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Biocides in urban wastewater treatment plant influent at dry and wet weather: Concentrations, mass flows and possible sources

Ulla E. Bollmann [a], Camilla Tang [b], Eva Eriksson [b], Karin Jönsson [c], Jes Vollertsen [d], Kai Bester [a,*]

[a] Aarhus University, Department of Environmental Science, Frederiksborgvej 399, 4000 Roskilde, Denmark
[b] Technical University of Denmark, Department of Environmental Engineering, Miljovej B113, 2800 Kgs. Lyngby, Denmark
[c] Lund University, Water and Environmental Engineering at the Department of Chemical Engineering, P.O. Box 124, 22100 Lund, Sweden
[d] Aalborg University, Department of Civil Engineering, Sohngaardsholmsvej 57, 9000 Aalborg, Denmark

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ABSTRACT

In recent years, exterior thermal insulation systems became more and more important leading to an increasing amount of houses equipped with biocide-containing organic façade coatings or fungicide treated wood. It is known that these biocides, e.g. terbutryn, carbendazim, and diuron, as well as wood preservatives as propiconazole, leach out of the material through contact with wind driven rain. Hence, they are present in combined sewage during rain events in concentrations up to several hundred ng L^{-1}.

The present study focused on the occurrence of these biocides in five wastewater treatment plants in Denmark and Sweden during dry and wet weather. It was discovered, that biocides are detectable not only during wet weather but also during dry weather when leaching from façade coatings can be excluded as source. In most cases, the concentrations during dry weather were in the same range as during wet weather (up to 100 ng L^{-1}); however, for propiconazole noteworthy high concentrations were detected in one catchment (4.5 μg L^{-1}). Time resolved sampling (12 × 2 h) enabled assessments about possible sources. The highest mass loads during wet weather were detected when the rain was heaviest (e.g. up to 116 mg h^{-1} carbendazim or 73 mg h^{-1} mecoprop) supporting the hypothesis that the biocides were washed off by wind driven rain. Contrary, the biocide emissions during dry weather were rather related to household activities than with emissions from buildings, i.e., emissions were highest during morning and evening hours (up to 50 mg h^{-1}). Emissions during night were significantly lower than during daytime. Only for propiconazole a different emission behaviour during dry weather was observed: the mass load peaked in the late afternoon (3 g h^{-1}) and declined slowly afterwards. Most likely this emission was caused by a point source, possibly from inappropriate cleaning of spray equipment for agriculture or gardening.

* *Corresponding author*. Tel.: +45 87158552.
E-mail addresses: kb@dmu.dk, kai.bester@uni-DUE.de (K. Bester).

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1. Introduction

Biocides and biocidal products are used in order to "*destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means*" (European Parliament and Council, 2012). In recent years, an increasing amount of houses is equipped with biocide-containing paints, renders and other building materials in order to prevent algae and fungi growth (Reichel et al., 2004). A mix of 3–5 different active ingredients, resulting in final biocide concentrations in the exterior render of up to 1% (w/w), is often used (Burkhardt et al., 2011). Primarily carbamates, triazines, isothiazolinones, and phenylureas are used as fungicides, bactericides or algaecides in polymeric renders and paints (Paulus, 2005). Triazoles are common fungicides in wood protection products (Schultz et al., 2007).

Laboratory tests have shown that the biocides may leach out of the materials during rain events when the building materials are wetted and thus enter urban surface waters via stormwater runoff (Schoknecht et al., 2003, 2009). Due to this, several studies have focussed on the occurrence of biocides in urban stormwater runoff and urban surface waters affected by building material. Concentrations up to several $\mu g\ L^{-1}$ have been detected in stormwater runoff in separated sewer systems (Bollmann et al., 2014; Bucheli et al., 1998a, 1998b; Burkhardt et al., 2007, 2009, 2011; Coutu et al., 2012; Wittmer et al., 2010). It is obvious that those biocides might be present not only in separated stormwater but also in combined sewer systems during wet weather periods. However, only a few studies on biocides in combined sewers have been performed so far – in all cases samples were taken as 24 h composite samples during wet weather periods or the weather conditions have been neglected. The observed concentrations in combined sewer systems at the inlet of wastewater treatment plants (WWTPs) range from a few $ng\ L^{-1}$ up to 2.5 $\mu g\ L^{-1}$ (Table 1).

