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Not only biocidal products: Washing and cleaning agents and personal care products can act as further sources of biocidal active substances in wastewater

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ABSTRACT

The emission sources of biocidal active substances in households have been under discussion since these substances have been detected frequently in municipal wastewater and receiving surface water bodies. Therefore, the goal of this study was to investigate the products responsible for the emission of these substances to wastewater.

We analysed the wastewater of two streets for a set of biocidal active substances. Time-proportional sampling was conducted for one week of each season during one year in each street. The 14 substances analysed with liquid chromatography coupled with tandem mass spectrometry were 1,2-benzisothiazol-3(2H)-one (BIT), C_{12}-benzalkonium chloride, carbendazim, 5-chloro-2-methyl-2H-isothiazol-3-one (CMIT), dichlorooctylisothiazolinone (DCOIT), N,N-diethyl-meta-toluamide (DEET), diuron, icaridine, 2-octyl-2H-isothiazol-3-one (OIT), piperonyl butoxide (PBO), triclosan, tebuconazole, terbutryn and tetramethrin. Using data available from household product inventories of the two streets, we searched the lists of ingredients for the products possibly being responsible for the emissions.

Except for four substances, all substances have been detected in at least 10% of the samples. Highest concentrations were measured for C_{12}-benzalkonium chloride with an average concentration in the daily samples of 7.7 μg/L in one of the streets. Next to C_{12}-benzalkonium chloride, BIT, DEET and icaridine were detected in all samples in average concentrations above 1 μg/L in at least one street. The results show that washing and cleaning agents were important sources for preservatives such as BIT and OIT, while triclosan was apparently mainly emitted through personal care products. The mosquito repelling substances DEET and icaridine were found throughout the year, with highest emissions in summer and autumn.

In conclusion, the results demonstrate that the sources of biocidal active substances in municipal wastewater are complex and that measures for the prevention of the emission of biocidal active substances into the aquatic environment have to be carried out under different legislations. This has to be taken into account discussing emission reduction at the source.

1. Introduction

Discussions on solving the problem of micropollutants in wastewater falter between end-of-pipe technologies, such as the improvement of removal technologies at sewage treatment plants, or proactive pollution prevention at the source (Kümmerer et al., 2015; Ternes et al., 2004). One possible source for chemicals that might enter the sewage system and end up as micropollutants are products in households. They can contain pest controlling substances, so-called biocidal active substances according to the Biocidal Products Regulation 528/2012 (Bollmann et al., 2014; European Union, 2013; Launay et al., 2016; Merel and Snyder, 2016). Until now, when biocidal active substances have been detected during monitoring studies, the specific products or materials releasing the substances within households remained unclear (Bollmann et al., 2014; Launay et al., 2016; Singer et al., 2010; Wittmer et al., 2011). It has already been shown by Wieck et al. (2016) based on

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Abbreviations: BIT, 1,2-benzisothiazol-3(2H)-one; BKC, alkyl (C_{12}) dimethylbenzyl ammonium chloride; CAR, carbendazim; CMIT, 5-chloro-2-methyl-2H-isothiazol-3-one; DCOIT, dichlorooctylisothiazolinone; DEET, N,N-diethyl-meta-toluamide; DIU, diuron; ESI, electrospray ionisation; ICA, icaridine; LC-MS/MS, liquid chromatography coupled with tandem mass spectrometry; LOQ, limit of quantification; MIT, 2-methylisothiazol-3(2H)-one; MWWC, measured average wastewater concentration; OIT, 2-octyl-2H-isothiazol-3-one; PBO, piperonyl butoxide; PWWC, predicted wastewater concentration; TCS, triclosan; TEB, tebuconazole; TER, terbutryn; TET, tetramethrin

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product inventories that personal care products and washing and cleaning agents could be important potential sources for biocidal active substances in wastewater. In contrast to most biocidal products, the ingredients of many washing and cleaning agents and personal care products, such as shampoo or washing agents, are directly emitted into the wastewater during use (Ternes et al., 2004). Studies that link product inventories to analytical results, enabling a better understanding on products potentially emitting the substances within one study site, are rare and urgently needed. The selection of analytes only based on the substances that have been already identified in prior studies, instead on the substances actually emitted in a study site, i.e. based on product inventories, has already been criticised by Daughton (2014). To the best of our knowledge, such studies are only available for other product categories such as pharmaceuticals (Herrmann et al., 2015), or wastewater types such as grey water (Eriksson et al., 2003).

