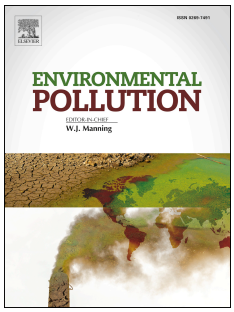

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Assessment of pesticide inputs into surface waters by agricultural and urban sources - a case study in the Querne/Weida catchment, central Germany

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Abstract

Pesticide inputs into surface waters may cause harmful effects on aquatic life communities and substantially contribute to environmental pollution. The present study aimed at evaluating the input pathways in the Querne/Weida catchment (central Germany) to efficiently target mitigation measures of pesticide losses. Relevant pesticide substances were measured in surface waters in agricultural and urban surroundings and in soil samples within the catchment area. Pesticides application data from farmers were analyzed. Additionally, batch tests were performed to determine sorption and degradation of relevant pesticides for site specific soil properties. Frequency of detection, number of pesticides and maximum concentrations were much higher in the surface water samples in mainly urban surroundings

compared to those in agricultural surrounding. The most frequently detected substances were glyphosate, AMPA, diflufenican and tebuconazole in surface water samples and diflufenican, boscalid, tebuconazole and epoxiconazole in the topsoil samples. Glyphosate and AMPA contributed to the highest concentrations in surface water samples (max. 58 µg L^{-1}) and soil samples (max. 0.19 mg kg^{-1}). In most cases, pesticide detections in surface water and soil were not consistent with application data from farmers, indicating that urban sources may affect water quality in the catchment area substantially. However, it was observed that pesticide substances remain in the soil over a long time supported by sorption on the soil matrix. Therefore, delayed inputs into surface waters could be suspected. For the implementation of reduction measures, both urban and agricultural sources should be considered.

Novel findings of the study: pesticide detections were not consistent with application data from farmers, urban sources contributed substantially to pesticide pollution of surface waters

Keywords: biocides; degradation; half-lives; persistence; sorption; urban sources

1. Introduction

Pesticides are an important group of anthropogenic organic pollutants in surface waters that may cause harmful effects on structure, biodiversity and function of aquatic life communities (Liess and von der Ohe, 2005; Lundqvist et al., 2019). Worldwide, multiple pesticide residues have been found in streams and other natural waters (Hagemann et al., 2019; Zhen et al., 2019; Curchod et al., 2020), where they have substantially contributed to environmental pollution. For Europe, the European Water Framework Directive (Directive 2000/60/EC) defined environmental quality standards (EQS) for priority pesticides to scientifically-determine good chemical and ecological states of surface waters. Monitoring of surface

waters in Germany often showed positive findings of pesticides that frequently exceeded EQS (LAWA, 2016; UBA, 2017; 2019).

Pesticides could enter natural waters via several different pathways. The occurrence of pesticides in surface waters originates either from point sources, e.g. farmyard runoff, wastewater treatment plants or non-point sources such as surface runoff, artificial drainage from agricultural fields, atmospheric deposition or spray drift (Gerecke et al., 2002; Müller et al., 2002; Wittmer et al., 2014; Munz et al., 2017). It was reported by several authors that pesticides in surface waters mainly originated from point sources of farmyard runoff (Müller et al., 2002; Bach et al., 2005).

In addition to being applied for agricultural purposes, the same pesticides are also found in numerous biocidal products in urban environments. Biocides, which are used for multiple purposes (e.g. protection of walls and facades), might enter surface waters via sewer systems, by storm water run-off wastewater treatment plants (WWTP) or combined sewer overflows (Bürgi et al., 2009; Wittmer et al., 2014; Mutzner et al., 2019). There are little data available on biocide consumption, use patterns and overall emissions to the environment. For the country of Switzerland, it was reported that urban biocide consumption is within the same range as agricultural pesticides (Bürgi et al., 2009) and thus, urban areas might contribute substantially to micropollutant burden of surface waters via wastewater effluents (Wittmer et al., 2011; Neale et al., 2017; Kienle et al., 2019).

The environmental fate of pesticides is mainly affected by their degradation rates. The sorption of pesticides on clay, organic matter or organo-clay complexes and the formation of non-extractable residues (NER) might decrease microbial availability of active ingredients in pesticides and thus slow biodegradation (Mamy et al., 2005; Al-Rajab et al., 2008). As a consequence, applied pesticides might accumulate over time in soils as shown by Silva et al. (2019) and could contribute to delayed inputs into surface waters. The formation of NER has been observed for various pesticides and was described to be strongly variable with the extraction procedure used (Loeffler et al., 2020; Muskus et al., 2020). Depending on their

78 classification type (1. sequestered, entrapped, 2. covalently bound to soil constituents, 3.
79 biogenic), NER are known to be a potential long-term source of slowly-released pesticide
80 residues to the environment (Schäffer et al., 2018).

81 Previous studies have shown that there is a lack of information on the relative contributions
82 of urban and agricultural sources and of delayed pesticide inputs from arable land to surface
83 water pollution. Therefore, the present study was aimed at evaluating the input pathways of
84 pesticides into surface waters in the Querne/Weida catchment in central Germany and to
85 efficiently target mitigation measures of pesticide losses. In this context, actual pesticide
86 application data from farmers within the catchment area were directly compared for the first
87 time to the pesticide findings in water and soil samples. Additionally, sorption and
88 degradation of pesticides were determined at site-specific soil properties for a better
89 understanding of their environmental behavior. The main objectives of the study were to:

90 i. quantify pesticide substances in surface waters in the watercourse of the catchment
91 ii. quantify pesticide substances in soil (topsoil and subsoil up to 5 m)
92 iii. analyze actual pesticide application data from farmers in the catchment area
93 iv. determine degradation rates and sorption coefficients of selected pesticides at site-
94 specific properties in a separate laboratory study
95 v. identify main input pathways for pesticides into surface waters.

96

97 **2. Material and methods**

98 **2.1 Study site**

99 The study was conducted in the Querne/Weida catchment located in Saxony-Anhalt (central
100 Germany) 20 km west of the city of Halle (Figure 1).

101

102 "((Figure 1: Location of the Querne/Weida catchment and sampling sites.))"

The entire catchment area covers 247 km². The selected sub-catchment comprises 150 km² with the largest portion (97 %) used as arable land. The main agricultural crops during the study period (2015-2016) were winter wheat (36 %), silage corn (16 %), winter barley and winter oilseed rape (13 %), sugar beets (6 %) and grain corn (4 %). Multiple towns are located within the catchment, with Querfurt being the largest (11,562 inhabitants) (see Fig. 1). In the catchment, 92 % of inhabitants were connected to the two central WWTPs and 8 % to small decentralized WWTPs which release their water to groundwater, to a septic tank or directly to surface waters.

The climate of the study site is subcontinental and characterized by low precipitation amounts with a long-term (1981 to 2010) precipitation level of 550 mm and maximum precipitation falling during the summer months (DWD weather station Querfurt-Lodersleben). Characteristic for the region are frequently occurring heavy rains which may be connected to erosion events (Schröder, 1985). The long-term average annual air temperature was 9.0 °C. The geology consists of Mesozoic rocks (shell limestone, mottled sandstone) which are largely covered by a loess layer. Main soil types at the study site are Chernozems and Luvisols (GLA, 1999).

2.2 Precipitation and discharge

Precipitation amounts were obtained from the German Weather Service station Lodersleben (elev. 204 m, 51°23 'N, 11°37 'E). Discharge amounts were registered at two gauge stations in the Kriebuschbach and Weida surface waters (see Fig. 1) by continuously measurement of water levels with pressure sensors (OTT CTD, OTT HydroMet GmbH, Germany) and periodic measurement of flow velocities (OTT C31, OTT HydroMet GmbH, Germany). Discharge amounts were calculated by the rating curve method (stage-discharge relation). Discharge data from the two gauge stations were stored at 15 min intervals by the data logger of the automatic water sampler (ISCO, 3700, Teledyne Inc., Los Angeles, CA, USA).

