Biocide emissions from building materials during wet weather: identification of substances, mechanism of release and transfer to the aquatic environment

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ABSTRACT

Biocides are added to or applied on building materials to prevent microorganisms from growing on their surface or to treat them. They are leached into building runoff and contribute to diffuse contamination of receiving waters. This review aimed at summarizing the current state of knowledge concerning the impact of biocides from buildings on the aquatic environment. The objectives were (i) to assess the key parameters influencing the leaching of biocides and to quantify their emission from buildings; (ii) to determine the different pathways from urban sources into receiving waters; and (iii) to assess the associated environmental risk. Based on consumption data and leaching studies, a list of substances to monitor in receiving water was established. Literature review of their concentrations in the urban water cycle showed evidences of contamination and risk for aquatic life, which should put them into consideration for inclusion to European or international monitoring programs. However, some biocide concentration data in urban and receiving waters is still missing to fully assess their environmental risk, especially for isothiazolinones, iodopropynyl carbamate, zinc pyrithione and quaternary ammonium compounds, and little is known about their transformation products. Although some models supported by actual data were developed to extrapolate emissions on larger scales (watershed or city scales), they are not sufficient to prioritize the pathways of biocides from urban sources into receiving waters during both dry and wet weathers. Our review highlights the need to reduce emissions and limit their transfer into rivers, and reports several solutions to address these issues.

KEYWORDS

Biocides, building materials, leaching, review, risk assessment, stormwater, surface water, wastewater

1. Introduction

According to the European Biocidal Product Regulation (BPR), which regulates the placing of biocidal products on the market, a biocidal product is a chemical substance or mixture that is used "*with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action*" (European Parliament and Council 2012). Assessments are underway for most biocides and their uses concerning their placing on the market. Biocides are widely used in buildings to prevent microorganism growth (mosses, fungi, bacteria, algae and lichens) on their surfaces. Among the 22 types of biocidal products defined by the BPR, four are currently applied in building materials: in-can preservatives (product type 6 of the BPR), film preservatives (product type 7), wood preservatives (product type 8) and masonry preservatives (product type 10). They can be incorporated into the material (flat concrete roofs, renders, paints, etc.) or used for surface post-treatment (roof tiles, wooden surfaces, etc.) (Paulus 2005; Van de Voorde et al. 2012). In general, 3 to 5 biocides are applied in order to broaden the spectrum of protection. They can account for up to 0.5% (w/w) of the total material, ranging from 300 to 4000 mg/m^2 (Burkhardt et al. 2011). Biocides are meant to migrate from the deeper layer to the surface of the coating to act on microorganisms (Paulus, 2005) and are hence released in runoff. Similarly, biocides used for post-treatment of building materials, such as cleaning agents for roof tiles (Van de Voorde et al. 2012), are leached during wet weather and also contribute to runoff contamination. After entering the sewer network, they can be released into the aquatic environment and have negative effects on aquatic life (Singer et al. 2010; Wick et al. 2010; Wittmer et al. 2010; Moschet et al. 2015; Ccanccapa et al. 2016).

The issue of biocide emissions from buildings is of increasing concern for the aquatic environment. First, their consumption is increasing due to the growing urbanisation (Steffen et al. 2011) and the evolution of building practices such as the implementation of multilayer external thermal insulation composite system, which offers good conditions for the growth of microorganisms, or the increasing use of flat roofs (Burkhardt et al. 2012; Wicke et al. 2015). Secondly, despite their impact on ecosystems and intensive use in urban areas, biocides are still poorly regulated in the aquatic environment and thus poorly monitored (Dulio et al. 2015; Geissen et al. 2015). For example, the Water Framework Directive (European Parliament and Council 2013) covers only 4 biocides (diuron, isoproturon, terbutryn and cybutryn), which are used as plant protection products (PPPs). Finally, regulations on the discharges of wastewater or specific actions intending to reduce certain pollutants (e.g., pharmaceuticals or pesticides) proved to be effective in improving surface water quality (Botta et al. 2012; Köck-Schulmeyer et al. 2012; Palma et al. 2014; Ccanccapa et al. 2016). Similar regulations are required for biocides. So far, much attention has been paid to agricultural sources. A number of policy measures have been introduced to reduce agricultural and urban sources of pesticides, whose active substances are sometimes also used as biocides (European Parliament and Council 2009a; Barzman et al. 2015; Lamichhane et al. 2016; Lechenet et al. 2017). However, in 2015, the NORMAN network and the German Federal Environment Agency organized a workshop on environmental monitoring of biocides in Europe and pointed out the need to acquire more data on biocide

concentrations in the aquatic environment for full risk assessment and to set up stormwater monitoring programs for source assignment (Pohl et al. 2015).

Numerous studies measured the emissions of biocides from building materials (Schoknecht et al. 2003; Jungnickel et al. 2008; Schoknecht et al. 2009; Burkhardt et al. 2011, 2012, Bollmann et al. 2016, 2017a). Many others focused on the contamination of receiving waters by biocides, which were mostly used as pesticides (Quednow and Püttmann 2007; Wick et al. 2010; Chen et al. 2012; Palma et al. 2014; Vorkamp et al. 2014; Ccanccapa et al. 2016). However, the link between the biocide emissions from buildings and their impact on receiving waters is rarely addressed (Burkhardt et al. 2011; Wicke et al. 2015). This link is difficult to establish because wet weather discharges are diffuse and biocidal substances have many other applications, especially in urban areas. Indeed, they are used as preservatives or cleaning agents (pharmaceuticals, personal care products, household products, pesticides etc.). In these cases, they unfortunately do not fall under the BPR (Wieck et al. 2016, 2018) but are covered by other regulations, such as Directive 91/414/EEC (European Parliament and Council 1991) for plant protection products or Regulation 1223/2009/EC for cosmetic products (European Parliament and Council 2009b). Therefore, the pathway between buildings and receiving waters is sometimes missing to assess the associated risk (Singer et al. 2010; Wick et al. 2010; Wittmer et al. 2010; Moschet et al. 2015; Ccanccapa et al. 2016).

In this context, the aims of this review were (i) to summarize the current state of knowledge concerning the leaching phenomenon and the urban water contamination by biocides used in buildings; (ii) to identify knowledge gaps and subsequent scientific research needed to address them, and (iii) to report policy and technical solutions in order to improve surface water quality. Therefore, four objectives were set to explore the fate of biocides used in building materials. The first one was to pinpoint the main biocides based on consumption data and leaching studies. Indeed, these substances could be transferred to runoff and thus contribute to the contamination of receiving waters via urban discharges during wet weather. The second one was to assess the key parameters influencing the leaching of biocides and their emission from paints, renders, roof sealants and treated tiles. The purpose was to generalize these emissions on a large scale (i.e., the watershed or city scales) and to provide technical options to prevent them from occurring. Mass balance between initial, remaining and released biocides was then addressed and the transformation processes that occurred in building materials were discussed. The third objective was to determine the urban sources of biocides and their different pathways to receiving waters during both dry and wet weathers. Data for biocides and their transformation products at different levels of urban water cycle (runoff, stormwater, combined sewer overflows, wastewater influents and effluents, rivers, and groundwater) were reviewed and compared to identify the main pathways, in order to help guiding actions of reduction after emissions. The final objective was to assess the environmental risk associated to the presence of biocides in receiving waters. Available data in receiving waters were compared to threshold values from regulation or ecotoxicological data. The comparison between the targeted biocides in this review and those actually monitored in the environment points out the missing data, which are required to assess global risk of biocides released from building materials, and policies that should be implemented in order to guide management and reduction of biocide uses, and thus achieving a better control of surface water quality.

2. Identification of the most used biocides in building materials

Many organic biocides are used in building materials or in post-treatment products. This section identifies biocides commonly used for these purposes. Three main sources related to buildings were singled out: roofs, wood materials and façades coated with renders and paints.

2.1. Roof treatments

The control of microorganisms or roots may take place at different parts of the roof. Biocidal substances can be used in deslagging or de-mossing products as a post-treatment for tiles. They can be used in roof paints or in bitumen roofing membranes for flat roofs.

2.1.1. Post-treatment of tiles

Biocidal products can be applied on roofs to fight stains, mold and algae, and to prevent lichen proliferation. Commercial formulations contain different active substances as quaternary ammonium compounds (QAC), isothiazolinones (dichlo-octylisothiazolinone and octylisothiazolinone) and terbutryn (Van de Voorde 2012; Gromaire et al. 2015; Pena-Poza 2018). According to Van de Voorde (2012), most of the de-mossing formulations for roofs available on the French market contain quaternary ammonium compounds, in particular benzalkonium (alkyldimethylbenzylammonium). Their manufacturing process leads to a mixture of homologues with different alkyl chain lengths (from 8 to 18 carbons) and benzalkoniums mainly with 12, 14 and 16 carbons (Ferrer and Furlong 2001; INRS 2005).

2.1.2. Roof paints

Biocidal substances are used in organic roof paints. The use of zinc pyrithione and terbutryn was reported by Jungnickel et al. (2008) and Van de Voorde (2012). Some other compounds such as isothiazolinones (OIT), phenylureas (diuron), carbamates (carbendazim, 3-iodo-2-propynylbutylcarbamate (IPBC)) or triazoles (propiconazole) were also mentioned (Jungnickel et al., 2008).

2.1.3. Herbicides in bitumen sheets for flat roofs

Mecoprop is an herbicide used in agriculture and in urban areas. It is often added to bitumen membranes for flat roofs to prevent roots from growing, thus maintaining roof sealing (Bucheli et al. 1998; Burkhardt et al. 2007). Unfortunately, these membranes are often over-used even though protection against root is not necessary (Wicke et al. 2015). This compound is originally registered as a plant protection product (PPP) but is currently used 3 times more as a root protection agent than in agriculture (Burkhardt et al. 2007).

2.2. Treatment of wooden elements

Permethrin, tolylfluanid, dichlofluanid or quaternary ammonium compounds have been widespread used since the 1980s to protect wood materials as well as azole fungicides (Kupper et al. 2005). In order to broaden their spectrum of activity, they can be applied as a mixture with

other organic or inorganic biocides, such as IPBC (Kukowski et al. 2016), copper or boron (Tiruta-Barna and Schiopu 2011; Lupsea et al. 2013). For example, tecubonazole and propiconazole are often used together because of their synergic effect. Also, copper based preservatives, such as copper azole, alkaline coper quaternary or copper pentachlorophenol are often used for wood (Janin et al. 2011; Sheng et al. 2013). In recent years, nanoparticles of silver, copper or zinc oxide were used (Kaegi et al. 2010; Kaiser et al. 2013) and more recently Pereyra et al. (2014) proposed the use of A-type zeolite containing Ag^{+}/Zn^{2+} as an inorganic antifungal for coatings.

