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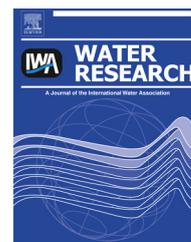
Dynamics of biocide emissions from buildings in a suburban stormwater catchment – Concentrations, mass loads and emission processes

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ABSTRACT

Biocides such as isothiazolinones, carbamates, triazines, phenylureas, azoles and others are used to protect the surfaces of buildings, e.g. painted or unpainted render or wood. These biocides can be mobilized from the materials if rainwater gets into contact with these buildings. Hence, these biocides will be found in rainwater runoff (stormwater) from buildings that is traditionally managed as "clean water" in stormwater sewer systems and often directly discharged into surface waters without further treatment. By means of a 9 month event-based high resolution sampling campaign the biocide emissions in a small suburban stormwater catchment were analysed and the emission dynamics throughout the single rain events were investigated. Five out of twelve of the rain events (peak events) proved significantly higher concentrations than the rest (average) for at least one compound. Highest median concentrations of 0.045 and 0.052 $\mu g\ L^{-1}$ were found for terbutryn and carbendazim, while the concentrations for isoproturon, diuron, N-octylisothiazolinone, benzoisothiazolinone, cybutryn, propiconazole, tebuconazole, and mecoprop were one order of magnitude lower. However, during the peak events the concentrations reached up to 1.8 and 0.3 $\mu g\ L^{-1}$ for terbutryn and carbendazim, respectively. Emissions of an averaged single family house into the stormwater sewer turned out to be 59 and 50 $\mu g\ event^{-1}\ house^{-1}$ terbutryn and carbendazim, respectively. Emissions for the other biocides ranged from 0.1 to 11 $\mu g\ event^{-1}\ house^{-1}$. Mass load analysis revealed that peak events contributed in single events as much to the emissions as 11 average events. However, the mass loads were highly dependent on the amounts of rainwater, i.e. the hydraulic flow in the receiving sewer pipe.

The analysis of the emission dynamics showed first flush emissions only for single parameters in three events out of twelve. Generally biocides seemed to be introduced into the stormwater system rather continuously during the respective events than in the beginning of them. Mass flows during the events did correlate to driving rain, whereas mass loads neither correlated to the length or the intensity of rainfall nor the length of dry period.

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1. Introduction

Building façades are exposed to wet conditions such as driving rain and undercooling condensation, and, hence, susceptible to growth of algae, fungi and bacteria. For preservative reasons, polymeric based coatings as renders and paints, which are very susceptible for microbial attack, are equipped with biocides (Reichel et al., 2004). These polymeric based renders and paints are commonly used as finishing coating on top of thermal insulation systems. Also other façade materials, such as polymer based paints for wooden surfaces, are preserved by biocides (Schoknecht and Bergmann, 2000). Biocides are regulated in the EU and defined in the European biocidal product directive (BPD) (European Parliament and Council, 2012) as substances designed "to destroy, deter, render harmless, prevent action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means."

Both renders and exterior paints can be equipped with film preserving compounds. It is known that triazines and phenylureas are used as algaecides and carbamates as fungicides, while isothiazolinones are used as bactericides for such purposes. Besides the use as film preservatives some of the biocides, primarily the ones with high water solubility, are only added to the products to increase shelf life of the formulated products until they are used (in-can preservatives) (EC, 2013a,b). The concentration per single biocide is about $0.1–2 \text{ g kg}^{-1}$ in render, which corresponds to $0.3–4 \text{ g m}^{-2}$ wall area (Burkhardt et al., 2011). In-can and film preservatives consist of mixtures of about one to eight different biocides, leading to a total content of biocides in render and exterior paints from 0.5% to 1% (Burkhardt et al., 2011). Additionally to the previous named biocides, triazoles are used for the preservation of wood, as they are very effective fungicides (Schultz et al., 2007). Besides usage in buildings also private gardening is a potential source for urban pollution (Fig. 1). Only use, (European) laws and regulations but not effects discriminate between biocides and pesticides. However, for most compounds it is quite clear for which purpose they are used in Denmark (Table 1).

The current literature that focuses on biocide leaching from materials relies on equilibrium partitioning and forced weathering. Schoknecht et al. (2003, 2009) and Styszko et al. (2014) demonstrated that triazine, phenylurea and iso-thiazolinone biocides can be washed off from construction material surfaces (paints and renders) in idealized laboratory experiments, in which materials were constantly soaked with water. Under forced rain in combination with drying periods (Burkhardt et al., 2009, 2011; Schoknecht et al., 2003, 2009) the biocides leach in considerable fractions from the respective materials (paints and renders). However, significantly higher amounts of rain were applied in these experiments than naturally occurring. The authors intended these experiments as first guidance and not as sound basis for massive assessment/modelling. In additional projects it has been found out, that the delivery rate of the biocides through the materials is diverse, even though the used renders are very similar, i.e. it depends on the exposure to weather (Burkhardt et al., 2012; Wangler et al., 2012).