130

131 ## 2.3 Water and soil sampling

132 Grab water samples were collected monthly from July 2015 to June 2016 at 9 sampling sites
133 (points – P1 to P9) in different surface waters (see Fig. 1). At two sampling sites, one with a
134 mainly agricultural surrounding (SP_{agr}) and one with a mainly urban surrounding (SP_{urb}),
135 water samples were taken with daily resolution and pooled to one composite weekly sample
136 from June 2015 to July 2016. For this purpose, automatic water samplers equipped with
137 polytetrafluoroethylene (PTFE)-tubes and 24 polypropylene bottles (ISCO, 3700, Teledyne
138 Inc., Los Angeles, CA, USA) were installed in the surface waters. Composite samples were
139 taken at weekly frequencies (7 aliquots every 24 hours). Water samples were transferred to
140 glass bottles and stored in the dark at 4℃ until a nalyses.

141 Topsoil samples (0-30 cm) were taken at 25 different sampling sites in the vicinity of surface
142 waters, in areas which were assessed to be vulnerable for erosion (see Fig.1). In addition,
143 soil samples were taken at five sampling sites at permanent soil observation plots up to a
144 depth of 5 m (S1-S5, see Fig. 1) by the core drilling method (PVC-Liner) with drill diameters
145 of 105 mm (Fa. Eijkelkamp Soil & Water, Netherlands).

146

147 ## 2.4 Analyses of water and soil samples

148 Water samples were measured unfiltered after suspended particles had deposited on the
149 bottom of the glass bottles. The samples were analyzed for 53 pesticide substances and the
150 degradation product of glyphosate (aminomethylphosphonic acid - AMPA) which were
151 assessed as environmentally-relevant based on previous monitoring studies of Saxony-
152 Anhalt. Nonpolar (less polar) substances (Table S1) were analyzed by gas chromatography
153 coupled to a mass spectrometer (GC-MS) (Shimadzu TQ 8050, Japan, column RXi-5 SIL
154 MS, 30 m x 0.25 mm x 0.2 µm, Restek GmbH, Germany) according to DIN EN ISO 10695
155 F6.

Neutral and basic substances (Table S1) were analyzed by high performance liquid chromatography coupled to a mass spectrometer (HPLC-MS) (MS: Thermo Q Exactive Orbitrap, HPLC: Thermo Pump HPG-3400 RS, column neutral substances: Thermo Accucore RP-MS, 100 x 2.1 mm, 2.6 µm particle size, column basic substances: Thermo Hypersil Gold, 50 x 2.1 mm, 3 µm particle size, Thermo Fisher Scientific, USA) according to DIN 38407-36 (2014). Acid substances (Table S1) were analyzed by HPLC-MS (MS: Thermo TSQ Quantum Ultra (Triple Quadrupole), HPLC: e Quan Online SPE, Thermo Fisher Scientific, USA, column: Agilent Zorbax Eclipse Plus C18, 150 x 2.1 mm, 3.5 µm particle size, Agilent Technologies, USA) according to DIN 38407-35 (2010). Glyphosate and AMPA were analyzed by HPLC-MS (MS: Agilent 6495-Triple quadrupole, HPLC: Agilent Binary Pump 1290, Agilent Technologies, USA, column: Macherey-Nagel Nucleodur HILIC, 125 x 2 mm, 3 µm particle size, Macherey-Nagel, Germany), Gerstel MPS autosampler (Gerstel GmbH & Co.KG, Germany) according to DIN 38407-22 (2001), modified with pre-column derivatization. The limit of determination (LOD) were in the range of 0.2 (Irgarol) and 10 ng L^{-1} (Glyphosat, AMPA) and the limit of quantification (LOQ) from 0.7 to 30 ng L^{-1}.

The soil was air-dried and passed through a 2 mm sieve. The analyses of selected soil properties were performed prior to laboratory study according to DIN ISO 10694 (1996) (OC content), DIN ISO 11261 (1997) and DIN EN ISO 11732 (2005) (total N), DIN EN 15933 (2012) (soil pH) and DIN EN ISO 11272 (2017) (dry density). The soil samples were analyzed for acid herbicides by extracting 20 g of soil with 20 mL acetonitrile, acidified with 12 mL 0.1 N sulfuric acid, shaken for 4 hours and centrifuged for 5 min at 3000 x g (Ultrafuge Filtron, Heraeus, Thermo Fisher Scientific, USA) and cooled for 30 min in ice water. For clean-up, 6 g of anhydrous magnesium sulfate and 1.5 g of natrium chloride were added to the extract. The tube was shaken for 1 minute and centrifuged for 5 minutes at 3000 x g (Ultrafuge Filtron, Heraeus) to separate the acetonitrile phase. Analysis of the extracts was done with liquid chromatography coupled to mass spectrometry (LC-MS/MS). Compounds were separated by reversed-phase LC using a Synergi Fusion RP (VWR, Germany) and detected by MS (4000 QTRAP, AB SCIEX GmbH, Germany). The LOD and LOQ were 0.002

and 0.005 mg kg^{-1} soil dry matter (DM), respectively. For analysis with GC-MS (GC 7000 QQQ –Triple Quadrupole, Agilent Technologies, USA), 4 mL of acetonitrile extract were blown off under a nitrogen stream by evaporation (XcelVap®, Biotage, Sweden) and re-dissolved in 1 mL of isooctane/acetone. The LOD and LOQ were 0.0025 and 0.005 mg kg^{-1}, respectively. For analyses of glyphosate and AMPA, a 5 g amount of soil was extracted with 10 mL of 0.6 M potassium hydroxide. The sample was shaken for 30 min and centrifuged for 30 min at 5000 rpm. A portion of 600 µL of 32 % hydrochloric acid was added to precipitate humic acids for 15 min. Four mL of the sample were diluted with 6 mL water and filtered through a 500 mg Chromabond®C18 ec filter. The filter was previously conditioned with 5 mL methanol and 1 mL water. Samples were analyzed with LC coupled to a triple quadupole MS (LC-MS/MS) (4000 QTRAP, AB SCIEX GmbH, Germany). Compounds were separated by an Unisol Amid Hilic column (Thermo Fisher Scientific, USA). The limit of detection was 0.025 and LOQ was 0.05 mg kg^{-1} soil DM.

2.5 Pesticide application data

For the analyses of pesticide application in the catchment area, farmers were contacted and asked to provide their pesticide application data for a retroactive period of 6 years (2011-2016). Farmers managing arable land adjacent to surface waters were primarily considered for the survey. The following information was requested as part of the survey: date of pesticide application, treated crop, indication of treatment, name of applied pesticide and amount (l ha^{-1}, g ha^{-1}). The amount of active ingredients of each pesticide was searched in the BVL (2020) database. Application data were delivered mainly as Excel® files. In response to the survey, we obtained detailed pesticide use data from 7 farms encompassing a total of 9,573 ha arable land (547 fields), corresponding to 66 % of the total farmland in the catchment area for the period of 2011 to 2016. Application data were tested for improper use by random checks with respect to application amounts, application date and indications. Therefore, it was proven whether the farmers were complying with the application regulations

which are included in the product use instructions for each pesticide (required for labelling of pesticide products) (PflSchG, 2012). Pesticide detections in surface waters were compared to the application data of farmland directly adjacent to the considered surface waters at a radius of approx. 3 km around the sampling point. Pesticide detections in the topsoil samples were compared directly to the application data from the respective field (if available). For the depth profiles at permanent soil observation plots, application data from farmers for a retroactive period of 10 years (2007-2016) were available for analysis. For all pesticide detections in water and soil samples, the days between last application and detection were calculated, if application data were available.

