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Discharge and fate of biocide residuals to ephemeral stormwater retention pond sediments

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ABSTRACT

Biocides used in paints and renders prevent algae and fungi growth but can wash off during wind-driven rain and enter urban environments. Retention ponds represent part of stormwater management that retain water and partly pollutants. However, it is poorly understood which percentage of biocides leached from facades reaches a pond and how efficiently biocides are retained inside ponds although biocides can have harmful environmental effects. Here, we combined measurements and modeling to address diffuse biocide loss and a pond's retention capacity in a delimited residential area of 3 ha, with detached houses connected to an ephemeral retention pond. Six stormwater events were sampled within 2 years and confirmed biocidal residuals at pond inflow. Model results revealed that during the sampled events only 11% of terbutryn leachate arrived at the pond while the major part of this biocide was diffusely lost in the residential area. Measured low terbutryn concentrations in the sediment (mean 2.6 ng g^{-1}) confirmed this result. Model results suggested that approximately 50% of terbutryn reaching the pond were retained and degraded. Our results are site-specific but suggest that biocide retention in ponds is limited, environmental entry pathways are diverse and that biocide use should be limited at its source.

Key words: biocides, retention pond, terbutryn, transformation products, urban stormwater management

HIGHLIGHTS

- Comparison of measured and modeled data suggests that diffuse losses are the major pathway (89%) of biocides.
- Only 11% of leached terbutryn arrived at the stormwater retention pond where about half was retained while the remaining half spilled over into the sewage system.
- Results imply diverse entry pathways of biocides and suggest measures at the source are best.

1. INTRODUCTION

Retention ponds are important parts of stormwater management in urban areas. Since 2009, the German Federal Water Act requires to avoid, retain or infiltrate stormwater locally (WHG 2009 §55). Besides stormwater, ponds can also retain pollutants from the inflowing stormwater including diverse contaminants (Sébastian *et al.* 2015). Two types of ponds can be distinguished: first, treatment wetlands often constructed primarily to remove pollutants and improve water quality (Kadlec & Wallace 2008), and second, retention ponds primarily designed for water retention that are dry during phases of low precipitation and/or high evaporation. The type of pond and its water variability are crucial to understanding the fate of pollutants. For example, while treatment wetlands in agriculture have been found to control pesticide dissipation (Imfeld *et al.* 2021) and remove pesticides (Maillard *et al.* 2011), pollutants in a retention pond connected to an urban catchment revealed low retention of pesticides (Sébastian *et al.* 2015). At the latter pond, pesticides occurred mainly in low concentrations of 2–286 ng g^{-1} in the sediment (Wiest *et al.* 2018). However, most studies in urban areas address pollutants in treatment wetlands or infiltration systems (Allinson *et al.* 2015; Tedoldi *et al.* 2016) and thus knowledge about pollutant retention in stormwater retention ponds is comparatively limited.

One example of contaminants in urban stormwater is biocides that act as active ingredients in coatings to prevent algae and fungi growth on façades. During wind-driven rain events, these biocides are partly washed off, enter the environment (Burkhardt *et al.* 2012) and may have detrimental effects on aquatic organisms (Musgrave *et al.* 2011) and soil microorganisms (Fernández-Calviño *et al.* 2021). Biocides also degrade into transformation products (TPs) that are often more mobile and persistent in the aquatic environment. TPs might have similar or even higher toxicity for various species compared to their parent compounds (Hensen *et al.* 2020). The focus of this study is on three commonly and complementary used biocides, namely diuron, octylisothiazolinone (OIT) and terbutryn, that act as herbicide, fungicide and algaecide, respectively. All of them can be toxic to environmental organisms even in low concentrations with predicted no-effect concentration (PNEC) values in the freshwater of 0.02 $\mu g\ L^{-1}$ for diuron, 0.013 $\mu g\ L^{-1}$ for OIT and 0.034 $\mu g\ L^{-1}$ for terbutryn (Paijens *et al.* 2019).

While various studies confirm biocide entry into urban stormwater (Burkhardt *et al.* 2012; Hensen *et al.* 2018; Wicke *et al.* 2021a) only a few studies so far focused on sediments in urban stormwater infrastructure as a target compartment of biocide pollution. Two studies sampled sediments in urban wetlands in Sweden (Flanagan *et al.* 2021) and in Australia (Allinson *et al.* 2015) and detected the biocide terbutryn only in one and in no sample, respectively. For retention ponds, there is little knowledge of the amount of biocides retained in pond sediment and we are not aware of a mass balance. Sébastian *et al.* (2015) analyzed samples of a detention pond for biocides used in film preservatives, such as terbutryn, irgarol, and isothiazolinone, but did not detect any of them in pond sediments.

Due to the utilization of terbutryn as an agricultural pesticide, several studies exist on its interaction with soil/sediment (Muir & Yarechewski 1982; Avidov *et al.* 1985). The sorption of terbutryn generally increases with pH and soil organic carbon (Johann *et al.* 2018). Degradation kinetics and formation of TPs in soil are described in Bollmann *et al.* (2017) pointing to a long half-life time of 231 days for terbutryn. Junginger *et al.* (2022) differentiated degradation pathways of terbutryn, namely biodegradation, photodegradation and abiotic hydrolysis, using compound-specific isotope analysis. Lower degradation rates of terbutryn were found with lower redox potentials (Muir & Yarechewski 1982) and less microbial activity (Avidov *et al.* 1985). As all biocides may have toxic impacts on the environment, it is important to understand their environmental fate including entry pathways and potential sinks such as ponds.

To assess the fate and risks of terbutryn in pond sediments, it is necessary to quantify the amount of biocides leached from facades in the contributing catchment. Biocide emissions depend on temperature, sunlight irradiation, amount of biocide used, precipitation amount, and antecedent moisture, among others (Paijens *et al.* 2019). Usually, limited data are available and only models can fill this gap including various assumptions and uncertainties. For example, Coutu *et al.* (2012) modeled yearly biocide emissions and concentrations in receiving surface waters for the city of Lausanne based on experimental data of Burkhardt *et al.* (2011); they arrived at total emissions for Lausanne of 900 kg $year^{-1}$. Paijens *et al.* (2021) calculated the annual mass load discharged from Paris to the Seine River using Monte Carlo simulations based on measurement data and estimation of stormwater proportions. The annual terbutryn load discharged by wastewater treatment plants was 10–20 kg $year^{-1}$, whereas the load from combined sewer overflow was by a magnitude lower (0.5–0.7 kg $year^{-1}$). However, these authors did not provide information about the amount of biocide originally leached from individual facades that might be important for investigations in smaller urban areas. The model software COMLEAM calculates biocide wash-off from facades (Burkhardt *et al.* 2021) and was already applied to urban areas studies (Wicke *et al.* 2022). In this study, we use COMLEAM to determine the biocide emissions of a residential area.

Besides emissions, the transport of biocides and the arrival at selected sinks such as surface water, soil or groundwater are important. Wicke *et al.* (2022) investigated a residential area in Berlin and established a 1.5-year mass balance to show that over 90% of emitted biocides were diffusely lost around buildings. Thus, ponds might only receive a small part of emitted biocides of a connected area. Besides the amount of biocide flowing into a pond, it is important to understand biocide accumulation and degradation within a pond to determine the biocides' fate over time and the possible biocide retention.