Previous studies showed that leaching from building materials is a major source of biocide pollution concerning urban waters (Burkhardt et al., 2007). Driven by rain, the biocides enter surface waters and soil, where they might undergo degradation processes. As rainwater runoff (stormwater) is often collected in separated sewer systems and either directly discharged into surface waters or infiltrated into groundwater, the contamination of stormwater is of special concern. Burkhardt et al. (2007) expected that urban biocide emissions lead to concentrations exceeding the European drinking water quality standard for pesticides (100 ng L^{-1} for single pesticide and 500 ng L^{-1} for total pesticide concentration (European Parliament and Council, 1998)) up to ten fold in the first flush of stormwater runoff. However, these values are only relevant for those biocides that are registered as pesticides as well, for all others no threshold value for drinking water exists and, hence, also substances, forbidden in agricultural usage, are still used as biocides without any regulation in respect to drinking water in Europe. Nevertheless, the presence of biocides exceeding effect levels in surface water would be in conflict with the European water framework directive (WFD) (European Parliament and Council, 2000). A new directive on priority substances under the WFD recommends annual average environmental quality standard (AA-EQS) for inland waters of 2.5 and 64 ng L^{-1} for cybutryn and terbutryn, and 200 and 300 ng L^{-1} for diuron and isoproturon, respectively (European Parliament and Council, 2013). The other biocides are not regulated under the WFD. Furthermore, the used biocides are toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment already at low concentrations. For example the effect concentration of cybutryn, which causes an effect in 10% of the test organisms
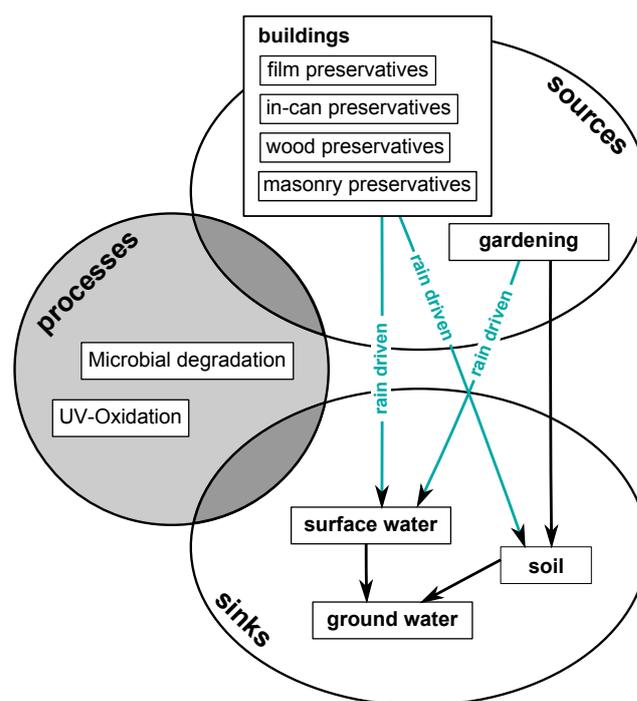
Fig. 1 – Sources, fate and sinks of biocides in urban stormwater.

Table 1 – Biocides covered within this study: Name, acronym, activity, log K_{ow}[a], water solubility (WS)[a], and predicted-no-effect-concentration (PNEC)[b]. According to European and Danish laws and regulations compounds marked (A) are exclusively used as biocides, (B) are used both as biocides and pesticides in Danish agriculture, compounds marked with (C) are used both as biocides and pesticides in Danish private gardening (in 2010).[c]

Group	Substance (acronym) characteristics	Formulae	Substance (acronym) characteristics	Formulae
Triazines	Terbutryn (TB)[A] Algaecide Log K_{ow}: 3.77 WS: 42 mg L^{-1} PNEC: 34 ng L^{-1}		Cybutryn, Irgarol 1051[A] (IRG) Algaecide Log K_{ow}: 4.07 WS: 20 mg L^{-1} PNEC: 1 ng L^{-1}	
Carbamates	Carbendazim (CD)[A] Fungicide Log K_{ow}: 1.55 WS: 3112 mg L^{-1} PNEC: 34 ng L^{-1}			
Phenylureas	Isoproturon (IP)[A] Algaecide Log K_{ow}: 2.84 WS: 92 mg L^{-1}		Diuron (DR)[A] Algaecide Log K_{ow}: 2.67 WS: 102 mg L^{-1} PNEC: 20 ng L^{-1}	
Isothiazolinones	Methylisothiazolinone (MI)[A] Bactericide/Fungicide Log K_{ow}: <0 WS: 9.6*10^5 mg L^{-1}		Benzoisothiazolinone (BIT)[A] Bactericide/Fungicide Log K_{ow}: 0.64 WS: 22,204 mg L^{-1}	
	Octylisothiazolinone (OIT)[A] Bactericide/Fungicide Log K_{ow}: 2.61 WS: 309 mg L^{-1} PNEC: 13 ng L^{-1}			
Triazoles	Tebuconazole (TBU)[B/C] Fungicide Log K_{ow}: 3.89 WS: 97 mg L^{-1}		Propiconazole (PPZ)[B] Fungicide Log K_{ow}: 4.13 WS: 11 mg L^{-1}	
	Mecoprop (MCPP)[A] Algaecide Log K_{ow}: 2.94 WS: 471 mg L^{-1}			

[a] Calculated with EPI Suite™ v4.10 of the US EPA (http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm).
[b] Referred in Burkhardt et al., 2009.
[c] According to the Danish EPA (Danish Environmental Protection Agency DEPA, 2011a,b).

(EC$_{10}$), is 10 ng L^{-1} (Mohr et al., 2008). Additionally, the predicted no effect concentrations (PNEC) of biocides are in the low ng L^{-1} range, e.g. terbutryn and carbendazim 34 ng L^{-1} or octylisothiazolinone 13 ng L^{-1} (Burkhardt et al., 2009).

