outer dyke, B: plateau, C: small scale depression, D: inner dyke, E: Elbe River backflow outlet, F: backwater inflow, G: backwater. Numbers 1–4 represent the paired sampling sites of each a plateau (P) and small scale depression (SD). The numbers I–IV represent the sampling sites in the backwater inflow with the three sampling heights (BIx-bottom–medium–top)
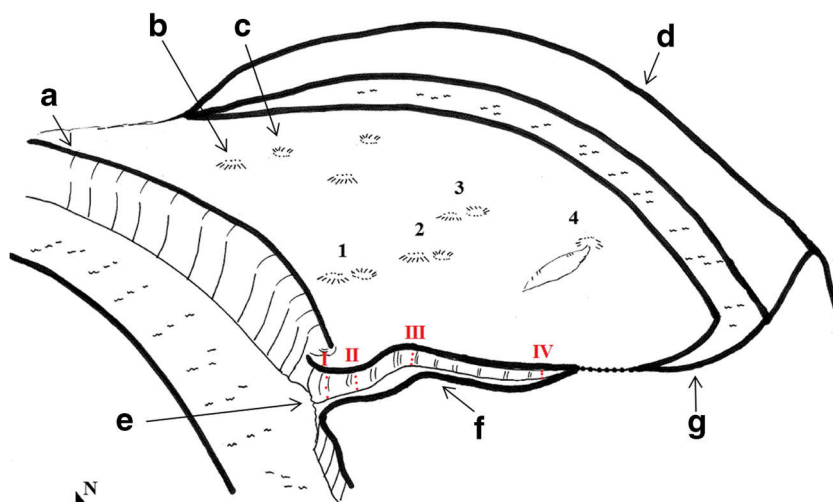
The River Basin community Elbe (FGG 2016) and the State Office of Environment, Agriculture and Geology of Saxony, Germany (LfULG Saxony 2016) provided comprehensive databases on pesticide concentrations in Elbe water samples over a considerable long monitoring period (1935–2015) at numerous sampling points. These data were used to conclude the literature database screening for potential pesticides in the catchment area of *Elsnig*.

2.4 Pesticide screening

2.4.1 Accelerated solvent extraction

Accelerated solvent extractions were performed using a Dionex ASE350 system and 10 ml stainless steel cells (Thermo Fisher Scientific Inc., Waltham, MA, USA). Therefore, 4 g of dried and sieved soil was thoroughly mixed with 1.7–1.8 g of diatomaceous earth (supplied from J.T. Baker, Center Valley, PA, USA). A cellulose filter was placed at the outlet of the cells to inhibit any solid particles to enter the collection vials, or clogging the outlet of the cell, respectively. Settings of the accelerated solvent extraction (ASE) method are listed in Table 1. The obtained extracts were transferred to a speed vac (Eppendorf concentrator 5301/ Eppendorf, Hamburg, Germany) operating at 60 °C and 2000 rpm to concentrate the extract to 1.0 ml final volume. Although some extracts showed only low or no turbidity immediately after the extraction, a greenish precipitate was developed during the course of the evaporation process. Consequently, the concentrated extracts were centrifuged for 20 min at 14,000 rpm (Eppendorf centrifuge 5417C/ Eppendorf, Hamburg, Germany). The received clear fluid was filled into LC-Vials and stored in the refrigerator until UHPLC-MS/MS measurement.

2.4.2 Pesticide standards

Pesticide standards were used for pesticide verification and quantification. Simazin (99.0% purity) was purchased from Fluka (Steinheim, Germany). 2-Hydroxy-terbuthylazine (97.5%) and ethofumesate (98.5%) were provided from Dr. Ehrenstorfer (Augsburg, Germany), and 2-hydroxy-atrazine (96%) was provided from Riedel-de-Haën (Seelze, Germany). Acetone and methanol (both LC-MS-grade), water (LC-MS grade), and formic acid (supra pur) were supplied by Merck (Darmstadt, Germany), and acetonitrile (LC-MS grade) was purchased from VWR (Fontenay sous Bois, France). Standard solutions for compound identification and quantification (external calibration) were freshly diluted from stock solutions before any measurement in a range between 0.001 and 10 μg/l, (50–200 μg/l ethofumesate only). Only linear calibration curves with a coefficient of determination > 0.99 were accepted for pesticide quantification. Peak areas of the standard solutions were checked for deviation throughout the measurement cycle.

Table 1 Settings of the accelerated solvent extraction (ASE) method

Parameter	Setting
solvent	acetonitrile: H_2O (2:1)
temperature	80 °C/100 °C
pressure	1500 PSI
heating time	5 min
static time	7 min
flush volume	70%
purge	60 s
static cycles	1

2.4.3 UHPLC-MS/MS

Pesticide analysis was carried out with the Waters ACQUITY® UHPLC system (binary pump, autosampler) coupled to a Waters Xevo TQ-S® triple-quadrupole mass spectrometer (Waters Technologies Corp., MA, USA). Liquid chromatography was performed using a KINETEX® 2.6 μm XB-C18 column (100 × 2.1 mm); for the target screening of 401 substances, a KINETEX® 2.6 μm Biphenyl column (100 × 2.1 mm) was used for separation of verified compounds (Phenomenex corp. Aschaffenburg, Germany). The LC mobile phase for pesticide screening and downstream analysis consisted of (A) water and (B) acetonitrile, both containing 0.1% formic acid (v/v). The elution gradient at a flow rate of 0.6 ml/min started at 10% B for 0.21 min, increasing to 90% B in 8 min, further increasing to 100% B for 2 min, held for 7 min, returning back to 10% after 1 min and re-equilibration resulting in a total runtime of 20 min.