2.6 Sorption and degradation laboratory study

For the laboratory study, homogenized soil samples from depth profiles (sorption study: 0-1 m, degradation study: 2-4 m) with the following soil properties were used: sandy silt, pH 7.8, 0.12 % of OC DM for degradation studies and clayey silt, pH 7.3, 1.29 % of OC DM for the sorption studies.

Sorption studies were performed by carrying out two classic batch test series (A & B). For each batch series, a solution consisting of synthetic rainwater (distilled water with 1.64 mg L^{-1} $KHCO_3$, 6.86 mg L^{-1} $NaNO_3$ and 40.04 mg L^{-1} $CaSO_4$ * 2 H_2O) spiked with the selected pesticide substances (purchased from HPC Standards GmbH and Sigma-Aldrich Laborchemikalien GmbH, Germany, 98.8-99.9 %) at different concentrations were prepared (concentrations in reference batch in µg L^{-1} = bentazone A: 120 & B: 30, diflufenican A: 0.5 & B: 2.7, epoxiconazole A: 94 & B: 180, glyphosate A: 170 & B: 400, imidacloprid A: 90 & B: 200, metazachlor A: 130 & B: 110, MCPA A: 140 & B: 110 and terbuthylazine A: 98 & B: 120).

For this purpose, pesticide substances were added to the synthetic rainwater, stirred at 40℃ for 12 h and then filtered (pressure filtration with 0.45 µm cellulose acetate filter, Sartorius Stedim Biotech GmbH). For the different approaches, soil dry matters of 226 g, 452 g, 903 g, 1355 g and 1806 g along with corresponding process water amounts to achieve liquid-solid

ratios of 8.5, 4.0, 1.7, 1.0 and 0.6 were filled in 2 L glass bottles. As reference for blank subtraction, process water without added soil was used. The batches were shaken overhead for 22 h at 10℃ in the dark and left for 2 h for s edimentation. Then samples were centrifuged for 20 min at 4000 rpm. Supernatants were decanted and filtered (pressure filtration with 0.45 µm cellulose acetate filter, Sartorius Stedim Biotech GmbH) and analyzed for the relevant pesticide substances with HPLC-MS according to 2.4. The difference between the initial pesticide concentration in solution and the concentration after equilibration was assumed to equal the amount of pesticides sorbed to the soil. The following isotherm model equations (1: HENRY, 2: FREUNDLICH) have been applied to determine the sorption coefficients (K_d, K_{Fr}):

$$K_d = \frac{q}{C_{eq}} \quad (1)$$

where Kd (L kg^{-1}) is the linear HENRY sorption coefficient, C_{eq} (mg L^{-1}) is the soil equilibrium concentration and q (mg kg^{-1}) is the amount of pesticides sorbed to the soil

$$q = K_{Fr} * C_{eq}^{n} \quad (2)$$

and K_{Fr} (mg^{1-n} L^{n} kg^{-1}) is the non-linear FREUNDLICH sorption coefficient, n is the FREUNDLICH exponent describing the non-linearity, C_{eq} (mg L^{-1}) is the soil equilibrium concentration and q (mg kg^{-1}) is the amount of pesticides sorbed to the soil. K_d and K_{Fr} values were normalized to the soil organic carbon content (f_{oc}, kg kg^{-1}) after equation 3:

$$K_{OC,}\ K_{FOC,} = \frac{K_{d,} K_{Fr}}{f_{oc}} \quad (3)$$

For examination of the microbial degradation, static batch tests (soil saturation extracts, method embedded in LfULG, 2004) were prepared under anaerobic conditions. Analogous to the sorption study, the homogenous, mixed soil samples were mixed with synthetic rainwater, which was spiked with the pesticide substances at a concentration of 200 µg L^{-1} (solution stirred at 40℃ for 12 h and then pressur e filtered). The produced suspensions with a liquid-solid ratio 0.3:1 were incubated in the dark in air-tight 1 L glass jars at 10℃. For the analyses, pore water was extracted by a stainless-steel pressure-filtration-cell equipped with

a 0.45 µm filter (cellulose acetate filter, Sartorius Stedim Biotech GmbH) up to 2 bar with N_2. The first sampling of pore water was conducted 1 day after preparation of soil saturation extracts, sufficient time for equilibration between liquid and solid phase (data not shown). Pore water samples were analyzed for pesticide substances according to 2.4 every 1-3 months (timewise increasing sampling intervals) in a time span of up to 333 days. Pesticide degradation was described using first-order kinetics:

$$C_t = C_0 * e^{(-k* t)} \quad (4)$$

Where C(*t*) is the concentration of the remaining pesticide substances (µg L^{-1}) at time *t*, C_0 is initial concentration of pesticides (measured in the pore water one day after soil application), and *k* the first-order rate constant of degradation (day^{-1}) determined by non-linear regression. The half-life time $T_{1/2}$ was calculated with the following equation:

$$T_{1/2} = \frac{\ln(2)}{k} \quad (5)$$

2.7 Statistical analyses

SPSS (vers. 26) was used to calculate correlations between discharge amounts and pesticide concentrations and to calculate regression coefficients for the sorption studies.

3 Results

3.1 Precipitation and discharge

Yearly precipitation during the study period amounted to 479 mm (2015) and 441 mm (2016) whereas the most precipitation fell during the summer months (May to September) with amounts of 287 and 246 mm in 2015 and 2016, respectively. One heavy rain event with 30 mm d^{-1} occurred on 5 July 2015. Average registered discharge in 2015 at the Kriebuschbach gauge station was 0.053 m^3 s^{-1}, with the lowest discharge accounting for 0.025 m^3 s^{-1} (15/08/05, 15/09/27) and highest discharge for 0.155 m^3 s^{-1} (15/08/18). In 2016, average

discharge was 0.054 m^3 s^{-1} and ranged between 0.016 m^3 s^{-1} (16/08/24-16/08/27) and 0.32 m^3 s^{-1} (16/02/23). The high discharge was associated with several heavy rain events in February 2016. Accumulated for the weekly intervals, highest discharge was observed in February 2016 (16/02/21- 28) (Figure 2).

"((Figure 2: Total pesticide concentration, number of positive findings and discharge at the Kriebuschbach gauge station in mainly agricultural surroundings (SP_{agr}).)"

Recorded mean discharge at the gauge station Weida in 2015 and 2016 was 0.28 and 0.22 m^3 s^{-1}, respectively. Maximum discharge during the study period was observed on 18 May 2015 (1.08 m^3 s^{-1}) and 23 February 2016 (0.65 m^3 s^{-1}). Lowest discharge was 0.17 m^3 s^{-1} in 2015 (15/06/08) and 0.11 m^3 s^{-1} in 2016 (16/09/15-16). Accumulated for the weekly intervals highest discharge was registered in August 2015 (15/08/10-17) (Figure 3).

"((Figure 3: Total pesticide concentration, number of positive findings and discharge at the gauge station Weida in mainly urban surrounding (SP_{urb}).)"

Compared to the long-term mean (2006-2016) of 0.091 m^3 s^{-1} (Kriebuschbach) and 0.308 m^3 s^{-1} (1966-2016, Weida) measured discharge in the study period was markedly lower.

3.2 Pesticide application

Analyses of pesticide use data in the catchment area showed an application of 112 different pesticide substances during the period of 2011-2016, whereas the number of applied pesticide substances ranged between 29 and 70 per farm and 1 to 58 per field. Types of applied pesticides were mainly herbicides (53 %) and fungicides (26 %). The proportion of applied insecticides, growth regulators and rodenticides was smaller with 10 %, 10 % and 1

%, respectively. Most frequently used pesticide substances are ranked as follows: (1.) tebuconazole, (2.) glyphosate, (3.) prothioconazole, (4.) diflufenican, (5.) trinexapac, (6.) florasulam, (7.) terbuthylazin, (8.) flufenacet, (9.) chlormequat, (10.) lambda-cyhalothrin, (11.) pendimethalin, (12.) metsulfuron, (13.) epoxiconazole and (14.) mepiquat. Indications of incorrect uses of pesticides by farmers (e.g. exceedances of allowed pesticide amounts) were not discernable.