In this study the stormwater in a suburban catchment was sampled with high temporal resolution and analysed with respect to biocide concentrations and mass loads to study the emission dynamics and detect first flush events. The temporal resolution was used to study whether a treatment of only a fraction of the runoff water for instance the first flush (which we take as the first 30% or less) would make sense. The study covered substances (Table 1) that are known to be used on the Danish building market (N-octylisothiazolinone (OIT), terbutryn (TB), diuron (DR)), as well as those that were analysed in previous studies (cybutryn (IRG), isoproturon (IP),

benzoisothiazolinone (BIT), carbendazim (CD), methyl-isothiazolinone (MI)). Furthermore, tebuconazole (TBU) and propiconazole (PPZ) were added to this study, as they are predominantly used in wood preservation (Schoknecht and Bergmann, 2000), while mecoprop (MCPP) is mainly used in roof protection (Bucheli et al., 1998), and is no longer sold for agricultural or gardening purposes in Denmark (DEPA, 2011a,b). Among the analysed biocides only propiconazole and tebuconazole are currently used in Danish agriculture (DEPA, 2011a); tebuconazole is used in urban gardening as well (DEPA, 2011b). The occurrence of some compounds analysed in the present study (carbendazim, triazines and phenyl-ureas), has been reported for urban stormwater (Burkhardt et al., 2012; Quednow and Püttmann, 2007, 2009, Wittmer et al., 2010), whereas, the isothiazolinones and triazoles

have, to the author's knowledge, never been reported in urban waters. The study was undertaken, first, to demonstrate the importance of biocide emission into rainwater catchments in Northern Europe, second, to test whether the assumption that no biocides will be emitted from suburban catchments into surface waters holds true, third, to study the dynamics of biocide emissions in rainwater catchments, and fourth, to study the influence of weather to the respective emissions.

2. Material and methods

2.1. Catchment

The stormwater runoff was collected in a catchment in Silkeborg (Denmark), which is a typical example of a Northern European suburban area. The catchment had previously been hydraulically analysed in detail as its stormwater management system was constructed in connection with an EU LIFE project (Silkeborg Municipality, 2009). The catchment is residential and covers in total 21.5 ha with 140 single family houses. Applying a calibrated runoff model the impervious area was determined to 7.1 ha, of which approximately 30% are streets or parking lots. The buildings in the catchment were surveyed and it was found that single family houses, garages, etc. are well-kept and often newly painted. In order to estimate the total façade area and the biocide treated surfaces, a survey of the catchment was conducted by walking through the streets and inspecting the surfaces visually. The status was documented on photographic images. The total façade area accounted for about 24,000 m^2. About 5% of the façades were equipped with renders and paints, 20% covered with painted wood, and 75% were brick façades, hence, maximum 25% of the total façade area was expected to be treated with biocides.

Based on a survey of aerial maps of the catchment, 22% of the façades drained to impervious surfaces of which on their side only a small fraction was connected to the stormwater sewer. The exact fraction of impervious surfaces draining to the stormwater sewer is not known for the test catchment; however, for a similar Danish catchment Thorndahl et al. (2006) found that only 42% of the impervious horizontal surfaces are connected to the stormwater sewer. Here of $^3/_4$ were roads and roofs which do not connect directly to a façade but do have a high degree of connectedness to the stormwater sewers. Based here on, an estimated 2–7% of the total façades actually was connected to the stormwater sewer.

The stormwater from the catchment was collected in a separated sewer system ending in a stormwater pond. The longest distance the water runs in the sewers was 1040 m while the shortest was 100 m. Since the pipe slope generally was more than 1%, the maximum runoff time for a typical storm event was about 15–20 min.

2.2. Sampling

The flow was measured continuously in a deep underground structure about 10 m upstream of the inlet to the stormwater pond. A full flowing magnetic flow-meter (Optiflux 2000, DN400, *Krohne*, Duisburg, Germany) was used with a flow rate dependent and estimated accuracy of 1–5%. An automatic

water sampler (ISCO 6712, *Teledyne ISCO*, Lincoln, NE, USA) was triggered by the flow-meter, allowing flow proportional stormwater sampling. The flow measurement cut-off level was 3 L s^{-1}, ensuring that the continuous trickle of infiltrating groundwater observed in the pipe did not trigger the water sampler. Sub-samples were collected for every 5 m^3 of water. Every three such sub-samples were mixed to a composite sample. The automatic sampler held 24 glass bottles, hereby allowing up to 360 m^3 of water to be sampled with a sampling resolution of 15 m^3. The samples were kept dark and at ambient temperature in the automatic sampler, which, due to the underground placement of the measuring structure was 6–12 °C all year round. After a storm event the bottles were exchanged with clean bottles within one week and kept refrigerated until they were analysed. The compounds were tested to be stable under these conditions as concentration changes were determined to be less than 8% in 7 days (except propiconazole which decreased 30% during the storage period). Within the sampling period between October 2011 and June 2012, a total of 8929 m^3 stormwater runoff entered the stormwater pond. As not every event was sampled, representatives of 2880 m^3 were sampled and analysed (191 samples from 12 events).

2.3. Weather during the experimental period

Rain events occurred with 0.1–4.3 mm h^{-1}. Between November 3rd and 25th it was a rather dry period with less than 0.3 m^3 entering the pond. The rain intensity in this catchment was thus considerably lower than the water exposure of 85 mm h^{-1} as used in the laboratory orientation experiments by Burkhardt et al. (2009, 2011) which has been used for catchment scale modelling repeatedly (Wittmer et al., 2011; Coutu et al., 2012a,b).

2.4. Analysis

The sample extraction was performed following Bester and Lamani (2010) with minor modifications. In a volumetric flask a 100 mL sample was spiked with 50 μL of a surrogate standard solution, containing a mix of deuterated biocides (1 μg mL^{-1} in methanol (gradient grade LiChrosolv, *Merck*, Darmstadt, Germany): isoproturon-D6, terbutryn-D5, cybutryn-D9, tebuconazole-D6, carbendazim-D4). In addition 3 mL of a 0.2 M phosphate buffer was added to adjust to pH = 7. A Bakerbond SDB-2 (6 mL, 200 mg) SPE-cartridge (*Mallinckrodt Baker*, Deventer, The Netherlands) was conditioned with 12 mL acetonitrile (gradient grade LiChrosolv, *Merck*, Darmstadt, Germany) and 12 mL Millipore-water, successively. After extracting the 100 mL sample (using a velocity of ∼2 mL min^{-1}) the cartridge was washed with 12 mL Millipore-water, slightly dried with vacuum and then eluted with 12 mL acetonitrile and 12 mL methanol. The combined eluates were condensed to 1 mL in a BÜCHI Syncore® multiport condenser (*Büchi*, Flawil, Switzerland) at 50 °C, 280 rpm, and 100 mbar for about 90 min. The extracts were transferred to 1.5 mL autosampler vials.