The electrospray ionization (ESI) was used in the positive mode. The capillary voltage was set to 2.13 kV and the cone voltage to 54 V. The desolvation temperature and source temperature were 500 °C and 150 °C, respectively. The desolvation gas flow was set to 1000 l/h and the cone gas flow at 150 l/h using nitrogen in both cases. Mass spectrometric detection in the MRM mode (see Appendix Table 5) was applied for screening as well as specific quantification of the pesticides. Nitrogen was used as the collision gas at a flow of 0.25 ml/min. The screening for pesticides was carried out using a mass-spectra library provided by Waters® (Waters Technologies Corp., MA, USA) embedded in the software MassLynx® (Waters Technologies Corp., MA, USA). The library included mass spectrometry transition data of 401 pesticides and some of their respective metabolites, which facilitated to perform measurements using multiple reaction monitoring (MRM) featuring two ions, one quantify-ion, and one qualify-ion, respectively. During the evaluation of the 401 pesticide screening data, several false positive peaks, i.e., detection of both quantify- and qualify-ion at the same elution time, occurred, which had to be reexamined with an analytical standard and then rejected from further analysis. For unambiguous detection and quantification of all those pesticides which had been identified by the pesticide screening, 4 MS-MS transitions were determined for each pesticide by use of IntelliStart a software tool embedded in MassLynx. The optimized LC-MS/MS parameters of target pesticides as well as their major chemical properties are listed in Appendix Table 5, and the limits of quantification (LOQ) are listed in Appendix Table 6. To this end, the extraction and LC-MS/MS method was applied to the *Elsnig* floodplain and backwater soil samples, whereby from the homogenized core material, five samples were extracted and measured individually for each point.

2.5 Statistical analysis

All statistical evaluations were carried out using R Studio, version 1.0.44 (RStudio Team 2016), with incorporated functions from the stats- and lawstat-package. Executed functions were used to assess variance in group means or medians, respectively (Kruskal and Wallis 1952). Hence, associated post-hoc tests were run to evaluate the source of variation. Data sets were checked for outliers using the Grubbs test (Field et al. 2012).

3 Results and discussion

3.1 Soil physico-chemical properties

In general, soil texture of the *Elsnig* floodplain samples is sandy loam, whereby the grain size differs slightly between sampling locations. The median values of the grain sizes of the small-scale depressions (SD1–4) were 24.3% sand, 51.0% silt, and 24.7% clay, respectively, and similar to those determined for the plateau samples (P1–4) with 27.5% sand, 48.2% silt, and 24.3% clay. On the other hand, the backwater inflow soil samples (BI1–12) show a distinct pattern in grain size distribution with increasing distance to the river bank, whereby those sampling sites located closer to the Elbe River show a coarser texture, dominated by sand (up to > 75%), independently of different elevation level. In contrast, sampling sites located more far away from the main inflow channel show a gradually finer texture. The grain size distribution of the backwater soils typically reflects the suspended solid transport characteristics of flooding waters, where increasing distance to the main stream results in decreased in flow velocity, thus increasing sedimentation of finer particles.

The clustered soil pH-values varied between 6.1 and 6.8 with a median of 6.5. Measured TOC levels range between 0.7 and 4.7% (median = 2.3%), respectively. An overview of the physico-chemical properties of the clustered floodplain soil samples is provided in Table 2.

In order to assess any correlations between individual soil properties, such as the classically observed regression between clay content and TOC (Mayer 1994), all physico-chemical properties were regressed against each other. While there was no correlation between soil pH with any other parameter, only weak positive correlations for TOC with silt ($R^2 = 0.50$) and TOC with clay ($R^2 = 0.56$) and TOC with CEC ($R^2 = 0.56$) were discovered, whereas a negative correlation was found with increasing sand content ($R^2 = 0.51$).

3.2 Inundation characteristics of the Elsnig floodplain

The hydrological information from the close by river gauge *Torgau* (~ 12.8 km upstream) was used to reconstruct the flooding events at the *Elsnig* site. In general, low water levels

Table 2 Median values of soil texture (sand, silt, and clay) (mass %), cation exchange capacity (CEC) (cmol$_c$/kg), total organic carbon content (TOC) (mass %), and pH value for the different sampling locations at the *Elsnig* floodplain. The x in the backwater samples stands for the four sampling points 1 to 4

Sampling location	Sand	Silt (%)	Clay	CEC (cmol$_c$/kg)	TOC (%)	pH (−)
Plateau (P1–4)	27.4	47.8	23.9	13.8	1.8	6.1
Small scale depressions (SD1–4)	24.3	51.0	24.7	14.2	2.6	6.2
Backwater bottom (BIx-b)	48.6	32.6	18.8	10.8	2.1	6.6
Backwater medium (BIx-m)	49.8	32.7	17.6	10.1	3.0	6.8
Backwater top (Bix-t)	50.6	31.3	18.1	10.5	2.5	6.7

around 20 cm were measured several times during the observation period (1935–2015). In contrast, the highest water level ever measured was during the flood event in 2002 on August 18th with 949 cm. Based on the raw discharge data at the gauge *Torgau*, the frequencies of flooding events that occur statistically every 5, 10, 20, 50, and 100 years (HQ5, HQ10, HQ 20, HQ50, and HQ100) were calculated and are plotted in Fig. 2. Additionally, the occurrence was separated in events before and after the year 2000. As can be seen, severe flooding events characterized by HQ20 to HQ100 occurred disproportionately more often in the shorter time period after the year 2000.