3.3 Detected pesticide substances in water samples

3.3.1 Grab water samples

In the monthly grab water samples, numerous pesticide substances were detected, ranging from 6 (P1) to maximum 35 (P6) different substances (Table S2). At five sampling sites (P2 to P6), pesticide substances were found in all analyzed water samples. The lowest number of detections was observed at sampling site P1 (Kriebuschbach) which is located adjacent to a forest (see Fig. 1). The highest number of pesticides detected was observed at sampling sites in the vicinity of urban areas (P5, P6, P9). The most frequently detected substances were bentazone, glyphosate and its metabolite AMPA, diflufenican, tebuconazole, terbuthylazine, metolachlor, carbendazim and MCPA (Figure 4).

"((Figure 4:.Number of positive detections and maximal concentrations of pesticides in surface water samples (grab water) in the catchment area.))"

The pesticides glyphosate, diflufenican, epoxiconazole and AMPA contributed to the highest concentrations in the water samples with maximum values of 58.0 µg L^{-1}, 17.0 µg L^{-1}, 8.2 µg L^{-1} and 5.4 µg L^{-1}, respectively (see Fig. 4, Table S2). The lowest maximum concentrations were detected for spiroxamine (0.013 µg L^{-1}), chlortoluron (0.015 µg L^{-1}) and

amidosulfuron (0.016 µg L^{-1}). Exceedances of the EQS were documented for diflufenican (EQS: 0.009 µg L^{-1}), bentazone (EQS: 0.1 µg L^{-1}) and epoxiconazole (EQS: 0.2 µg L^{-1}).

3.3.2 Weekly composite water samples

In the composite water samples, in mainly agricultural surroundings (SP_{agr}), nine different pesticide substances were detected during the study period overall (Table 1).

"((Table 1: Minimum, maximum, mean concentrations and frequency of detection of pesticide substances in the weekly composite water samples with mainly agricultural surroundings (SP_{agr}) during the study period of 15/06/19 to 16/07/31 (n=59), pesticide types and their use for agricultural (agric) or dual (urban and agricultural) purposes"))

The most frequently detected substance was glyphosate (9 % of water samples), followed by AMPA, fenpropimorph and quinmerac with 7 % frequency of detection, respectively. Glyphosate and AMPA also contributed to the highest concentrations of maximum 0.20 and 0.21 µg L^{-1} and on average of 0.021 and 0.025 µg L^{-1}, respectively (Table 1). At SP_{agr}, positive detections were found in 26 % of analyzed water samples. Maximum total pesticide concentrations were observed during the period from 15/10/25 to 15/11/22 and on 15/12/06, associated with increasing discharge in times of pesticide application or with temporal delay to pesticides application (see Fig. 2). In contrast to SP_{agr}, at the sampling point in a mainly urban surrounding (SP_{urb}), higher concentrations of pesticide substances and a higher frequency of detection was observed (Table 2, see Fig. 3).

"((Table 2: Minimum, maximum, mean concentrations and frequency of detection of pesticide substances in the weekly composite water samples with mainly urban surroundings (SP_{urb})

364 during the study period of 15/06/19 to 16/07/31 (n=59), pesticide types and their use for
365 agricultural (agric), urban or dual (urban and agricultural) purposes))"

366

367 Here, 24 different substances were present and 90 % of analyzed water samples showed
368 positive detections. The most frequently determined substances were glyphosate, bentazone
369 and AMPA with 63 %, 51 % and 39 % frequency of detection, respectively. The main
370 detected pesticide types were herbicides (19 substances), whereas fungicides and
371 insecticides were found less frequently (3 fungicides, 2 insecticides). A total of 11 of the
372 detected substances are known to be used for dual (agricultural and urban) or solely urban
373 purposes. The highest mean concentrations were measured for glyphosate (0.15 µg L^{-1}),
374 prochloraz (0.08 µg L^{-1}) and AMPA (0.04 µg L^{-1}), whereas prochloraz, glyphosate, MCPA and
375 dichlorprop contributed to the highest maximum concentrations of 4.0, 0.9, 0.4 and 0.3 µg L^{-1},
376 respectively. Pesticide substances were found throughout the whole course of the year
377 (Figure 3). Total pesticide concentrations in the water samples were positive correlated with
378 discharge amounts ($r=0.57$, $p<0.05$, $n=59$). Highest total pesticide concentrations were
379 observed on 15/08/20, accompanied by high precipitation amounts during the period of
380 15/08/16 to 15/08/18 (54 mm) and increasing discharge amounts (4.4 L m^{-3}).

381

382 **3.4 Detected pesticide substances in soil samples**

383 The soil of the catchment area was characterized by pH values in the range of 7.3 to 7.9 and
384 organic carbon (OC) contents of 0.07 to 0.8 % depending on the soil depth (Table S3).

385 In the analyzed soil profiles, 22 different substances were found (Table 3).

386 "((Table 3: Detected pesticide substances in topsoil (n=30) and subsoil (n=5), sampling date:
387 15/11/01), number of detections (Detect.) and minimal (Min) and maximal (Max)
388 concentrations (Concentr.)))"

Concentrations ranged from 0.003 to maximum 0.19 mg kg^{-1} dry matter (DM). The most frequently detected substances in the topsoil were diflufenican (87 %), boscalid (67 %), tebuconazole (60 %), epoxiconazole (57 %) and pendimethalin (47 %). Glyphosate and its metabolite AMPA contributed to the highest concentrations of 0.19 and 0.17 mg kg^{-1} DM, respectively but were only detected in 13 % and 17 % of the considered topsoil samples, respectively. Most detected substances were only present in the topsoil, however some pesticides (e.g. diflufenican, epoxiconazole, MCPA, S-metolachlor, glyphosate) were also measured in the subsoil (>30 cm depth). Residues of MCPA were detected throughout the entire soil profile to a depth of 4.8 m. Glyphosate was found in significant concentration (0.19 mg kg^{-1} DM) at a depth of 2.10 m.

3.5 Pesticide sorption and degradation

Calculated non-linear Freundlich isotherm coefficients (K_{FR}) provided the best fit of the sorption data with coefficients of determination (R^2) in the range of 0.393 to 0.977 (on average: 0.855, Table 4). The K_{FR} isotherm coefficients covered a wide range, from 0.39 to 50.1 mg^{1-n} L^n kg^{-1} (Table 4).

"((Table 4: Henry (K_d) and Freundlich (K_{Fr}) sorption coefficients and half-lives ($T_{1/2}$) of selected pesticide substances (anaerobe degradation)))"

The sorption of the seven selected pesticide substances according to the K_{FR} (K_d) values increased in the following order: bentazone < MCPA < terbuthylazine < metazachlor < imidacloprid < epoxiconazole < glyphosate.

The calculated $T_{1/2}$ values ranged from 26 to 1420 days (Table 4) and increased as follows: terbuthylazine < glyphosate < MCPA < diflufenican < metazachlor < bentazone < epoxiconazole < imidacloprid. For imidacloprid, no half-life time was determinable, as no

significant decrease in concentration over the observed experimentation time was determined.