The analysis was performed by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) using electrospray ionization in positive mode (ESI(+)) on

an Ultimate 3000 dual gradient low pressure mixing HPLC-system (*Dionex*, Sunnyvale, CA, USA) coupled to an API 4000 triple-quadrupole-MS (*AB Sciex*, Framingham, MA, USA). The separation was performed at 5 °C using a Synergy Polar-RP column (*L* = 150 mm, ID = 2 mm, particles = 4 μm, *Phenomenex*, Torrance, CA, USA). Contrary to Bester and Lamani (2010) an acidic eluent was avoided to improve retention in the HPLC column. Acidification took place post column by adding a flow of 0.03 mL min^{-1} of 0.2% formic acid in water via a T-piece between column and ion-source in order to support the ionization process. The neutral multi-step HPLC-gradient consisted of water (A) and methanol (B): 0–3 min 0% B, 3–5 min 0 → 50% B, 5–15 min 50 → 80% B, 15–15.5 min 80 → 100% B, 15.5–19 min 100% B, 19–20 min 100 → 0% B, 20–25 min 0% B.

Recoveries ranged between 74 and 105% (except methylisothiazolinone (47%) and N-octylisothiazolinone (49%)). The recovery rates were not used to correct the presented results. The limits of detections (LODs) were below 1 ng L^{-1} for all substances, except methylisothiazolinone (4 ng L^{-1}). Every set of 24 samples was extracted together with a blank, in order to exclude contamination during sample preparation. Detailed information about recoveries, LODs, and mass spectrometric data is provided in the supplementary material (S1 & S2).

2.5. Driving rain

Driving rain I_{WDR} (Burkhardt et al., 2012; Blocken and Carmeliet, 2012; Blocken et al., 2013), i.e. the rain that actually hits the façade surfaces, is usually calculated as

$$I_{WDR} = \frac{2}{9} C_R C_T OWI_{Rain} U \cos \theta \qquad (1)$$

with C_R = roughness coefficient; C_T = topography coefficient, O = obstruction factor, W = wall factor, U = wind speed, I_{Rain} = rain intensity, θ = angle of the wind. In a given catchment driving rain is linearly dependent on wind speed and rain intensity, considering that effects from wind direction will level out in a catchment of reasonable size (Eq. (2)):

$$I_{WDR} = C_C I_{Rain} U \qquad (2)$$

with C_C being a catchment specific factor including $\frac{2}{9} C_R C_T OW$. Assuming that the cumulative mass of released biocide is proportional to the accumulated runoff from a façade – as for example reported by Burkhardt et al. (2012) – the mass flow of a compound M_{WDR} during the respective rain event becomes:

$$M_{WDR} = C_C C_S I_{Rain} U \qquad (3)$$

with C_S being a substance specific constant including e.g. the façade area containing the compound, different usage pattern or release mechanisms. Some of the parameters controlling the release mechanism are pH-value of the water, K_{ow} or K_{oc} of the compound resulting in K_d values for the respective render/biocide system, as studied by Styszko et al. (2014). The product $C_C C_S$ can be found by plotting mass flows vs. the product of rain intensity and wind speed. In our approach we took I_{Rain} equalling the total hydraulic flow at the outlet of the catchment of the respective event divided by the area of the catchment. The average wind speed was gained from a weather station during the respective event. The mass flow M_{WDR} (Eq. (5)) was calculated from the mass load per event

m_{event} (Eq. (4)) and the event length t_{event}. The mass load per event, hence, the sum of each subsample mass load, was calculated from the concentration c_{sample}, the hydraulic flow Q_{sample} and the sampling length t_{sample} of each subsample within the respective event:

$$m_{event} = \sum \frac{c_{sample} * Q_{sample}}{t_{sample}} \qquad (4)$$

$$M_{WDR} = \frac{m_{event}}{t_{event}} \qquad (5)$$

3. Results and discussion

3.1. Concentrations

The median and average concentrations of the analysed biocides for all 191 analysed stormwater samples are shown in Fig. 2. The box plot shows concentrations for all biocides, focussing around a median. However, also some outliers, which usually originated from a few events with concentrations exceeding the median by one or two orders of magnitude (peak events), were detected as well. A more detailed discussion about frequency and possible causes for occurrence of these peak events is given in paragraph 3.2. Compounds found in all analysed samples with high median concentrations were carbendazim and terbutryn (45 and 52 ng L^{-1}), while they occurred with up to 306 and 1840 ng L^{-1} in peak events, respectively. Diuron, isoproturon, propiconazole, and iodocarb as well as mecoprop were detected with median concentrations between 2 and 7 ng L^{-1}. However, these substances were not detected in all samples. Some biocides, e.g. methylisothiazolinone and benzoisothiazolinone, were only detected in a few events, but in these cases with high
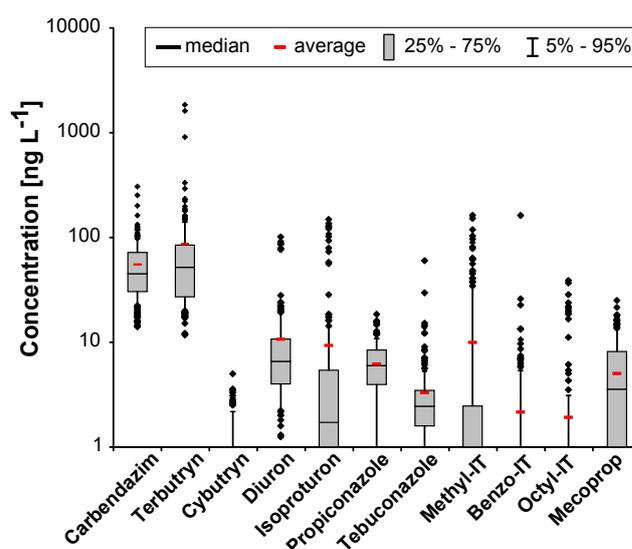
Fig. 2 – **Concentrations of different biocides in the studied catchment from Oct. 2011 to June 2012. In order to enable the calculations, concentrations smaller than the LOD were set to zero (Abbreviation IT: Isothiazolinone).**