2.3. Paints and renders

In recent years, organic renders and paints have been increasingly used. Unfortunately, they are vulnerable to the growth of microorganisms on their surfaces (Shirakawa et al. 2002; Burkhardt et al. 2012). In order to protect these materials, biocides are added to coating formulations (Paulus 2005). Some studies focused on the leaching of biocides from buildings, to determine whether it contributes to water pollution in urban areas or not. Isothiazolinones (Schoknecht et al. 2003, 2009, 2013; Bester and Lamani 2010), triazines (Schoknecht et al. 2003, 2009, 2013; Jungnickel et al. 2008; Bester and Lamani 2010; Burkhardt et al. 2011, 2012; Wangler et al. 2012; Styszko et al. 2014, 2015; Bollmann et al. 2016), phenylureas (Schoknecht et al. 2003, 2009, 2013; Bester and Lamani 2010; Burkhardt et al. 2011, 2012; Wangler et al. 2012; Styszko et al. 2014, 2015), carbamates (Schoknecht et al. 2003, 2009, 2013; Jungnickel et al. 2008; Bester and Lamani 2010; Burkhardt et al. 2011, 2012, Styszko et al. 2014, 2015) and triazoles (Styszko et al. 2014, 2015) appear to be the most commonly used-substances in building materials.

2.4. Most used organic biocidal substances in building materials

The literature review described above highlights 20 organic biocidal substances of concern which are among the most used or applied in building materials. The present review focuses on the following biocidal substances: isothiazolinones (methylisothiazolinone (MIT), benzisothiazolinone (BIT), chloro-methylisothiazolinone (CMIT), octylisothiazolinone (OIT), dichloro-octylisothiazolinone (DCOIT)), phenylureas (diuron, isoproturon), carbamates (carbendazim, iodopropynyl carbamate (IPBC)), triazines (terbutryn, cybutryn, terbuthylazine), mecoprop, azoles (propiconazole, tebuconazole, thiabendazole), permethrin, quaternary ammonium compounds (benzalkonium, dodecyl-dimethyl ammonium (DDAC)), zinc pyrithione.

3. Leaching of biocides from building materials

This section reviews the data concerning the quantity of biocides emitted from buildings and the parameters influencing the leaching. Most of the studies on leaching processes focused on paints and renders (Schoknecht et al. 2009; Burkhardt et al. 2011; Wangler et al. 2012; Styszko et al. 2015; Bollmann et al. 2015a; Erich and Baukh 2016; Urbanczyk et al. 2019a). Emissions from roof maintenance practices are far less documented (Van de Voorde et al. 2012; Gromaire et al. 2015).

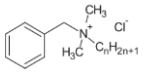
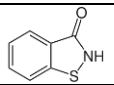
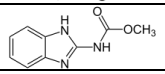
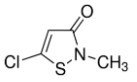
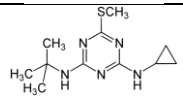
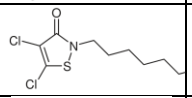
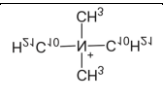
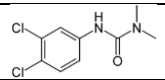
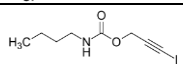
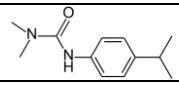
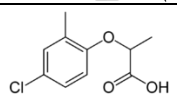
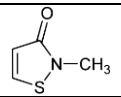
3.1. Key parameters influencing leaching behaviour

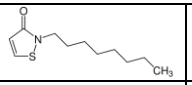
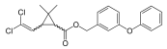
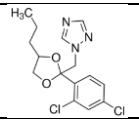
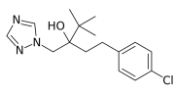
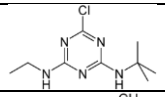
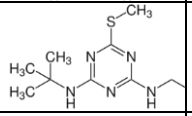
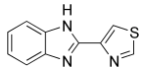
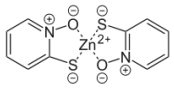
According to Uhlig et al. (2019) the leaching of biocides follows 5 steps: (i) transport of the absorbed water within the coating, (ii) desorption of the biocide from the material and dissolution in water, (iii) transport of the biocide through the material, (iv) degradation of the biocide via photolysis and hydrolysis and (v) transfer of the biocide to water on the material surface. At the render-water interface, a partitioning equilibrium is established between the material and the water. Biocides are washed off by runoff and the remaining part migrates from the deeper layers of the material to the surface in order to restore this equilibrium (Styszko et al. 2015). Three mechanisms for the transport of biocides in polymeric renders have been suggested (Schoknecht et al. 2009; Wangler et al. 2012): (i) evaporative transport, (ii) transport through the polymer and (iii) diffusion through the water-filled pores, the predominant mechanism (Schoknecht et al. 2009; Wangler et al. 2012; Erich and Baukh 2016). Given the nature of the mechanisms involved, the leaching process is influenced by many factors such as temperature, time span between two rain events, UV exposure, biocide properties, render composition, weather conditions, etc. (Burkhardt et al. 2012; Wangler et al. 2012; Erich and Baukh 2016; Urbanczyk et al. 2019a).

One of the major parameters influencing leaching is the physical and chemical properties of the biocides. Among them, hydrophobicity, solubility and stability seem to be key parameters. Table 1 reports some properties of biocides of interest, highlighting two features:

- The structures and physico-chemical properties of biocides are very different. Log K_{ow} (hydrophobicity) ranges from -0.83 (MIT) to 9.33 (zinc pyrithione), water solubility from under 0.005 mg/L (permethrin) up to 960,000 mg/L (MIT), log K_{oc} (partition between the particulate and dissolved phases) from 1.08 (MIT) to 5.43 (benzalkonium) and Henry's constant K_H (volatility) from 10^{-12} (carbendazim) to 10^{-7} atm.m^3.mol^{-1} (permethrin, DCOIT). Consequently, the variety of physical and chemical properties makes it complex to analyse biocides with a single analytical procedure (analytical column, extraction steps, chromatographic systems, etc.). Additionally, their persistence in water, expressed as the half-life (DT50), varies from less than a day to more than 2000 days, depending on the compound.
- It is difficult to gather information on biocides since many values can be found in the literature for a given parameter. Hence, several values are reported in table 1 for log K_{ow} or DT50.

Table 1. Physico-chemical properties and ecotoxicological data of biocides of concern

Biocide MW (g/mol)	Structure	Log Kow	pKa	WS (mg/L)	Log Koc[a,l]	K_H (atm.m^3.mol^{-1})[b]	DT50 in fresh waters (days)	PNEC value in fresh water (µg/L)	EC50 *daphnia magna* (mg/L) 48h	Bioconcentration factor (BCF)[l]
Benzalkonium chlorides C12-C16 304.5-388.7		1.69-3.42[c]		100000[d]	5.43		30[e]	S12-S16 – 0.415[s] S12 – 0.04[α]	0.041[β]	10.79
BIT 151.2		0.64[f]		22204[b]	1.53		>50[g]	-	0.85[γ]	3.16
Carbendazim 191.2		1.51[j]	4.20[h]	1.55[b]	2.39	1.5*10^{-12}	42[k]-350[l]	0.034[v]	0.087[u]	27
CMIT 149.6		-0.34[l]-0.4[m]		Highly soluble[n]			3[m]-6.6[n]	0.049[h]	0.16*[e]	<54
Cybutryn 253.4		2.58[f]-3.95[l]	4.1[j]	20[b]	2.4	5.3*10^{-9}	30[o]	0.001[v]	2.4[h]	250
DCOIT 282.2		3.59[b]-4.9[m]		27[m]	3.35	1.9.10^{-7}	<1[p]	0.008[v]	0.0052[e]	108.6
DDAC (C10) 326.6		-0.41[q]		650[r]			30[s]	0.38[s]	0.062[q]	81
Diuron 233.1		2.71[m]-2.85[f,j]		102[b]	2.59	5.3*10^{-10}	113[a]-2190[m]	0.02[v]	5.7[h]	2
IPBC 281.1		2.4[m]-2.81[f,j,l]		436[b]		6.9*10^{-9}	7-139[t]	0.026[v]	-	19.33
Isoproturon 206.3		2.50[f,j,l]		92[b]	2.14	1.9*10^{-9}	30[p]-1560[h]	0.021[u]	0.56[u]	3.6
Mecoprop 214.6		-0.19[l]-0.1[f,j]	3.74[j]	471[b]	1.41	1.8*10^{-8}	31[i]	44[u]	200[u]	3.16
MIT 115.2		-0.83[l]-0.5[m]		960000[b]	1.08	5*10^{-8}	18,2[n]-30[m]	3.9[h]	0.16*[e]	3.16

OIT 213.3		2.45[f,j]-2.61[b]		309[b]	2.13	$3.6*10^{-7}$	>30[p]	0.013[v]	0.32[e]	19.21
Permethrin 391.3		6.1[u]		<0.005[u]	4.59	$4.6*10^{-8}$ - > $4.5*10^{-7}$ [u]	<3[u]	0.00047[u]	0.00127[u]	500-570[u]
Propiconazole 342.2		3.72[j,l]	1.09[h]	11[b]	2.82	$14*10^{-9}$	6.4[v]-30[i]	6.8[u]	4.8[e]	180
Tebuconazole 307.8		3.5[l]-3.7[j]	5.00[h]	97[b]	3	$5.1*10^{-10}$	28[i]	1[u,e]	4[e]	78
Terbuthylazine 229.7		3.04[j]-3.4[l]	2[j]	6.6[l]	2.34	$1.6*10^{-11}$ [h]	77[i]	0.06[u]	21.2[h]	34
Terbutryn 241.4		3.65[f,j,l]	4.30[h]	42[b]	3.30	$9.1*10^{-9}$	354[i]	0.034[v]	2.6[h]	41.47
Thiabendazole 201.2		2.39[l,h,w]	4.73 & 12[h,w]	31[w]	2.40	$1.4,10^{-11}$ [w]	203[h,w]	1.2[W]	0.81[W]	96.5[W]
Zinc pyrithione 317.7		9.33[x]		8[y]			<1[z]	0.0026[v]	0.034[e]	

*Value for CMIT/MIT (3/1) mixture

[a]Gustafson (1989); [b]Bollmann et al. (2014b), modelled data; [c]Chem Spider, modelled data; [d]Sigma Aldrich; [e]European Parliament and Council (1998); [f]Wittmer et al. (2010); [g]Bürgi et al. (2009); [h]University of Hertfordshire, PPDB; [i]PAN Pesticides Database; [j]Wick et al. (2010); [k]Cuppen et al. (2000); [l]INERIS; [m]Paulus (2005); [n]European Parliament and Council (2015b); [o]EQS (2011); [p]Ekblad (2014); [q]European Parliament and Council (2015c); [r]European Chemical Agency; [s]European Parliament and Council (2015a); [t]Juergensen et al. (2000); [u]European Parliament and Council (2014); [v]European Parliament and Council (2015d); [w]European Parliament and Council (2008); [x]Sánchez-Bayo and Goka (2005); [y]Burkhardt et al. (2009); [z]Yamada (2007); [α]Uhl et al. (2005); [β]Kreuzinger et al. (2007); [γ]Nautiel, SDS.

