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Biocides in Soils of Urban Stormwater Infiltration Systems—Indications of Inputs from Point and Non-point Sources

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Abstract Urban stormwater contains various micropollutants, such as biocides, which are washed off from facades during wind-driven rain events. Biocides can reach the groundwater via stormwater infiltration systems (SIS), although the soil layer acts as a reactive barrier preventing the leaching of biocides but producing transformation products (TPs). Little is known about the occurrence and concentration of biocides in SIS soils, their distribution and temporal behavior. Here, we present a first systematic screening of three commonly used biocides (diuron, octylisothiazolinone (OIT), terbutryn) and four TPs of terbutryn in 46 French and German SIS. Overall, biocide occurrence in SIS topsoils was ubiquitous but low, while point source inputs to specific SIS were high but rare. Low concentrations (< 2ng g^{-1}) of terbutryn were detected in 78% of the SIS. Maximum concentrations occurred in recently constructed SIS, suggesting that this is due to higher biocide loads entering the SIS. The frequent detection of terbutryn supports the idea that it is a non-point source marker, as it is relatively stable in soil ($t_{1/2}$ > 90 days) and widely used in renders and paints. In contrast, high concentrations of diuron (168 ng g^{-1}) and OIT (58 ng g^{-1}) were observed in only one sample, suggesting an urban point source contamination, possibly from a freshly repainted facade. The distinction between source types provides a basis for targeted measures to prevent biocide entry to groundwater. Altogether, this

Highlights

- The biocide terbutryn was detected in 78% of the 46 investigated stormwater infiltration system (SIS) soils
- Low (<2 ng g^{-1}) concentrations of terbutryn suggest that it is a non-point source marker
- High concentrations of diuron and OIT in only one sample suggest point source contamination
- Higher concentrations of terbutryn in new SIS suggest biocide input as the prevailing factor
- Biocides should be considered in SIS design and monitoring

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study opens the door to a more systematic consideration of micropollutant dissipation and ecotoxicological effects in SIS design and monitoring.

Keywords Biocides · Stormwater infiltration · Terbutryn · Transformation products

1 Introduction

In urban areas, stormwater infiltration systems (SIS) are constructed to temporarily retain and locally infiltrate stormwater. SIS are thus an essential part of sustainable urban drainage systems or integrated stormwater management approaches (Fletcher et al., 2015). SIS may also retain common urban pollutants, such as heavy metals or nutrients. However, biocides in stormwater may reach groundwater following infiltration into SIS (Pinasseau et al., 2020), thus threatening groundwater quality.

Biocides used in renders and paints on facades are often an overlooked group of micropollutants in urban stormwater. They wash off during wind-driven rain events and disperse into the environment (Burkhardt et al., 2011). Biocides are found in stormwater (Bollmann et al., 2014), surface water (Wittmer et al., 2011), waste water treatment plants, combined sewer overflow (Paijens et al., 2021), standing water in SIS (Linke et al., 2021), soil (Bollmann, Fernández-Calviño, et al., 2017a) and in groundwater (Hensen et al., 2018; Pinasseau et al., 2020). They can have adverse impacts on organisms in aquatic environments (Paijens et al., 2019). Several factors affect the accumulation, transformation and potential leaching of biocides from SIS to groundwater, including soil type, percolation rate, organic content, and half-life time (Vega-Garcia et al., 2022). In addition, preferential flow in SIS macropores can facilitate the transport of biocides to groundwater. Older SIS tend to have more macropores, increasing the risk of groundwater contamination (Bork et al., 2021).

In this context, the present study focuses on three common and complementary used biocides approved as film preservatives (ECHA, 2023): diuron, octylisothiazolinone (OIT), and terbutryn. In 2015, these three substances were the most commonly used biocides in German facade renders and paints, with total amounts ranging from 50 to 100 tons per year. In comparison, the amount of other biocides used in Germany ranged from 10 to 50 tons per year (Gartiser et al., 2015). Diuron and terbutryn are classified as priority substances in the EU Water Framework Directive and were banned for agricultural use in 2007 (EC, 2002) and 2022 (EC, 2022), respectively.

Sorption and degradation are the main processes that control the accumulation and dissipation of biocides in soil, depending on soil characteristics, hydro-climatic conditions and the physico-chemical properties of the biocide (Reiß et al., 2021). Biocides degrade via photolysis at facades and via biodegradation in soil, following leaching from the facade (Bollmann et al., 2016; Bollmann, Fernández-Calviño, et al., 2017a; Junginger et al., 2022). Measurements of both biocides and transformation products (TPs) can help the evaluation of potential biocide accumulation and ongoing degradation in SIS. However, few studies have evaluated the occurrence of biocides in SIS soils, limiting the ability to design effective barriers. One study that focused on pesticides in both surface water and retention pond soils found biocides only in the surface water, but not in the soil (Allinson et al., 2015). In another study, the biocide terbutryn was found in one of 17 samples of soil in urban stormwater retention ponds—systems that typically have limited infiltration (Flanagan et al., 2021). In a recent study, the soil of a stormwater retention pond had low terbutryn (up to 26 ng g^{-1}) and OIT concentrations (1 ng g^{-1}) while terbutryn TPs were systematically below 1 ng g^{-1} (Linke et al., 2022). Overall, these results suggest that soil in retention ponds or SIS act as biocide sink, where biocides chronically leached from facades into stormwater can accumulate and dissipate depending on their half-life times ($t_{1/2}$) and sorption. However, knowledge of the distribution and concentration ranges of urban biocides in SIS is mostly lacking.