concentrations (up to 162 ng L^{-1}), possibly indicating transport in polymer paint particles.

The concentrations of phenylureas (median: diuron 7 ng L^{-1}, isoproturon 2 ng L^{-1}) were in the same range as experienced by Burkhardt et al. (2012), and Wittmer et al. (2010) for surface waters. The diuron concentrations were considerably lower than in French urban river water (9000 ng L^{-1}), though (Blanchoud et al., 2004). The concentration of carbendazim (median 45 ng L^{-1}) is comparable to Burkhardt et al. (2012). The results obtained for terbutryn from Swiss surface water (median < 10 ng L^{-1} (Wittmer et al., 2010)) agree well to those found in the present study (median 52 ng L^{-1}), while it was lower as found by Quednow and Püttmann (2007, 2009) in German surface waters (50–5000 ng L^{-1}). No comparison data is available for the isothiazolinones. The differences in the substance pattern between the German, French and Swiss studies and the present study may originate from the different building structures in the respective areas and, hence, different materials in use. In general, the detected concentrations in the stormwater runoff were considerably lower than in the direct material leachate (10–1000 μg L^{-1}) from a freshly treated building complex (Burkhardt et al., 2011). The comparison of the stormwater concentrations from this study with the ecotoxicological data from Burkhardt et al. (2009) shows that the median concentrations of carbendazim, N-octylisothiazolinone, and terbutryn were in the same range as the PNEC-values. However, in some events also other biocides exceeded the PNEC values by far. In addition, the detected median concentration of terbutryn was similar to the fresh water AA-EQS of 64 ng L^{-1}, as recommended by the European water framework directive (European Parliament and Council, 2013) for this compound. Also cybutryn exceeded the AA-EQS level of 2.5 ng L^{-1} in some stormwater samples.

Several studies report atmospheric deposition of pesticides (e.g. Bester et al., 1995; Buser, 1990; Dubus et al., 2000). To exclude that the results in this study were influenced by atmospheric deposition of pesticides (which would especially be relevant for isoproturon and less for diuron) a comparison to the Danish monitoring for atmospheric deposition was conducted. It showed that during the sampling period only in March/April 2012 low deposition rates of isoproturon could be detected (DMU, 2012; DCE, 2013), while diuron deposition was not detectable at all — none of the other compounds were analyse in deposition samples in that region as they had been removed from the target list because they never occurred in earlier years. The occurrence of biocides in infiltrating groundwater was tested to be negligible as well, since concentrations in the stormwater pipe between the storm events were below the detection limits. Therefore, the concentrations detected in the stormwater runoff were supposed to be emitted during the respective storm event.

3.2. Mass loads per event

In addition to the concentrations, the mass loads for the twelve analysed events were determined individually. The mass loads per event ranged from no emissions to 76 mg event^{-1} (terbutryn). For most of the biocides the mass loads per event were usually comparable between the events while some events with several times higher mass loads could be detected as well. These outlier events were identified by GRUBB outlier test ($\alpha = 95\%$) in this normal distributed data set of 12 events (DAVID test) (Danzer, 2007). For the calculation of the average mass loads per event these outlier events were excluded and shown separately in Table 2, but they were not excluded in the further discussion of the mass loads (a dot-plot showing the variability of the mass loads can be found in suppl. mat. S3). However, it has to be mentioned that the outlier identification was based on the total mass load per event and conducted separately for each substance, since the occurrence of peak events were compound specific: while an event was a peak event for one compound, it was usually quite regular for other compounds.

On average about 8 mg terbutryn were emitted into the Silkeborg catchment during each rain event; within the outlier event even more than 70 mg. Except carbendazim (7 mg) and methylisothiazolinone (1.6 mg), the average mass loads were below 1 mg per event for all other biocides. Nevertheless, in some outlier events the mass loads were also very high for

Table 2 – Mass loads per event of different biocides in the Silkeborg catchment (Oct. 2011–June 2012, 12 rain events). Up to two outlier events (peak events) were identified by Grubb-outlier test ($\alpha = 95\%$). The parameter "Emissions per average house" includes all houses (painted and unpainted) in the catchment.