In this study, we aim to determine (a) typical biocide loads from a well-defined urban area and losses on the way to a retention pond and (b) a biocide mass balance for the pond and hence assess its remediation potential.

Our study area is a homogenous, clearly delimited 3-ha residential area of one-family dwellings built during the last 13 years. It represents a typical residential development area of Germany and other European countries. The connected retention pond has limited infiltration capacity. We conducted measurements of diuron, OIT, terbutryn and four TPs in urban stormwater entering the pond. In parallel, we analyzed terbutryn and its TPs in sediment samples over a period of 2 years. We then used the model COMLEAM and the urban rainfall–runoff model RoGeR_WB_Urban (Steinbrich *et al.* 2021) to calculate continuous terbutryn emissions and pond inflow. Finally, we combined all data to establish a 13-year mass balance of terbutryn in pond water and sediments.

2. METHODS

2.1. Study area

The study area is a part of Nussdorf, a district of the city Landau in southwestern Germany (49° 13′ 29.3088″ N 8° 6′ 17.3124″ E) located in the foothills of the northern Upper Rhine Valley, covered with loess loams (approximately 10 m). Clays, marls and limestone banks in deeper layers act as aquicludes (Stadt Landau in der Pfalz 2004). The study area comprises 46 detached houses built since 2009 (Table S1, Supplementary material). Two pipes collect stormwater runoff (Pipe East and Pipe West) and discharge into a 1,219 m^2 retention pond where stormwater remains, evaporates, slowly infiltrates or spills over into the sewage system (Figure S1, Supplementary material). Pipe West collects runoff from 30 houses adjoining two streets, and Pipe East from 16 houses built along one street (Figure 1). Connected catchment areas are 19,462 m^2 at Pipe West and 10,199 m^2 at Pipe East.

Vegetation differs within the pond: reed grows at Pipe West, and grass at Pipe East. Clearing takes place once a year during winter. At Pipe West, continuous seepage creates saturated soil and small puddles which was already observed during pond construction. Only little infiltration losses can be expected due to the low water permeability values of the predominant loess soils. Their hydraulic conductivity values are in the range of 5.5×10^{-7}–1.6×10^{-8} m s^{-1} (Stadt Landau in der Pfalz 2004). The total retention volume of the stormwater retention pond is 625 m^3 and groundwater is 8–10 m below ground (Stadt Landau in der Pfalz 2004). The average width and length of the pond are 58 and 21 m. The average depth from the terrain surface is 1.4 m. All weather data were available from a station about 0.6 km west of the pond (Agrarmeteorologie Rheinland-Pfalz 2022), except for wind direction data which were obtained from the Weinbiet weather station of the German Weather Service, located 17 km north.

2.2. Sampling of stormwater and sediments

First, stormwater was sampled at Pipe East and Pipe West during two events to investigate biocide occurrence. Following a two-step approach (Linke *et al.* 2021), sampling continued after concentrations were found to be above-defined test criteria, here the PNEC value. Then, the campaign was extended to test a possible connection between biocides in stormwater and pond sediments. For this purpose, four campaigns consisted of sediment sampling during dry conditions followed by water and sediment sampling shortly after a storm event, approximately 1 month later (Figure 1).

Water samples were taken as grab samples at both pipes using 1-L brown water bottles previously washed with deionized water. During six events in the years 2019–2021, water was collected in a stainless steel container and then filled into the bottles. For the third and fourth events, an additional sample was collected, about 2 h after the first, to determine intra-event variability. For these events, the mean biocide concentration was calculated. Water samples were kept cool until preparation started, usually within 2 days after sampling. Duplicate samples were taken during the first three events.

Sediment samples were collected by digging a 0.3 × 0.3 m pitch of approximately 0.1 m depth. Vegetation was removed and the sediment was homogenized in a large container. At selected locations, sediment was sampled up to 0.3 m depth in 0.1 m steps. All samples were filled into plastic bags, immediately cooled, and prepared for analysis directly after sampling or frozen if this was not possible. To avoid resampling of disturbed sediments, samples were taken about 0.5 m away from the previous locations. Yet, this was not possible for samples directly at the pipes. A reference sample was taken outside the pond during each sampling campaign. In total, 116 sediment samples were collected (Tables S2–S4, Supplementary material). Figure S2, Supplementary material shows a map of sampling locations.

2.3. Measurement of soil moisture and redox potential

After the first sampling campaign, soil moisture and redox potential were measured by portable instruments across the pond to assess influencing factors of biocide concentrations in pond sediments (Table S5, Supplementary material). Volumetric soil moisture was determined by an ML3 Theta Probe (Delta-T Devices, Cambridge, UK) connected to the readout device Moisture Meter HH2 (Umwelt-Geräte-Technik GmbH, Münchberg, Germany) and redox potential using a redox probe (Paleo terra, Amsterdam, the Netherlands).