4. Discussion

4.1 Detected pesticide substances in surface waters

Numerous positive detections of up to 35 different substances were found in the studied surface waters. Most detected substances were herbicides (70 %) whereas fungicides and insecticides only had a proportion of 21 % and 9 %, respectively. Herbicides also contributed to the highest concentrations. These results are in line with previous studies (e.g. UBA, 2019) and correspond to their consumption amounts (see 3.2). In comparison to surface water sampled by automatic samplers (composite water samples), grab water sampling accounted for higher maximum concentrations of pesticide substances. This presumably resulted from the different applied sampling approaches. While automatic sampling of composite water samples is not suitable to determine peak concentrations, grab water sampling may detect maximum concentrations when performed immediately after a rain event. Nevertheless, composite water sampling is assumed to be more favorable because an average pesticide load of surface waters and the chronic exposure for aquatic organisms can be evaluated (Wittmer et al., 2014). Event based (hydrograph-based) sampling is considered to be the best sampling strategy for evaluating pesticide inputs into surface water, but it is also analytically costly (Xing et al., 2013; Wittmer et al., 2014; UBA, 2019). Beyond the sampling strategy, the employed materials that were in contact with the water sample should also be considered. During usage of automatic sampling devices, the water samples are in contact with various materials, depending on the device type. Nonpolar substances, in particular, with a relatively high log octanol-water coefficient as well as cationic substances might be sorbed to these materials, resulting in an underestimation of the actual pesticide concentrations. The automatic sampling device used in this study was equipped with PTFE-tubes and polypropylene bottles, whereas composite water samples were transferred weekly

into glass bottles. As demonstrated by previous studies, PTFE and glass materials not lead to substantial losses of pesticide substances (UBA, 2019). Underestimations of substances caused by the polypropylene bottles cannot be excluded, however, since a modification of the used automatic sampling device was not feasible in this study. Most frequently-detected substances were bentazone, glyphosate, AMPA, diflufenican and tebuconazole. Glyphosate contributed to the highest concentrations, measured in the vicinity of an urban area. These results are confirmed by other studies (e.g. Wittmer et al., 2010; LAWA, 2016; van Bruggen et al., 2018). The predominance of glyphosate and AMPA in environmental samples was assessed as the result of the frequent application of glyphosate-based herbicides and higher application rate compared to other herbicides in agricultural (Benbrook, 2016) and urban areas (Skark et al., 2014; Okada et al., 2020). Also, in our study, glyphosate was the second most frequently used agricultural pesticide in the catchment area. As previously shown, glyphosate and AMPA are prone to off-site transport with water erosion and thus might contribute to pollution of surface waters (Bento et al., 2019). However, it is known that AMPA is also a degradation product of household and industrial phosphonate detergents and thus can be found in WWTPs outlets (Grandcoin et al., 2017).

In accordance with previous studies (e.g. UBA, 2019) the pesticides diflufenican and epoxiconazole were frequently found and detected at high concentrations of 17.0 and 8.2 µg L^{-1}, respectively, in the grab water samples. These high concentrations were observed in the surface water samples in the vicinity of an urban area. While diflufenican could be used as herbicide in urban areas the fungicide epoxiconazole is known rather for agricultural purposes. With the rank 4 (diflufenican) and 13 (epoxiconazole), however, both substances belong to the group of most frequently used agricultural pesticides in the studied catchment (see 3.2). In contrast to our study, however, Martínez et al. (2000) found diflufenican in river water and ground water in very low concentrations never surpassing a level of 0.1 µg L^{-1}, caused by the low water solubility of < 0.05 mg L^{-1} (25 °C) (Lecomte et al., 2001). Nevertheless, it was stated that more adsorbing pesticides like diflufenican may be transported in surface waters by runoff and erosion after heavy rain events (Lecomte et al.,

2001; Larsbo et al., 2016) or by preferential flow through macro pores (Holten et al., 2019). Lecomte et al. (2001) reported concentrations of up to 2 mg L^{-1} in the first runoff after simulated rainfall 24 h after pesticides application. Furthermore, much higher losses from sealed surfaces (asphalt, concrete surface and gravel) than from arable fields were reported for diflufenican and other urban herbicides by Spanoghe et al. (2005). Caused by the very low affinity for water (octanol/water partition coefficient (log K_{ow}): 4.2) (PPDB, 2020), diflufenican adsorbed strongly to asphalt with the formation of dislodgable residues (Spanoghe et al., 2005). Thus, diflufenican which is known to be persistent ($T_{1/2}$: up to > 365 days, Bending et al., 2006), may remain available for loss to the environment for a long time. Such runoffs from sealed surfaces and/or from arable land could be an explanation for the determined long temporal distance between detection and application (Table 5) and the in-part extremely high diflufenican concentrations found in our study. Also, farmyard runoff from sealed surfaces after cleaning of crop protection sprayers, as stated in several studies (e.g. Müller et al., 2002; Bach et al., 2005), may be a possible input pathway.

"((Table 5: Detected pesticide substances in water and soil samples (listed after frequency of detection) related to the application time (for soil samples only, analyses of 5 soil depth profiles)))"

In accordance with various studies (Doussett et al., 2014, LAWA, 2019), bentazone was frequently detected in surface waters of the studied catchment, which can be explained by its high mobility (Li et al., 2003) and its persistence in the soil-water system (Pareja et al., 2012). Rapid degradation, however, was observed for the aerobic topsoil with half-lives of 17 days, whereas no bentazone was detected in the leachate of lysimeters (Schuhmann et al., 2019). In contrast, very slow degradation of bentazone was reported for the subsoil with $T_{1/2}$: of 515 days in 70-80 cm soil depth (Rodríguez Cruz et al., 2008). This observation was confirmed by the determined $T_{1/2}$ for bentazone in our laboratory study of 839 days. Thus, delayed

inputs of bentazone, independent of the actual application, cannot be excluded. This assumption can be proofed by the analysis of application data from farmers showing a temporal delay from more than 4 up to more than 5 years between application and detection of bentazone in surface water samples (Table 5). However, it should be taking into account that the entire farmland was not included in the survey (66 % of farmland, in particular farmland adjacent to surface waters) and thus it cannot be completely excluded that the lack of data might have caused this strong temporal delay between application and detection. Nevertheless, long transport processes of pesticides to surface waters due to long-term storage in the subsoil were also reported elsewhere (Sandin et al., 2018).

The pesticides fenpropimorph, MCPA, tebuconazole and mecocrop were also found frequently in the surface water samples of the studied catchment. These pesticides can be used for both non-agricultural and agricultural purposes. In urban areas, mecocrop and MCPA are applied as herbicides on lawns (Gerecke et al., 2002), as root protection agents in flat-roof sealings (mecocrop) or as wood preservatives (fenpropimorph) (BAuA, 2020). Various studies showed high concentrations of mecocrop in roof runoff, which may be transported by rain events into WWTPs or directly into surface waters by combined sewer outflow or separate sewers (Gerecke et al., 2002). Thus, one can assume that the water quality in the catchment area of our study site was affected substantially by urban sources. This assumption was confirmed by the occurrence of wastewater tracers, which were found in all surface water samples (data not shown). High concentrations of caffeine, saccharine and cyclamate indicate the input of untreated wastewater, because these substances are known to be more than 90 % degraded in WWTPs (Scheurer et al., 2009). Furthermore, the impact of urban pesticide inputs was confirmed by the detected pesticide substances in analyzed composite water samples. At the sampling site with a mainly urban surrounding (SP_{urb}), the number of positive detections as well as the number of detected substances and concentrations were higher compared to the site in a mainly agricultural surrounding (SP_{agr}). Furthermore, the analysis of application data from farmers showed that several pesticide

524 substances with dual uses were not applied in the last 6 years in the catchment area (see
525 Table 5).