Schoknecht et al. (2009) and Burkhardt et al. (2012) showed that biocides from the same family can have similar leaching behaviour (as for triazines or phenylureas). This is not a generic rule, as in the case of isothiazolinones (DCOIT and OIT). Moreover, it was expected that water solubility (WS) and hydrophobicity (log K_{ow}) would be correlated with the calculated desorption constant (K_d), which was not the case in practice. According to Styszko et al. (2014), K_{ow} and K_d were correlated only at neutral pH, pH at which the K_{ow} is often given. However, the pH of the water-filled pores is basic and the pH of the runoff on the surface is more acidic. The same authors have shown that concentrations of biocides in runoff are considerably lower than their water solubilities. The nature of the material, such as the composition of the render (e.g. the organic fraction), led also to different emissions. Emissions of carbamates, isothiazolinones and triazines were influenced by the render composition unlike phenylureas. The silicone render led to fewer biocide emissions, probably because of a higher organic matter fraction (Styszko et al. 2014, 2015; Bollmann et al. 2016, 2017b).

Regarding environmental conditions, Jungnickel et al. (2008) highlighted the impact of rain intensity and cumulative rain duration after application of the compound, on its concentration in runoff. Significant concentrations can be observed especially after low-intensity rainfall (0.3 mm/h). According to Wangler et al. (2012) and Burkhardt et al. (2011, 2012), a rise in temperature tends to increase the release of biocides from façades, possibly due to faster diffusion. The partitioning and chemical interaction may change with temperature. At higher temperatures, chemical interactions may be reduced, leading to higher release. Also, biocides can be degraded by environmental conditions (hydrolysis, biodegradation or direct and indirect photolysis (Fenner et al. 2013)), resulting in lower emissions of the parent compounds but higher emissions of transformation products over time.

3.2. Release of biocides from buildings during rain events

The quantity of biocides emitted from leaching in runoff is not constant over time and, as described previously, depends on various parameters. Leaching of biocides mostly occurs within the first months after application (Bollmann et al. 2016, 2017b) and tends to decrease exponentially with time (Jungnickel et al. 2008; Wittmer et al. 2011b). In addition, this leaching is discontinuous (Bollmann et al. 2016; Schoknecht et al. 2016) and depends on rain events. Even though the main part remains in the material, biocides can still be released after numerous rain events (Burkhardt et al. 2011): Riechel et al. (2015) and Hensen et al. (2018) showed the release of compounds even after more than 15 years. It is therefore difficult to estimate the quantities of biocides emitted from buildings during rainy weather. These emissions were studied on two scales. Some lab or building-scale studies investigated the leaching behaviour in order to assess the emissions under controlled conditions. Based on these findings, release models were developed to simulate the emissions on a larger scale.

3.2.1. Small-scale emissions

Table 2 reports cumulative emissions found in the literature and the percentages of losses from the material compared with the initial quantity. Concerning paints and renders, the values are highly variable from one compound to another but also for a given compound. For instance, cumulative emissions ranged from 0.6 to 178 mg/m^2 for carbendazim, from 0.5 to 1012 mg/m^2

for terbutryn, from 6 to 1730 mg/m^2 for diuron, from 2.5 to 1376 mg/m^2 for OIT or from 56 to 5041 mg/m^2 for BIT (biocides are listed in increasing order of water solubility). For most of the biocides, the main part remains in the material. The percentages of losses vary from 1 to 33% for carbendazim, from 1 to 34% for terbutryn, from 7 to 62% for diuron, from 2 to 29% for OIT. However, biocides just used as in-can preservatives are not expected to remain in the material in the long term. For instance, Schoknecht et al. (2009) reported leached quantities up to 100% of the initial quantity of BIT in the material. Emission differences observed between compounds are linked to their physicochemical properties. In particular, releases tend to increase with water solubility. Variability between studies is also linked to the different experimental procedures which have been performed: lab-scale or real building, exposure to water, initial quantity of substances etc. Schoknecht et al. (2009) compared emissions from three different leaching tests on the lab scale and demonstrated the importance of the contact time with water. Only a few studies investigated leaching of biocides from paints and renders under natural weather conditions. Burkhardt et al. (2012) and Bollmann et al. (2016, 2017b) exposed panels coated with renders and paints to natural weather during at least one year. They measured higher emissions of biocides compared to those obtained following the EN 16105 (CEN 2011) procedure used by Schoknecht et al. (2013), possibly due to a higher initial amount of biocides in the material. However, the percentages of leached biocides assessed under natural weather were slightly lower compared with those obtained in the lab-study. Consequently, considering a same initial amount of biocides, the EN 16105 procedure could overestimate both the emission rates and the associated risk assessment.

Table 2. Cumulative emissions of biocides from leaching experiment on the lab-scale or semi-technical scale and percentages of biocides leached (DR, diuron; IP, isoprotuon; TB, terbutryn; CB, cybutryn; CBZ, carbendazim; TEB, tebuconazole; BZK, benzalkonium)

Reference	Material	Concentration of each biocide	Exposition to water	Cumulative emissions in mg/m² (% of losses)												
				DR	IP	TB	CB	CBZ	IPBC	DCOIT	OIT	BIT	MIT	TEB	MCPP	BZK
Burkhardt et al. (2011)	Render	1500 g/m2	Sprinkling	435 (29)		315 (21)	285 (19)	105 (7)								
	Marketed sealants	4.8 g/m2 (Preventol® B2)	Sprinkling												12.4 (0.2)	
		3.0 g/m2 (Herbitect®)													1.1 (0.04)	
Styszko et al. (2015)	Silicone render	11.4 µg/g	Immersion	2.9-5.0 (7-12)	8.9-12.1 (21-29)	0.5-2.2 (1-5)	0.5-4 (1-9)	0.8-2.7 (2-6)	1.1-2.1 (3-5)	0.02-0.24 (0.1-0.6)	2.5-13.6 (5-29)	61.8-142	106-295	0.2-1.1 (1-3)		
	Acrylate render	11.4 µg/g		4.8-8.0 (12-19)	12.8-15.8 (29-36)	28-62	1.7-6.1 (3-13)	7.5-34 (18-77)	1.1-3.2 (3-8)	0.05-0.2 (0.1-0.5)	60-217	82.8-189	211-465	1.3-3.6 (3-8)		
Schoknecht et al. (2009)	Acrylate render + silicon paint	2250-3000 mg/m2	Irrigation	6-15	8-21	1-5	1-4	0.6-1.3	3-7	0.5-1	9-22	56-155				
			Short-term immersion	59-180	114-239	16-53	17-47	73-178	23-82	5-14	11-254	448-836				
			Permanent immersion	399-739	735-1484	96-300	97-270	5-30	164-332	18-37	634-1376	3100-5041				
Schoknecht et al. (2013)	Render	780 mg/m2	Short-term immersion	99 (12.7)		25 (3.2)		19 (2.4)	46 (5.9)	5 (0.6)	97 (12.4)					
	Paint	230 mg/m2		57 (24.8)		9 (3.9)		15 (6.5)	36 (15.7)	4 (1.7)	54 (23.4)					
Wangler et al. (2012)	Organic render	2100-2400 mg/m2	Sprinkling	622-1451 (30-45)	618-1534 (29-64)	324-919 (14-34)	285-727 (12-30)		421-1234 (20-51)	94-299 (4-12)	128-502 (6-21)					
	Render + silicone paint	2800-3000 mg/m2		1570-1730 (53-62)	1613-1841 (58-60)	624-1012 (22-34)	650-988 (23-33)		823-1547 (29-50)	202-595 (7-19)	296-620 (10-20)					
Jungnickel et al. (2008)	4 commercial roof paints		Immersion			10-25		10-60								
Bucheli et al. (1998)	Bitumous roofing membranes		Spraying												0.026-0.26	
	3 roofs (5100 m2)		Natural weather during 5 days												0.12	
Riechel et al. (2015)	Green roof with bituminous membrane		Natural weather during 7 months												0.24	
Bollmann et al. (2016, 2017b)	Silicone render	1.2 g/kg for terbutryn and 6.2 g/m2 for OIT	Natural weather during 1.5 y			65 (3)					120 (2)					
	Acrylate render	1.7 g/kg for terbutryn and 13.6 g/m2 for OIT				150 (3)					250 (2)					
Burkhardt et al. (2012)	Render	2250 mg/m2	Natural weather during 1 y	225 (9.5)	440 (18.4)	15 (0.6)	15 (0.6)		84 (3.5)	1 (0.05)	48 (2.0)					
	Render and paint	3000 mg/m2		180-400 (7.5-13)	499-573 (16-23)	50-10 (2.1-3.5)	54-122 (2.3-5.1)		147-311 (6.2-10.4)	2-15 (0.1-0.5)	59-116 (2.5-3.9)					
Gromaire et al. (2015)	Old clay tiles	5900 mg/m2	Natural weather during 13 m													152 (2)
	Concrete tiles															1683 (27)

Concerning mecoprop used in roof sealant, emissions vary from 0.026 to 12.4 mg/m² (Bucheli et al. 1998; Burkhardt et al. 2011; Riechel et al. 2015). Bucheli et al. (1998) compared emissions from two roofs equipped with two different bituminous roofing membranes containing the product Preventol B2® and with different rooftop greening. The values of emissions differ from one order of magnitude between both roofs (from 26 to 260 µg/m^2) because of contrasting residence times, bituminous sealing membranes, microbial activities at the membrane surface and root intensity and their penetration into the membranes. Burkhardt et al. (2011) also investigated the leaching of mecoprop from roof at the semi-technical scale (2.5 m²). Cumulative emissions were 1 mg/m^2 for Preventol B2® and 12 mg/m^2 for Herbitect® (HE, half as concentrated as B2), which represent 0.04 and 0.2 % of the initial amount, respectively. The ethylhexylester of mecoprop in product Herbitect® is less susceptible to hydrolysis than polyglycolester in B2, which means that the emissions of mecoprop in runoff from product Preventol B2® are higher. Compared to emissions reported by Bucheli et al. (1998), higher emissions were observed because of the test procedure: Burkhardt et al. (2011) performed eleven sprinkling events of 5 h over 70 days, which corresponds to 1100 mm of water (annual rainfall in Zürich) and Bucheli et al. (1998) sprayed 18 L/m^2 of tap water on flat roofs within 30 min only once. Riechel et al. (2015) measured mecoprop release from a real green roof with bituminous membrane containing mecoprop and calculated leaching rates of 0.24 mg/m².