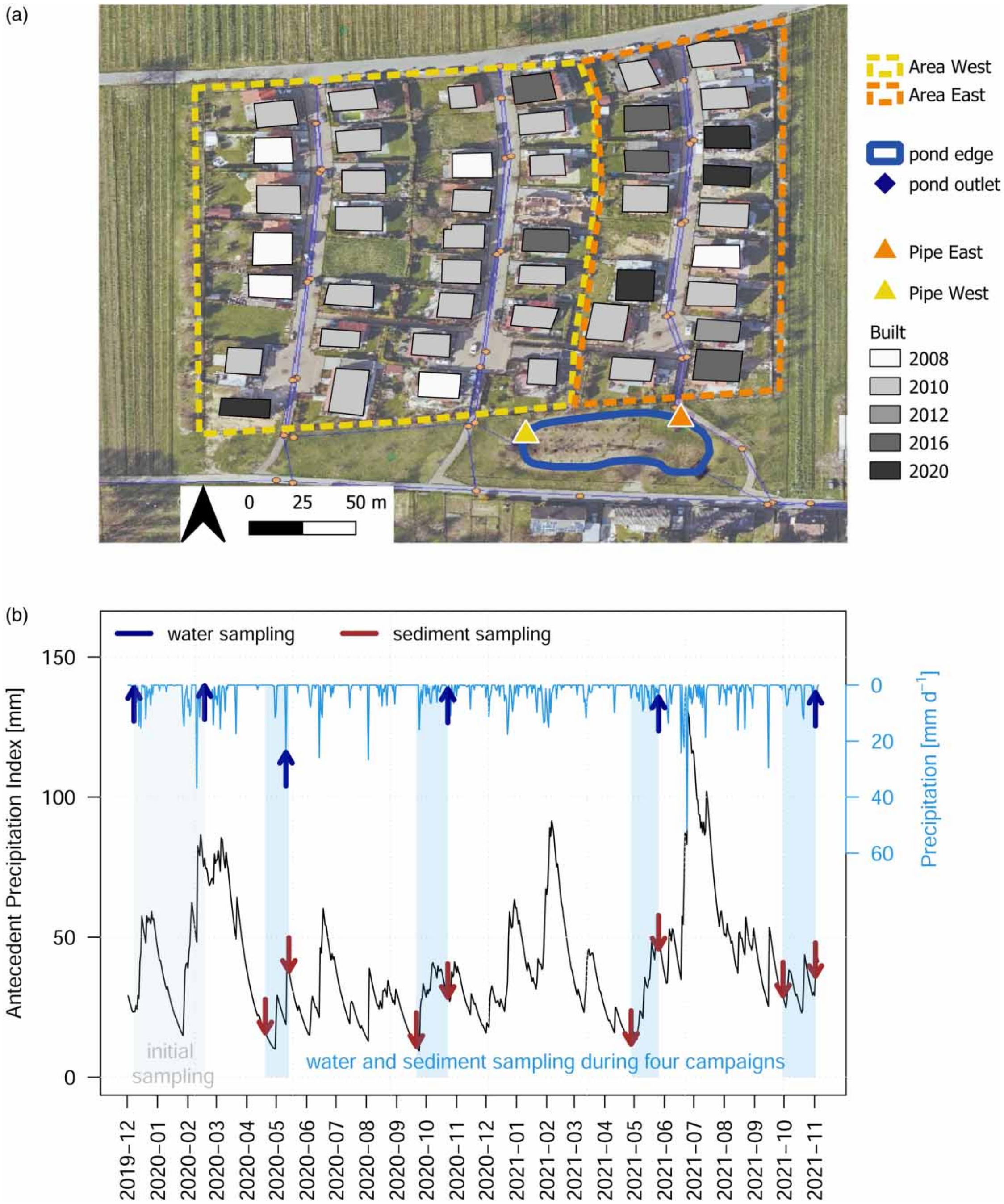

Figure 1 | Spatial and temporal overview of sampling campaigns. (a) Aerial view of the study area with two pipes collecting stormwater from areas West and East (Background picture by Stadt Landau in der Pfalz). (b) Arrows indicate days of water and sediment sampling. The blue line is daily precipitation and the black line is the antecedent precipitation index (API). The API was calculated according to Kohler & Linsey (1951). Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/nh.2022.075.

2.4. Physicochemical properties of environmental samples

Water samples of event 3 were analyzed for major ions to determine possible groundwater contributions to pond inflow. Concentrations of chloride, nitrate, sulfate, sodium, potassium, magnesium and calcium were determined by ion chromatography (Dionex ICS-1100, Thermo Fisher Scientific Inc., USA).

Grain size, organic matter (OM) and total carbon content were determined for sediment samples taken during campaign 1. The grain size was determined with a Malvern Mastersizer following the procedure outlined by Abdulkarim *et al.* (2021). The content of OM and carbon were determined using loss on ignition, drying samples at 105 °C and combusting them subsequently at 550 and 900 °C (Heiri *et al.* 2001).

2.5. Preparation and analytics of environmental samples

2.5.1. Stormwater samples

Stormwater samples were analyzed for three biocides (diuron, terbutryn and OIT) and four TPs (diuron-desmethyl, terbuthylazine-2-hydroxy, terbutryn-desethyl and terbumeton). Table S6, Supplementary material provides an overview of the analyzed substances. Pesticide standards were purchased from Neochema GmbH (Bodenheim, Germany) except diuron-d6 (HPC standards GmbH, Borsdorf, Germany) and OIT (LGC Standards, Teddington, Middlesex, UK). Analysis was performed as shown by Linke *et al.* (2021). Briefly, samples were filtered, prepared using solid phase extraction and analysed by HPLC-MS/MS (Agilent Technologies, Inc.; 1200 Infinity LC system and 6430 Triple Quad; Waldbronn, Germany). Acetonitrile (LC-MS grade, VWR International GmbH, Darmstadt, Germany) was used for stock solution preparation and as an organic mobile phase in chromatography. Limits of detection (LOD), limits of quantification (LOQ) and recovery rates were assessed by procedures outlined in Linke *et al.* (2021); Table S7, Supplementary material gives the results.

2.5.2. Sediment samples

The preparation of sediments was conducted using an extraction protocol similar to Droz *et al.* (2021). Sediments were sieved to 2 mm. 5 g of sample was filled up to 50% of water content and put into a centrifuge tube (50 mL, Fisher Scientific, Darmstadt, Germany). To each sample, 3 mL of a mixture of pentane:dichlormethane (3:1 v/v) was added (Carl Roth GmbH + Co. KG, Karlsruhe, Germany). Samples were vortexed for 5 s, put into an ultrasound bath for 5 min, vortexed for 1 min, and centrifuged at 5,000 RPM (Thermo Scientific Heraeus Megafuge 16R). The supernatant was sampled and put into a new glass vial. The previous steps were repeated three times until 9 mL of supernatant was obtained. This supernatant was completely vaporized under nitrogen flow and resuspended in 1 mL of acetonitrile. 75 mg of magnesium sulfate anhydrous and 12.5 mg of PSA Silica were added (Sigma Aldrich, Taufkirchen, Germany). Samples were vortexed for 30 s, centrifuged for 5 min and the supernatant was transferred into a vial. Measurements of two biocides (terbutryn and OIT) and three TPs (terbuthylazine-2-hydroxy, terbutryn-desethyl and terbumeton) were conducted via HPLC-MS/MS using the same method as for the water samples. LOD, LOQ and recovery rates are given in Table S8, Supplementary material.

2.6. Mass balance of terbutryn in the pond

2.6.1. Modeling terbutryn in stormwater inflow to pond

We chose terbutryn as a sample biocide to continuously model biocide inflow to the pond from the start of pond construction until the end of sampling (01.01.2008–04.11.2021). We used a rainfall–runoff model (RoGeR_WB_Urban) to calculate the amount of stormwater runoff entering the pond and a leaching model (COMLEAM) for the terbutryn load leached from the area connected to the pond. Both models have individually been applied and successfully tested in various urban areas. Our study combined both models to obtain daily terbutryn loads in stormwater entering the pond. Precipitation and temperature data were obtained from the weather station (Agrarmeteorologie Rheinland-Pfalz 2022) and potential evapotranspiration was calculated according to Haude (1954).

RoGeR_WB_Urban is a 1D rainfall–runoff model adapted to urban areas (Steinbrich *et al.* 2021). We used a 10 min time-step and a 1 m × 1 m resolution to adequately simulate runoff generation and summed up to arrive at daily values. COMLEAM is a model used to simulate the leaching of substances from buildings (Burkhardt *et al.* 2021). It first calculates wind-driven rain and corresponding facade runoff using data on precipitation, wind speed and wind direction. Thereafter, hourly biocide emission is quantified based on stored emission functions. In our study area, no information about initial terbutryn concentration on individual facades was available. We, therefore, estimated the facade area painted with terbutryn to be 50% of the total facade area excluding windows (3,649 m^2 in Catchment East and 6,016 m^2 in Catchment West, respectively). We chose initial terbutryn concentration and emission data from encapsulated biocides and arrived at an initial terbutryn concentration of 2,250 mg m^{-2} which was within the expected range of 200–3,000 ppm in dry films of coatings (Burkhardt *et al.* 2012). The age of the buildings was set to the date of their first appearance in aerial images. At both inlet pipes, we coupled COMLEAM terbutryn emissions with stormwater inflow to the pond calculated by RoGeR_WB_Urban. At both inlet pipes, the obtained terbutryn concentrations were compared to samples collected during six measured events using a Nash–Sutcliff efficiency (NSE) index (McCuen *et al.* 2006). We optimized NSE to determine a loss factor for the area, i.e. how much terbutryn was lost in the contributing residential area before entering the pond.

