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Occurrence and fate of synthetic musk fragrances in a small German river

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HIGHLIGHTS

- Investigation of synthetic musks in water samples and fishes in a small catchment.
- Effects can be observed better in small water bodies (e.g. source characterization).
- Combined sewer overflow cause episodic and highly dynamic concentration peaks.
- Degradation of HHCB depends on the water temperature.
- Fishes are suitable indicators of bioaccumulative substance entry in surface waters.

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ABSTRACT

The polycyclic musks tonalide® (acetyl hexamethyltetraline = 1-(3,5,5,6,8,8-hexamethyl-6,7-dihydronaphthalen-2-yl)ethanone, AHTN), galaxolide® (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta(*g*)-2-benzopyrane, HHCB) and the degradation product HHCB-lactone were determined in water samples and brown trouts (*Salmo trutta fario*) of the river Ammer, a small catchment in the state of Baden-Württemberg, south-west Germany. The Ammer receives the effluent discharge of two municipal wastewater treatment plants (WWTPs) with 90,000 population equivalents. The wastewater contributes 14% of the total discharge of the river (average 1.0 m^3/s). Water samples were collected monthly at 12 sampling points from June 2010 to May 2011. Downstream the WWTPs the median concentrations of HHCB, AHTN and HHCB-lactone were 0.26 μg/L, 0.06 μg/L and 1.0 μg/L, respectively. The effluent of the WWTPs was identified as main source of the synthetic musks in the surface water. The ratio of HHCB-lactone/HHCB showed significant seasonal variations indicating the influence of the water temperature on the degradation of HHCB in the surface water.

A total of 251 trout was caught in two campaigns in October 2010 at 12 sampling points. The median concentrations of HHCB and AHTN in the trouts downstream the WWTPs significantly increased to 10.8 μg/g lipid weight (LW) and 3.7 μg/g LW, respectively.

1. Introduction

Fragrance substances are used in various everyday products such as perfumes, deodorants and other personal care products, room sprays and detergents. Until the end of the 19th century predominantly natural fragrances (isolated from plants and animals) were used. Nowadays synthetic fragrances are increasingly applied, offering the advantage of constant and reproducible quality.

Representatives of this class of fragrances are nitro musks and polycyclic musks. Due to toxicological aspects, their persistence and bioaccumulation tendency the nitro musks (e.g. musk xylene and musk ketone) were recommended for authorization under REACH [1] and voluntarily banned by the International Fragrance Association (IFRA). In contrary the polycyclic musks galaxolide® (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(*g*)-2-benzopyrane, HHCB) and tonalide® (acetyl hexamethyl tetraline = 1-(3,5,5,6,8,8-hexamethyl-6,7-dihydronaphthalen-2-yl)ethanone, AHTN) are used in high quantities. Due to their lipophilicity and persistence these substances tend to accumulate in fatty

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tissues causing magnification in the food chain. Within a short time the musk compounds used were detected in water and aquatic organisms as well as in human fat, blood and breast milk [2–7].

Global production of polycyclic musk compounds in the year 2004 amounted to about 1000 t (for HHCB) and 5000 t (for AHTN). The consumption in the EU in 2004 for HHCB was 1307 t and 247 t for AHTN [8,9]. Due to these high amounts produced and consumed and their persistence, HHCB and AHTN are nowadays ubiquitous substances. They can be detected in various environmental and human samples such as water, sediments and organisms (e.g. mussels, crabs, various fish species) [2,8–11]. Remarkably high concentrations were found in human fat (28–189 μg/kg for HHCB, 8–33 μg/kg for AHTN), human blood (average 0.77 μg/L for HHCB and 0.27 μg/L for AHTN) and breast milk (16–108 μg/kg HHCB, 11–58 μg/kg AHTN) [3,8,9,12,13]. These findings reflect the high bioaccumulation tendency of HHCB and AHTN in accordance to the water–octanol partition coefficients ($\log K_{ow}$) of 5.9 and 5.7 for HHCB and AHTN, respectively. After usage the compounds reach the aquatic environment via domestic wastewater, where they can interfere with fish and other organisms. According to REACH, HHCB is classified as dangerous for the environment and very toxic for aquatic organisms, with the warning H410 (very toxic to aquatic life). The predicted no-effect concentration (PNEC) of HHCB according to REACH is 4.4 μg/L. The aquatic toxicity is stated as no observed effect concentration (NOEC) of 0.093 mg/L for fish.

HHCB and AHTN concentrations in wastewater treatment plant (WWTP) influents are significantly influenced by production and regiospecific consumption of the synthetic musks and the influent composition (ratio domestic and industrial wastewater). In influents of WWTPs in USA the synthetic musks were detected at concentrations from 0.04 to 12.7 μg/L for HHCB and 0.1–5.4 μg/L for AHTN [14,15]. HHCB and AHTN concentrations in influents of German WWTPs were 1.9 μg/L and 0.6 mg/L, respectively [16]. Large fluctuations of the concentrations were also reported for WWTP influents from Spain and Western Balkan (0.03–25.0 μg/L for HHCB and <0.05–1.93 μg/L for AHTN [17]. Due to the lipophilic properties of the synthetic musks the samples of the investigations mentioned above were analyzed with particles. Remarkable amounts of HHCB and AHTN reach the WWTP particle-bonded. Removal via the sludge path is reported to be one of the main elimination processes in conventional wastewater treatment [16–19]. Smaller proportions of HHCB are biologically degraded to HHCB-lactone in WWTPs operating with activated sludge [16,19]. A wide range of HHCB and AHTN concentrations is reported for WWTP effluents. HHCB and AHTN were determined in concentrations from 0.01 μg/L to 3.3 μg/L for HHCB and from 0.01 μg/L to 0.81 μg/L for AHTN [10,14,15,17]. HHCB and AHTN are removed in conventional WWTPs (activated sludge process) to 80–90% [17].