The accumulation of biocides can have adverse environmental effects on soil and water organisms. Two biocides commonly used in film preservatives, terbutryn and diuron, were originally developed as agricultural pesticides. There are several studies on their environmental impacts (Muir, 1980; Sedgley & Boersma, 1969), including effects on microbial activity (Auspurg et al., 1988). However, the concentrations and frequency of application in agriculture differ from those of urban biocides. Recent studies also investigated the effects of biocide emissions from facades on soil microorganisms. In bioassays, biocide leachate from buildings did not affect soil organisms, although it did affect aquatic organisms (Vermeirssen et al., 2018). The adverse effects of terbutryn and diuron depend on the exposure time and organism type (Fernández-Calviño et al., 2021; Prado & Airoldi, 2001). After 40 days of exposure, terbutryn had stronger effects on soil microorganisms than after short-term exposure (Fernández-Calviño et al., 2021). Diuron also negatively altered microbial activity (Prado & Airoldi, 2001) and macro-organisms such as earthworms, although effects decreased following the exposure period (Wang et al., 2022). OIT rapidly degraded in soil and TPs did not accumulate (Bollmann, Fernández-Calviño, et al., 2017a). In microtox tests, OIT is more toxic than its TPs and terbutryn. However, further studies are needed to assess the impact of biocides on soil organisms (Bollmann, Fernández-Calviño, et al., 2017a). In particular, the environmental impacts of low but chronic concentrations in SIS soils are largely unknown.

Here, we address the lack of systematic monitoring of biocides and TPs in SIS soils, which currently limits the evaluation of potential environmental impacts on soil and groundwater. The purpose of this study was thus to characterize and compare the occurrence and accumulation of biocides in urban SIS of two cities, Freiburg (Germany) and Strasbourg (France). Biocides including terbutryn, diuron and OIT and terbutryn TPs, were measured in 46 SIS. SIS ages range from 2 to 19 years, built from 2003 to 2020. Residential buildings have the same year of construction as the connected SIS. We hypothesized that older SIS accumulate more biocides if biocide loads in stormwater reaching the SIS are greater than degradation or leaching rates. In addition, biocide inputs occur from both point and non-point sources. In the urban context, we consider point sources to originate from construction works and to be defined as discernible, confined and discrete conveyances (Clean Water Act, US, 2002). Non-point sources represent diffuse inputs that produce low but steady concentrations with unknown long-term effects. Both types of inputs need to be investigated to account for acute and chronic toxicity effects. Sampling of urban SIS soils can provide information on the dominant type of inputs. Thus, the environmental significance of this study is to provide a basis for risk assessment and targeted measures to prevent biocide inputs to SIS and groundwater. The specific objectives of the present study are to examine whether (a) non-point and point sources of biocides in SIS can be distinguished, (b) biocide concentrations are higher in newer facilities, and (c) biocide concentrations are higher in soil with higher organic carbon or clay content due to higher sorption potentials.

2 Materials and Methods

In total, 55 SIS were selected in the two cities. Initially, only terbutryn was measured in 9 SIS in the city of Freiburg to assess whether concentrations in soils exceeded detection limits. A second sampling included an additional 46 SIS. Three common and complementary used biocides were analyzed, namely diuron, OIT, and terbutryn. Four TPs of terbutryn with analytical standards available were analyzed to evaluate degradation, i.e., terbutryn-2-hydroxy, terbutryn-sulfoxide, desethyl-terbutryn, and desethyl-2-hydroxy-terbutryn. In addition, acetochlor, a selective pre-emergence herbicide was analyzed. It is no longer approved for use in the EU as of 2012 (EU, 2011), but was part of an existing measurement routine and therefore included in the analysis. An overview of the substances analyzed, is provided in Table S1.

2.1 Study Area

The study area consists of SIS in the city of Freiburg, Germany, and in the intercommunal structure including the city of Strasbourg (Eurométropole de Strasbourg), France (Fig. 1). Table 1 provides an overview of the SIS and samples per district in both cities with sampling dates; Table S2 provides the location of each district. All SIS collected water from residential areas, typically consisting of multi-family houses. All SIS were covered by a vegetated soil layer, usually with rye grass (*Lolium perenne*). In Germany, SIS are built according to technical standards (DWA, 2005). France has adopted similar guidelines, although no official standards exist (Tedoldi et al., 2020). Renders and paints of two districts contained terbutryn as previously evaluated (Hensen et al., 2018; Linke et al., 2021). In the remaining districts, renders and paints could not be identified.