Characterization of surface types next to houses helps to understand losses directly at the base of facades. We thus calculated the percentages of partly sealed (i.e. permeable pavements) and unsealed (vegetated soil) areas in a buffer of 1 m around houses based on available GIS data.

2.6.2. Mass balances of water and terbutryn in pond

We neglected infiltration losses to groundwater due to the low infiltration rates of prevalent soils. In our mass balance approach, inflowing stormwater was assumed to fill up the pond, partly evaporate and spill over into the sewage system. Terbutryn in stormwater was assumed to remain in standing water, infiltrate into the sediment or leave the pond via the outlet. Degradation of terbutryn took place by photodegradation in standing water and by biodegradation in the sediment. Our mass balance approach consists of two storages, namely standing pond water and pond sediment. Both contain water and terbutryn concentrations in daily time steps. Details of individual model calculations are provided in section A of the Supplementary Material.

3. RESULTS AND DISCUSSION

3.1. Measured concentrations of biocides and TPs

3.1.1. Biocides and TPs in stormwater

We detected all measured substances at both inflow pipes although detections differed for the individual events (Figure 2). Diuron, diuron-desmethyl, terbutryn, and terbutryn-desethyl were above LOQ during all six events, OIT during four, terbuthylazine-2-hydroxy, and terbumeton during two events, though not always at both pipes. These findings suggested active and significant leaching of biocides from facades in our investigated residential area, although detrimental environmental impacts are known for a long time (Burkhardt *et al.* 2011) and information about possible mitigation measures for biocide reduction is available (Wicke *et al.* 2021b).

Measured biocide concentrations compared with other studies, for example, with measurements in urban stormwater infiltration systems for terbutryn, between 3 and 1,800 ng L^{-1} with median values ranging from 30 to 100 ng L^{-1} (Hillenbrand *et al.* 2016). Generally, concentrations at Pipe East were higher than at Pipe West. These differences could partly be explained by more recent buildings in Catchment East or by different biocide amounts and types used in paints and renders. We observed high variability of concentrations between events at both pipes for all substances. This variability was within the expected range since biocide emissions depend on various factors, such as moisture, temperature, remaining biocide concentration in the paint and/or render and on precipitation intensity (Paijens *et al.* 2019). Most substances showed the highest concentrations during the third event with the highest precipitation (Table S10, Supplementary material). As we did not take flow-proportional samples, our measurements are not necessarily representative of entire events. But for all three biocides, they exceeded PNEC values for surface water at least during one event. Without further dilution, this corresponds to a possible risk for ecosystems and calls for further investigations (Linke *et al.* 2021).

3.1.2. Biocides and TPs in sediment

We detected terbutryn in 85 out of 116 sediment samples, 54% of these samples showed a concentration below 1 ng g^{-1} (Figure 2). At Pipe East, only 32 out of 57 samples had concentrations above LOD with a maximum concentration of 2.7 ng g^{-1} in samples collected during campaign 4. At Pipe West, 53 of 59 samples had concentrations above LOD and were taken during different campaigns, 6 had concentrations above 10 ng g^{-1} (Figure S3, Supplementary material). Flanagan *et al.* (2021) found higher terbutryn concentration in urban stormwater pond sediments in Sweden (100 ng g^{-1}), although terbutryn was only quantified in one out of 32 samples. The reason for the low concentrations of terbutryn found in our sediment samples could be a lower input. We found the highest concentrations close to the outlet of Pipe West, both before (maximum 26 ng g^{-1}) and after (maximum 25 ng g^{-1}) storm events during various campaigns (Figure 3). Two effects could be responsible for these findings. First, sorption might be higher directly at the pipe since all inflow enters here and terbutryn loads of small events might not reach distant locations. Second, we observed saturated soil during all sampling campaigns and measured low redox potentials (−90 mV) during campaigns 3 and 4, which might have retarded the degradation of terbutryn as observed in experimental studies by Muir & Yarechewski (1982).