Biocide	Mass load[a] ± standard deviation [mg event^{-1}] without peak events	Mass load of the highest peak event [mg event^{-1}] (number of peak events)	Emissions per average house per event [μg event^{-1} house^{-1}]
Carbendazim (CD)	7.0 ± 6.0	No peak event identified	50
Terbutryn (TB)	8.3 ± 5.6	77 (1)	59
Cybutryn (IRG)	0.02 ± 0.03	0.2 (1)	0.1
Diuron (DR)	0.8 ± 0.6	10.1 (1)	6
Isoproturon (IP)	0.4 ± 0.3	15.3 (2)	3
Propiconazole (PPZ)	0.6 ± 0.4	2.3 (1)	4
Tebuconazole (TBU)	0.4 ± 0.3	No peak event identified	3
Methylisothiazolinone (MI)	1.6 ± 3.5	No peak event identified	11
Benzoisothiazolinone (BIT)	0.1 ± 0.2	2.6 (2)	1
N-Octylisothiazolinone (OIT)	0.03 ± 0.05	3.7 (2)	0.2
Mecoprop (MCPP)	0.8 ± 0.7	No peak event identified	6

[a] In order to enable the calculation of the average values mass loads < LOD were set to zero.

those substances with low mass loads in average events. It is interesting to note that events with peak loads contributed about as much to the total biocide loads of the catchment as the standard events, since only every 10th event was a peak event with about ten times higher mass load.

The occurrence of peak events might simply be caused by the inhomogeneity and patchiness of the rain as rain differs temporarily but also spatially within events. However, it cannot completely be excluded that these peak events were due to compound specific mobilization caused by special weather conditions or fresh applications (see suppl. material S4). November 2011 was extremely mild with friendly weather and temperature up to 15 °C; thus, new paintings etc. cannot be excluded. Peak events may also have been observed by Coutu et al. (2012b) – in that paper modelled concentrations for the Vuachère basin are compared to those measured with low temporal resolution. In some cases the model predictions in that paper matched measured concentrations very accurately, while for others significant deviations were detected. Possibly the temporal resolution in the older study was not high enough to be able to demonstrate the first flush effects in the catchment as such.

The Silkeborg catchment covers about 140 single family homes. Only a few of them are to some extend equipped with render or paint. The rest of the houses are mainly covered by painted wood or masonry (bricks). A comparison with emission rates from artificial walls (Burkhardt et al., 2012) shows that observed emissions (normal as well as peak) agree to the hydraulic characterization of the present catchment, taking the fraction of treated surfaces into account (see suppl. material S4). Assuming that the Silkeborg catchment is representative for other suburban residential catchments, emissions to surface water per average house were calculated, only taking the total mass load as well as the number of houses in the catchment into account, but disregarding the fraction of treated surfaces as well as the connection rate of the walls to the sewer (Table 2). This can be used in order to provide a comparable number for the emissions from a random suburban catchment with similar building structure, for which the actually biocide-equipped façade area or the amount of façades directly connected to the sewer system is only known as being similar to the Silkeborg catchment. The average emissions of a single family house turned out to be 59 and 50 μg event^{-1} house^1 terbutryn and carbendazim, respectively. Emissions for the other biocides ranged from 0.1 to 11 μg event^{-1} house^1 (Table 2). Even considering the low fraction of treated surfaces, this catchment based assessment results in considerably lower emissions than those assessed by Wangler et al. (2012) based on pure fresh render façades ignoring the ratio of transfer of water from the walls into either the soil or the stormwater sewers. Thus, this transfer rate is essential for emissions into surface water. The difference between our emission data and the older work is probably the fraction that is emitted into the soil. However, in the assessments for the European biocidal product directive (European Parliament and Council, 2012) it is considered that the mass flow into the soil is the only one for suburban regions, while obviously also the runoff into surface waters is relevant (this study).

It was tested, on whether the mass load per event on a catchment scale was dependent on diverse weather conditions. Correlation tests ($N = 12$, terbutryn: $N = 11$) showed that the length of dry period preceding the event, the length of rainfall and the wind direction had no influence on the mass flow on the catchment scale (R^2 of a linear correlation < 0.1 (See suppl. material S5)). Contrary, the tebuconazole emissions were (linearly) dependent on the accumulated hydraulic flow with a positive correlation of $R^2 = 0.64$ ($N = 12$). The linear correlation ($N = 12$ for all compounds, except terbutryn: $N = 11$) between mass flow and wind driven rain (expressed as the product of rain intensity and wind speed, see paragraph 2.5) lead to positive correlation coefficients up to $R^2 > 0.96$ for propiconazole and tebuconazole but also for carbendazim, terbutryn, and methylisothiazolinone correlation coefficients $R^2 > 0.66$ were determined (Fig. 3). Hence, it could be concluded that the accumulated hydraulic flow per event (rain amount) and, more important, the wind driven rain had an influence on mass flows on the catchment scale at least on selected biocides. In addition, the analysis of the slope in Fig. 3, hence, the product C_CC_S allowed conclusions about the emission processes. As the product C_CC_S is the same for terbutryn and carbendazim (0.55 and 0.51, respectively) it can be concluded that these compounds are emitted and used in a very similar way in this catchment. Contrary, C_CC_S for propiconazole and tebuconazole are similar to each other (0.08 and 0.03, respectively), but differ widely from those for the other compounds. As tebuconazole and propiconazole are predominantly used in wood protection while terbutryn and carbendazim are used in paints and renders this difference might indicate different usage or release mechanisms. However, despite the similar usage of terbutryn, carbendazim, and methylisothiazolinone, the release factors for these three compounds were expected to be quite different as their lipophilicity (K_{ow}) is quite different. At this stage, the emissions seem to be triggered by
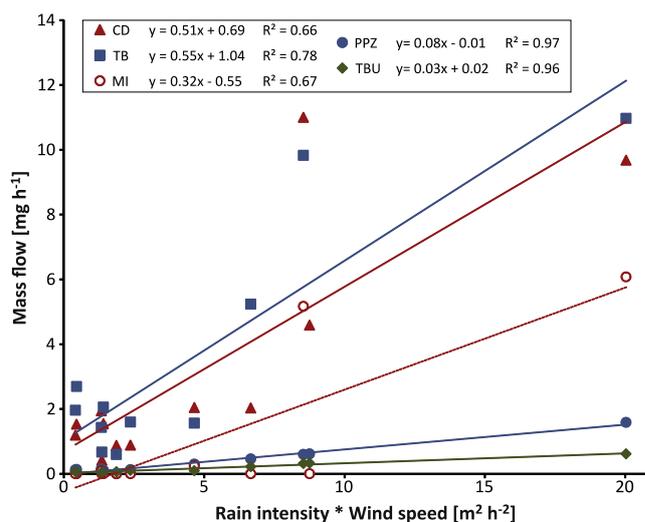
Fig. 3 – Mass flows of biocides (M_{WDR}) in relation to rain intensity (I_{Rain}) times wind speed (U) in the Silkeborg stormwater catchment (Shown are all compounds with $R^2 > 0.48$; Abbreviations: CD: Carbendazim, TB: Terbutryn, MI: Methylisothiazolinone, PPZ: Propiconazole, TBU: Tebuconazole; one peak event for terbutryn is excluded).