So far, emissions of benzalkonium to runoff have been poorly documented but a two-part study was conducted to characterize and quantify the level of benzalkonium in runoff from treated roofs. The first part (Van de Voorde et al. 2012) is a laboratory scale study and the second one (Gromaire et al. 2015) a 1-year in-situ pilot scale study. Test benches, covered with old clay tiles or concrete tiles on which commercial de-mossing product was applied (5900 mg/m^2), were exposed to natural weather conditions during 13 months. After 640 mm of rain, cumulative emissions from old clay tiles (152 mg/m^2) were much lower than those from concrete tiles (1683 mg/m^2) and represented only 2% of the initial amount, against 27% for concrete tiles. This result highlights once more the influence of the material. These roof scale data are valuable for simulating benzalkonium emissions, but no assessment has yet been done at the watershed scale and is hence needed.

Many data on emissions of biocides from building materials are reported in the literature even if they are scarcer for MIT, tebuconazole, mecoprop and benzalkoniums. Many leaching tests were performed following different protocols at different scales: lab scale, semi-technical scale, building scale and under lab conditions or natural weather conditions. As cumulative emissions depend on test procedures (e.g. exposure by immersion or spraying, time of exposure, amount of water, duration of the experiment, orientation of the specimen, etc.) and on specimens (nature of the material, initial quantity of biocides, age etc.), a high variability was observed. These differences highlight once again the difficulty of comparing values from studies that do not follow the same procedure. Standardized methods are therefore needed so that leachability can be compared between several materials. An interlaboratory study was conducted by Schoknecht et al. (2013) and showed that the procedure described in EN 16105 (CEN 2011) is suitable for investigating the leachability of active ingredient in coatings, as similar results were observed between and within laboratories. However, these methods only enable biocide emissions to be

estimated under laboratory conditions, not under natural weather conditions, and hence introduce uncertainties to assess real biocide emissions from building materials in the environment. Indeed, as already mentioned in this review, many parameters can influence leaching of biocides. Natural weather conditions are difficult to reproduce because of their unpredictable nature. Another limit of the reported studies concerns the risk assessment. The different procedures could lead to an over- or underestimation of emissions and to the corresponding risk assessment. Only scarce studies assess the toxicity of the leachates though this would be a relevant tool for assessing potential environmental impact (Bandow et al. 2018). For instance, Vermeirssen et al. (2018) conducted ecotoxicity test on leachates and demonstrated that combining standardized leaching tests with standardized bioassays is a valuable tool to assess the environmental risk of biocide releases from façade renders and to rank the different materials according to potential ecotoxicity.

3.2.2. Modelling studies

The objectives of the modelling studies are (i) to understand the mechanism involved on a small scale, (ii) to generalize the emission data from small to larger scales, such as city or the watershed, and (iii) to assess the risk for aquatic ecosystems. A few studies developed diffusion-based models, as it was supposed to be the controlling mechanism of leaching. Wangler et al. (2012) and Styszko and Kupiec (2018) included dry periods in their models in order to allow biocide redistribution within the material. Results were in the range of experimental data from lab scale experiments. Also, several studies (Lupsea et al. 2013; Styszko et al. 2014; Bollmann et al. 2015a) described biocide partition between the material and the water as a major mechanism which controls leaching. Erich and Baukh (2016) took three mechanisms into account: water diffusion, biocide transfer to water and biocide diffusion. The first one was assumed to be the fastest. Then, two cases were distinguished: (i) biocide diffusion was the slowest mechanism and thus biocide emissions were proportional to the square root of water exposure time or (ii) transfer to water was the slowest mechanism and thus emissions were proportional to water exposure time. From these observations, Uhlig et al. (2019) proposed a mathematical approach in order to determine the mechanism controlling leaching at a given moment from experimental data (treated materials exposed to natural weather conditions). Desorption, diffusion and degradation processes were different for the three studied biocides (diuron, terbutryn and OIT), which led to different emission curves. Also, the authors suggested that changes in weather conditions might change mechanisms or factors controlling the release of biocides. Wittmer et al. (2011b) developed a model to simulate the losses of diuron from a façade in order to assess the significance of this phenomenon under realistic outdoor conditions on a small scale. The model is based on the sum of two exponential functions to simulate both a fast and a slow diffusion process. The model was based on the applied amounts of biocides in façade materials and on rainfall. However, the amount of rainfall that reaches façades and turns into runoff is difficult to predict as it depends on the rain intensity, the wind speed or the location of the building (Blocken and Carmeliet 2004; Blocken et al. 2009). The results showed that only a third of the initial amount was leached after the equivalent of 6 years of rainfall in the Swiss Plateau, which is consistent with experimental data on the lab scale. These examples underline the ability of models to simulate the emissions but also the complexity to calibrate numerous parameters and mechanisms. Moreover, these models are limited and cannot be extrapolated to the city scale

because (i) they imply too many processes to which biocides are subjected to allow rapid computation and (ii) they did not consider spatial variations. Coutu et al. (2012a; 2012b) developed therefore another type of model to simulate leaching of biocides (terbutryn, carbendazim and diuron) at the city scale. They used a two-region model: (i) the biocide in the façade and (ii) the biocide in the flow over the façade surface (Coutu et al. 2012a). Then, they coupled their model at the city scale with basin scale hydrologic and biocide transport submodels to simulate degradation, sorption or dilution into the separate storm sewer (Coutu et al. 2012b). The façade models were calibrated using the same experimental laboratory data of Burkhardt et al. (2011) as Wittmer et al. (2011b) and extrapolated at the city of Lausanne (Switzerland). The models allowed assessing the biocide emissions at the city scale (900 kg/y for Lausanne) and predicting the concentrations in the receiving river with an overall good match between calculated and experimental data. Generally, modeled concentrations were slightly underestimated. Thanks to this model, risk assessments were performed and showed a low probability of exceeding the predicted no effect concentrations (PNEC) values (9% for diuron, 5% for carbendazim and 0% for terbutryn).

Models are therefore valuable tools for assessing biocide loads that are discharged to runoff. Using such models could be a first step to risk assessments but it relies on the availability of many informations, such as the consumption data or sale volumes, the amount of rainfall available for façade leaching or the façade surface area, which are often not available. Moreover, the variability of watersheds and cities makes generalisation of models and risk assessments complex because of different land-uses and impervious surfaces, the age and the orientation of buildings, the weather conditions etc. (Gaylarde et al. 2011). Many uncertainties also remain: spatial variability of rainfall, particulate contamination for more hydrophobic biocides such as benzalkonium chlorides, variety of sewer discharges (stormwater discharges, combined sewer overflows and WWTP discharges during wet weather). Therefore, further research should be done to improve large-scale models with the objectives to complete and validate all data in order to calibrate, evaluate performance and recalibrate if necessary.

3.2.3. Reduction of biocide releases from buildings during rain events

The reported studies concerning leaching of biocides from building materials pointed out some solutions to reduce emissions at source, depending on construction type and product used. The comparison between the two products Preventol B2® and Herbitect® (Burkhardt et al. 2011) demonstrates that improving product formulations with respect to the release of hazardous substances is an effective source control measure to reduce the impact of construction materials on receiving waters. As a result, the three main manufacturers of bituminous membranes in Switzerland no longer use product B2 and they have revised their formulations in order to obtain the same leaching characteristics as HE. Another way to reduce the leaching of biocides from building materials is the encapsulation of biocides in polymer microspheres (Andersson et al. 2015; Nordstierna et al. 2010) or in the silica of the material (Edge et al. 2001), which slows down their release. Similarly, Wangler et al. (2012) showed that adding a top coating (paint) without biocide limits emissions and still protects the façade. Concerning roof treatment practices, Gromaire et al. (2015) suggested that de-mossing products should be used as a curative rather than a preventive treatment when needed. The dose must be reduced and adapted to the

material (ceramic vs. concrete for tiles), the level of proliferation, and to the age of tiles (new tiles are less porous and thus emit more benzalkoniums). The choice of materials (e.g., silicone vs. acrylate renders) could constitute a solution to reduce emissions of biocides at source (Gromaire et al. 2015; Styszko et al. 2014). Wicke et al. (2015) reported the intensive uses of mecoprop in bituminous membranes, even if root protection is not required. In the light of these observations, the Senate of Berlin provided recommendations to avoid unnecessary emissions of this compound (SenStadtUm 2013).

3.3. Mass balance

In order to understand the fate of biocides during leaching, mass balances were performed between the initial mass of biocides, the remaining amount in the material and the emitted part into runoff (Schoknecht et al. 2009, 2013; Burkhardt et al. 2012; Wangler et al. 2012; Bollmann et al. 2016, 2017b). Indeed, biocides in building materials are exposed to environmental conditions and can be transformed over time by several processes, e.g. hydrolysis, biodegradation, direct and indirect photolysis (Fenner et al. 2013) and, in most cases, transformation products (TPs) are formed as a result of incomplete degradation (Hensen et al. 2018). TPs of some biocides are directly formed in the material itself by photodegradation, which is the most common degradation process (Burkhardt et al. 2012; Breuer et al. 2012; Luo et al. 2013; Bollmann et al. 2016, 2017b; Hensen et al. 2018). Identified photodegradation products are reported in table 3.

Several studies reported a mass balance deficit: the amount released and the amount remaining in the material did not correspond to the initial quantity of biocides in the material (Schoknecht et al. 2009, 2013; Burkhardt et al. 2012; Wangler et al. 2012; Bollmann et al. 2016, 2017b). In particular, a significant mass balance deficit was observed for easily photodegradable compounds such as IPBC, OIT, DCOIT or terbutryn. Wangler et al. (2012) found a deficit of 55%, 62% and 43% for OIT, DCOIT and IPBC, respectively, on a lab scale. Burkhardt et al. (2012) and Bollmann et al. (2016, 2017b) exposed panels to natural weather conditions and reported a deficit of 35% for terbutryn and more than 70% for OIT, as shown in figure 1. In order to explain these deficits, the presence of TPs both in materials and runoff were investigated. 6 out of the 15 searched TPs (8 for terbutryn and 7 for OIT) have been detected in the façade and runoff. Cumulative emissions of TPs ranged from 8 to 40 mg/m^2 for terbutryn and from 2 to 75 mg/m^2 for OIT. A peak in the emission of the major OIT TP, octylamine, was detected in early summer because of higher UV-degradation at this time of year. The quantity of TPs that leached represented 2 to 4% and the quantity of TPs remaining in panels was twice as high as these values. The majority of the TPs remained in the material and did not leached out. However, the older the material, the more TPs might undergo leaching. Burkhardt et al. (2011) quantified the descyclopropyl-cybutryn (M1), a TP of both cybutryn and terbutryn, in runoff from spiked panels exposed to natural weather conditions. They reported low M1 concentration just after application followed by a progressive increase with time until it finally exceeds cybutryn or terbutryn concentration.