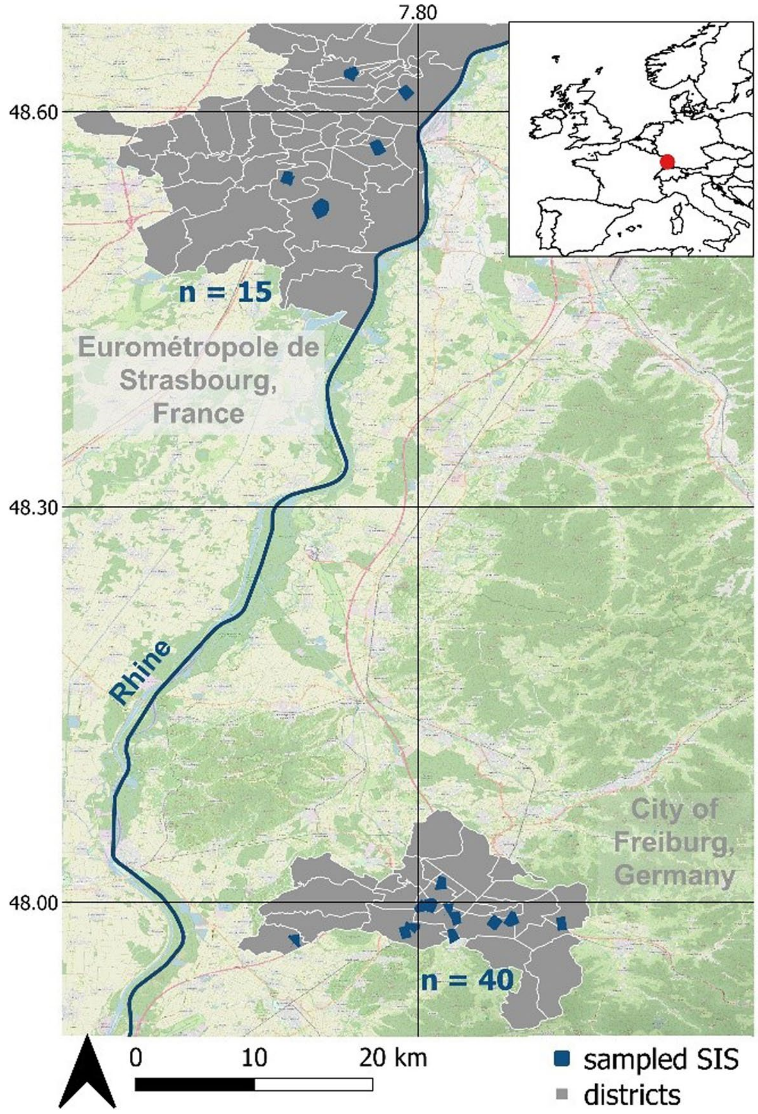

Fig. 1 Location of SIS in the cities of Freiburg (Germany) and Strasbourg (France)

2.2 Soil Sampling

Soil samples were collected from 9 SIS in three districts of Freiburg in 2020 and 2022 (Table 1). Five additional soil samples were collected outside of the SIS. These included four soil samples across entry pathways in the district of Wiehre and one below a building's facade in the district of St. Georgen. In the second campaign, 69 samples in were collected from May to June 2022 in 46 SIS in Freiburg and the Strasbourg area. For sampling, we used a spade to dig a pit of 0.3 × 0.3 × 0.1 m. All samples were collected near the inflow of the SIS, where the highest biocide concentrations were expected. Because some SIS had multiple inflows, one sample per inflow was collected from each SIS. In the first campaign, SIS soil was collected at different depths; i.e., 25 samples at 0–0.1 m and 2 additional samples at 0.1–0.2 m depth to investigate the occurrence of biocides at depth and thus possible leaching to deeper soil layers. For the second campaign, only the first 10 cm of topsoil was collected with the vegetation removed. Samples were transported on ice and frozen at -20°C until biocide analysis.

Table 1 Sample collection from the 55 SIS in 2020 and 2022

District No.	City	District	SIS built	# of samples	# of SIS	Sampling date
0.1	Freiburg	Vauban	2000	11	2	24-02-2020
0.2	Freiburg	Wiehre	2007	4	2	25-02-2022
0.3	Freiburg	St. Georgen	2011	10	5	25-02-2022
1	Freiburg	Weingarten	2003	1	1	18-05-2022
2	Freiburg	Mooswald	2006	8	4	16-05-2022
3	Freiburg	Oberwiehre	2006	6	2	18-05-2022
4	Freiburg	St. Georgen	2008	8	3	04-05-2022
5	Freiburg	Weingarten 2	2010	5	4	18-05-2022
6	Freiburg	Ebnet	2010	1	1	18-05-2022
7	Freiburg	Munzingen	2012	3	1	03-06-2022
8	Strasbourg	Robertsau	2014	1	1	08-06-2022
9	Strasbourg	Ostwald	2015	5	3	08-06-2022
10	Strasbourg	Souffelweyersheim	2016	7	6	08-06-2022
11	Strasbourg	Neudorf	2017	6	4	08-06-2022
12	Strasbourg	Illkirch-Graffenstaden	2018	1	1	08-06-2022
13	Freiburg	Haslach	2019	16	14	04-05-2022
14	Freiburg	St. Georgen 2	2020	1	1	04-05-2022

2.3 Soil Characteristics

Gravimetric water content was determined by drying the samples at 105°C for 24 h. For loss on ignition, samples were burned at 550°C for organic content and at 950°C for carbon content (Heiri et al., 2001). Grain sizes were analyzed by laser diffraction using a Malvern Mastersizer according to the method described by Abdulkarim et al., 2021.