Several compounds used as biocides are toxic to aquatic organisms and long-term adverse effects in the aquatic environment cannot be excluded already for low concentrations (Mohr et al., 2008). An effect concentration of 10 $ng\ L^{-1}$, causing effects in 10% of the test organisms chlorophytes (green algae) (EC_{10}), was calculated for the antifouling biocide cybutryn (Mohr et al., 2008). Predicted no effect concentrations (PNEC) were estimated to be in the low $ng\ L^{-1}$ range for several biocides (Burkhardt et al., 2009). According to the list of priority pollutants under the water framework directive (WFD) (European Parliament and Council, 2013), recommended annual average environmental quality standards (AA-EQS) for inland waters are 2.5 and 64 $ng\ L^{-1}$ for cybutryn and terbutryn, and 200 and 300 $ng\ L^{-1}$ for diuron and isoproturon, respectively. The other biocides used in building material are not regulated under the WFD.

Biocides are used in different applications in connections with buildings: as in-can preservatives, as well as film preservatives in building materials like render or paint and wood protection products. Beyond that, most biocides have a broad usage spectrum and it is known that most of the compounds used in façade coatings have other application forms as well (see Table 2). They are also used as preservatives for various types of materials, e.g. leather or rubber, as well as industrial working fluids (European Commission, 2013a, 2013b). In addition, some compounds (Cybutryn (IRG) and dichloro-N-octylisothiazolinone (DCOIT)) are used in antifouling paints for ships (Thomas et al., 2002). Several compounds used as biocides are or have been used as plant protection products (PPPs) as well (Danish Environmental Protection Agency, 2011a, 2011b), in order to "*protect plants or plant products against all harmful organisms*" and "*destroy undesired plants*" (European Parliament and Council, 1991).

Due to various possible diffuse sources for biocides in urban waters it is difficult to track individual sources. Gerecke et al. (2002) used the enantiomeric ratio of mecoprop (MCPP) in order to decide whether the compound originated from agriculture or from urban roof top sealants (bitumen sheets). At that time the racemate was used in rooftop materials, while only the R-enantiomer was applied in agriculture. Singer et al. (2010) assumed that the main sources for carbendazim and terbutryn are rather households and other constant sources than building façades, since the influent loads in combined sewer were relatively independent from the stormwater content in the samples. However, no analysis in completely dry weather conditions was performed within that study.

So far, only 24 h composite samples of combined sewage have been analysed, hence, no higher time resolution is available in the literature. Since either sampling took place during wet weather or the weather conditions have been neglected in the previous studies, the occurrence of biocide originating from leaching from buildings can neither be

Table 1 – Concentrations of biocides in WWTP in-and effluent [$ng\ L^{-1}$].

WWTP	CD	TB	DR	IP	PPZ	TBU	MCPP	IRG	OIT	DCOIT	Reference
Influent	110–920	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Kupper et al. (2006)
Effluent	50–980										
Influent	n.a.	n.a.	n.a.	n.a.	4–27	n.d. – 8	n.a.	n.a.	n.a.	n.a.	Kahle et al. (2008)
Effluent					5–40	1–10					
Prim. Eff.	110 ± 30	70 ± 20	60 ± 30	90 ± 100	n.a.	n.a.	870 ± 590	10 ± 4	n.a.	n.a.	Singer et al. (2010)
Tert. Eff.	70 ± 10	20 ± 4	40 ± 10	30 ± 20			1010 ± 590	5 ± 1			
Influent	110	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2	6	Chen et al. (2012)
Effluent	114								0.5	5	
Influent	n.a.	5–183	28–2526	1–90	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Masiá et al. (2013)
Effluent		9–46	29–2393	2–102							

n.a.: not analysed n.d.: not detected.