Based on the gauging data, the inundation characteristics of the *Elsnig* floodplain were reconstructed based on a recent digital elevation model (BfG 2016). All terrain elevations were calculated based on the reference of a HQ10 flooding event, divided into 8 classes and listed in Table 3, and the position of the sample locations was expressed as meters below water surface. Thus, the most inundated area (class 4–3.5 m below water surface) lies in the lowest part of the Elsnig site at the backwater inflow, and the least flooded area (0.5–max m below water surface) is located at the plateaus. Additionally, the absolute numbers of flooding days

Fig. 2 Frequency of characteristic flood events at the river gauge *Torgau* (~ 12.8 km upstream of the sampling site *Elsnig*)

exceeding this flood level as well as the frequency were calculated and also listed. As can be seen from Table 3, the backwater inflow will be inundated 1263 days (4.31% of all gauging data) by water levels exceeding HQ10 events. On the other hand, the highest elevations located at the plateau next to the dike were only flooded over 42 days in total (0.14%). The data also indicate that flooding of the inflow of the backwater occurs 30 times more often compared to the highest sections of the floodplain. Accordingly, the inflow of the backwater is most likely to be frequently inundated, while the major part of the floodplain is only affected when there are higher flood events. Additionally, a rather steep river bank on both sides of the stream inhibits a uniform inundation of the *Elsnig* floodplain. Therefore, flooding will mainly occur from the backwater and inflowing water will flood the rest of the terrain from behind and not directly from the stream. This pattern suggests that the soil in the lower areas will be exposed to pesticide containing flood water more frequently as those located at higher elevations. Moreover, the most elevated parts of the floodplain were inundated mostly in the 1940s, when several flood events in spring and winter occurred as well as during the serious flood events in 2002, 2006, and 2013. Inundation of the floodplain areas belonging to the next lower class (1–0.5 m) occurred in almost all decades at least one time during the observation period, except the 1990s, when no flooding of these areas was calculated. The class of 4–3.5 m, i.e., the inflow of the backwater, was affected of high water levels almost every year, particularly during winter and spring. At those seasons, more than 80% of the flooding occurred.

3.3 Pesticides in river water samples

The potential pesticide contamination in the river Elbe water samples near the test site was estimated by database analysis using information from the River Basin community Elbe (FGG 2016) and the State office of Environment, Agriculture and Geology of Saxony, Germany (2016). For this study, the sampling point *Dommitzsch, links* (river-km 172.6) was selected, as it is located close to the *Elsnig* (river-km 167) sampling site and it is the associated water quality sampling station of the reference gauge *Torgau*.
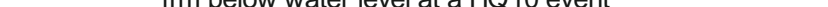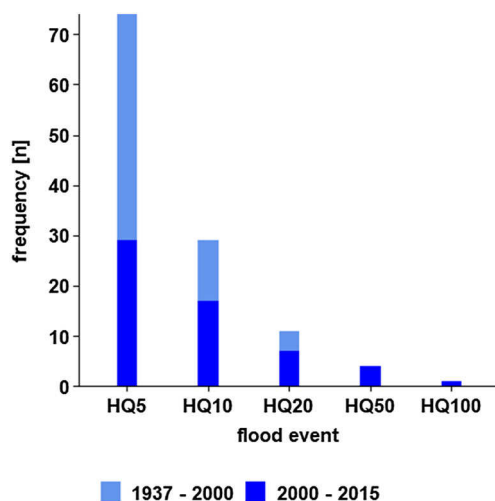
Table 3 Inundation frequency (%) and calculated inundation classes for flooding event ≥ HQ10. Note that the classes indicate the elevation of the sampling site below water surface at HQ10. Class 4–3.5 m defines the low-lying areas such as the backwater inflow and class 0.5–max m represents the areas with highest elevation in the plateau close to the dyke. Data were taken from the reference gauge *Torgau* (1935–2015). Total water observation levels (*n* = 29,281)

backwater inflow	[m] below water level at a HQ10 event							highest plateau
	4 - 3.5	3.5 - 3	3 - 2.5	2.5 - 2	2 - 1.5	1.5 - 1	1 - 0.5	0.5 - max
events [*n*]	1263	833	456	344	169	115	70	42
frequency [%]	4.31%	2.84%	1.56%	1,17%	0.58%	0.39%	0.24%	0.14%

Compounds were selected from the databases using the detection frequency in river water samples as well as associated concentration levels > LOQ. As a result, 50 major pesticides were selected from the database of weekly water samples from the location *Dommitzsch*, of which 40 were detected at least one time during 1 year with >LOQ. Out of those 50 the 13 most critical (highest detection frequency and concentration > LOQ) are listed in Table 4. Additionally, the total number of times the individual pesticide has been monitored is also provided (*n*). Some pesticides such as atrazine have been monitored throughout the entire period (*n* = 669), whereas some pesticides such as dimethoate have been only recently added to the monitoring program (*n* = 52). As mentioned, atrazine was the pesticide detected in all the samples, whereby in 523 or 78% of all samples, the concentration exceeded LOQ and only in 146 or 22% the concentrations were below LOQ and could only be determined qualitatively.