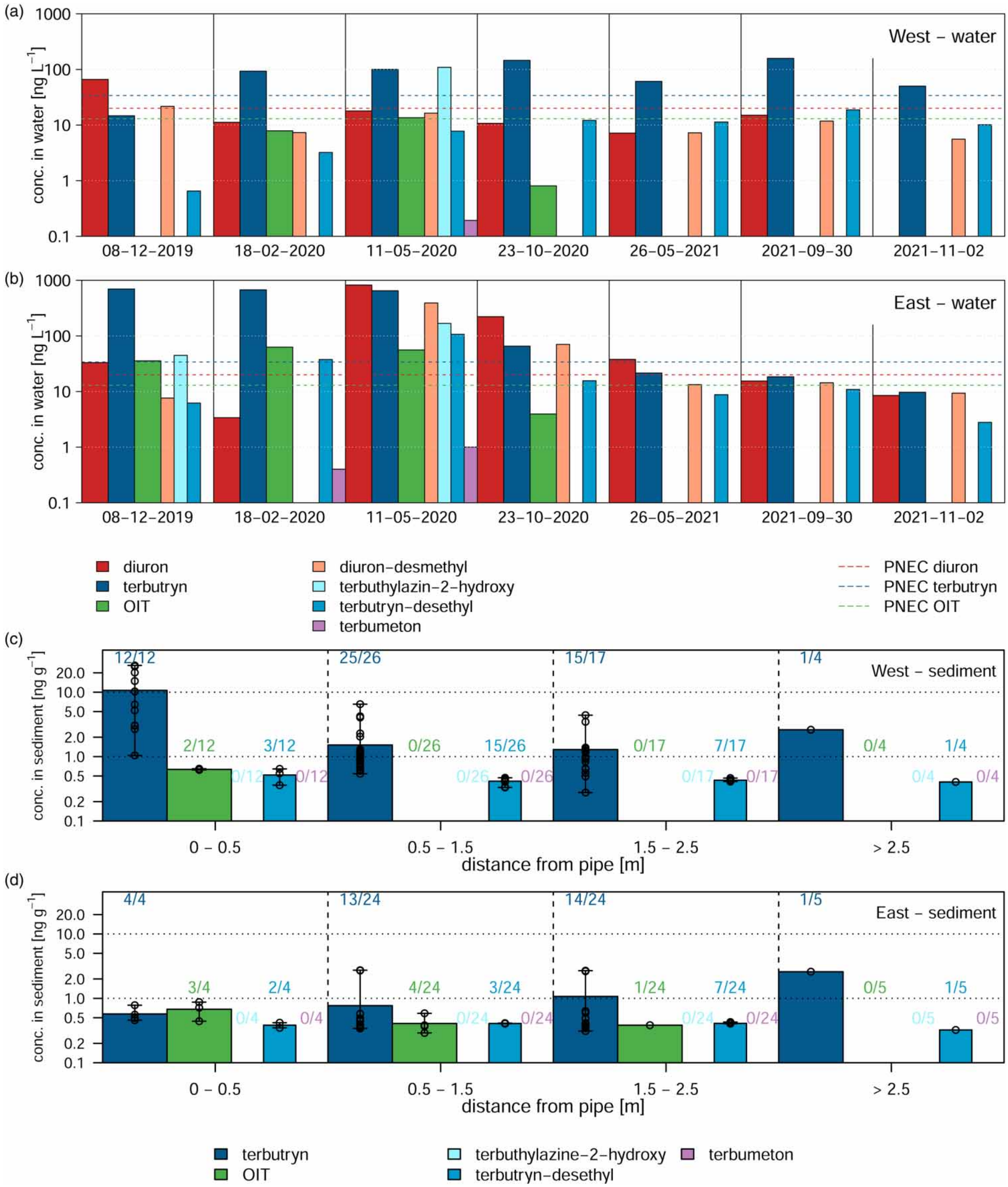

Figure 2 | Biocides and TPs in environmental samples. (a) and (b) show concentrations in stormwater inflow for Pipe West and Pipe East. PNEC values refer to surface water (Table S6, Supplementary material). (c) and (d) show concentrations of terbutryn, OIT and TPs in sediment close to Pipe West and Pipe East sorted by distance from pipes. Bars show mean measured values, arrows show minima/maxima and points individual samples. Colored numbers above bars refer to quantifiable samples (>LOQ) out of the total number of samples taken. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/nh.2022.075.

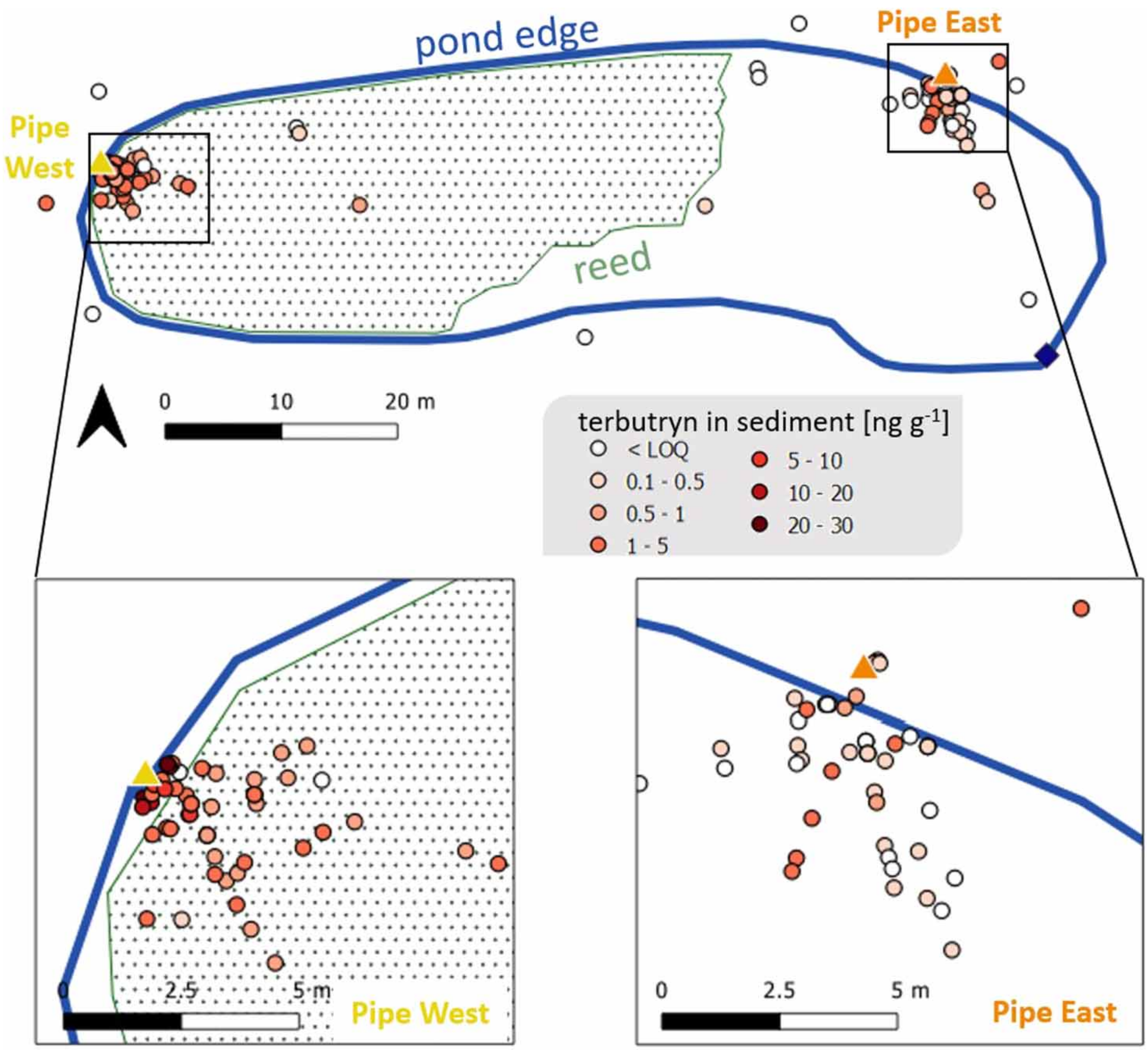

Figure 3 | Spatial pattern of terbutryn concentrations in the retention pond. Each point corresponds to one collected sample. Zooms detail the surrounding of pipes.

Terbutryn-desethyl was the only TP detected in sediment samples and was found in low concentrations (<1 ng g^{-1}) close to both pipes. In the first and second campaigns, about half of the measured samples contained terbutryn-desethyl (63 and 55%), but all samples during the third and fourth campaigns were devoid of this TP. More was found at Pipe West, sometimes even in samples that did not contain the parent compound terbutryn. We explain this observation by terbutryn degradation due to photolysis in standing water (Hensen *et al.* 2020) or by terbutryn-desethyl formed on and leached from facades (Bollmann *et al.* 2016). In general, differences in detected TPs during different campaigns might be due to different pre-conditions such as soil moisture and temperature, and due to varying concentrations in inflowing stormwater (Figure 2). Also, Bollmann *et al.* (2017) frequently detected this TP below recently painted facades in Denmark and showed in a laboratory experiment an accumulation of terbutryn TPs over time. This we could not detect in our study, as our inflow concentration was continuously low. Moreover, we did not detect terbuthylazine-2-hydroxy and terbumeton in sediment, although both are reported to form on facades (Bollmann *et al.* 2016). We attribute this finding to higher LODs and lower concentrations in stormwater.

Diuron and diuron-desmethyl were not detected at all. OIT was detected in 10 out of 116 (8%) sediment samples, mostly directed at the pipes, both before and after rain events. Two samples at Pipe West contained OIT and eight at Pipe East. This corresponded to collected stormwater samples that contained more OIT at Pipe East. Concentrations of OIT in sediments were all below 1 ng g^{-1}. The half-life time of OIT in the soil is 9 days (Bollmann *et al.* 2017). This degradation might explain the absence of OIT in most sediment samples. TPs of OIT could not be assessed due to missing laboratory standards.

Overall, terbutryn concentrations were low in the entire pond, higher close to the pipe outlets and highest at Pipe West (Figure 3). For 35 samples collected during campaign 1, we measured grain sizes and LOI, 25 of them had terbutryn above LOQ but did not show a significant correlation with OM (Figure S4, Supplementary material). Overall, OM (median = 7%) and clay content (median = 4%) were similar all over the pond. Grain sizes were silty-sandy. We also measured soil moisture during campaigns 2–4. As expected, soil moisture was higher (mean value of 55%) after precipitation events than before (31%). Higher soil moisture might promote terbutryn degradation (Lechón *et al.* 1997), but soil saturation might cause the opposite and explain the maximum concentrations found at Pipe West, as explained above.