2.4 Soil Sample Preparation and Analysis

Sample preparation followed the solid-liquid extraction protocol of Gilevska et al., 2022. Briefly, 5 g of sieved (2 mm) samples adjusted to 50% water content was filled into a centrifuge tube. 3 mL of solvent (DCM: Pentane, 3:1 v/v) was added. Samples were vortexed for 5 s, placed in an ultrasonic bath for 5 min, vortexed for 1 min and then centrifuged at 5000 RPM for 20 min (Thermo Scientific Heraeus Megafuge 16R). The supernatant was transferred to a fresh glass vial. These steps were repeated twice until 9 mL of supernatant was obtained. The supernatant was evaporated under a N_2 stream and re-suspended in 1 mL of Acetonitrile (LC-MS grade, VWR International GmbH, Darmstadt, Germany). 12.5 mg of PSA Silica and 75 mg of $MgSO_4$ were added (Sigma Aldrich, Taufkirchen, Germany). The sample was vortexed again for 30 s and centrifuged for 5 min (5000 RPM). The supernatant was transferred to a new glass vial and stored at -20°C until analysis.

Terbutryn in samples from the first campaign was quantified by gas chromatography-mass spectrometry (GCMS-QP2010 Ultra, Shimadzu) using helium as the carrier gas and a column of Trace Gold TG-ZB5 (5% Diphenyl/ 95% Dimethyl-Polysiloxan, Fisher Scientific). The injection mode was splitless. The temperature program was as follows: 1 min at 50°C, 30°C min^{-1} to 175°C, 4°C min^{-1} to 180°C, 2°C min^{-1} to 210°C, 30°C min^{-1} to 320°C, with 1 min hold time. Limit of detection (LOD) was 0.08 ng L^{-1} and limit of quantification (LOQ) LOQ 0.23 ng L^{-1}. Table 2 shows recovery rates.

Samples from the second campaign were analyzed using ultra-high-pressure liquid chromatography (UHPLC, Dionex/Thermo Scientific UltiMate Dionex 3000) coupled to a triple quadrupole mass spectrometer (Thermo Scientific TSQ Quantiva). Further details of the methods are given in Junginger et al., 2022. The UHPLC allowed simultaneous analysis of three biocides, terbutryn, diuron, OIT, one pesticide, acetochlor and four TPs of terbutryn (terbutryn-2-hydroxy, terbutryn-sulfoxide,

Table 2 LOD, LOQ, recovery rates, and measurement uncertainty for GCMS and LC-MS analysis

Substance	Measured	LOD [ng g^{-1}]	LOQ [ng g^{-1}]	Recovery [%]	SD of recovery [%]	Measurement uncertainty [%]
terbutryn	GC-MS (2020-22)	0.08	0.23	59.3	16	17
	LC-MS (2022)	0.03	0.10	68.4	15	12
TerOH		0.09	0.27	9.5	4	12
TerSO		0.02	0.06	22.5	5	12
TerDesE		0.04	0.11	60.1	18	12
TerdesEOH		0.15	0.44	5.6	3	12
Diuron		0.04	0.93	49.1	10	12
OIT		0.05	0.19	13.3	14	12
Acetochlor		0.04	0.11	37.3	2	12

desethyl-terbutryn, and desethyl-2-hydroxy-terbutryn. LOD, LOQ and recovery rates are included in Table 2.

2.5 Catchment Areas of SIS

We estimated the facade area in the districts connected to each SIS of the second campaign. Estimates were based on available GIS information by assigning adjacent buildings or parts of buildings to the runoff receiving SIS. We assessed facade areas by considering building length and width (GIS), counting the number of floors and assigning 3 m of facade per floor. We assumed that windows and balconies reduced the facade area by 50%. Table S3 details these estimates. Hydraulic loads of SIS were defined by DWA (2005) as

$$hl = \frac{c_a}{SIS_a} \quad (1)$$

With hl as the hydraulic load, c_a as the catchment area and SIS_a as the area of the SIS. The results for each SIS are given in Table S3. Biocide loads of SIS were defined here as

$$bl = \frac{f_a}{SIS_a} \quad (2)$$

With bl as the biocide load and f_a as the facade area.

2.6 Data Analysis

Data were analyzed with R (Version 4.2.1) using R Studio (2022.07.1). The Spearman Rank Correlation Coefficient (Best & Roberts, 1975) was used to evaluate correlations between terbutryn concentrations, age of SIS, organic content, clay content and facade area to SIS area.

3 Results and Discussion

3.1 Biocides and TPs in SIS—First Campaign

The first campaign confirmed terbutryn transport via stormwater from facades to SIS soils. Terbutryn concentrations in 9 SIS ranged from < LOD up to 1 ng g^{-1} with only two of 25 samples above LOQ (Fig. 2, see Table 2 for value of LOD and LOQ). No measurable concentration of terbutryn was found in samples collected from deeper layers, confirming previous studies that most biocides are retained in the top 0.1 m (e.g. for diuron Li et al., 2021).