In a second step, pesticide loads in the Elbe River water for the substances with either high number of observations (atrazine, terbuthylazine, metazachlor, and metolachlor) or continuous detection > LOQ during the last 5 years (chlorotoluron, isoproturon) were calculated using the discharge data of the gauge *Torgau* and the water quality data from station *Dommitzsch*, links (see Fig. 3). At this point, it should be noted that the calculated loads merely represent an underestimation of the actual loads of these pesticides as loads < LOQ were not taken into account. Thus, only those values, which pose quantitative information, were used. As can be seen, there are several events with relatively high pesticide loads between 2 and 5 kg/day and even some with extreme high loads exceeding 20 kg/day as for atrazine in 2002, metazachlor in 2010, and metolachlor in 2013. Additionally, it becomes obvious that total loads of some pesticides such as atrazine decrease over the years, from approx. 3 kg/day in 2002 to less than 0.2 kg/day in 2012. The same trend in river Rhine water samples has been shown by Bach and Frede (2012), with approximately 18 kg/day of atrazine in 1994 and a decline to 0.13 kg/day in 2004 measured at the water quality station *Cologne*. The strong reduction in atrazine concentrations over the years is attributed to its ban by the European Union regulators in the early 1990s, whereby the high loads even until 2005 can be explained by the persistence of the substance and consequent drainage through the vadose zone to the groundwater even years after ban (e.g.,

Table 4 Selected detection frequencies and minimum and maximum pesticide concentrations [ng/l] in the Elbe River water samples at the sampling location *Dommitzsch, links* (river-km 172.6)

Substance	Total *n*	Detection frequency (*n*)	*n* > LOD	*n* > LOQ	min (ng/l)	max (ng/l)
Atrazine	669	100.0	146	523	7	270
Chlorotoluron	255	100.0	4	251	5	110
Isoproturon	254	100.0	0	254	2	120
Diuron	255	98.8	52	200	5	58
Terbuthylazine	669	90.1	75	528	7	340
γ-HCH (lindane)	411	81.8	73	263	2	7
Metazachlor	669	55.0	173	195	10	290
Metolachlor	669	49.3	147	183	10	270
Ethofumesate	407	41.3	108	60	10	110
Simazine	463	34.6	118	42	8	28
Clomazone	255	25.9	47	19	5	24
Acetochlor	203	12.8	7	19	10	100
Dimethoate	52	1.9	0	1	16	16

Fig. 3 Calculated pesticide loads (kg/day) based on weekly water quality sampling at reference station *Dommitzsch, links* and discharge data from gauging station *Torgau*. Pesticides were selected based on high number of observations or continuous detection > LOQ
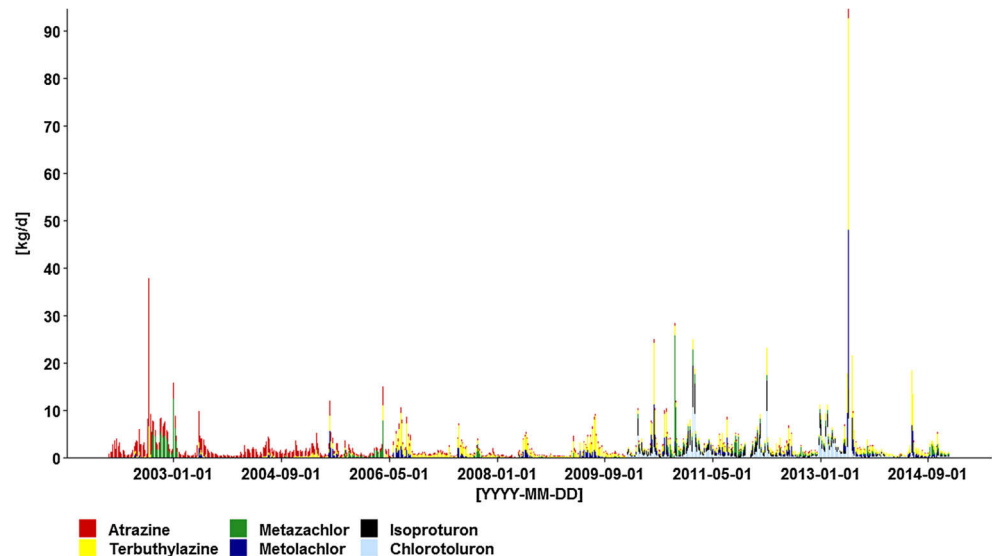
Jablonowski et al. 2009; Vonberg et al. 2014). In the following years, atrazine was mainly substituted by terbuthylazine, which belongs to the same substance group of triazine derivatives, as the most common herbicide for maize cropping (Guzzella et al. 2003; Schulte et al. 2012), whereby maize is one of the predominant crops of the rural district *Nordsachsen* (river upstream), which explains the continuous detection > LOQ in the water samples from 2006 onwards. Additionally, the substances isoproturon, metolachlor, and chlorotoluron are also detectable in the river water samples in non-negligible quantities, whereby the temporal occurrence varies between the pesticides. Isoproturon and chlorotoluron were mainly detected after 2010 and metolachlor in the period between 2005 and 2009. To identify the contamination source and pathways, Huber et al. (2000) performed a modeling study. The results revealed that inputs of pesticides into surface waters can be explained by pesticide translocation via surface runoff, tile drains, and leaching from agricultural sides, whereby surface runoff was estimated to be the major diffuse source. While surface and subsurface runoff are known to be the most important drivers of pesticide dislocation and contamination into surface waters, and therefore, of surface water contamination, only a few studies focused on the contribution of flood events to remobilization and translocation of contaminant loads. For example, Krein et al. (2013) highlight the crucial importance of flood event observation in contaminant transport studies. The same picture can be seen for our data, where the loads of the selected pesticides were considerably higher during flood events. For instance, the total load of atrazine during the flood event in 2006 was 23.8 kg over the time period between 29th of March and the 12th of April, while the annual load for the same year excluding the flood event was only 21.5 kg. Consequently, the amount of transported atrazine during the flood event was

