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Occurrence of micropollutants in the wastewater streams of cruise ships

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ABSTRACT

Nowadays the protection of the marine environment raises increasing academic and public attention. The issue of organic micropollutants is of equally high importance for the marine ecosystems. Maritime vessels are considered to significant sources of micropollutants especially if the ship carries many passengers, which is often true for cruise ships which frequent attractive and sensitive sea areas. The emission pathways for micropollutants include wastewater discharges and sewage sludge disposal. The findings of the German research and development project NAUTEK contribute to bridging the knowledge gap about micropollutant emissions from cruise ships. As expected, micropollutants were detected in both the blackwater and greywater on board, emitted from either the passengers or certain ship operations. In total, 16 out of 21 target substances were detected. Peak concentrations of pharmaceuticals could be found mainly in blackwater (peak conc. Carbamazepine 3.9 µg/L, lbuprofen 29 µg/L, Diclofenac $0.04 \ \mu g/L$), while greywater is mainly characterized by substances such as ointment residues, UV-filters and flame retardants (peak conc. Diclofenac 0.65 µg/L, Bisphenol A 8 µg/L, Tris(1-chloro-2-propyl) phosphate 136 μ g/L). Further analyses suggest a gradual removal of the micropollutants by the onboard MBR plant (MBR effluent peak conc. Carbamazepine 0.47 µg/L, Ibuprofen 6.8 µg/L, Diclofenac 0.3 µg/L). Findings of this research provide a critical stepstone for shaping technical solutions for onboard micropollutants removal and water resource recycling.

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1. Introduction

It is borne out by cruise operators' figures that every year more than 20 million passengers embark on a cruise trip. For many years, the cruise ship industry has been one of the fastest growing tourism sectors worldwide and its passenger count has been increasing rapidly. Similarly, the ongoing construction of many new cruise ships shows how optimistic the cruise industry is about the future. However, the cruise industry should be held accountable for numerous environmental problems, including critical emissions such as exhaust gases and wastewater. In view of the latter, the creation and maintenance of luxurious conditions aboard results in high water and resource consumption and hence high wastewater discharge. In addition, further wastewater streams are derived from

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laundries, galleys and from other activities like ship cleaning. In view of the existing legal regulations (primarily Annex IV of MARPOL Convention which contains regulations for the prevention of pollution by sewage from ships), most of the operating cruise ships are equipped with wastewater treatment systems. Specific statements regarding treatment performance cannot be made due to missing administrative plant monitoring.

In the maritime context only blackwater is officially regarded as wastewater. In most cases, greywater is nonetheless also treated on board of cruise ships, which seems appropriate in view of the actual pollution loads from greywater.

There is still significant room for treatment system improvements. The latest technical developments are aimed at integrating nutrient removal mainly into market available treatment systems. Since it was proven that micropollutants harm aquatic life [1] the issue of micropollutants has become an important topic on the world's task list for wastewater treatment improvement. Micropollutants encompass substances such as pharmaceuticals,

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Specification	of	target	substances.	
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Compound	Subordinated group	CAS number	Method for analysis	Reference substance ^a	Measurement uncertainty [%]
Pharmaceuticals					
Carbamazepine	Anticonvulsant	298-46-4	HPLC/MS-MS	Sigma	60-80
Dimenhydrinate	Antiemetic	523-87-5	GC/MS	Sigma	70-100
Ibuprofen	Analgesic and anti-inflammatory	15687-27-1	HPLC/MS-MS	Fluka	50-90
Diclofenac	Analgesic and anti-inflammatory	15307-86-5	HPLC/MS-MS	Sigma	55-65
Naproxen	Analgesic and anti-inflammatory	22204-53-1	HPLC/MS-MS	Sigma	70
Propyphenazone	Analgesic and anti-inflammatory	479-92-5	GC/MS	Fluka	94
Metoprolol	Beta blocker	37350-58-6	HPLC/MS-MS	Sigma	85-120
Atenolol	Beta blocker	29122-68-7	HPLC/MS-MS	Sigma	10
Bezafibrate	Cholesterol-lowering drug	41859-67-0	HPLC/MS-MS	Sigma	65-100
Clofibric acid	Cholesterol-lowering drug	882-09-7	HPLC/MS-MS	Fluka	70-80
Clarithromycin	Antibiotic	81103-11-9	HPLC/MS-MS	Sigma	80-85
Sulfamethoxazole	Antibiotic	723-46-6	HPLC/MS-MS	Fluka	80-90
Trimethoprim	Antibiotic	738-70-5	HPLC/MS-MS	Sigma	75
Ethinyl estradiol	Estrogen	57-63-6	GC/MS	Sigma	80
Verapamil	Antiarrhythmic	52-53-9	HPLC/MS-MS	Sigma	60
Caffeine	Analeptic	58-08-2	GC/MS	-	20-45
Personal Care Products	•				
Benzophenone	UV filter	131-57-7	GC/MS	Fluka	75-95
Methylbenzyli-dene camphor	UV filter	36861-47-9	GC/MS	Fluka	62
Tonalide	Fragrance	21145-77-7	GC/MS	SAFC	50-60
Chemicals	-				
Bisphenol A	Plastic Softener	80-05-7	GC/MS	Fluka	85-110
Tris(1-chloro-2-propyl) phosphate (TCPP)	Flame retardant	13674-84-5	GC/MS	Fluka	100