The concentrations in this study were an order of magnitude lower than two other studies sampling soil in ponds (Flanagan et al., 2021) and below facades (Bollmann, Fernández-Calviño, et al., 2017a). Flanagan et al. (2021) found terbutryn in one out of 17 ponds sampled with concentrations up to 100 ng g^{-1}. Below

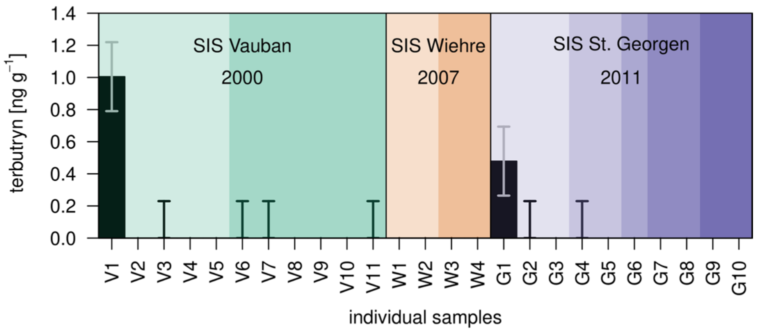

Fig. 2 Terbutryn concentration in SIS soil. Colors separate districts, each shade representing a unique SIS. Gray lines indicate standard deviation; black lines indicate measurements below LOQ. Measurements below LOD are blank

the facades, terbutryn concentrations of 10 to 100 ng g^{-1} were reported in two of 17 samples (Bollmann, Fernández-Calviño, et al., 2017a). Similar terbutryn concentrations (< LOD to 26 ng g^{-1}) were found in a stormwater retention pond (Linke et al., 2022). However, concentration differences may be due to different paints and initial terbutryn concentrations, age of buildings, different weather conditions and other factors that vary between study areas (Paijens et al., 2019).

Terbutryn was most abundant in the oldest SIS (SIS Vauban), suggesting accumulation over time and therefore higher chronic release to SIS than degradation and leaching from SIS soils. Higher organic content in soil column cores from SIS Vauban than from SIS Wiehre (Bork et al., 2021) may explain the increasing terbutryn adsorption. Two additional samples collected at 0.1 to 0.2 m depth in SIS Vauban show terbutryn concentrations below the LOQ, suggesting limited vertical transport of terbutryn. As terbutryn concentrations confirm biocide transport to the investigated SIS, the study was extended to SIS of different ages.

3.2 Biocides and TPs in SIS—Second Campaign

This section discusses explanatory variables of biocide and TP concentrations in 46 SIS from two cities. According to the research objectives, possible explanatory variables include point and non-point sources, SIS age and soil characteristics such as organic carbon content and clay content.

3.2.1 Point and Non-point Sources

Biocide occurrence in SIS varied for each compound (Fig. 3). Terbutryn was detected in 78% of samples (<LOQ to 1.7 ng g^{-1}). In contrast, diuron (58 ng g^{-1}) and OIT (168 ng g^{-1}) were present in high concentrations in a single SIS. Besides biocides, the herbicide acetochlor was observed in two districts in Strasbourg. Although acetochlor has not been allowed as an active ingredient in commercial formulations in the EU since 2012 (EU, 2011) and the grace period ended in 2013, it may have originated from the use of old stocks in urban areas. The half-life time of acetochlor of about 90 d in soil suggests a recent use.

We assume a diffuse source for terbutryn in all districts, whereas diuron and OIT occur punctually and at high concentrations, which may be associated with recent repair work or construction. Both OIT and diuron were present in one newly built district. OIT and diuron also have lower K_{oc} values than terbutryn and were thus expected to sorb less to organic matter in soils (Table S1). In addition, degradation in soil is fastest for OIT (DT_{50} = 9 d) and much slower for terbutryn (DT_{50} = 90 - 231 d) and diuron (DT_{50} >2500 d) (Bollmann, Fernández-Calviño, et al., 2017a; Junginger et al., 2022). Thus, it was expected that OIT associated with chronic non-point sources should not be present in most samples because it biodegrades rapidly (Bollmann, Fernández-Calviño, et al., 2017a) or be photodegraded directly on facades before reaching SIS soils (Bollmann, Minelgaite, et al., 2017b). Since diuron sorbs less to organic material and has a longer half-life than terbutryn, it may be transported to deeper soil layers, and even reach groundwater. Diuron may also interact with dissolved organic matter to form diuron-DOM complexes, which could facilitate transport (Thevenot et al., 2009). The amount of diuron contained in the applied renders and paints was unknown and may be less than the original amount of terbutryn, although typical concentration ranges were the same for diuron and terbutryn (Gartiser et al., 2015). Since OIT degrades rapidly