Table 3. Identified phototransformation products of biocides

Biocides	Abbreviation	Phototransformation products	Chemical formula	Precursor ion (m/z)	Références
Carbendazim		2-aminobenzimidazole	$C_7H_7N_3$		Urbanczyk et al. (2019b)
CMIT		Acetic and formic acids			Krzeminski et al. (1975)
DCOIT		N-octanal		128,00	Sakkas et al. (2002)
		N-octyl isocyanate			
		N-cotyl amine		129,00	
		N-octyl actamide		171,00	
		N-n-octyl oxamic acid		201,00	
OIT	TP-214	2-octylthiazol-2(3 H)-one	$C_{11}H_{19}NOS$	214,13	Bollmann et al. (2017b)
	TP-158	N-octylformamide	$C_9H_{19}NO$	158,15	
	TP-184a	N-octylprop-2-enamide	$C_{11}H_{21}NO$	184,17	
	TP-172	N-octylacetamide	$C_{10}H_{21}NO$	172,17	
	TP-130	Octylamine	$C_8H_{19}N$	130,16	
	TP-216	N-octyl malonamic acid	$C_{11}H_{21}NO_3$	216,16	
	TP-198	2-octyl-1,2-oxazol-3(2 H)-on* 3-octyl-1,3-oxazol-2(3 H)-one*		198,15	
	TP-184b	N-ethenyl-N-octylformamide*	$C_{11}H_{21}NO$*	184,17	
	TP-188			188,16	Bollmann et al. (2017b) Hensen et al. (2018)
	TP-182			182,15	
	TP-144			144,14	
Diuron	TP-219	1-(3,4-dichlorophenyl)-3-methylurea (DCPMU)	$C_0H_8Cl_2N_2O$	219,01	Hensen et al. (2018) Urbanczyk et al. (2019b)
	TP-215a	3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea	$C_9H_{10}ClN_2O$	215,06	
	TP-215b	3-(4-chloro-3-hydroxyphenyl)-1,1-dimethylurea	$C_9H_{12}ClN_2O_2$	215,06	
Cybutryn	TP-214	Desethyl-terbutryn (M1)	$C_8H_{15}N_5S$	214,11	Hensen et al. (2018) Bollmann et al. (2016)
Terbutryn	TP-258	Terbutryn sulfoxide	$C_{10}H_{19}N_5OS$	258,14	Bollmann et al. (2016)
	TP-196	Desthiomethyl-terbutryn	$C_9H_{17}N_5$	196,16	
	TP-168	Desthiomethyl-desethyl-terbutryn	$C_7H_{13}N_5$	168,13	
	TP-140	Desthiomethyl-desbutyl-terbutryn	$C_6H_9N_5$	140,09	
	TP-212	2-hydroxy-terbutryn	$C_9H_{17}N_5O$	212,15	
	TP-184	Desethyl-2-hydroxy-terbutryn	$C_9H_{13}N_5O$	184,12	
	TP-226	Terbumeton	$C_{10}H_{19}N_5O$	226,17	
	TP-186		$C_6H_{11}N_5S$	186,10	Hensen et al. (2018)
	TP-210		$C_9H_{15}N_5O$	210,14	
	TP-256		$C_{10}H_{18}N_5SO$	256,16	

* assumption

For TP investigation, two different cases are reported: (i) mass balance is closed with TPs and (ii) mass balance is not closed even if TPs were taken into account, as illustrated by the figure 1. Indeed, in the case of terbutryn, the mass balance was closed with eight TPs but it was not the case for OIT, although seven TPs were included. This remaining deficit was attributed to vaporisation (octylamine is considerably more volatile than OIT), undetected TPs or complete mineralization via acetic and formic acids (Bollmann et al. 2016, 2017b).

Recently, Urbanczyk et al. (2019b) showed that the photodegradation of biocides (OIT, terbutryn, diuron and carbendazim) was much slower in presence of pigments in paints (e.g., TiO_2, α-Fe_2O_3, Fe_3O_4) because of their interaction with light. The fastest photodegradation was observed for OIT contrary to carbendazim, which was not significantly photolyzed. Little difference in the degradation rates was observed between the three pigments but different TP patterns were observed for both terbutryn and OIT.

This section pointed out that the investigation of biocide emissions from building materials should integrate the monitoring of TPs to assess mass balances. Photodegradation plays a key role in the TP production. However, even if known TPs are taken into account, mass balances are still not closed for a majority of biocides, such as OIT. Further work is required to elucidate the processes involved in TP production, to identify missing TPs and to prove their complete mineralization or vaporization, if appropriate. High-resolution mass spectrometry and non-targeted approaches are relevant tools for the identification of molecular structures of TPs (Bletsou et al. 2015; Bollmann et al. 2016, 2017b). However, physico-chemical properties, ecotoxicity and environmental fate of TPs are often unknown (Hensen et al. 2018), thus significantly limiting risk assessment of biocides from building materials.

4. Transport of biocides and occurrence in the aquatic environment

The previous section highlighted that biocides and TPs are released from building materials in runoff. They can be discharged into surface water or contaminate groundwater via infiltration processes. Pathways of biocides from buildings to receiving environment are many and varied, including WWTP effluents and combined sewer overflows in the case of combined sewer systems, or stormwater discharges in the case of separate sewer systems. In this section, levels of concentration of biocides in urban discharges during dry and wet weather conditions and surface water are reviewed. The values reported are compared to regulatory threshold for drinking water, groundwater and surface waters along with ecotoxicological values in order to assess the potential impact of discharges to receiving waters. To our knowledge, no study reported the level of zinc pyrithione contamination in freshwater, stormwater or WWTP waters. This compound is difficult to analyse and to quantify in water because of possible trans-chelation with other metals, such as copper or iron, which forms more stable complexes (Thomas 1999; Bones et al. 2006).

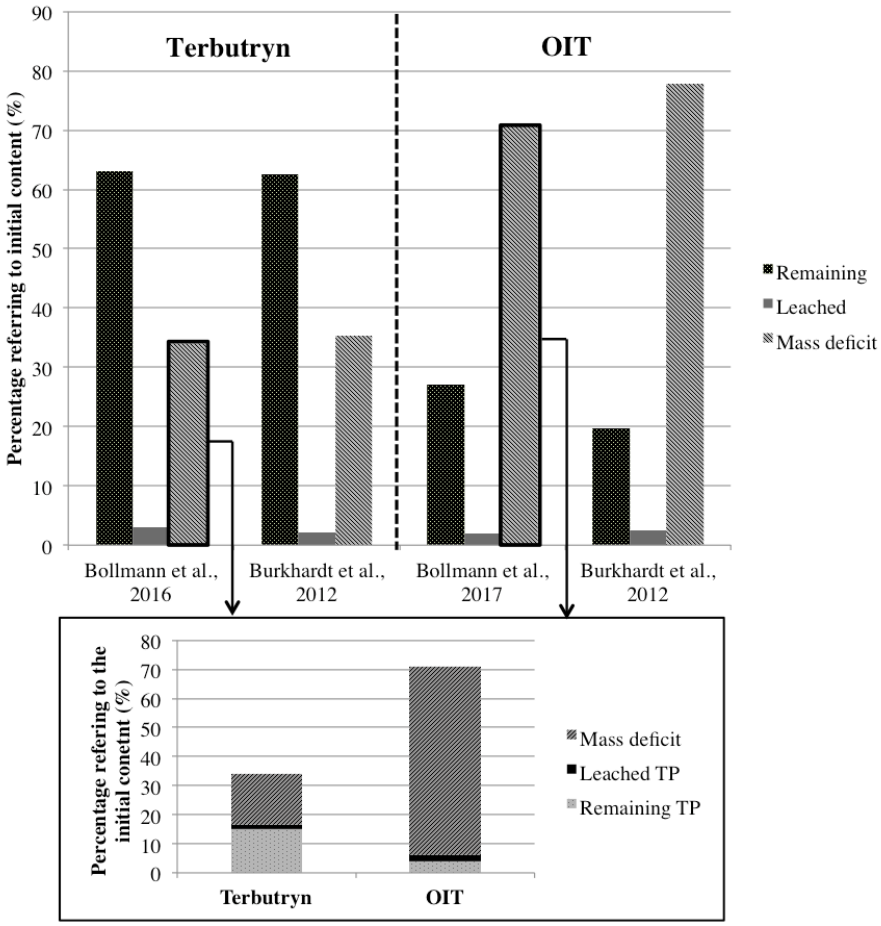


Fig. 1 Mass balance (%) of terbutryn and OIT from artificial walls coated with acrylate renders in which biocides were added (seven biocides in the study of Burkhardt et al. (2012) and just the biocide of interest in the other two studies). Panels were exposed from one year to 19 months to natural weather conditions according to Bollmann et al. (2016), Bollmann et al. (2017b) and Burkhardt et al. (2012). Top charts did not include TPs in mass balances contrary to bottom chart, in which eight TPs of terbutryn and seven TPs of OIT (from photolysis) were included (adapted from Bollmann et al. (2016) and Bollmann et al. (2017b)).

4.1. Discharge to receiving waters

4.1.1. Façade runoff

Concentrations measured in façade runoff were often found in the range of a few mg/L at the beginning of the experiment and about tens of µg/L at the end. For example, in Burkhardt et al. (2011), concentrations of diuron and carbendazim in runoff were 7 and 0.7 mg/L respectively at the beginning of the experiment, under laboratory conditions. After the equivalent of 6 years of rainfall in the Swiss Plateau, concentrations were up to 2 orders of magnitude lower with 70 µg/L for diuron and 40 µg/L for carbendazim. Under natural weather conditions, Burkhardt et al. (2012) reported concentrations of diuron in façade runoff between 10 and 25 mg/L in the first months and close to 2 mg/L after one year of exposure. Terbutryn was detected in a similar amount in Burkhardt et al. (2012) and Bollmann et al. (2016) studies, from 1-5 mg/L in the first months to less than 1 mg/L after one year-exposure. The M1 TP of terbutryn and cybutryn was

also detected at up to 12 mg/L in Burkhardt et al. (2012) study. Bollmann et al. (2016) detected the four main TPs of terbutryn (i.e., terbutryn sulfoxide, 2-hydroxy-terbutryn, desethyl-terbutryn and desethyl-2-hydroxy-terbutryn) in façade runoff at concentrations ranging from 0.05 to 1.5 mg/L. Concentrations of OIT ranged from less than 20 µg/L to 14 mg/L and six out the seven studied TPs were detected in most of the samples, at up to 8.8 mg/L for N-octyl oxamic acid (Bollmann et al. 2017b).