526

527 **4.2 Dynamic of pesticide concentrations in surface water**

528 Surface water samples at SP_{urb} showed positive detections throughout the entire year (90 %
529 of analyzed samples), while at SP_{agr} pesticide substances only were found seasonally-
530 associated with times of pesticides application (26 % of analyzed samples). These results
531 are in accordance with previous studies (Wittmer et al., 2014). Wittmer and Burkhardt (2009)
532 noted that increased inputs of agricultural pesticides into surface waters usually occur during
533 the application seasons. In contrast, substances from urban areas can enter surface waters
534 throughout the year. The authors reported that substances released from an urban and an
535 agricultural area showed different concentration dynamics. Peak discharges after rainfall
536 events in agricultural areas were considerable lower compared to urban areas, because
537 water was adsorbed and subsequently released by the unsealed soils. In the urban areas,
538 water flowed off the sealed surfaces (e.g. roads, paved areas, roofs) without any delay and
539 may directly reach surface waters via rainwater sewers or combined sewer systems via
540 overflow basins of WWTPs. This discharge dynamic in urban areas was also confirmed by
541 the detected correlation between total pesticide concentrations and discharge amounts at
542 SP_{urb}, while no correlation was observed at SP_{agr}. For agricultural pesticide losses, two main
543 sources were discussed: diffuse losses from agricultural soils (overland flow, preferential
544 flow, drainage) on the one hand and point sources by spills on roads or farmyards on the
545 other hand (Müller et al., 2002; Bach et al., 2005). Diffuse losses were described by
546 increasing pesticide concentrations with increasing discharge during rain events in the
547 application season (Wittmer et al., 2010). This dynamic was observed in our study at SP_{agr},
548 with detection of agricultural substances directly during application season or with temporal
549 delay associated with increasing discharge after application times. In contrast, point sources
550 may cause extremely high but short-duration concentration peaks (Wittmer et al., 2010), as

551 detected in the surface water in urban areas of our study. Furthermore, pesticide substances
552 with solely urban use were found at SP_{urb}, but were not present at SP_{agr}. Glyphosate, as a
553 typical pesticide applied also in urban areas, was detected in 63 % of analyzed samples at
554 SP_{urb}, also outside of typical agricultural application times and in partly high concentrations.
555 In accordance with our results, Hanke et al. (2010) noted that more than a half (60 %) of the
556 glyphosate load during rain events originates from urban areas. Nevertheless, the presence
557 of typical agricultural pesticides in the surface water of SP_{urb} indicates that both agricultural
558 and urban sources displayed an impact on surface water quality in the studied catchment.

559

560

561 **4.3 Detected pesticides in soil, pesticides sorption and degradation**

562 In the soil samples, numerous different substances were detectable. Multiple pesticide
563 residues of ≥ 2 or even ≥ 5 pesticides in more than a half of analyzed top soil samples of
564 European arable soils were also reported previously (Hvězdová et al., 2018; Silva et al.,
565 2019). Thereby concentration levels of pesticide residues were in many cases noticeable (36
566 % of soils with ≥ 3 pesticides exceeding 0.01 mg kg^{-1} (Hvězdová et al., 2018). Detected
567 pesticide concentrations in the soil profiles of our study, however, were in total on a lower
568 level. In most cases, pesticide concentrations did not exceed 0.01 mg kg^{-1}. Diflufenican,
569 boscalid, tebuconazole and epoxiconazole were the most frequently detected substances in
570 the considered topsoil samples. These results are in line with other studies (Hvězdová et al.;
571 2018; Silva et al., 2019). Diflufenican is known to be a pesticide that becomes tightly sorbed
572 to soil components, with high variability in degradation rates, and thus may accumulate upon
573 repeated use at the same site (Bending et al., 2006). Linear sorption coefficients (K_d) of
574 arable soils in the range of 207 to 694 L kg^{-1} were reported by Benoit et al. (2008).
575 Unfortunately, we could not determine sorption coefficients of diflufenican in the laboratory
576 study because the maintained solution concentration was too low (low water solubility of
577 diflufenican). Half-lives of diflufenican were given with a significant variability, in a range of 65

to 621 days in the field and 41.4 to 318 days in the laboratory (PPDB, 2020). The $T_{1/2}$ value of 76 days observed in our laboratory study (see Table 4) was in the reported range. Nevertheless, the detected diflufenican residues in the soil profiles, up to several years after their application, indicate a high spatial variability of degradation in the field, depending on soil properties and sorption on soil matrix, as also shown by Bending et al. (2006). The frequent findings of diflufenican in soil samples correspond to the similarly high frequency of detection in surface water samples, suggesting pesticide inputs by erosion and run-off as reported by Larsbo et al. (2016).

The high detection frequency of the substances boscalid, tebuconazole and epoxiconazole in the considered soil samples corresponds to their common use as broad-spectrum fungicides and their environmental properties. These substances were evaluated as moderate to strong sorbing, less water soluble (4.6-36 mg L^{-1}) and persistent (PPDB, 2020). Thus, it is not unexpected that the pesticides were widely detectable in different environmental compartments as shown by various authors (Smalling et al., 2013; Hvězdová et al., 2018; Silva et al., 2019). It was reported previously that these substances tend to accumulate in soil profiles and form long-term residues, particularly as a result of repeated application (Lewis et al., 2016). Degradation half-lives in the field were stated in the range of 26 to 312 days and in the laboratory of 103 to 1214 days (boscalid), > 365 days (tebuconazole) and 98 to 2236 days (epoxiconazole) (PPDB, 2020). Our laboratory study resulted in a $T_{1/2}$ value of 1420 days for epoxiconazole, which is in line with the values noted in literature. For tebuconazole a trend for increasing persistence with increasing dose rate was observed in several laboratory studies (e.g. Papadopoulou et al., 2016). Previous studies reported that the strong sorption of these fungicides might slow mineralization by reducing their availability to microorganisms (Herrero-Hernández et al., 2011; Passeport et al., 2011). Furthermore, the formation of NER maintains a proportion of desorbable mobile residues (Passeport et al., 2011). Sorption coefficients normalized to soil OC contents (K_{FOC}) were noted in a range of 1909 to 2676 mg^{1-n} L^{n} kg^{-1} for boscalid (PPDB, 2020), 438-1691 mg^{1-n} L^{n} kg^{-1} for tebuconazole and 280-2647 mg^{1-n} L^{n} kg^{-1} for epoxiconazole (Passeport et al., 2014). The

606 K_{FOC} values for epoxiconazole with 1429 mg^{1-n} L^{n} kg^{-1} observed in our laboratory study were
607 in line with the values from literature. Thus, it can be suggested that the formation of long-
608 term residues of the three considered fungicides may explain the strong temporal delay
609 between detection of substances in soil and application by farmers. Otherwise, it should be
610 noted that tebuconazole also can be used for seed treatment, which was not documented by
611 farmers but also may led to tebuconazole residues in the soil.

612 Contrary to the study of Hvězdová et al. (2018), we frequently found pendimethalin in the
613 considered soil profiles, with 47 % of positive detections. This was unexpected because the
614 pesticide was not applied from farmers during the last 10 years at the 5 analyzed depth soil
615 profiles. Pendimethalin can be assumed as a persistent ($T_{1/2}$: 39.8-187 days, DT_{90}: 144-582
616 days) and moderately volatile substance (PPDB, 2020). It has the potential for migrating
617 significantly through the air, whereas concentrations rapidly declined with distance from
618 application (Vighi et al., 2017). Nevertheless, it is possible that pendimethalin may be
619 occurring in regions near and down-wind of application areas (Vighi et al., 2017). This could
620 be an explanation for the positive pendimethalin detections in the soil samples independent
621 from its application in our study, particularly as pendimethalin belonged to the group of
622 frequently used herbicides within the considered catchment area (rank 11, see 3.2).
623 Furthermore, the repeated application of pendimethalin or/and the occurrence of
624 pendimethalin in mixtures with other pesticides could enhance its persistence in the
625 environment (Kaur and Bullar, 2019).