usage rate in the catchment and water contact to the render system (driving rain as originating from wind, rain and topography in the catchment) (both included in C_C), as well as partitioning render/water and the loss rate (e.g. by photolysis) (both included in C_S (compare Styszko et al., 2014)). Similar connections between mass loads and driving rain were found by Jorgenson and Young (2010) and Luo et al. (2014). However, in those experiments insecticides were applied in mimicking spray and, hence, loosely attached to surfaces and not incorporated in polymers as in this study. For this reason, the reservoirs were quickly depleted and the dependency load vs. cumulative water runoff volume was not linear, as in our study.

3.3. Dynamics

The high-resolution flow-proportional sampling enabled new findings about the dynamics of the biocide emissions during the rain events. The main issue to test was, whether the release of the biocides is constant during the rain event or a fast release of biocides occurs in the beginning of the event and diminishing later on (first flush). Doing so, conclusions can be drawn on, whether biocides accumulate during dry weather on surfaces (like dust), where they might be loosely attached and are released via first flushes, or are leached out of the materials during the rain event. In addition, it allows designing treatment systems that e.g. treat only the first fraction of the water. Bertrand-Krajewski et al. (1998) defined the first flush phenomenon when 80% of the pollutant load is emitted during the first 30% of discharge volume. Delayed release rates would result in a post flush phenomenon – low or no emissions in the first part of discharge volume and high emissions later in the event. A simple graphical test for the first flush behaviour is the relation between the emitted mass and the accumulated (hydraulic) flow, which would result in an upwards curved (convex) line in case of first flush, while a post flush would result in a downwards curved (concave) line.

Neither first nor post flushes could be detected for any compound in 5 out of 12 events. Independent from the actual flow, the concentrations were already in the first subsample in the same range as the median concentrations from all samples in the respective event (Fig. 2), and stayed constant over the entire storm event. An example for these commonly detected events is shown in Fig. 4a (an overview over all 12 events is shown in suppl. mat S6). A first flush would occur if the biocide release is very fast in the beginning, due to an accumulation of biocides on the surface of the façade or in dust, and slowing down as soon as this is washed off. Contrary to the expectations of a first flush, a linear relation was commonly observed during the events (Fig. 4b) which indicates continuous emission of the biocides from the facades. This was also observed by Burkhardt et al. (2011), who analysed stormwater runoff from a small urban catchment in Switzerland. Continuous emissions during short time rain events also agree well to the models based on laboratory experiments developed by Wangler et al. (2012) and Schoknecht et al. (2009) who discuss a diffusion based process as the controlling mechanism for the release of biocides from render. They do find however decreasing values during the lifetime of a material. Nevertheless, this cannot be expected to be seen on a catchment scale as renovation/refurbishing is constantly ongoing in a catchment.