110% of the "normal" annual total load in 2006. The same pattern was calculated for terbuthylazine, with 48.1 kg throughout the year and 25.5 kg during a short flood event, which accounts for 53% of the normal annual total load. Same patterns were also observed for the flood events in 2002 and 2013.

The monthly loads of atrazine, chlorotoluron, isoproturon, and terbuthylazine during their individual observation period are summarized in Fig. 4. In general, there was a significant difference ($p < 0.0001$) between monthly loads of the pesticides with highest mean ranks during summer month. These findings are consistent with observations of the water supplier union in the Elbe catchment (AWE 2016), which show, for example, highest concentrations of terbuthylazine during the summer months in Elbe River water samples at *Dresden* (river-km 50). The phenyl urea pesticides isoproturon and chlorotoluron, which are often applied as pre- and post-
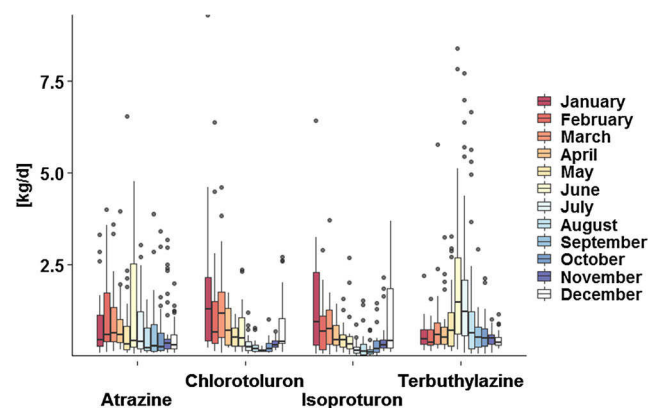

Fig. 4 Summarized monthly loads of atrazine, chlorotoluron, isoproturon, and terbuthylazine during the observation period (2002–2014) based on weekly water sampling. Dots mark extrema and were tested for outliers using the Grubbs outlier test (Field et al. 2012)

emergence herbicides in numerous crops (e.g., spring and winter wheat, barley, and rye) (Chhokar et al. 2008), exhibit equally significant differences ($p < 0.0001$) among monthly loads with highest mean load ranks from December to April. As mentioned, isoproturon and chlorotoluron are herbicides mainly applied from early September/October to spring (April/May), whereas terbuthylazine is mainly used in maize production, where application starts from May to early summer. Based on the correlation between application timing and detection in the stream water, it is likely that these substances are mainly transported via run-off and not via the groundwater, as transport in the groundwater will cause mixing and damping of the signal and, therefore, lower the correlation. In general, appropriate estimation of pesticide translocation pathways is impeded by the various ways pesticides may enter the environment over point or diffuse sources. On the one hand, the substances can be translocated and contaminate surface waters after field application via run-off, drainage, or spray drift or they might enter the surface water by sewage waters, where the pollution source traces back from improper cleaning of pesticide application instruments as well as inappropriate disposal on the farm yard (Karanasios et al. 2010). Especially, the latter will cause a quick response in the pesticide concentrations measured in the stream, as the flow paths are generally short. At the catchment scale, studies have elucidated that 40 to 90% of surface water contamination by pesticides can be due to point source pollution (Carter 2000; Kreuger and Nilsson 2001).

Based on the detection frequencies, it can be hypothesized that pesticides with high detection frequencies in the river water samples will be also present in the floodplain soil samples as a result of adsorption or deposition processes of polluted suspended sediments. Under this assumption, pesticides such as terbuthylazine or atrazine are rather likely to appear in the soils. On the one hand, the long-term monitoring history ($n = 669$) of both pesticides in combination with detection frequencies > 90%, of which findings > LOQ constitute to the major part, indicate a considerable probability of verifying these pesticides in soil samples as well. On the other hand, although the phenyl-urea pesticides diuron, chlorotoluron, and isoproturon exhibit in fact a smaller number of total observations ($n = 255$, 255, and 254, respectively), these pesticides occurred continuously in the water samples of the last 5 years with respect to the available data (2010–2014), with detection frequencies > 98% (> LOQ).

3.4 Pesticides in floodplain soils

Two pesticides and two pesticide metabolites were detected and quantified in the floodplain soils, namely simazine, ethofumesate, 2-hydroxy-atrazine, and 2-hydroxy-terbuthylazine (see Fig. 5 and Appendix Table 7), whereby only the two pesticide parent compounds simazine and

ethofumesate detected in *Elsnig* soil samples were also listed in the water monitoring database. Additionally, the two degradation products 2-hydroxy-atrazine, and 2-hydroxy-terbuthylazine are metabolites of atrazine and terbuthylazine, which were detected in the water samples in high concentrations and throughout the entire weekly monitoring period from 2002 to 2014. Interestingly, atrazine itself as the parent compound of 2-hydroxy-atrazine could not be detected in the soil samples, even if atrazine is known to be relative persistent in soils with half-lives of 29 to 75 days (PPDB 2019). Nevertheless, this general finding support the hypothesis that floodplain soils represent a memory of the pollution history of the catchment area, as they are periodically flooded and characterized by continuous suspended or dissolved contamination inputs from the stream as already stated by Förster et al. (2009).