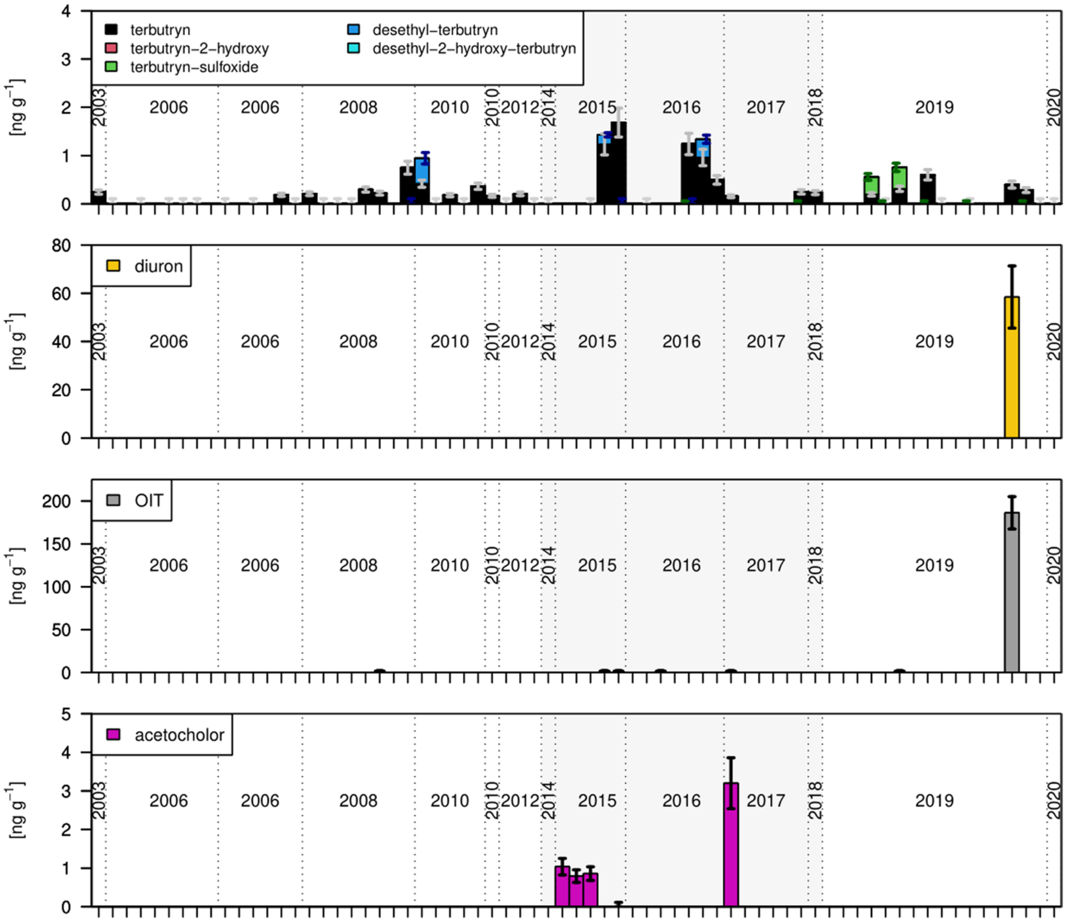

Fig. 3 Concentrations of terbutryn, diuron, OIT and acetochlor in SIS. Error bars represent standard deviation. Concentrations below LOQ but above LOD are shown as lines at the bottom. Dotted lines show different districts with oldest SIS at the left side and newest at the right side. The gray shaded area indicates samples collected in Strasbourg

in soil (Bollmann, Fernández-Calviño, et al., 2017a) and diuron is mobile and quickly transported to deeper soil layers (Thevenot et al., 2009), the relatively high concentrations found in the present study point to even higher concentrations prior to sampling. Thus, high concentrations of OIT and diuron indicate a point source input from a recently painted facade. Terbutryn, which is more stable subject to higher sorption, may be regarded as better marker for diffuse inputs in SIS soils.

Soil samples were collected at the inflow to the SIS as concentrations were expected to be the highest. The extent of contamination within the SIS was not determined. A study in an urban flood detention pond suggested that biocide contamination was highest at the inflow but also occurred within the pond (Linke et al., 2022), which may be similar to contamination in SIS investigated here. We did not evaluate seasonal changes since all samples of the second campaign were collected within the same season and year, i.e., from May to June 2022. No seasonal changes of terbutryn could be observed in a study of soil samples collected in spring and autumn over two years (Linke et al., 2022). Also, no change in biocide concentration was observed before and after a rain event, suggesting that other factors dominate biocide concentrations in soil (Linke et al., 2022).

The terbutryn TPs, terbutryn-sulfoxide and desethyl-terbutryn, were measured in two and three samples, respectively, that also contained terbutryn. Terbutryn-sulfoxide was above LOD but below LOQ in six samples. Desethyl-terbutryn was detected in three samples. While TPs are partially formed on facades through photodegradation, they are also formed in soil by biodegradation (Junginger et al., 2022). Terbutryn-2-hydroxy and desethyl-2-hydroxy-terbutryn have a higher mobility than terbutryn-sulfoxide, although their sorption affinity to soil is lower, which may explain why they were not detected here. Terbutryn TPs in mixtures may be more toxic in aquatic systems than terbutryn itself (Hensen et al., 2020). Noteworthy, the toxic potency of terbutryn TPs may be underestimated because the uncertainty associated with the quantification of terbutryn TPs may be high due to low and often variable recovery rates during extraction from soil (generally < 50%; Table 2).

As biocides measured in the urban context were originally used in agriculture, information on substances in agricultural soils was available. Pesticide concentrations in agricultural soils can be higher than biocide concentrations in SIS and are mostly dependent on the amount of pesticide applied and on the time since application. For example, terbutryn and acetochlor have not been detected in agricultural soils recently, probably because they were banned in agriculture in 2007 and 2013, respectively (Kosubová et al., 2020). Overall, this supports the idea that biocide input is the determining factor for biocide concentrations in SIS and that acetochlor was from a recent source.

3.2.2 *Influence of SIS Age on Biocide Occurrences in SIS*

The age of the SIS and the corresponding houses built at the same time, varied from 2 to 19 years. Terbutryn was found as a diffuse input in all districts, which enabled comparison of concentrations at different SIS ages. As expected, higher concentrations of terbutryn were found in more recently (< 7 years) constructed SIS (Fig. 4). The highest concentrations of diuron and OIT were found in a district built in 2020 (Fig. 3). In general, terbutryn-sulfoxide was found in recently built districts (2016, 2017, 2019), while desethyl-terbutryn was present in older districts (2010, 2015, and 2016). This suggests a preferential formation and/or slower degradation of the latter TP due to terbutryn biodegradation (Junginger et al., 2022). However, both TPs may have already formed on the facade (Bollmann et al., 2016).