626 It was revealed in our study that Glyphosate and AMPA contributed to the highest
627 concentrations in the considered soil samples. These observations are in line with the results
628 of Silva et al. (2018, 2019), whereby in our study the frequency of detection (13 and 17 %)
629 and concentrations (0.19 and 0.17 mg kg^{-1}) were comparable lower. Silva et al. (2018, 2019)
630 noted a detection frequency of 45 % for both substances and concentrations of 2.05 mg kg^{-1}
631 (glyphosate) and 1.92 mg kg^{-1} (AMPA). Glyphosate residues were not only detected in the
632 top soil but also at a depth of up to 4.50 m in our study. These results contradict previous

studies that only found glyphosate and AMPA sporadically and at low concentrations in deeper soil layers and groundwater, indicating that the leaching of these compounds is generally unlikely and negligible (e.g. Poiger et al., 2017). Also, in the lysimeter study of Bergström et al. (2011), glyphosate residues only were detected in the topsoil (0-30 cm) and in the 30-60 cm layer in a clay soil 748 days after application. These observations were explained by the high sorption of glyphosate to the soil matrix, which indicates a low risk of leaching (Klier et al., 2008; Gros et al., 2020). However, it was stated that translocation processes of glyphosate sorbed to soil particles in clay soils are possible due to preferential flow through macropores (Al-Rajab et al., 2008). The negatively charged glyphosate molecule is known to sorb strongly to the soil matrix, particularly at high soil OC and clay contents, depending on soil pH (Al-Rajab et al., 2008). Thus, glyphosate can interact strongly with organic matter (e.g. peptides, carbohydrates) and mineral surfaces (e.g. goethite, montmorillonite) caused by the variety of binding sites (Gros et al., 2017; Ahmed et al., 2018). In the literature, a wide range of K_{Fr} values between 0.6 to 2751 mg^{1-n} L^{n} kg^{-1} for glyphosate were reported (Vereecken, 2005; Wang et al., 2005; Gros et al., 2017). We obtained a K_{Fr} value of 50 mg^{1-n} L^{n} kg^{-1} for glyphosate, which was in line with the noted range. Various studies noted that a high proportion of the initial glyphosate (up to nearly 70 %) was in-part present in the soil as NER (Mamy et al., 2005; Al-Rajab et al., 2008). It is known that the formation of NER reduces their availability to degrad microorganisms by stabilization. Otherwise, these bound residues could become available and take part in biodegradation and leaching and thus may contribute to delayed contaminations of ground- and surface waters (Mamy et al., 2005; Al-Rajab et al., 2008). Glyphosate residues in the studied soil profiles at a depth of up to 4.5 m were found in our study in the absence of AMPA, indicating that glyphosate was more persistent than expected. Rapid microbial degradation of glyphosate in soil has been reported by numerous authors with the occurrence of AMPA, the most predominant degradation product, which is known to be more persistent (e.g. Borggaard and Gimsing, 2008; Mamy et al., 2005). The lysimeter study of Gros et al. (2020) also noted a rapid degradation of glyphosate with recoveries in soil of < 3

% and < LOD for glyphosate and AMPA, respectively. However, the enrichment of ^{15}N and ^{13}C and the absence of glyphosate and AMPA leachates indicated further degradation products and/or the formation of NER. In our laboratory study, the $T_{1/2}$ for glyphosate was determined to be 33 days and thus in accordance with the range reported previously (<1 to 180 days) (Mamy et al., 2005; Bergström et al., 2011; Tang et al, 2018; PPDB, 2020). Nevertheless, the strong sorption of glyphosate in the soil matrix as established in the accompanying laboratory study may reduce glyphosate availability and increase its persistence in soil as noticed by Okada et al. (2019). This assumption was confirmed by the observed temporal delay between application and detection of glyphosate of 60 days to maximum more than 10 years.

For the strobulurin fungicides pyraclostrobin, azoxystrobin and dimoxystrobin as well as the insecticide imidacloprid, either a strong temporal delay between detections in soil profile and application by farmers or no association with their application (imidacloprid) was observed. This presumably was caused by the chemical properties of these substances, which are known to be strong sorbing (log K_{OC}: 2.4-4.0) and moderately to strong persistent (DT_{90}: 80 to >1000 days) (PPDB, 2020) and thus were commonly found in soil profiles (Hvězdová et al., 2018). Persistence in soils was confirmed in our laboratory study for imidacloprid. Here, $T_{1/2}$ value was not determinable because no significant decrease in concentration was observed over the entire study period of 333 days. In addition, the use for seed treatment for some of these substances (imidacloprid, azoxystrobin), which was not documented by farmers, could also be a possible explanation that findings were not related to their application data by farmers.

Conclusions

Numerous pesticide substances were detected in the water and soil samples within the considered catchment area, where they might substantially contribute to environmental pollution. Analyses of pesticide application data from farmers showed in most cases that

pesticide detections in water and soil samples were not consistent with their application. Analyses of soil samples and the accompanying batch tests showed that primarily strong sorbing substances might accumulate in the soil over long periods, exhibiting strong temporal delay compared to their application. This persistence presumably resulted from a decreased microbial availability and thus delayed degradation of the pesticides. It can be assumed by the present study that both agricultural and urban sources affect the water quality in the catchment area substantially. Urban inputs, however, led to the highest pesticide concentrations and the highest number of detected pesticide substances over the entire course of the year. Thus, the urban use of pesticides should receive more attention when establishing reduction measures in the future. In this context, the following proposals can be suggested: sensitization of inhabitants, more transparency for labelling of biocide products, monitoring of biocide consumption, expansion of sewage treatment plant connections in rural areas and, additionally, better education of local farmers to avoid point sources from cleaning of crop protection sprayers on farmyards. In addition, all measures for erosion protection and the substitution of persistent substances would be appropriate to avoid delayed pesticide inputs into ground- and surface waters. In further studies, the formation of degradation products and NER should be considered more in detail.

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Supplementary Material

"((Table S1:.List of analyzed substances and analytical technology))"

"((Table S2: Number of detected pesticide substances and exceedances of environmental quality standards (EQS) and highest concentrations in the monthly grab water samples (n=12) of the sampling sites P1 to P9 during the study period (2015/07/22 to 2016/06/23))".

"((Table S3:.Physicochemical properties of soils (soil depth profiles, average value, n=5) (sampling date 2016/11/11))"

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“Figure 4:.Number of positive detections and maximal concentrations of pesticides in surface water samples (grab water) in the catchment area.”

Table 1: Minimum, maximum, mean concentrations and frequency of detection of pesticide substances in the weekly composite water samples with mainly agricultural surrounding (SP_{agr}) in the study period of 15/06/19 to 16/07/31 (n=59), pesticide types and their use for agricultural (agric) or dual (urban and agricultural) purposes

Substances	Frequency of detection (%)	Concentration (µg L^{-1})			Use (type)
		Min	Max	Mean	
AMPA[1]	7.0	0.12	0.21	0.025	-
boscalid	1.8	0.01	0.01	0.005	agric (h)
diflufenican	3.5	0.005	0.006	0.002	dual (h)
fenpropimorph	7.0	0.008	0.036	0.003	dual (f)
glyphosate	8.8	0.03	0.20	0.021	dual (h)
imidacloprid	3.5	0.0007	0.0008	0.0004	dual (i)
metazachlor	1.8	0.03	0.03	0.006	agric (h)
quinmerac	7.0	0.01	0.01	0.006	agric (h)
tebuconazole	3.5	0.011	0.014	0.005	dual (f)

1: aminomethylphosphonic acid: metabolite of glyphosate, h: herbicide, f: fungicide, i: insecticide

Table 2: Minimum, maximum, mean concentrations and frequency of detection of pesticide substances in the weekly composite water samples with mainly urban surrounding (SP_{urb}) in the study period of 15/06/19 to 16/07/31 (n=59), pesticide types and their use for agricultural (agric), urban or dual (urban and agricultural) purposes