^a Standard/pure substance of each substance to establish the analytical method for this substance.

personal care products, endocrine disruptors, anti-flame retardants and many more. Because of a lack of specific legal requirements, reducing the micropollutants emissions from (cruise) ships are apparently not yet on the ship owners' agenda.

For the first time, the cooperative R&D project "Sustainable Solutions for Wastewater Treatment and Reuse on Cruise Liners (NAUTEK)" places the micropollutants issue in the context of wastewater management aboard cruise ships. Why investigate the occurrence of micropollutants aboard? First, the ashore discharge standards - after some time – are expected to become relevant for the offshore regions. Second, in line with continuous efforts for energy saving, waste or greywater reuse solutions will potentially play an important role. While reflecting on reuse solutions the micropollutants issue can be a critical bottleneck. To address all these open questions, the project NAUTEK focused on the development of a "future-proof" modular wastewater treatment scheme.

The present article aims to provide a comprehensive overview about the occurrence of selected micropollutants in different wastewater streams aboard cruise ships. In detail, black and greywater streams on cruise ships were subjected to in-depth investigations for the first time. The sampling methods and analyses were carried out by Hamburg University of Technology (TUHH), Germany, within the scope of the cooperative R&D project "Sustainable Solutions for Wastewater Treatment and Reuse on Cruise Liners (NAUTEK)" and in cooperation with a large cruise operator. The findings presented in this article provide essential criteria for the concrete design of techniques to be used for onboard micropollutants removal.

2. Methods

After establishing sampling points, accurate sampling, and sample processing as well as using high-end analytical methods for micropollutants detection, as illustrated in details below.

2.1. Selection of target substances

The determination of target substances was based on their

likelihood of appearance onboard cruise ships, either originated from passengers or certain cruise ship operations. For example popular painkillers, beta blockers, and also typical compounds of sun protection products and ship cleaning agents were worth considering. Further conversations with the pharmacy staff and doctors onboard a cruise ship as well as in-depth literature review particularly dealing with the occurrence and fate of micropollutants in the aquatic environment - were conducted. Finally, 21 micropollutants were selected as target substances. The selected compounds belong to the following groups: pharmaceuticals (16 substances), personal care products (3 substances) and chemicals (2 substances). Table 1 specifies the tested substances. It comprises the CAS Number, the parameter classification, the specific method for analysis, the distributor of the reference substance and the specific measurement uncertainty.

2.2. Sampling

In total 12 sampling episodes took place on four different medium-sized cruise ships (total capacity 2600–3300 persons) during calls at Hamburg Port, Germany. The grab sampling was carried out during passenger disembarkation and embarkation. It is worth noting that all cruise ships subject to the investigations were equipped with nearly similar membrane bioreactor systems as shown in Fig. 1. Generally, the plant operation was not geared to support nitrification and the denitrification tank was bypassed. Only one cruise ship had a denitrification system in operation.

Appropriate sampling points were identified and implemented with the assistance of the ship crews (also displayed in Fig. 1). In total four wastewater streams were sampled: the blackwater vacuum tank, the mixed greywater stream, the laundry greywater and the final effluent (MBR-permeate). Table 2 provides an overview of the different sampling episodes indicating number of samples taken from each cruise ship. The sampling frequency depended on ships calling at Hamburg Port within the investigation period. There was no sampling after mixing black- and greywater due to the absence of collecting tank or mixing tank upstream from the treatment plant. Download English Version:

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