Higher concentrations found in recently built SIS could be related to greater biocide emissions from recently painted buildings connected to the SIS and thus large biocide loads entering into the SIS. Burkhardt et al., 2012 reported highest biocide emissions in the first year after painting in a field study, while Bollmann et al., 2016) observed the highest emissions of terbutryn and OIT in the first 6 to 12 months after painting (Bollmann, Minelgaite, et al., 2017b). However, biocides wash-off was found even 13 years after construction (Linke et al., 2021), underscoring that older buildings connected to SIS are continuously emitting biocides at low concentrations. This long-term, chronic leaching was also reported in a previous study, where biocide leaching occurred 14 years after construction (Hensen et al., 2018).

The biocide occurrence between the cities of Freiburg and Strasbourg, and thus between the examples from Germany and France, did not differ significantly. Higher concentrations of terbutryn were observed in Strasbourg, where SIS were constructed more recently. The SIS in Strasbourg were 4 to 8 years

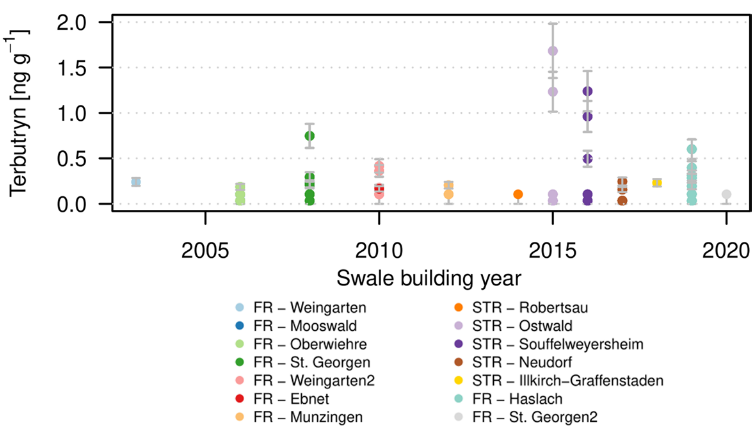

Fig. 4 Terbutryn concentration as a function of SIS age. Vertical lines indicate the recovery uncertainty for terbutryn

old, while in Freiburg they were 3 to 19 years old. This supports the finding that biocide wash off was highest after painting (Burkhardt et al., 2012). However, it was not possible to conclude that the use of biocides differed between France and Germany, although there may be differences between substances, since diuron and OIT were found only in Freiburg.

Other factors influencing the transfer of biocide loads from facades to SIS include the initial biocide concentrations in the paints and renders and hydro-climatic forcing (Paijens et al., 2019). No information was available for paints and renders in 14 districts sampled in 2022. Catchment parameters, such as impervious area or surface type, may also affect the loss of biocide runoff before it reaches the SIS (Wicke, Matzinger, et al., 2021a). Diffuse biocide losses from contributing catchments can reach up to 89% of leached biocides (Linke et al., 2022). The average annual temperature was similar in Strasbourg and Freiburg (11.6°C and 11.2°C), but the annual precipitation was higher in Freiburg, i.e., 977 mm compared to 650 mm in Strasbourg (German Weather Service, station Freiburg 1994-2020; Meteo France, station Strasbourg-Entzheim 1994–2020). Typically, more precipitation and more wind-driven rain results in higher biocide emissions from individual facades (Vega-Garcia et al., 2020). This indicates that climatic differences between Freiburg and Strasbourg cannot explain the higher biocide concentrations found in the Strasbourg SIS.

After entry into a SIS, sorption and degradation of biocides are the main processes that influence the amount of biocides in soil. This is highly dependent on soil characteristics, which can change with time. While clay content did not vary with the age of the SIS, the soil organic content of SIS soil decreases in newer SIS (Fig. S1). Some outliers with high organic content (loss on ignition at 550°C > 40 %) include SIS with wood chips as the topsoil layer. The decrease in soil organic content over time has been described previously and may indicate soil development in SIS over time (Bork et al., 2021).

3.2.3 *Influence of Facade Areas on Biocide Concentrations in SIS*

The variation in facade area between districts may also explain the differences in terbutryn concentrations in the SIS. Overall, the facade area contributing to terbutryn fluxes into the SIS did not determine terbutryn accumulation (Fig. 5). The hydraulic loads, i.e., the catchment area divided by the SIS area (from 1.2 to 14.3, Eq. 1), were within the limits recommended by the DWA (2005) and thus comparable in terms of potential biocide leaching. The terbutryn concentration did not vary as a function of estimated facade area divided by SIS area (biocide load, bl, Eq. 2). However, the potential for biocide leaching from facades to SIS varied widely, although more than 90% of the SIS have a ratio of facade to SIS area of less than 10. Larger facade areas connected to SIS reflect the contribution of taller (>5 floors) buildings, for example, in the districts of Haslach and Ostwald (Table S3). Note that terbutryn was only detected in 36 out of 46 SIS, so this result is only valid for SIS with terbutryn concentrations