3.2. Mass balance of terbutryn in the pond

3.2.1. Modeled terbutryn in stormwater inflow and comparison to measured data

Compared to the observed data, the modeled terbutryn concentration overestimated the measured concentrations during all events up to two orders of magnitude (Figure 4). We did not take stormwater samples proportional to flow, thus measured concentrations should only be treated as rough estimates for daily concentrations. But also simulated values included various uncertainties, such as missing information about initial terbutryn concentrations, about facade areas containing biocides, or about exact dates of biocide application, because these were estimated from aerial images. However, these first simulations did not consider losses of biocides on the way to the pond. A substantial part of the contributing facades was observed to drain on permeable pavements or even gardens around the houses. Hence, a substantial part of facade runoff probably infiltrated the vicinity of buildings and did not reach the pond. These diffuse biocide losses were not incorporated in the concepts of our models and could only be quantified by a loss factor comparing modeled with observed biocide concentrations (Figure 4). The first comparisons yielded negative values of NSE, −1.13 for Pipe West and −0.85 for Pipe East. An optimized NSE was reached for a loss factor of 11%, 0.44 for Pipe East and −0.71 for Pipe West. This factor was compared to another study that found 25% of diuron wash-off from facades in the connected rainwater channel (Burkhardt *et al.* 2021). Modeled terbutryn concentrations were above PNEC value (34 ng L^{-1}) in 87 and 88% of events at Pipe East and West, respectively (Figure S5, Supplementary material). Our loss factor further suggests that 89% of leached biocides entered the environment without reaching the pond. This puts serious restrictions on the efficiency of end-of-pipe measures for biocide control.

To check the plausibility of these diffuse biocide losses, we characterized surface types adjacent to the facades. In our GIS analysis, approximately one-third consisted of vegetated soil, i.e. was unsealed, while the remaining part consisted of

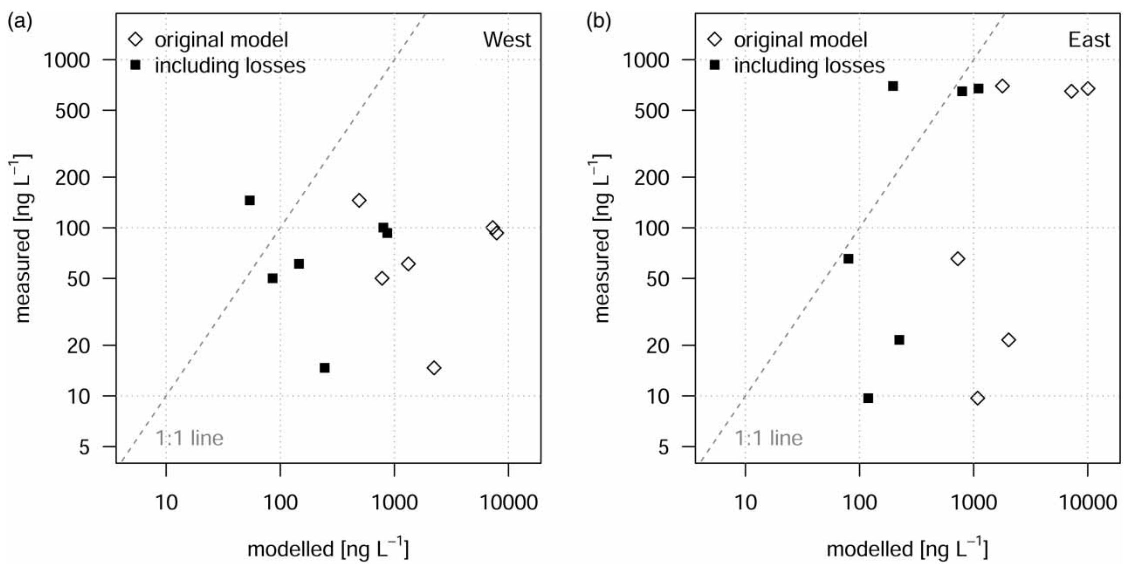

Figure 4 | Measured and modeled terbutryn concentrations during six events for pipes (a) West and (b) East. Empty squares show values before optimization. Filled squares show optimized simulations including losses thus reducing modeled values by a factor of 11%.

permeable pavements. See Figure S7, Supplementary material for a picture of typical houses and their surroundings. Also, residential streets that diverted stormwater runoff to the pond were covered by permeable pavements. On these pavements, water and biocide losses may be expected. They depend on surface detentions and infiltration characteristics which are highly variable and change over time (Schaffitel *et al.* 2020).

3.2.2. Mass balance of terbutryn in pond sediment

Our mass balance approach yielded a maximum terbutryn concentration in pond sediments of 4.2 ng g^{-1} with mean concentrations of 1.9 ng g^{-1}. The modeled value is close to the mean measured sediment concentration of 2.6 ng g^{-1} (Figure S6, Supplementary material). Terbutryn loads arriving in the pond were between 0.1 and 0.9 g per ha and year. Wicke *et al.* (2022) calculated a 3-year diuron emission of 305 g from which only 3.4 g arrived in the sewer system in an area of 1.85 ha. This corresponds to ten times higher diffuse biocide loss but to a similar load of 0.6 g per ha and year compared to the present study.

For our mass balance, we excluded groundwater inflow to the pipes by measuring the ions at samples taken at event 3. Ion concentrations were typical for stormwater and did not suggest any groundwater inflow to pipes (Table S9, Supplementary material).

Our mass balance approach could further be used to separate annual terbutryn amounts for inflow, storage, outflows and processes (Figure 5). We calculated the mass balance for 13 years since the start of construction and included the increasing number of houses. As a result, 11% of leached terbutryn reached the pond. We calculated this reducing factor by comparing measured and modeled terbutryn concentration during six events (see section 3.2.1). Incoming terbutryn partly reached the overflow (6% of leached terbutryn) or remained in the pond to finally infiltrate into the sediment (5% of leached terbutryn). Thereby, terbutryn is degraded by photodegradation in standing water and by biodegradation in the sediment. Photodegradation in pond water amounted to 98 mg per year, 0.9%, and biodegradation in pond sediments to 360 mg per year, 3.5%. During several years, the amount of degraded terbutryn in sediments was higher than influxes due to additions from previous years. Years with constructions in the contributing catchment were periods with the highest terbutryn inflow.