In general, simazine showed lowest concentrations at individual sampling points ranging between 0.008 and 0.061 μg/kg followed by 2-hydroxy-terbuthylazine (0.21 and 0.66 μg/kg), 2-hydroxy-atrazine (0.04 and 6.04 μg/kg), and ethofumesate (12.90 and 21.49 μg/kg). Here, it has to be noted that ethofumesate was detected neither in the plateau (P) nor small scale depression (SD) samples. In the backwater inflow samples no significant ($p > 0.05$) difference between sampling locations (bottom, medium, or top) was observed. In general, the water solubility of ethofumesate is much larger (50 mg/l) compared to the other pesticides, whereby the water solubility decreases in the following order ethofumesate >> 2-hydroxy-terbuthylazine > 2-hydroxy-atrazine > simazine (PPDB 2019), which might have caused downward leaching of ethofumesate (below the 30 cm of sampling) in the plateau (P) and small scale depression (SD) samples since last inundation, as flooding occurs much less frequently at higher landscape elevation. Furthermore, there was a significant difference ($p < 0.05$) between the pesticide/metabolite concentrations for the different sampling locations plateau (P), small scale depression (SD), and backwater inflow (BI), whereby the backwater inflow locations with medium and lowest elevation showed highest concentrations and were significantly higher than those sampled at the P and SD. The latter showed lowest mean rank-sums of all locations (see Fig. 5).

Considering the individual occurrence of triazine pesticides in soil samples, median concentration values for 2-hydroxy-atrazine were highest in backwater inflow samples (bottom and medium location), with significant ($p < 0.05$) difference to the plateau (P) samples. Scherr et al. (2017) measured 2-hydroxy-atrazine residues at a median concentration of 26.6 μg/kg, while also no atrazine residues were found, for an alluvial floodplain soil of the Elbe River in the Czech Republic. In comparison to the highest concentration found at our site (6.04 μg/kg), these concentrations are rather high, even if the same soil depth 0–30 cm was sampled. The still high concentrations of atrazine metabolites (2-hydroxy-

Fig. 5 Determined pesticide concentrations (µg/kg) of 2-hydroxy-atrazine, ethofumesate, simazine, and 2-hydroxy-terbuthylazine in the *Elsnig* floodplain soil samples
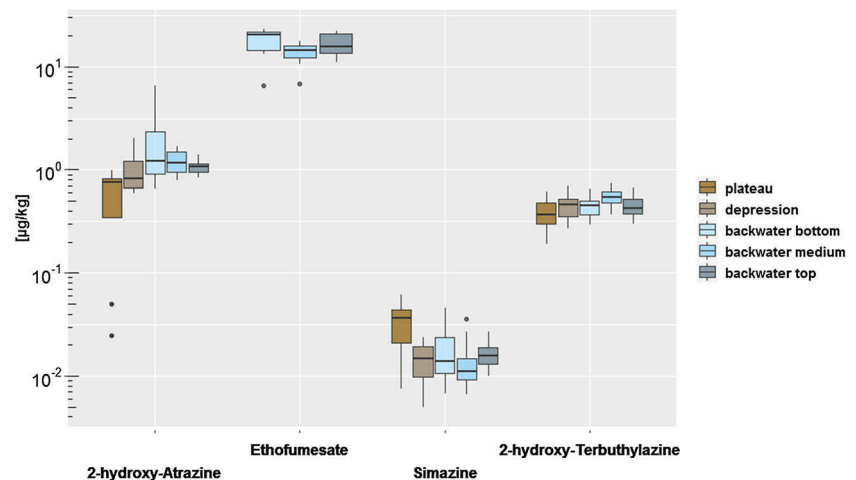
atrazine) years after ban indicate the persistent nature of the compound. This persistent behavior has been exemplarily shown by Jablonowski et al. (2009) who measured ^{14}C labeled atrazine as well as 2-hydroxy-atrazine concentrations in an agriculturally used outdoor lysimeter of 1.0 and 42.5 µg/kg, respectively, in the top and 3.4 and 17.7 µg/kg of atrazine and 2-hydroxy-atrazine in the subsoil 22 years after last atrazine application. Compared to simazine and 2-hydroxy-terbuthylazine, 2-hydroxy-atrazine concentrations were significantly higher ($p < 0.0001$) independently from the sampling location (bottom, medium, top), which was also confirmed by Scherr et al. (2017), who stated that the median 2-hydroxy-atrazine concentrations were > 2 times higher than 2-hydroxy-terbuthylazine, and 3 times higher than the median simazine residues in their floodplain soil samples.

For the *Elsnig* soil samples, simazine, on the other hand, showed significantly ($p < 0.0001$) higher values in the plateau (P) samples compared to all other sampling locations, although, the measured values were always below 0.1 µg/kg. The higher concentrations detected in the plateau might be a result of the low water solubility of simazine, and therefore, preferential translocation on fine sediments, which are sedimented on the plateau and less at the backwater inflow. Additionally, the low concentrations can be explained by less frequent inundation of the plateau region and, therefore, limited inputs.