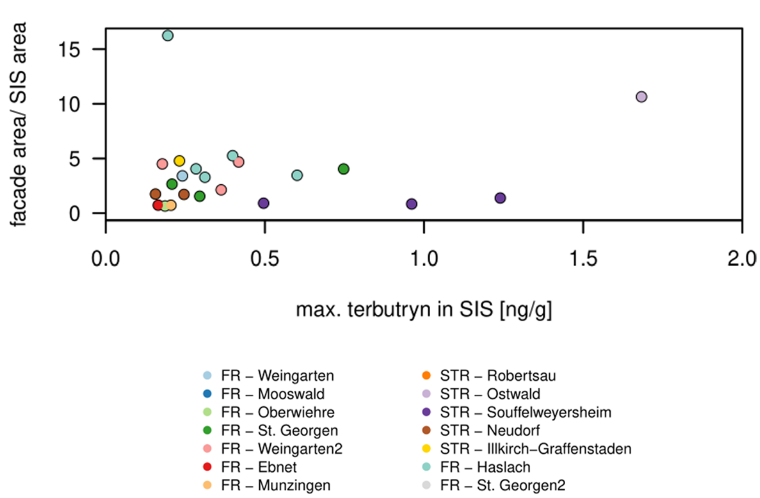

Fig. 5 Facade area/ SIS area ratios as a function of maximum terbutryn concentration in SIS

above the LOD. In addition to the facade area, other factors such as diffuse losses (Linke et al., 2022) and the dilution along the flow path may influence the terbutryn load entering a SIS, and thus the final biocide concentration in SIS.

3.2.4 Soil Clay and Organic Matter Contents

The organic matter content ranged from 0.5 to 71%, with a median value of 6.5% (loss on ignition). Soil texture analysis showed mostly silt in the SIS of Strasbourg. In Freiburg, the samples were mostly silty-loam to sandy-loam (Fig. S2). Clay content ranged from 0.2 to 13.2% with a median of 3.7%. Most samples were within the range of guidelines for SIS construction (DWA, 2005). We expected higher terbutryn concentrations with higher organic content and higher clay content since terbutryn ($logK_{oc} = 3.3$) has the lowest mobility, followed by diuron ($logK_{oc} = 2.6$) and OIT ($logK_{oc} = 2.1$) (Paijens et al., 2019). Organic matter and clay contents in SIS soils did not correlate with terbutryn concentrations ($p < 0.05$; Fig. S3). However, some SIS with higher terbutryn concentrations have higher organic content. Overall, this suggests that the mass input of terbutryn into SIS during runoff events mainly controlled terbutryn concentrations rather than soil characteristics.

4 Conclusions

The objective of this study was to assess the occurrence of biocides and to identify non-point and point sources of biocide inputs to the SIS by using grab soil samples only. Distinguishing between non-point and point sources may help to assess the fluxes and the impacts of biocides in urban ecosystems, including groundwater. Non-point source inputs of terbutryn prevail over point source inputs of diuron, OIT and the prohibited herbicide acetochlor. Most importantly, our results emphasize that biocide input is the dominant factor explaining biocide concentrations in SIS soils. The lack of significant biocide accumulation in soil over years may reflect both decreasing biocide emissions and biocide degradation over time. Selected measured soil characteristics, such as clay content and organic content, have no significant influence on biocide concentrations.

Leaching of biocides to groundwater via SIS may also occur. Here, design guidelines of SIS could be adapted to meet water quality thresholds, especially for biocides (Helmreich et al., 2022). Due to their widespread distribution, the best way to prevent the environmental impact of biocides leached from facades is to reduce them at the source (Wintz et al., 2022). Several options are available, including biocide-free paints, different facade materials such as brick or glass, and green facades (Wicke, Tatis-Muvdi, et al., 2021b). Soil and sediment of SIS might be contaminated not only with biocides but also with other micropollutants. At the end of their life-time, SIS soil might need to be disposed of at a special waste facility depending on their overall contamination (Flanagan et al., 2021). Other contaminants, such as free dissolved heavy metals at low pH values, may have greater effects than biocides. Still, mixtures of biocides and TPs can alter ecosystems.

In the future, screening of biocide concentrations and loads in SIS may be combined with modeling approaches (Perera et al., 2021) to quantify transformation and vertical transport of biocides from SIS soils to groundwater and to assess the associated ecotoxicological risks. For example, frequent detection of biocides indicates chronic exposure of soil organisms to biocides, although degradation processes on the way from the facades to the SIS soils were confirmed by the occurrence of terbutryn TPs. Knowledge on long-term toxicity of low concentrations of biocides in mixtures is particularly scarce for soils. Measurement methods such as environmental DNA can help to investigate and evaluate changes in soil due to biocide use and potential resistance of soil organisms against biocides (Amarasekara et al., 2023).

Overall, this study opens the door to more systematic monitoring of pollutant mixtures in SIS collecting stormwater runoff and the associated risks.

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07.10.2022), Eurométropole de Strasbourg (Limites de communes: https://data.strasbourg.eu/explore/dataset/limites_de_communes/export/?disjunctive.nom, last access and download 11.10.2022). Maps were created using QGIS Version 3.16.3.

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Declarations

Conflict of Interest The authors declare no competing interests.

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