In roof runoff, concentrations of mecoprop varied from 1.5 to 4 µg/L and very high concentrations (500 µg/L) were measured after a long dry period in summer. Similar concentrations were measured by Burkhardt et al. (2011), from 1-10 µg/L to 400 µg/L. For benzalkoniums, Van de Voorde et al. (2012) measured concentrations in roof runoff (sum of C12 and C14 benzalkoniums) ranging from 5 to 30 mg/L immediately after treatment. It took 5 to 7 months for the concentration to drop down below the EC50 value for fish (280 µg/L (USEPA 2006)). After 640 mm of rainfall (i.e., the annual rainfall in Paris), concentrations in runoff remained above 4 µg/L, which is one order of magnitude higher than the PNEC value of 0.415 µg/L (European Parliament and Council 2015c).

4.1.2. Stormwater

Only a few studies measured concentrations of biocides in separate stormwater pipe system or combined sewers overflows (CSOs), which are a mixture of stormwater and wastewater. The biocide concentrations in stormwater and CSOs are reported in table 4. Most of these studies focused on biocides also used as PPP (phenylureas, triazines, carbendazim, mecoprop, etc.). In stormwater, concentrations ranged from tens of ng/L to a few µg/L. According to table 4, diuron, carbendazim, mecoprop and isoproturon have been detected with the highest concentrations, up to 12 µg/L in the case of diuron. In the frame of the OgRe project (Wicke et al. 2015), the quality of stormwater from different catchments (old buildings, new buildings, commercial area, residential area and road area) was monitored during one year (table 4). Higher concentrations of mecoprop, carbendazim, diuron and terbutryn were measured in the catchment with old buildings, because of recent refurbishment. A strong correlation was established between diuron and carbendazim concentrations and the number of façades coated with render. Another correlation was established between terbutryn concentrations and the roof surface in the catchment because of its use in roof paints while a lowest correlation with the number of façades coated with render was observed. Mecoprop was detected in all the studied catchments because of its use in bituminous membranes. It is interesting to note that concentrations in building runoff are in the mg/L range, which suggests significant dilution of biocides in stormwater with runoff from other impervious surfaces, or infiltration in case of pervious surfaces. Burkhardt et al. (2011) examined the different pathway of biocides from buildings to stormwater receiving waters and compared the occurrence of terbutryn, carbendazim, diuron and mecoprop in building runoff and at three levels of the stormwater sewer: (1) one 0.5ha subcatchment included in (2) a 11ha subcatchment and (3) at the discharge into a small river. Diuron was diluted between the building runoff and the discharge. For other compounds, concentrations were in the same order of magnitude at the three levels. At the discharge to the receiving waters, median concentrations were about 100 ng/L for both biocides but could reach 1.8, 1.1 and 10 µg/L for terbutryn, carbendazim and mecoprop respectively.

Table 4. Concentrations in ng/L (min-max) of biocides used in building materials in stormwater (sampling in separate stormwater sewer pipes) and combined sewer overflows

Biocides	Concentrations in stormwater (ng/L)	Concentrations in combined sewer overflows (ng/L)	Country	Reference
Carbendazim	<20-1500 45 <3-1568	 15-42	Germany Denmark France Germany	Wicke et al. (2015) Bollmann et al. (2015) Gasperi et al. (2013) Launay et al. (2016)
BIT	<4 <30-1600		France Germany	Gasperi et al. (2013) Wicke et al. (2015)
OIT	<4 <30-60 <0.77-67		France Germany Germany	Gasperi et al. (2013) Wicke et al. (2015) Hensen et al. (2018)*
Diuron	<10-55 <5-11997 30-1750 40-80 <30-600 <0.39-4.9	480 90-1600 68-681 43-81	Denmark France France France Germany Germany Switzerland Germany	Birch et al. (2011) Gasperi et al. (2008, 2013) Zgheib (2009) Bressy (2010) Wicke et al. (2015) Launay et al. (2016) Burkhardt et al. (2007) Hensen et al. (2018)*
Isoproturon	<10-44 <5-1017 <10-140 50 <30-120	200 <60 25-180	Denmark France France France Germany Germany	Birch et al. (2011) Gasperi et al. (2008, 2013) Zgheib (2009) Bressy (2010) Wicke et al. (2015) Launay et al. (2016)
Cybutryn	52 <4 <20-20		Denmark France Germany	Bollmann et al. (2015b) Gasperi et al. (2013) Wicke et al. (2015)
Terbutryn	<4 <10-360 1-160	<60-160 9-210	France Germany Germany Germany	Gasperi et al. (2008, 2013) Wicke et al. (2015) Launay et al. (2016) Hensen et al. (2018)*
Terbuthylazine	<10 <30-260	200	Denmark Germany	Birch et al. (2011) Wicke et al. (2015)

Propiconazole	40	<60-210	France France	Bressy (2010) Gasperi et al. (2013)
Tebuconazole	<20-90		Germany	Wicke et al. (2015)
Mecoprop	<20-6900 <1-10	100-378	Germany France Germany	Wicke et al. (2015) Gasperi et al. (2013) Launay et al. (2016)

* Sampling in swales

4.1.3. Wastewater during dry and wet weather conditions

Concentrations in untreated and treated wastewater are useful (i) to determine the origin of biocides between runoff from buildings and domestic uses in the case of combined sewer networks and (ii) to compare the pathways of biocides into receiving waters (WWTP effluents vs. urban discharges during wet weather). Data on the occurrence of biocides in WWTP influents and effluents from recent studies are reported in figure 2. They are quite numerous for biocides also used as a PPP, such as phenylureas and triazines. Influent and effluent concentrations were of the same order of magnitude, ranging from a few ng/L to hundreds of ng/L (figure 2). It is interesting to note that concentrations in effluents sometimes exceeded those in influents, particularly for phenylureas, carbendazim and mecoprop. Wick et al. (2010) measured 26 biocides in two WWTPs. For most of them, concentrations in effluent were higher or of the same order of magnitude than those in influent. For example, diuron was detected at 23-68 ng/L (WWTP 1-WWTP 2) in influents and at 25-182 ng/L in effluents; mecoprop was detected at 252-37 ng/L in influents and at 203-72 ng/L in effluents; carbendazim was detected at 41-143 ng/L in influents and 48-88 ng/L in effluents. Likewise, Guillossou et al. (2019) measured higher concentrations of diuron in effluents (42 ng/L) than in influents (36 ng/L) but with a significant variability. High concentrations of permethrin (up to 425 ng/L) compared to the other biocides were reported in influents in two studies (Kupper et al. 2006; Gómez et al. 2007). This could be explained by its very widespread use as an insecticide (human and veterinary pediculicide (Başer et al. 2003), mothproofing on wool (Friedman et al. 1979; Ingham et al. 2012)). Figure 2 reveals a significant variability for a given compound in influents (I) and effluents (E), explained by the size of the watershed where the WWTP was located (from 1,500 to 1,000,000 inhabitants), the type of treatments, the sewer system (combined or separate), the local use and consumption of biocides or different weather conditions (Wittmer et al. 2010).

Bollmann et al. (2014a) compared the concentrations of 13 biocides (triazines, carbamates, isothiazolinones, phenylureas, triazoles and mecoprop) in wastewater during dry and wet weather conditions for 5 urban WWTPs in Denmark and Sweden. Most biocides were emitted during both wet and dry weather conditions, with the exception of mecoprop and isoproturon, which were only observed during wet weather conditions. Terbutryn, carbendazim and diuron were mostly emitted during rainy weather while tebuconazole inputs were similar for both weather conditions.

Few data are available for quaternary ammonium compounds (QACs) in WWTPs. Concentrations measured in influents during dry weather ranged from a few µg/L to hundreds of µg/L (table 5), depending greatly on local activities (Kreuzinger et al. 2007) since QACs are extensively used in hospitals or laundry products. Concentrations were lower in effluents, from hundreds of ng/L to a few µg/L. Only 5 studies concern isothiazolinones in table 5. However, sometimes, the analytical protocols did not allow their detection and their quantitation (LOQ) at trace levels: LOQ were as high as 100 ng/L (Wick et al. 2010) and the limits of detection (LOD) 85 ng/L (Rafoth et al. 2007). Rafoth et al. (2007) detected concentrations exceeding 1 µg/L in WWTP influents but other publications have reported lower levels (a few ng/L) or did not detect isothiazolinones in untreated or treated wastewater (table 5).

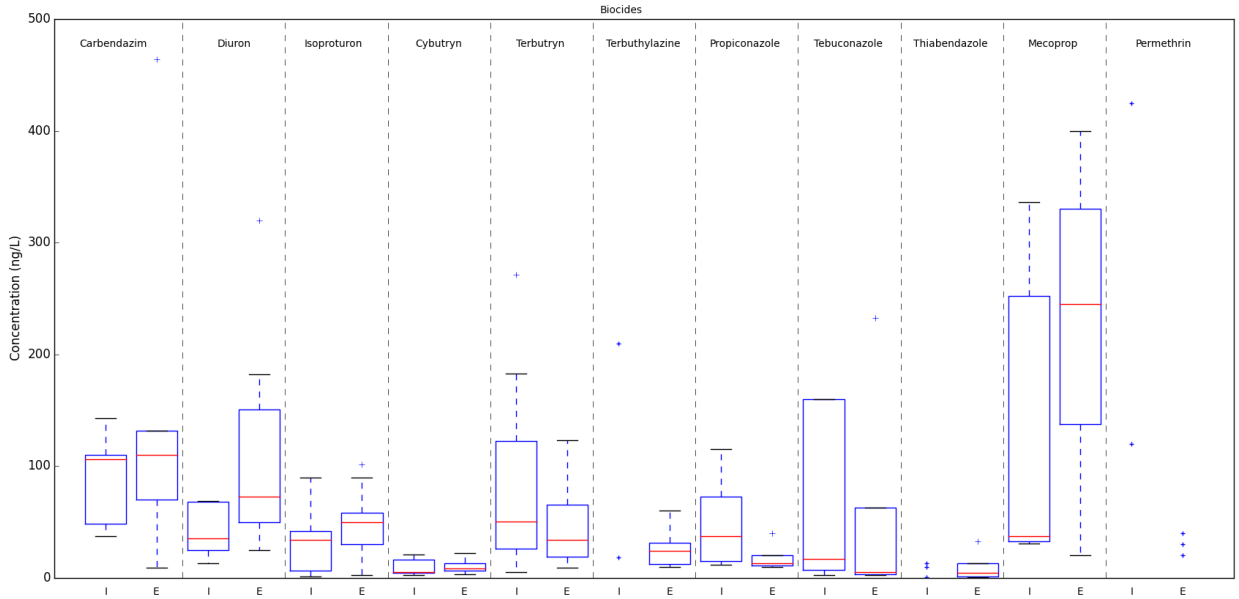


Fig. 2 Concentrations (ng/L) of biocides also used as PPP in influents and effluents of WWTP (Öllers et al. 2001; Kupper et al. 2006; Burkhardt et al. 2007; Gómez et al. 2007; Kahle et al. 2008; Bartelt-Hunt et al. 2009; Benvenuto et al. 2010; Morasch et al. 2010; Singer et al. 2010; Stamatis et al. 2010; Wick et al. 2010; Chen et al. 2012; Clara et al. 2012; Gros et al. 2012; Barco-Bonilla et al. 2013; Campo et al. 2013; Margot et al. 2013; Masiá et al. 2013; Luft et al. 2014; Bollmann et al. 2014a; Mailler et al. 2015; Launay et al. 2016; Peris-Vicente et al. 2016; Wluka et al. 2016). I: influents and E: effluents. These box plots were developed with average values available in the literature. Red line corresponds to the median value. The box corresponds to the first and the third quartiles. The bars linked to the box by dotted lines are the first and ninth deciles. Single crosses are extreme values or all values when data were not sufficient to create a box plot.