HHCB and AHTN are amongst the most commonly detected synthetic organic compounds in surface water. Occurrence and concentration levels of the synthetic musks depend on the discharge of wastewater and the individual dilution of the wastewater in the surface water.

HHCB and AHTN have been identified in various German surface water samples. Heberer et al. [20] investigated water samples from rivers, lakes and canals in Berlin. Highest concentrations of the synthetic musks (12.5 μg/L for HHCB and 6.8 μg/L for AHTN) were determined in the small brook Whule in Berlin which is mainly composed of wastewater effluent. Maximum concentrations were detected at sampling points where WWTP effluents were discharged. Average concentrations of 0.37 μg/L for HHCB and 0.2 μg/L for AHTN were detected in the river Ruhr [16]. Comparable concentration ranges from 0.04 to 1.8 μg/L (HHCB) and < 0.005–0.36 μg/L (AHTN) were found in other surface waters affected by wastewater discharge [10,18,21,22]. According to the high dilution of the discharged wastewater in the Hudson river HHCB and AHTN were detected at concentration ranging from 0.004 to 0.026 μg/L and from 0.005 to 0.023 μg/L [23]. The authors mentioned that the population size has an obvious influence on the volume of domestic wastewater discharge and thereby the quantities of synthetic musks released into the river. HHCB-lactone, the degradation product of HHCB, was not detectable in the water samples (LOQ < 0.01 μg/L). The HHCB-lactone concentrations in the German river Ruhr were in the range of 0.02–0.03 μg/L (HHCB 0.06 μg/L) [16]. The ratio HHCB-lactone/HHCB was reported to be constant downstream the WWTPs indicating less degradation of HHCB.

The lipophilic synthetic musks tend to sorb on particles and various studies document the bioaccumulation of HHCB and AHTN in aquatic organism. The concentrations depend strongly on the species of fish, the region and the individual occurrence and the entry type of the synthetic musks (e.g. point source WWTP).

Bioaccumulation factors of HHCB and AHTN are reported in wide range of 20–1584 (HHCB) and 40–670 (AHTN) [23–25] indicating species-dependent accumulation and metabolism of the synthetic musks. Gatermann et al. [24,25] determined the bioconcentration factors (BCFs) of HHCB and AHTN in tertiary treatment ponds receiving municipal wastewater. For different species BCFs were found in a wide range (from 1700 L/kg for eel to 44,000 L/kg for mussels). The polycyclic musks assumably undergo a fast metabolism and are released into the water in form of one or more polar metabolites [26–28].

Tissue concentrations of brown trouts from remote alpine lakes in Switzerland were in the range of 0.02 μg/g–0.05 μg/g lipid weight (LW) for AHTN and 0.04 μg/g–0.23 μg/g LW for HHCB. Presumably the synthetic musks reach remote alpine lakes via atmospheric transport and deposition [29]. Comparable concentrations were found in fish from Taihu Lake (China) for HHCB (maximum 0.05 μg/g LW) and AHTN (0.007 μg/g LW) although this lake has been severely impacted by wastewater input [30]. Concentrations in higher ranges were found in fish from wastewater affected surface waters. In a German wide study breams (*Abramis brama*) from the rivers Danube, Rhine, Elbe, Saar, Mulde and Saale were investigated. Highest concentrations were determined in fish from the Saar with maximal 11.1 μg/g LW for HHCB and 0.38 μg/g LW for AHTN. In breams from the rivers Danube, Elbe and Saale the tissue concentrations ranged from 1.24 μg/g to 1.38 μg/g LW (HHCB) and 0.12 μg/g to 0.16 μg/g LW [31]. A pilot study reported 19fold (HHCB) and 28fold (AHTN) higher values for the synthetic musks in fish tissue from rivers in the USA [32]. This demonstrates the regional differences in the HHCB/AHTN ratio and the differing concentration levels caused by specific production and consumption of the synthetic musks. HHCB-lactone, the degradation product of HHCB, was confirmed in environmental samples from Norway [33]. The concentrations of the lactone in marine fish muscle were in the range from 0.01 μg/g LW to 0.62 μg/g LW.

The purpose of this study was to investigate the occurrence and fate of HHCB and AHTN in a small catchment in timely and spatial resolution. The river Ammer, located in south-west Germany, receives the wastewater of two municipal wastewater treatment plants. Downstream of the WWTPs the river is not affected by additional wastewater discharge over a distance of more than 10 km.

Additionally, the synthetic musks were analyzed in brown trouts (*Salmo trutta fario*) to investigate the bioaccumulation of the compounds along the river. To determine possible seasonal variations of the concentrations in the surface water, samples were taken monthly in 12 consecutive sampling campaigns.