However, during three out of the 12 events first flush behaviour was detected for terbutryn, methylisothiazolinone, cybutryn and diuron as demonstrated in Fig. 5 for terbutryn. In the beginning of the event remarkable high concentrations for terbutryn were detected (up to 1840 ng L^{-1}, qualifying this first flush event also as a peak event), which decreased very fast to a level of below 100 ng L^{-1}. Also for carbendazim slightly higher concentrations in the beginning and a decrease afterwards were observed during this event. However, the other biocides had rather constant concentrations during the entire rain event. Hence, the long dry weather period prior to the event is presumably not the only main reason for this
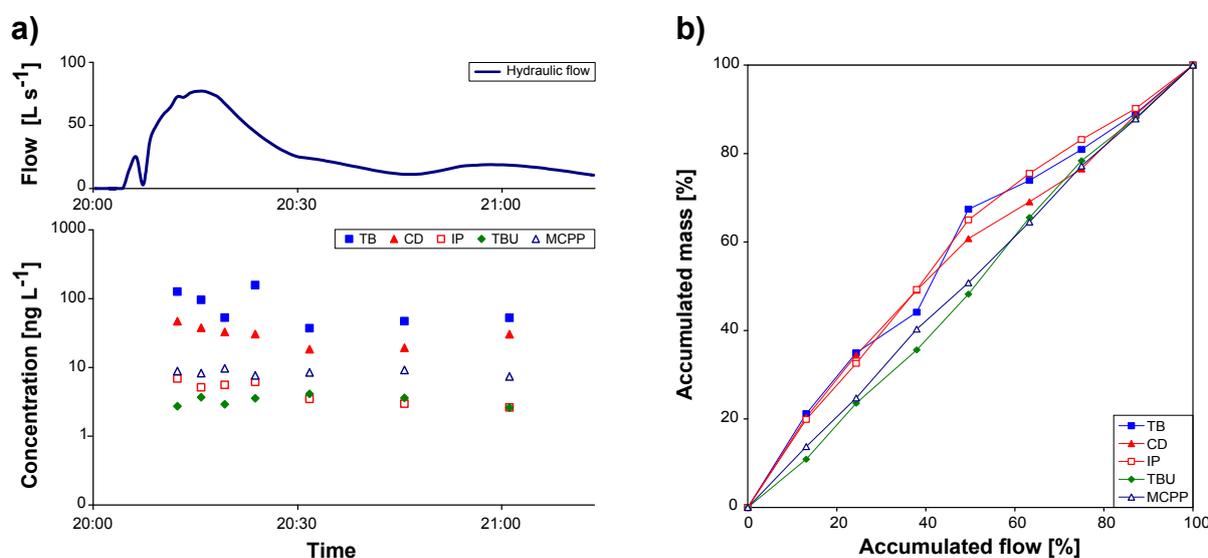
Fig. 4 – Common biocide concentration dynamics during a rain event (a) and evaluation of first flush dynamics in a common rain event (b). Abbreviations: TB: Terbutryn, CD: Carbendazim, IP: Isoproturon, TBU: Tebuconazole, MCPP: Mecoprop.
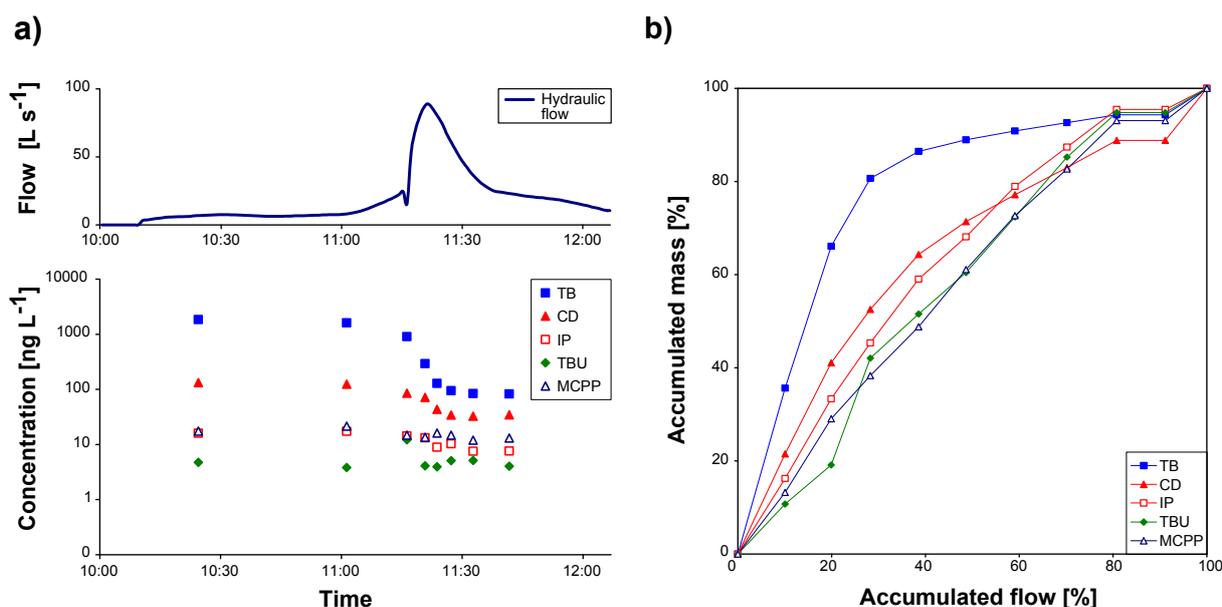
Fig. 5 – **Biocide concentration dynamics (a) and evaluation of first flush dynamics in the rain event on November 25th, 2011 (b): occasionally occurring first flush for terbutryn after a long dry period. Abbreviations: TB: Terbutryn, CD: Carbendazim, IP: Isoproturon, TBU: Tebuconazole, MCPP: Mecoprop.**

behaviour. Additionally, for cybutryn, also post flush behaviour was detected in two separated events, meaning, more was emitted at the end than during the event. The little dynamic that can be detected is probably due to variability or patchiness of rainfall (and wind speed) that occur on 10–100 m scale. It can be excluded that effects similar to dust mobilization are relevant as in such a case first flushes would occur regularly and for all compounds. Also occurrence in infiltration water can be excluded as stated in paragraph 3.1.

4. Conclusions

The different concentration profiles in the stormwater runoff events can be ascribed to different emission pathways and application forms of the biocides (Fig. 1). First of all, the constantly emitted biocides as terbutryn, carbendazim, isoproturon, diuron, tebuconazole, propiconazole, and mecoprop were detected in most of the samples. These compounds are used as film preservatives (EC, 2013a,b) and slowly released to the environment (Burkhardt et al., 2012; Wangler et al., 2012). In contrast to these, benzoisothiazolinone and methylisothiazolinone were only detected in a few selected samples during some rain events. Rain homogeneity modelling indicated that this is probably rather due to the patchiness of rain than to one-time emissions e.g. via abrasion of polymer particles or fresh applications which could go along with the usage as in-can preservatives (EC, 2013a,b) and their high water solubility and low K_{ow} values (Table 1).

In general, this study showed that:

1) Biocide emissions are not only important in certain city centres (Burkhardt et al., 2009; Quednow and Püttmann, 2007, 2009, Wittmer et al., 2010), but also in Northern European suburbs, though the thermal insulation systems with polymeric top render are less common in these regions.
2) The constantly high emissions in suburban regions raise the question whether the risk assessments for these compounds – saying in suburban areas 100% will be infiltrated into the ground – need to be refined, particularly with regard to surface waters.
3) It could be demonstrated that it is not efficient to focus on first flushes when assessing treatment options of stormwater with respect to biocides.
4) Even though the application of the different biocides in construction materials is very similar, the emission behaviour on the catchment scale in respect of first flush etc. is very different.

Acknowledgement

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.02.033

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