Substances	Frequency of detection (%)	Concentration (µg L^{-1})			Use (type)
		Min	Max	Mean	
amidosulfuron	1.7	0.018	0.018	0.005	agric (h)
AMPA[1]	38.9	0.03	0.18	0.04	-
bentazone	50.8	0.01	0.04	0.009	agric (h)
chlorotoluron	3.4	0.01	0.08	0.006	agric (h)
dichlorprop	18.6	0.02	0.33	0.015	agric (h)
diflufenican	3.4	0.003	0.004	0.002	dual (h)
dimethoate	3.4	0.02	0.07	0.006	dual (i)
diuron	1.7	0.05	0.05	0.006	urban (h)
fenpropimorph	16.9	0.008	0.03	0.004	dual (f)
flufenacet	1.7	0.08	0.08	0.006	agric (h)
flurtamone	1.7	0.09	0.09	0.006	agric (h)
glyphosate	62.7	0.04	0.90	0.15	dual (h)
imidacloprid	3.4	0.0007	0.0007	0.0004	dual (i)
isoproturon	3.4	0.017	0.15	0.007	dual (h)
MCPA	16.9	0.01	0.42	0.015	dual (h)
mecocrop	16.9	0.01	0.14	0.01	dual (h)
metamitron	3.4	0.02	0.11	0.007	agric (h)
metazachlor	1.7	0.02	0.02	0.005	agric (h)
metolachlor	5.1	0.01	0.05	0.006	agric (h)
prochloraz	18.6	0.01	4.00	0.08	agric (f)
quinmerac	3.4	0.01	0.06	0.006	agric (h)
tebuconazole	6.8	0.01	0.08	0.007	dual (f)
terbuthylazine	11.9	0.01	0.04	0.007	agric (h)
Tribenuron-methyl	3.4	0.01	0.02	0.005	agric (h)

1: aminomethylphosphonic acid: metabolite of glyphosate, h: herbicide, f: fungicide, i: insecticide

Table 3: Detected pesticide substances in topsoil (n=30) and subsoil (n=5), sampling date: 15/11/01), number of detections (Detect.) and minimal (Min) and maximal (Max) concentrations (Concentr.)

	Topsoil (0-30 cm)		Subsoil (30-90 cm)		Subsoil (>100 cm)	
	Detect.	Concentr. ($mg\ kg^{-1}$ DM) (Min-Max)	Detect.	Concentr. ($mg\ kg^{-1}$ DM) (Min-Max)	Detect.	Concentr. ($mg\ kg^{-1}$ DM) (Min-Max)
AMPA[1]	5	0.03-0.17	-	-	-	-
azoxystrobin	4	0.003-0.005	-	-	-	-
beta-cyfluthrin	1	0.004	-	-	-	-
boscalid	20	0.003-0.06	-	-	-	-
diflufenican	26	0.003-0.06	2	0.003-0.01	-	-
dimoxystrobin	3	0.003-0.003	-	-	-	-
epoxiconazole	17	0.003-0.03	1	0.003	-	-
glyphosate	4	0.03-0.09	-	-	3	0.01-0.19
imidacloprid	1	0.003	-	-	-	-
lambda-cyhalothrin	1	0.003	-	-	-	-
MCPA	4	0.003-0.014	2	0.008-0.01	1	0.01
metamitron	4	0.003-0.01	-	-	-	-
metazachlor	1	0.01	-	-	-	-
S-metolachlor	5	0.003-0.01	1	0.01	1	0.01
nicosulfuron	1	0.005	-	-	-	-
pendimethalin	14	0.003-0.04	2	0.003-0.01	1	0.007
prochloraz	5	0.003-0.02	-	-	-	-
propiconazole	1	0.03	-	-	-	-
pyraclostrobin	1	0.005	-	-	-	-
quinmerac	1	0.003	-	-	-	-
tebuconazole	18	0.003-0.09	2	0.003-0.004	-	-
terbuthylazin	10	0.003-0.01	1	0.004	-	-

1: aminomethylphosphonic acid: metabolite of glyphosate, DM: dry matter

Table 4: Henry (K_d) and Freundlich (K_{Fr}) sorption coefficients and half-lives ($T_{1/2}$) of selected pesticide substances (anaerobe degradation)

Substances	K_d $L\ kg^{-1}$	R^2	K_{Fr} $mg^{1-n}\ L^n\ kg^{-1}$	n	R^2	$T_{1/2}$ days
bentazone	0.7	0.075	n. d.	n. d.	n. d.	839
diflufenican	n. d.	n. d.	n. d.	n. d.	n. d.	76
epoxiconazole	23.6	0.834	18.4	0.86	0.941	1420
glyphosate	455.9	0.899	50.1	0.63	0.952	33
imidacloprid	4.8	0.320	0.67	0.41	0.942	n. d.
MCPA	1.6	0.441	0.39	0.66	0.393	34
metazachlor	2.5	0.828	0.49	0.41	0.977	398
terbuthylazin	3.1	0.694	1.11	0.61	0.926	26

n. d.: not determinable, due to no significant decrease in concentration (degradation studies), too low solution concentrations or concentration changes (sorption studies)

Table 5: Detected pesticide substances in water and soil samples (listed after frequency of detection) related to the application time (for soil samples only analyses of 5 soil depth profiles)

Water samples	Days between detection and application		Soil samples	Days between detection and application	
Detected substances	Min	Max	Detected substances	Min	Max
bentazone	1556	1893	diflufenican	30	3650
glyphosate	11	298	boscalid	730	730
AMPA	11	298	tebuconazole	150	1095
diflufenican	1	193	epoxiconazole	150	150
tebuconazole	6	139	pendimethalin	n.a.[1]	n.a.[1]
terbuthylazin	15	370	terbuthylazin	365	3285
S-metolachlor	23	370	S-metolachlor	365	3285
carbendazim	n.a.	n.a.	AMPA	60	n.a.[1]
MCPA	n.a.	n.a.	prochloraz	365	n.a.[1]
imidacloprid	n.a.	n.a.	MCPA	365	n.a.[1]
fenpropimorph	65	372	glyphosate	60	n.a.[1]
isoproturon	197	227	metamitron	1460	1460
mecocrop	42	103	azoxystrobin	730	n.a.[1]
diuron	n.a.	n.a.	dimoxystrobin	730	730
metamitron	55	362	metazachlor	2920	2920
epoxiconazole	20	204	imidacloprid	n.a.[1]	n.a.[1]
propiconazole	44	44	lambda-cyhalothrin	2920	2920
chloridazon	820	820	propiconazole	180	180
nicosulfuron	92	372	pyraclostrobin	180	180
quinmerac	362	362	quinmerac	n.a.[1]	n.a.[1]
acetamiprid	785	785			

n. a.: no application in the last 6 years, n.a.[1]: no application in the last 10 years

Highlights

- Higher pesticide pollution of surface waters in mainly urban surroundings
- Glyphosate, AMPA, diflufenican and tebuconazole most frequently detected substances
- Pesticide detections were not consistent with application data from farmers
- Pesticides remained in soil over a long period, favored by sorption on soil matrix

Authors statement to Decision Letter for ENVPOL_2020_3439

Many thanks for the helpful comments from the reviewers to our manuscript entitled:

” Assessment of pesticide inputs into surface waters by agricultural and urban sources - a case study in the Querne/Weida catchment, central Germany”.

We agree with the reviewers and changed the manuscript accordingly. In our revisions, we have considered all comments and remarks of both reviewers. As suggested by reviewer#1, the section on the sorption studies was revised substantially to provide a better understanding. Furthermore, all information that was required by both reviewers were implemented in the method and discussion section. Units were changed to a consistent format in all Figures and Tables, as rightly stated by reviewer#1. In our revised manuscript changes were made in the text, Figure 2, Figure 3 and Figure 4, Table 4, Supplementary Material and Highlights.