2-Hydroxy-terbuthylazine was found with highest concentrations in medium elevation backwater (BI) samples, which were significantly ($p < 0.0001$) higher compared to the plateau (P) and backwater inflow (BI) samples at higher elevation (BI*x*-top). Scherr et al. (2017), on the other hand, detected simazine only in one out of 75 soil samples at a concentration of 8.7 µg/kg (max. = 0.061 µg/kg in this study (P4)) and 2-hydroxy-terbuthylazine was found in 82% of the soil samples, with median concentrations of 12.3 µg/kg, compared to maximum values of 0.66 µg/kg at the *Elsnig* site.

As mentioned, the detections of simazine and the two transformation products of atrazine and terbuthylazine reflect the results of the river water data, whereby especially atrazine and terbuthylazine were continuously detected in water samples over a long period in considerable concentrations. Therefore, it is likely that a deposition of these compounds, or metabolites took place, particularly in the backwater inflow, even during smaller inundation events. Even if simazine was also banned in the EU in 2004 (EC 2004), it could still be found sporadically in water samples of the Elbe River, but mostly in fairly low concentrations throughout the floodplain samples. Here, it has to be taken into account that simazine as well as atrazine as the parent compound of 2-hydroxy-terbuthylazine will still be released to the environment as impurities in the application formulation of terbuthylazine. Based on its importance in maize cropping, which is predominant in the *Elsnig* region, terbuthylazine application (> 2000 tons active ingredient used in Germany in 2014 (FAOSTAT 2017)) could represent one recent source for both banned pesticides simazine and atrazine (EFSA 2011). The application regulation for terbuthylazine in the EU permits up to 3% wt impurity of terbuthylazine based formulations with simazine and 0.1% wt impurity with atrazine (EC 2011). Therefore, the occurrence of simazine in such low concentrations in *Elsnig* samples is probably associated to the translocation of both compounds by the river water and sedimentation in the floodplain soil. As mentioned, the detection of both triazine hydroxyl transformation products as well as simazine is, for instance, the consequence of the long-term persistence of atrazine (Jablonowski et al. 2009) in combination with its vast application history and the constant replenishment with parent compound, which is expressed in the appreciable loads of terbuthylazine parent compound in the Elbe River. To this end, simazine as well as atrazine residues are known to persist under anoxic conditions; thus,

floodplain contamination may arise from river sediment deposition. Additionally, it has been shown that triazine compounds are likely to adsorb to soil mineral and organic fractions (Radović et al. 2014; Stipicevic et al. 2015).

Finally, remarkable ethofumesate concentrations (Fig. 5; Appendix Table 7) occurred only in the backwater inflow samples more close to the river bank, giving indication that the contamination was waterborne and that smaller flood events carry most of the substances or that more frequent flooding events will lead to higher compound deposition. The soil properties, particularly clay and total organic carbon content, might substantially influence the fate of the pesticides (Arias-Estevez et al. 2008) after they have been transported into the floodplain. Only weak correlations (but without statistical significance) between the soil physico-chemical properties (TOC, CEC, pH, or grain size) and the pesticide residues could be found. This gives room to the hypothesis that not the soil properties rather than the inundation characteristics play a major role in the residue loads and patterns found at the different landscape positions within the floodplain.

4 Summary and conclusion

Pesticide concentrations and loads of Elbe River water samples from 2002 to 2014 were analyzed to identify potential contaminants of the floodplain soils adjacent to the area of *Elsnig*. Therefore, a literature screening of river water pesticide contamination was performed to estimate the loads, and samples along an inundation gradient were taken from the topsoil of the floodplain area. These samples were analyzed for pesticide residues using LC-MS/MS. The determination of the pollution characteristics of the floodplain area was performed by linking the inundation characteristics of the floodplain to the pesticide loads from the water samples and to the measured pesticide concentrations of the soil samples. The results from analyzing the database of the river water contamination showed that 13 pesticides could be detected in high frequency and concentrations exceeding the limit of detection (LOD). Out of these, atrazine and terbuthylazine were the post prominent ones with detection frequencies of 100 and 90% in weekly water samples, respectively. Additionally, both pesticides showed high maximum concentration up to 270 and 340 μg/l. Looking at the pesticide loads, a temporal pattern could be also detected, whereby atrazine banned already in 1991 in the EU showed high loads until 2006. Terbuthylazine as the substitute for atrazine showed up with relative high loads since 2006 and exceeded 10 kg/day during single flooding events, indicating the potential risk of the substance to the aquatic environment.