4. CONCLUSION

In a 3-ha residential area of single-family dwellings, measured biocide concentrations in stormwater had high variability but were within the expected range. We showed that a combination of a water balance model and a leaching model can be useful to assess biocide fate in such an environment. A comparison of measured and modeled data suggested diffuse losses of 89% of

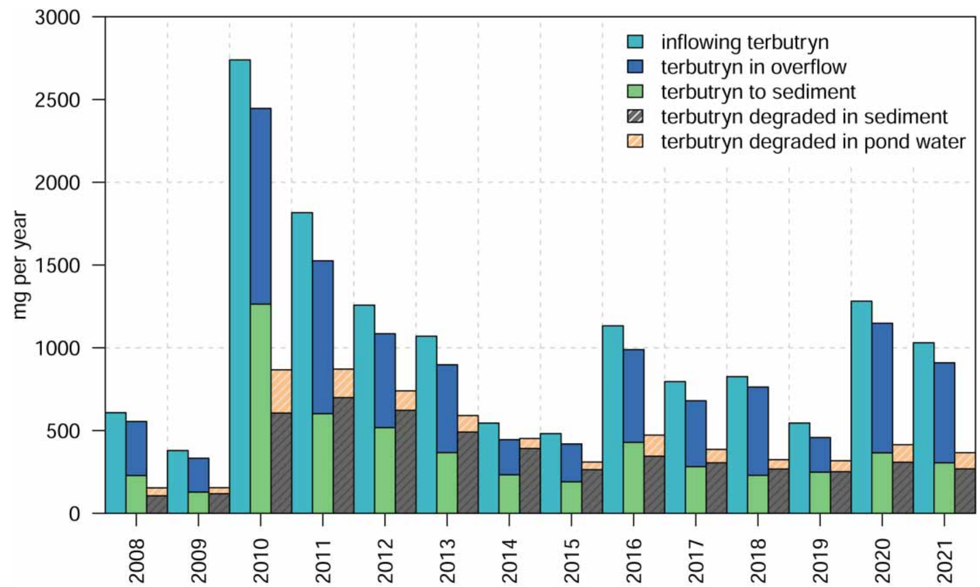

Figure 5 | Amount of terbutryn arriving at different storages in mg per year. Inflowing terbutryn amount accounts for diffuse losses (11% of leached biocide).

the leached biocide terbutryn on its way to a stormwater retention pond. There, overall low terbutryn concentrations in pond sediments and a 13-year mass balance suggested that only approximately 50% of the inflowing terbutryn was retained and degraded, while the remaining 50% spilled over into the sewage system. Our results are site-specific, and include various assumptions and uncertainties, but suggest that biocide retention in ponds is limited and environmental entry pathways are diverse in urban settings. Thus, end-of-pipe measures for urban biocide mitigation have limited efficiency. To prevent biocide emissions, measures should concentrate on the source.

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AUTHOR CONTRIBUTIONS

J.L., F.P. and F.L. conceptualized the study; F.L., J.L. and M.B. performed sampling and data visualization. F.L., L.S., O.O., F.P. prepared samples and analysed data. H.L. and F.L prepared the model. F.L. wrote the original draft. All authors wrote, reviewed, edited and approved the final version of the manuscript.

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DATA ANALYSIS

Data analysis and visualization were done in R (Version 4.2.0) using R Studio (Version 2022.02.3).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Abdulkarim, M., Grema, H. M., Adamu, I. H., Mueller, D., Schulz, M., Ulbrich, M., Miocic, J. M. & Preusser, F. 2021 Effect of using different chemical dispersing agents in grain size analyses of fluvial sediments via laser diffraction spectrometry. *Methods and Protocols* **4**. doi:10.3390/mps4030044.

Agrarmeteorologie Rheinland-Pfalz 2022 *Wetterstation Landau-Nussdorf: 89/NUD*. Agrarian meteorology Rhineland-Palatinate.

Allinson, G., Zhang, P., Bui, A., Allinson, M., Rose, G., Marshall, S. & Pettigrove, V. 2015 Pesticide and trace metal occurrence and aquatic benchmark exceedances in surface waters and sediments of urban wetlands and retention ponds in Melbourne, Australia. *Environmental Science and Pollution Research* **22**, 10214–10226. doi:10.1007/s11356-015-4206-3.

Avidov, E., Aharonson, N., Katan, J., Rubin, B. & Yarden, O. 1985 Persistence of terbutryn and atrazine in soil as affected by soil disinfestation and fungicides. *Weed Science* **33** (4), 457–461.

Bollmann, U. E., Minelgaite, G., Schlüsener, M., Ternes, T., Vollertsen, J. & Bester, K. 2016 Leaching of terbutryn and its photodegradation products from artificial walls under natural weather conditions. *Environmental Science & Technology* **50**, 4289–4295. doi:10.1021/acs.est.5b05825.

Bollmann, U. E., Fernández-Calviño, D., Brandt, K. K., Storgaard, M. S., Sanderson, H. & Bester, K. 2017 Biocide runoff from building facades: degradation kinetics in soil. *Environmental Science & Technology* **51**, 3694–3702. doi:10.1021/acs.est.6b05512.

Burkhardt, M., Zuleeg, S., Vonbank, R., Schmid, P., Hean, S., Lamani, X., Bester, K. & Boller, M. 2011 Leaching of additives from construction materials to urban storm water runoff. *Water Science and Technology* **63**, 1974–1982. doi:10.2166/wst.2011.128.

Burkhardt, M., Zuleeg, S., Vonbank, R., Bester, K., Carmeliet, J., Boller, M. & Wangler, T. 2012 Leaching of biocides from façades under natural weather conditions. *Environmental Science & Technology* **46**, 5497–5503. doi:10.1021/es2040009.

Burkhardt, M., Rohr, M., Wicke, D., Tatis-Muvdi, R., Rouault, P., Zerball-Van Baar, P. & Dünnbier, U. 2021 Urbanes Niederschlagsabwasser: Emissionen, Belastungen und wirksame Massnahmen. *Aqua & Gas* **10**, 34–41.

Coutu, S., Rota, C., Rossi, L. & Barry, D. A. 2012 Modelling city-scale facade leaching of biocide by rainfall. *Water Research* **46**, 3525–3534. doi:10.1016/j.watres.2012.03.064.

Droz, B., Drouin, G., Maurer, L., Villette, C., Payraudeau, S. & Imfeld, G. 2021 Phase transfer and biodegradation of pesticides in water-sediment systems explored by compound-specific isotope analysis and conceptual modeling. *Environmental Science & Technology*. doi:10.1021/acs.est.0c06283.

Fernández-Calviño, D., Rousk, J., Bååth, E., Bollmann, U. E., Bester, K. & Brandt, K. K. 2021 Short-term toxicity assessment of a triazine herbicide (terbutryn) underestimates the sensitivity of soil microorganisms. *Soil Biology and Biochemistry*, 108130. doi:10.1016/j.soilbio.2021.108130.

Flanagan, K., Blecken, G.-T., Österlund, H., Nordqvist, K. & Viklander, M. 2021 Contamination of urban stormwater pond sediments: a study of 259 legacy and contemporary organic substances. *Environmental Science & Technology* **55**, 3009–3020. doi:10.1021/acs.est.0c07782.

Haude, W. 1954 *Zur praktischen Bestimmung der aktuellen und potentiellen Evaporation und Evapotranspiration*. Schweinfurter Dr. und Verlag-Ges. *Mitteilungen des Deutschen Wetterdienstes* **8**, 81–94 (in German).

Heiri, O., Lottter, A. F. & Lemcke, G. 2001 Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology* **25**, 101–110.

Hensen, B., Lange, J., Jackisch, N., Zieger, F., Olsson, O. & Kümmerer, K. 2018 Entry of biocides and their transformation products into groundwater via urban stormwater infiltration systems. *Water Research* **144**, 413–423. doi:10.1016/j.watres.2018.07.046.