Table 5. Concentrations (µg/L) of QACs and isothiazolinones in WWTP influents and effluents

Biocides	Concentrations in WWTP influent (µg/L)	Concentrations in WWTP effluent (µg/L)	Country	References
Σ Benzalkonium (C12-C18)	22.4-306.8 <0.006-3458 38.2-251.9 420 <0.008-3.72	0.088-1.6 0.1-6.6 0.192-3.5 <10	Austria Austria Austria France USA	Clara et al. (2007) Kreuzinger et al. (2007) Martínez-Carballo et al. (2007) Deborde et al. (2016) Ferrer and Furlong (2001)
DDAC (C10)	13-200 <0.006-210 13-41 46-930	0.06-0.79 0.024-0.85 0.004-0.85 <30	Austria Austria Austria France	Clara et al. (2007) Kreuzinger et al. (2007) Martínez-Carballo et al. (2007) Deborde et al. (2016)
BIT	<0.1 1.7-3.2 <0.0022 <0.8	<0.05 ND* <0.0012	Germany Germany China Denmark	Wick et al. (2010) Rafoth et al. (2007) Chen et al. (2012) Bollmann et al. (2014a)
CMIT		<0.03	Netherlands	Speksnijder et al. (2010)
DCOIT	<0.01 ND* 0.0055-0.0061 <0.001	<0.005 ND* 0.0034-0.0064	Germany Germany China Denmark	Wick et al. (2010) Rafoth et al. (2007) Chen et al. (2012) (Bollmann et al. 2014a)
MIT		<0.04	Netherlands	(Speksnijder et al. 2010)
OIT	<0.01-0.012 ND* 0.0021-0.0025 <0.2	<0.005 ND* 0.0004-0.0006	Germany Germany China Denmark	(Wick et al. 2010) (Rafoth et al. 2007) (Chen et al. 2012) (Bollmann et al. 2014b)

* No LOD value is provided in the paper

4.1.4. Discussion on biocide pathways into receiving waters

Comparing concentrations in both matrices is interesting to assign sources (households or leaching from buildings). For most biocides, concentrations in stormwater, CSOs and wastewater are in the same order of magnitude. This means, that urban discharges in dry and wet weather conditions, are likely to contaminate the receiving waters. For some biocides (carbendazim, terbutryn, terbuthylazine), concentrations in CSOs are similar to those in wastewater, showing that household sources may be equivalent to those from buildings. For a few compounds (diuron, isoproturon, propiconazole, mecoprop), concentrations in CSOs are higher than the ones in wastewater. Consequently buildings appear to be the main source of these biocides in receiving waters. Although comparing concentrations is a first approach to assess the contribution of both

pathways, comparing mass loads would be more relevant. According to the authors' knowledge, the OgRe project (Wicke et al. 2015) was the first one to estimate biocide loads from Berlin stormwater discharged to natural waters. Loads of mecoprop were estimated at 106 kg/y, those of carbendazim at 10 kg/y and those for terbutryn and diuron at less than 10 kg/y. This work has to be pursued further with more biocides and extended to other European cities, as land-use could be different.

4.2. Occurrence of biocides in rivers and groundwater

4.2.1. Rivers

Table 6 shows concentrations in surface water of some biocides of interest. Most of the biocides that were measured in surface water were quantified worldwide during sampling campaigns not specifically devoted to rain events. Concentrations generally range from a few ng/L to tens of ng/L. However, diuron, isoproturon, terbuthylazine, permethrin and mecoprop were detected at significantly higher concentrations, i.e., up to 8.6, 5.5, 12.6, 1.7 and 1.8 µg/L, respectively. Data is still lacking for some other biocides that are not reported in table 6, such as isothiazolinones, QAC or zinc pyrithione. Only a few studies have reported concentrations of QAC in surface water, results ranged from a few ng/L to up to 55 µg/L according to Ding and Liao (2001), Ferrer and Furlong (2001) and Kreuzinger et al. (2007). Similarly, there has been little investigation on isothiazolinones in environmental compartments. Concentrations are often below LOD or LOQ (Rafoth et al. 2007; Speksnijder et al. 2010; Wick et al. 2010; Chen et al. 2012). However, Baranowska and Wojciechowska (2013) reported high level for CMIT (>5 µg/L). Also, Bürgi et al. (2009) categorized BIT and OIT as highly toxic (low EC50, LC50 or NOEC for a few aquatic organisms and low PNEC value) and concentrations in Swiss surface water were in the range of 0.1 - 1 µg/L, making them compounds of interest.

Table 6. Surface water concentrations (ng/L) of some biocides used either in building materials or as PPP.

	Concentrations in surface water (ng/L)									
Country	France	Germany	Spain	Switzerland	Other European countries	North America	Brazil	China	Australia	Tanzania
References	a	b	c	d	e	f	g	h	i	j
Carbendazim	1	<2.5-116	0.04-11.6	2.9-206	<0.33-269	21-360	<8	6.6-610		
IPBC		<5		<30						
Diuron	20-5600	2-41	7.5-8550	1.1-310	<0.51-290	<1-910	<8	26-51		
Isoproturon	10-61	<1-115	2.4-9.1	1.1-5500	1-340					
Cybutryn		0.9-12		<4.5-6	0.1	<7	7.7-15.9			
Terbutryn	10	5.3-5600	0.9-30.5	<4.5-50	1-22	<10			1-22	
Terbuthylazine	10	2.3-372	0.1-12600	5-40	<3-254.4		102.2			
Propiconazole	12	4.2-7		1.9-65	<4.5-44	<3-291		10	2-22	
Tebuconazole	14	2.2-12	1.7-15.4	1.9-86	<2.7-120	<3-53	5.6-60.6		21	
Thiabiendazole		0.1-21	0.01-1		<10-53	<3.9-153.2		<0.01		170
Permethrin	14				<0.5-97	<0.003-18	<375-1650	370		
Mecoprop	5-30	3-147		4-1750	1.7-30	5.1-94				

a: Blanchoud et al. (2004); Botta et al. (2012); Direction régionale et interdépartementale de l'environnement et de l'énergie d'Ile-de-France (DRIEE) (2016); b: Quednow and Püttmann (2007); Van Pinxteren et al. (2009); Loos et al. (2010); Wick et al. (2010); Reemtsma et al. (2013); Wluka et al. (2016); c: Claver et al. (2006); Benvenuto et al. (2010); Gros et al. (2012); Köck-Schulmeyer et al. (2012); Campo et al. (2013); Herrero-Hernández et al. (2013); Masiá et al. (2013); Ccanccapa et al. (2016); d: Öllers et al. (2001); Singer et al. (2010); Bonvin et al. (2011); Wittmer et al. (2011a); Moschet et al. (2015); e: Bonwick et al. (1995); Benvenuto et al. (2010); Stamatis et al. (2010); Matamoros et al. (2012); Emelogu et al. (2013); Kalogridi et al. (2014); Palma et al. (2014); Vorkamp et al. (2014); Antić et al. (2015); Chitescu et al. (2015); Stipaničev et al. (2017); f: Bartelt-Hunt et al. (2009); Murray et al. (2010); Battaglin et al. (2011); Struger et al. (2011); Weston and Lydy (2012); Sengupta et al. (2013); Metcalfe et al. (2016); g: Pinheiro et al. (2011); Caldas et al. (2013); Robles-Molina et al. (2014); h: Chen et al. (2012); Heeb et al. (2012); i: Allinson et al. (2015); j: Kishimba (2004)

Surface water concentration is expected to be at least one order of magnitude lower than of the one for urban discharges because of a dilution effect (Gros et al. 2007). However, when compared to WWTP effluents or stormwater (table 4 and figure 2), surface water concentrations are of the same order of magnitude. For example, average concentration of carbendazim ranges from 9 to 530 ng/L in WWTP effluents, from <3 to 1600 ng/L in stormwater and from 1 to 610 ng/L in surface water. Moreover, significant variability is observed. Indeed, measured concentrations depend on several parameters (Köck-Schulmeyer et al. 2012): the sampling points close to WWTP discharges generally give higher frequencies of detection and higher concentrations (Loos et al. 2010; Singer et al. 2010; Bonvin et al. 2011); the season of the year, higher quantities of biocides also used as pesticides can be observed during the pesticide application period (Quednow and Püttmann 2007; Wittmer et al. 2011a; Kalogridi et al. 2014; Antić et al. 2015); and the hydrological and weather conditions (e.g. river flow and rain intensity). For example, Palma et al. (2014) observed higher concentrations for most pesticides analyzed (including diuron, isoprotuon, terbuthylazine and mecoprop) after the first rainfalls than during the preceding wet period. Wicke et al. (2015) sampled surface water from a small river in Germany during dry and wet weathers. The reported level of biocides was mostly correlated to rainy events. The mean concentration of mecoprop was 240 ng/L, while diuron and terbutryn were detected at 50 ng/L. OIT was only detected twice but its concentration could reach 1.2 µg/L. These observations highlight again the presence of multiple pathways of biocides into receiving waters: urban discharges and diffuse sources. However these studies did not identify primary sources of emissions between buildings, domestic, agriculture etc.