In the soil samples of the heterogeneous floodplain, the compounds ethofumesate, simazine, and the two main metabolites of atrazine and terbuthylazine (2-hydroxy-atrazine and 2-hydroxy-terbuthylazine) were detected and quantified, revealing that the pollution of the *Elsnig* floodplain are to a certain extent directly linked to the detection frequency of pesticides in the river water samples. The two metabolites 2-hydroxy-atrazine and 2-hydroxy-terbuthylazine were detected in relatively high concentrations all over the floodplain. Additionally, the detection of simazine in the floodplain samples indicates that pesticides whose approval has expired for more than 20 years can still be present in the non-metabolized state. The hypothesis that the backwater inflow channel soil samples would exhibit higher pollution levels compared to the floodplain soil located at higher elevation could only partly be confirmed. On the example of ethofumesate and simazine, this relationship between inundation frequency, coupled with water solubility of the substance, and residual concentrations could be found. Ethofumesate, a water soluble compound, was detected in low lying backwater inflow samples only, in an area of frequent inundation, whereas simazine, the less water soluble compound, exhibited highest concentrations in the samples taken at the floodplain plateau, at locations at the site with less frequent inundations but also characterized by finer soil texture pointing to sedimentation of finer sediments, onto which hydrophobic pesticides can bind to. Additionally, both transformation products 2-hydroxy-atrazine and 2-hydroxy-terbuthylazine showed significantly higher concentrations in at least one of the different elevation levels of the backwater inflow samples, which were also higher compared to those measured in the floodplain plateau or small scale depression samples. Furthermore, there was no evident correlation between observed soil properties (soil texture, TOC, and pH) and pesticide concentrations in the *Elsnig* floodplain, indicating that the concentration differences are mainly caused by the inundation characteristics. However, the (specific) input pathways of pesticides over diffuse sources into the rivers, their translocation by the river waters, and the input into adjacent sink areas during flood events remain largely unknown. Thus, this study may motivate for more extensive pesticide monitoring campaigns in floodplain soils in order to elucidate and compare environmental fate structures within different river basins and soil types.

Appendix

Table 5 Optimized LC-MS/MS parameters of target compounds as well as their major chemical properties

Pesticide	CAS	Monoisotopic mass (Da)	t_R (min)	MRM (m/z)	Cone (V)	Collision energy (eV)
Ethofumesate	26225-79-6	286.08	6.64	287.06 > 258.99	38	8
				> 161.09		20
				> 133.13		28
				> 121.04		16
Simazine	122-34-9	201.08	2.56	201.99 > 131.98	34	18
				> 124.05		16
				> 103.95		24
				> 96.02		22
2-Hydroxy-atrazine	2163-68-0	197.13	1.23	198.09 > 156.13	34	14
				> 114.11		20
				> 86.08		22
				> 69.03		30
2-Hydroxy-terbuthylazine	66753-07-9	211.14	1.66	212.10 > 156.02	36	16
				> 114.02		24
				> 85.99		22
				> 68.96		32

Table 6 Methodological LOQ for the two detected pesticides ethofumesate and simazine and the two metabolites 2-hydroxy-atrazine and 2-hydroxy-terbuthylazine found in the *Elsnig* floodplain soil

	Ethofumesate	Simazine	2-Hydroxy-atrazine	2-Hydroxy-terbuthylazine
LOQ (µg/kg)	0.1	0.01	0.02	0.02

Table 7 Determined pesticide concentrations (µg/kg) of *Elsnig* floodplain and soil samples. LOQ = limit of quantification. Sample labeling P = plateau samples, SD = small scale depressions, and BI = backwater samples, respectively

	Ethofumesate (µg/kg)			Simazine (µg/kg)			2-Hydroxy-atrazine (µg/kg)			2-Hydroxy-terbuthylazine (µg/kg)		
	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max
P1		< LOQ		0.042	0.041	0.049	0.04	0.02	0.05	0.21	0.19	0.30
P2		< LOD		0.010	0.008	0.011	0.72	0.67	0.74	0.43	0.38	0.47
P3		< LOQ		0.033	0.026	0.037	0.90	0.82	0.99	0.55	0.52	0.62
P4		< LOQ		0.048	0.036	0.061	0.80	0.77	0.87	0.33	0.30	0.36
SD1		< LOQ		0.010	0.005	0.012	0.72	0.69	0.77	0.33	0.27	0.35
SD2		< LOQ		0.018	0.013	0.019	1.95	1.82	2.01	0.47	0.42	0.52
SD3		< LOQ		0.010	0.007	0.022	0.98	0.87	1.06	0.43	0.30	0.52
SD4		< LOQ		0.019	0.018	0.024	0.61	0.60	0.62	0.65	0.52	0.70
BI1-b	14.69	6.64	23.25	0.020	0.016	0.028	6.04	5.21	6.61	0.55	0.47	0.65
BI1-m	12.90	6.82	15.81	0.010	0.001	0.011	1.63	1.48	1.67	0.51	0.41	0.59
BI1-t	15.53	10.94	22.34	0.019	0.017	0.020	1.11	1.04	1.41	0.34	0.31	0.46
BI2-b	21.49	21.36	22.13	0.044	0.042	0.046	1.32	0.97	1.79	0.38	0.30	0.48
BI2-m	16.78	15.17	17.77	0.020	0.008	0.036	1.36	1.11	1.48	0.61	0.44	0.69
BI2-t	15.89	12.82	20.32	0.020	0.013	0.027	1.01	0.92	1.26	0.39	0.30	0.49
BI3-b		< LOQ		0.010	0.007	0.012	0.85	0.65	0.90	0.35	0.29	0.41
BI3-m		< LOQ		0.008	0.007	0.011	0.97	0.92	1.05	0.45	0.36	0.54
BI3-t		< LOQ		0.012	0.010	0.013	1.03	0.84	1.20	0.59	0.47	0.67
BI4-b		< LOQ		0.010	0.008	0.012	0.85	0.92	0.90	0.48	0.46	0.51
BI4-m		< LOQ		0.015	0.014	0.017	0.85	0.78	0.96	0.66	0.53	0.75
BI4-t		< LOQ		0.016	0.014	0.018	1.03	0.86	1.21	0.51	0.39	0.56

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