Hensen, B., Olsson, O. & Kümmerer, K. 2020 A strategy for an initial assessment of the ecotoxicological effects of transformation products of pesticides in aquatic systems following a tiered approach. *Environment International* **137**, 105533. doi:10.1016/j.envint.2020.105533.

Hillenbrand, T., Tettenborn, F., Fuchs, S., Toshovski, S., Metzger, S., Tjoeng, I., Wermter, P., Hecht, D., Kersting, M., Werbeck, N. & Wunderlin, P. 2016 Maßnahmen zur Verminderung des Eintrages von Mikroschadstoffen in die Gewässer – Phase 2, UBA. *UBA Texte* **60**, 235.

Imfeld, G., Payraudeau, S., Tournebize, J., Sauvage, S., Macary, F., Chaumont, C., Probst, A., Sánchez-Pérez, J.-M., Bahi, A., Chaumet, B., Gilevska, T., Alexandre, H. & Probst, J.-L. 2021 The role of ponds in pesticide dissipation at the agricultural catchment scale: a critical review. *Water* **13**, 1202. doi:10.3390/w13091202.

Johann, S., Schwerd, R. & Scherer, C. R. 2018 Verhalten von aus Baustoffen ausgelaugten Bioziden bei der Bodenpassage. *Bauphysik* **40**, 369–378. doi:10.1002/bapi.201800006.

Junginger, T., Payraudeau, S. & Imfeld, G. 2022 Transformation and stable isotope fractionation of the urban biocide terbutryn during biodegradation, photodegradation and abiotic hydrolysis. *Chemosphere* **305**, 135329. doi:10.1016/j.chemosphere.2022.135329.

Kadlec, R. H. & Wallace, S. 2008 *Treatment Wetlands*. CRC Press, Boca Raton, CA. ISBN: 978-1-56670-526-4.

Kohler, M. A. & Linsey, R. K. 1951 Predicting the runoff from storm rainfall, Research Paper Weather Bureau, vol. 34. *US Department of Commerce*.

Lechón, Y., Sánchez-Brunete, C. & Tadeo, J. L. 1997 Influence of the laboratory incubation method on chlorotoluron and terbutryn degradation in soil. *Journal of Agricultural and Food Chemistry* **45**, 951–954.

Linke, F., Olsson, O., Preusser, F., Kümmerer, K., Schnarr, L., Bork, M. & Lange, J. 2021 Sources and pathways of biocides and their transformation products in urban storm water infrastructure of a 2 ha urban district. *Hydrology and Earth System Sciences* **25**, 4495–4512. doi:10.5194/hess-25-4495-2021.

Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S. & Imfeld, G. 2011 Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment. *The Science of the Total Environment* **409**, 2317–2324. doi:10.1016/j.scitotenv.2011.01.057.

McCuen, R. H., Knight, Z. & Cutter, A. G. 2006 Evaluation of the Nash–Sutcliffe efficiency index. *Journal of Hydrologic Engineering* **11**, 597–602. doi:10.1061/(ASCE)1084-0699(2006)11:6(597).

Muir, D. C. & Yarechewski, A. L. 1982 Degradation of terbutryn in sediments and water under various redox conditions. *Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes* **17**, 363–380. doi:10.1080/03601238209372327.

Musgrave, H., Tattersall, C., Clarke, S. & Comber, S. 2011 Technical support for the impact assessment of the review of priority substances under directive 2000/60/EC: substance assessment: terbutryn. *European Commission (DG Environment)* 59. Available from: https://circabc.europa.eu/sd/a/d6673532-e862-4d40-ab5f-8aaffc766f58/DEHP.pdf. Last accessed 10 July 2022.

Paijens, C., Bressy, A., Frère, B. & Moilleron, R. 2019 Biocide emissions from building materials during wet weather: identification of substances, mechanism of release and transfer to the aquatic environment. *Environmental Science and Pollution Research International*. doi:10.1007/s11356-019-06608-7.

Paijens, C., Bressy, A., Frère, B., Tedoldi, D., Mailler, R., Rocher, V., Neveu, P. & Moilleron, R. 2021 Urban pathways of biocides towards surface waters during dry and wet weathers: assessment at the Paris conurbation scale. *Journal of Hazardous Materials* **402**, 123765. doi:10.1016/j.jhazmat.2020.123765.

Schaffitel, A., Schuetz, T. & Weiler, M. 2020 A distributed soil moisture, temperature and infiltrometer dataset for permeable pavements and green spaces. *Earth System Science Data* **12**, 501–517. doi:10.5194/essd-12-501-2020.

Sébastian, C., Becouze-Lareure, C., Lipeme Kouyi, G. & Barraud, S. 2015 Event-based quantification of emerging pollutant removal for an open stormwater retention basin – loads, efficiency and importance of uncertainties. *Water Research* **72**, 239–250. doi:10.1016/j.watres.2014.11.014.

Stadt Landau in der Pfalz 2004 *Bebauungsplan ND5: Textliche Festsetzungen, Stadtverwaltung Landau in der Pfalz*. p. 1.

Steinbrich, A., Leistert, H. & Weiler, M. 2021 Roger – ein bodenhydrologisches Modell für die Beantwortung einer Vielzahl hydrologischer Fragen. *Korrespondenz Wasserwirtschaft* **14**, 94–101.

Tedoldi, D., Chebbo, G., Pierlot, D., Kovacs, Y. & Gromaire, M.-C. 2016 Impact of runoff infiltration on contaminant accumulation and transport in the soil/filter media of sustainable urban drainage systems: a literature review. *The Science of the Total Environment* **569–570**, 904–926. doi:10.1016/j.scitotenv.2016.04.215.

WHG 2009 §55 Bundesministerium der Justiz und für Verbraucherschutz. Gesetz zur ordnung des wasserhaushalts (Wasserhaushaltsgesetz, WHG).

Wicke, D., Matzinger, A., Sonnenberg, H., Caradot, N., Schubert, R.-L., Dick, R., Heinzmann, B., Dünnbier, U., Seggern, D. v. & Rouault, P. 2021a Micropollutants in urban stormwater runoff of different land uses. *Water* **13**, 1312. doi:10.3390/w13091312.

Wicke, D., Tatis-Muvdi, R., Rouault, P., Zerball-Van Baar, P., Dünnbier, U., Rohr, M. & Burkhardt, M. 2021b Bauen und Sanieren als Schadstoffquelle in der urbanen Umwelt: Abschlussbericht. *UBA Texte* **155**, 108.

Wicke, D., Tatis-Muvdi, R., Rouault, P., Zerball-Van Baar, P., Dünnbier, U., Rohr, M. & Burkhardt, M. 2022 Emissions from building materials – a threat to the environment? *Water* **14**, 303. doi:10.3390/w14030303.

Wiest, L., Baudot, R., Lafay, F., Bonjour, E., Becouze-Lareure, C., Aubin, J.-B., Jame, P., Barraud, S., Kouyi, G. L., Sébastian, C. & Vulliet, E. 2018 Priority substances in accumulated sediments in a stormwater detention basin from an industrial area. *Environmental Pollution (Barking, Essex 1987)* **243**, 1669–1678. doi:10.1016/j.envpol.2018.09.138.

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