Sampling for biocidal active substances in municipal wastewater requires a thorough selection of the sampling location and sampling strategy. To differentiate between emissions from the outside of houses, such as leaching of material preservatives from facades, and substances used within households, samples should be taken in sewer systems with separate stormwater sewers. To get hold of single pulses of biocidal active substances, grab samples would not provide sufficiently high resolution in time. Time-proportional sampling with a sampling frequency of at least 15 min should at least be applied (Ort et al., 2010a). For the detection of micropollutants in wastewater, e.g. biocidal active substances, several sample preparation and analytical methods are available that cover a range of biocidal active substances. In the majority of studies, these methods are using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) (Chen et al., 2012; Singer et al., 2010; Wick et al., 2010). Electrospray ionisation (ESI) should be applied if a broad spectrum of substances is to be analysed and the use of labelled surrogate standards is important to account for ion suppression or enhancement (Wick et al., 2010). With these methods, biocidal active substances have been detected frequently in wastewater, which is the main exposure pathway for urban-use biocidal active substances to surface water (Singer et al., 2010). N,N-diethyl-meta-toluamide (DEET), an active substance repelling mosquitos, was for example detected in 100% of effluent samples of 90 sewage treatment plants across Europe; diuron (DIU), a herbicidal material preservative, in 77% of the samples and triclosan (TCS), a disinfectant and preservative, in 41% (Loos et al., 2013). 2-octyl-2H-isothiazol-3-one (OIT), 1,2-benzisothiazol-3(2H)-one (BIT), dichlorooctylisothiazolinone (DCOIT), icaridine (ICA), triclosan and carbendazim (CAR) were also frequently found in wastewater influent in China (Liu et al., 2017). Quaternary ammonium compounds, such as benzalkonium chloride (BKC), are discussed to promote resistance development against antibiotics and have been detected in influent of sewage treatment plants in concentrations of 170 μg/L and bind in high amounts to particles (Östman et al., 2017; Sütterlin et al., 2007; Zhang et al., 2015). This highlights the importance to monitor both, the aqueous phase and suspended particulate matter (Barco-Bonilla et al., 2010; Ort et al., 2010a).

In view of the considerations above, the main objective of this study was to allocate detections of biocidal active substances in municipal wastewater to possible emission sources within households. For the first time, this was possible for biocidal active substances in municipal wastewater because of existing product inventories of the households in the sampling area. This area was deliberately chosen as study site because the existing infrastructure allowed the assumption that all analysed biocidal active substances resulted from a use within households. The possible sources discussed in this study are, besides biocidal products, personal care products and washing and cleaning agents. Furthermore, we wanted to investigate whether product inventories suffice to characterise the emission of biocidal active substances from households to wastewater. Time-proportional sampling of wastewater of one neighbourhood was conducted during one year and 14 biocidal active substances were chosen for analysis using LC-MS/MS.

2. Methods

2.1. Sampling site and sampling strategy

2.1.1. Sampling site

As sampling site, we selected a neighbourhood in Schleswig-Holstein in the north of Germany. The neighbourhood consisted of 132 single-family houses mainly built between 1970 and 1980, with two wastewater streams (supplementary material S1) connecting 49 houses (street A) and 89 houses (street B) with the municipal sewer system. Based on information collected during interviews with the inhabitants of the streets, 113 inhabitants live in street A and 223 inhabitants in street B (Wieck et al., 2018). This neighbourhood was selected because (i) no professional users of biocides were discharging wastewater to the sewage system, (ii) no agricultural holdings were present and (iii) it had a separate sewer system for stormwater and the households' wastewater, thus ensuring that all analysed biocidal active substances resulted from a use within households. Due to the separate sewer system no runoff from facades and thereto related emission of biocidal active substances or emissions from the professional use of plant protection products should be present in the sampled wastewater.

Additional to the optimal infrastructure for a representative sampling of biocidal active substances in municipal wastewater, this sampling site was selected because recent product inventories of household products connected to the sampled sewers were available (Wieck et al., 2016; sampling area is "neighbourhood A"). These inventories contained data on biocidal products, personal care products and washing and cleaning agents. Product inventories of 29 households in street A (59% of the households) and 60 households in street B (67%) were obtained. Demographic data showed no significant differences between the inhabitants of street A and B. The only exception was that significantly more children of age 3 and 6 years (95% CI = -0.181 to -0.022; $p = 0.013$) lived in street B. Wieck et al. (2016) reported that with 53 years, the average age of the interviewees was higher than the German average age (44 years). The products that were inventoried also did not contain significantly different numbers of biocidal active substances except for TCS which was only used in toothpastes inventoried in street B.

2.1.2. Sampling procedure

Composite samples were taken daily for 14 h during approximately one week in each season to catch possible daily input variations and to reflect the differing use of products in the different seasons (Table 1). In spring, samples were taken only in street B due to technical reasons, in summer the sampling period in both streets was extended to 10 days due to problems during sampling. Teledyne Isco 6712 Portable Samplers (Teledyne Isco, Lincoln, USA) placed into manholes in the two streets were used for sampling. Each sampler contained 24 polypropylene bottles with a volume of 500 mL each. Automated sampling

Table 1
Description of the sampling campaign.

Season	Sampling locations	Sampling dates	Number of 14 h-samples	Number of days 1 h-samples were analysed separately
Spring	Street B	07.–13.04.2016	7	1
Summer	Street A	04.–14.08.2016	8	2
	Street B	04.–14.08.2016	5	1
Autumn	Street A	06.–12.10.2016	6	1
	Street B	06.–12.10.2016	7	2
Winter	Street A	12.–18.01.2017	5	2
	Street B	12.–18.01.2017	6	3