In order to estimate the potential risk for aquatic organisms, concentrations in receiving waters need to be compared with threshold values such as PNEC or median effective concentration (EC50) for sensitive organisms or environmental quality standards (EQS, Directive 2008/105/EC) for priority substances listed by the Water Framework Directive. EQSs are annual average concentrations that should not be exceeded in European surface water. This value is set at 200, 300, 65 and 2.5 ng/L for diuron, isoproturon, terbutryn and cybutryn, respectively. As shown in table 6, these concentrations can be exceeded across European countries. However, no annual data is available. In addition, European Directive 98/83/EC on the quality of water intended for human consumption set the maximum concentrations of each pesticide at 100 ng/L and the total concentration of pesticides at 500 ng/L. Despite this Directive, the concentration levels of individual compounds or mixtures are occasionally higher in surface water. However, analyses are often run on a restricted number of compounds, making it difficult to conclude that the total concentration of pesticides is not exceeded.

As shown in Table 1, PNEC values range from 0.47 ng/L (permethrin) to 44 µg/L (mecoprop). Among the 20 biocides shown in table 1, only 5 have PNEC greater than atrazine (0.6 µg/L (INERIS)), which is a priority substance of the Water Framework Directive. With respect to PNEC values, most of the listed biocides (quaternary ammonium compounds, carbendazim, CMIT, diuron, isoproturon, terbuthylazine, permethrin and sometimes cybutryn and terbutryn) are expected to have an impact on aquatic organisms at lower concentrations than atrazine. However, only four of them (diuron, isoproturon, terbutryn and cybutryn) are priority substances listed in the Water Framework Directive. Moreover, although mean concentrations of the other biocides did not exceed PNEC values, it occasionally happens. It is important to note that these

ecotoxicological values do not take into account synergistic and toxic cocktail effects although several studies have reported adverse effects of pesticide or biocide mixtures on aquatic organisms (Adam et al. 2009; Christen et al. 2014; Hua and Relyea 2014; Gandar et al. 2017; Gamet-Payrastre and Lukowicz 2017; Lukowicz et al. 2018).

EC50 values range from 1.27 µg/L (permethrin) to 21.2 mg/L (terbuthylazine). According to the data reported in table 6, only permethrin concentrations exceeded sometimes the EC50 values. Bioconcentration is assessed using the bioconcentration factor (BCF). As most of BCF are below 100 (except for cybuthrin, permethrin and propiconazole) it indicates that biocides tend to accumulate very little in organisms.

Concerning TPs in surface water, most studies focus either on pesticides or on mechanisms in surface water. But TPs resulting from photodegradation on the surface of buildings are not necessarily the same as those resulting from biodegradation in the river. As a result, there is little data on the TPs listed in table 3 for surface water. Singer et al. (2010) measured the desethyl terbutryn at a level of 10 ng/L both upstream and downstream a WWTP discharge in Switzerland, Moschet et al. (2014) measured this compound at concentrations lower than 5.5 ng/L in Switzerland and Wick et al. (2010) between 0.7 and 12 ng/L in German rivers. Moschet et al. (2014) measured also DCPMU, a diuron TP originating from hydrolysis or degradation in soil, at concentrations ranging from less than 10 to 22 ng/L. These levels were similar to those of diuron.

A few studies reported a decreasing trend of biocide concentrations from one year to the next because of bans on some compounds or changes in agriculture practices (Botta et al. 2012; Köck-Schulmeyer et al. 2012; Palma et al. 2014; Ccanccapa et al. 2016; Direction régionale et interdépartementale de l'environnement et de l'énergie d'Ile-de-France (DRIEE) 2016). These examples of source reduction in agriculture are very promising steps towards protection of surface water, and such regulatory measures could also be used for the reduction at source of biocide emissions from buildings. Conversely, Palma et al. (2014) reported higher concentrations of terbuthylazine in 2011-2012 than in 2006-2007, Quednow and Püttmann (2007) did not observe any decrease of terbutryn between 2003 and 2006 despite its ban as a pesticide in 2003. This latter finding suggests the presence of some other local sources of these compounds linked to their uses as biocides.

4.2.2. Groundwater

In a context of increasing urbanization, infiltration systems are becoming a widespread approach for stormwater management (Tedoldi et al. 2016), which raises the question of the contamination of groundwater. Bollmann et al. (2014b) studied the occurrence of a few biocides used in building materials (terbutryn, cybutryn, carbendazim, mecoprop, isoproturon, diuron, tebuconazole, propiconazole, MIT, BIT, OIT) in infiltrating groundwater from a separated sewer system but none of them were detected. More recently, Hensen et al. (2018) investigated the transfer of three of them (OIT, diuron, terbutryn) and their TPs to groundwater via stormwater infiltration systems in an urban area. Runoff was collected in swales and percolated on underground trenches. For OIT and terbutryn, concentrations and quantification frequencies were higher in swales than in trenches because of retention or rapid degradation in soil

(Bollmann et al. 2017a). On the contrary, diuron was more frequently quantified in trench samples than in swales, which suggests other inputs or release from soil. In groundwater, OIT and its TP-214 were infrequently detected (14 % for both) and the maximum concentration of OIT was 1.4 ng/L. Diuron and its TP-219 were often quantified (100% and 82%, respectively) at higher concentrations after the infiltration system, up to 8.8 ng/L (i.e. an eight-fold increase) and 7.3 ng/L respectively (a mean four-fold increase). Concentrations of diuron found in groundwater were higher than those in swale and trench samples. This result again showed that diuron might be continuously released from soil. In groundwater, terbutryn and its TP-214 were mostly quantified with maximum concentrations of 7.6 and 3.3 ng/L respectively. These observations strongly suggest that diuron and terbutryn entered the groundwater via the infiltration system. For all studied compounds, concentrations in groundwater were far below the threshold value (100 ng/L for individual pesticides) set by the European Directive 98/83/EC. Further work is needed for other biocides used in building materials and their TPs, as it is clear that they can enter groundwater via infiltration systems.

5. Conclusion and outlook

This review highlighted that biocides used in building materials are of major concern regarding the quality of receiving waters. Widely used in buildings but also as pesticides or in households or cosmetic products, they are ubiquitous in surface water and groundwater with concentrations close to regulatory thresholds at which they can have biological effects. Many studies investigated biocidal emissions from building materials, allowing the constitution of a list of biocides used in buildings, which should be monitored in receiving waters: methylisothiazolinone, benzisothiazolinone, chloro-methylisothiazolinone, octylisothiazolinone, dichloro-octyl-isothiazolinone, diuron, isoproturon, carbendazim, iodopropynyl butylcarbamate, terbutryn, cybutryn, terbuthylazine, mecoprop, propiconazole, tebuconazole, thiabendazole, permethrin, benzalkonium, dodecyl-dimethyl ammonium and zinc pyrithione. Some studies proposed models at the scale of a city or a watershed in order to predict the biocide loads into receiving waters. Literature results indicated that biocide concentrations in stormwater, CSOs and wastewater, were in the same order of magnitude. It was proved that urban discharges in both dry and wet weather conditions could contaminate the receiving environment. In rivers, several studies reported concentrations of cybutryn, carbendazim, QAC, permethrin and phenylureas exceeding PNEC values, which imply an environmental risk for aquatic organisms.

However, many gaps in knowledge have been identified, preventing the full assessment of the environmental risks related to biocides from buildings and the proposal of new regulations. First, the present review has pointed out that (i) data is scarcer for MIT, tebuconazole, mecoprop and benzalkoniums and almost absent for zinc pyrithione in building leachates, and (ii) data is also missing for isothiazolinones, IPBC, zinc pyrithione and QAC in surface water. Additionally, transformation products are still poorly investigated although they represent crucial information to close the mass balance between the remaining stock in materials and the emitted mass loads.

Future work should hence focus on the improvement of both analytical and experimental protocols. Limits of detection and quantification for zinc pyrithione, IPBC and isothiazolinones have to be improved in order to allow their detection and quantification at trace levels. Harmonized methods, such as EN 16105 procedure (CEN 2011), are required so that leachability can be compared between several materials. Concerning the biocide transfer into receiving waters, the comparison of concentrations is not sufficient to prioritize the major pathways. Comparing mass loads would be more relevant and helpful for risk assessment. Models can be valuable tools to assess biocide mass loads into receiving waters. However, much information is required including, consumption data or sales volumes, amount of rainfall reaching façades and turned into runoff, façade surface area, etc., which are often not available. Additionally, the representativeness of the already developed models and the quality of their inputs have to be improved by considering the variability of watersheds or cities and the complexity of sewer networks. Moreover, these approaches were based on individual chemical substances, which is insufficient for risk assessment and further research on cocktail effects or in-situ bioassays appears crucial.

The review also highlighted several potential technical solutions and policy actions to reduce biocide emissions from building materials and their transfer to receiving waters. The first solution should be the improvement of products formulations such as adding a top-coating on render without biocide or the encapsulation of biocides in polymer microspheres or silica, which slows down their release. Concerning roof treatment practices, the application of products containing biocidal substances should be restricted to specific cases where technical problems justify the requirement of roof de-mossing, and doses that are employed to treat these problems should be limited. Another solution is based on the regulation concerning both the ban of the most toxic substances and the addition of biocides in monitoring programs, which are not taken into account in the actual European survey programs. For instance, (i) OIT and DCOIT are among the most toxic substances presented in this work, but their concentrations in the aquatic environment are still unknown; (ii) QAC are rarely monitored but concentrations generally exceeded PNEC values, in particular concerning benzalkonium C12; and (iii) compounds like diuron and isoproturon, which are banned as PPP but still used as biocides, should be banned as PNEC values are often exceeded in rivers. Finally, our review underlines the necessity of a close link between researchers and industrials or policy makers (cf. the two examples for mecoprop, see paragraph 3.2.3) to reduce biocide emissions and limit their transfer into rivers, and, as a consequence, to significantly improve water quality in urban areas.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest

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ABBREVIATIONS

BCF, bioconcentration factor; BIT, 1,2-benzisothiazol-3(2H)-one; BPR, biocidal product regulation; BZK, benzalkonium; CB, cybutryn; CBZ, carbendazim; CMIT, 5-chloro-2-methyl-4-isothiazolin-3-one; CSO, combined sewer overflows; DCOIT, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one; DDAC, dimethydidecyl ammonium chloride; DR, diuron; EC50, half maximal effective concentration; IP, isoproturon; IPBC, Iodopropynyl butylcarbamate; LOD, limit of detection; LOQ, limit of quantification; MCPP, mecoprop; MIT, 2-methyl-4-isothiazolin-3-one; MW, molecular weight; ND, not detected; OIT, octhilinone; PNEC, predicted no effect concentration; PPP, plant protection product; QAC, quaternary ammonium compounds; TB, terbutryn; TEB, tebuconazole; TP, transformation product; UV, ultraviolet; WS, water solubility; WWTP, wastewater treatment plant; ZnPT, zinc pyrithione.

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