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Bioconcentration of polycyclic musks in fathead minnows caged in a wastewater effluent plume☆

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ABSTRACT

The synthetic polycyclic musks HHCB (Galaxolide®) and AHTN (Tonalide®) were monitored in fathead minnows (FHMs) caged for a month at various locations in the North Saskatchewan River (NSR), upstream and downstream of the Gold Bar wastewater treatment plant that serves the city of Edmonton, AB, Canada. In addition, the distribution of these musk compounds in the river was predicted using the fugacity-based Quantitative Water Air Sediment Interface (QWASI) model. In FHMs caged 0.15 km downstream of the wastewater outfall, mean concentrations of HHCB and AHTN were 7.4 and 0.4 μg g^{-1} wet weight, respectively. These are among the highest reported concentrations of these musk compounds in fish exposed to treated wastewater. The musk concentrations in FHMs were significantly lower further downstream of the outfall. High bioconcentration factors (BCFs) in FHMs that exceeded 10^4 higher than estimated concentrations in water indicated that there were low rates of biotransformation of the musks in the fish. In the FHMs caged at the site closest to the wastewater outfall, HHCB concentrations in FHMs were comparable to the body burdens that have been reported to moderate expression of vitellogenin in female rainbow trout, indicating that fish in the NSR downstream of the wastewater outfall may be at risk of anti-estrogenic effects. The QWASI model applied to six individual river sections of the NSR predicted that the largest fluxes of HHCB and AHTN would be for downstream transport in water, which explains why FHMs accumulated elevated concentrations of the musks at the furthest downstream site, 9.9 km from the wastewater discharge.

1. Introduction

Synthetic musks are a group of compounds that are used as fragrances in cosmetics, detergents, fabric softeners and household cleaning products. Nitro-musks were the first group of synthetic fragrances to be produced commercially, but these compounds have been largely replaced by the polycyclic musks, of which HHCB (Galaxolide®) and AHTN (Tonalide®) are the most widely used synthetic fragrances (Homem et al., 2015). Both of these compounds have been widely detected in the effluents of domestic wastewater treatment plants (Clara et al., 2011; Sumner et al., 2010; Yang and Metcalfe, 2006; Heberer, 2002), as well as in the tissues of fish collected from aquatic environments near urban centers (Lange et al., 2015; Zhang et al., 2013; Reiner and Kannan, 2011; O'Toole and Metcalfe, 2006; Gatermann et al., 2002). HHCB and AHTN bioaccumulate in aquatic organisms (Zhang et al., 2013; Klaschka et al., 2013; Gatermann et al., 2002), but the ranges of bioconcentration factors (BCFs) reported in the literature vary widely. Rimkus (1999) suggested that the large range of BCFs can be explained by differences in the rate at which musks are biotransformed and eliminated in fish species.

HHCB and AHTN exhibit endocrine disrupting activities. Schreurs et al. (2002) reported that both HHCB and AHTN act as estrogen receptor modulators when tested with *in vitro* reporter gene assays, indicating potential for either estrogenic or anti-estrogenic activity, depending on the cell line and the estrogen receptor subtype used in the test system (i.e. ERα or ERβ). These compounds also exhibit antagonist activities for estrogen, progesterone and androgen receptors, having greater potency for the progesterone receptor (Van der Burg et al., 2008; Schreurs et al.,

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2005). Both AHTN and HHCB also increased expression of ERα and vitellogenin in the livers of male medaka, *Oryzias latipes* (Yamauchi et al., 2008). In the yeast estrogenicity screening (YES) assay, HHCB did not exhibit agonistic activity, but was a strong antagonist of the human ERα (Simmons et al., 2010). In the same study, HHCB acted as an agonist of the rainbow trout ERα in an *in vitro* reporter assay and also blocked the capacity of estradiol (E2) to induce vitellogenin in immature female rainbow trout *in vivo* (Simmons et al., 2010). In addition to interactions with steroid receptors, HHCB and AHTN were shown to inhibit several steroidogenic enzymes in microsomes prepared from the liver of common carp, *Cyprinus carpio* (Schnell et al., 2009). Fernandes et al. (2013) found that HHCB was a weak inhibitor of oxyandrogen production in the testes of male European sea bass, *Dicentrarchus labrax*.

In the present study, we report the concentrations of HHCB and AHTN accumulated in the tissues of fathead minnows (*Pimephales promelas*) caged *in situ* for one month in the North Saskatchewan River (NSR) at locations upstream and downstream of the Gold Bar wastewater treatment plant serving the city of Edmonton, AB, Canada. Jasinska et al. (2015) previously reported changes in various biomarkers of exposure to contaminants in wastewater in fathead minnows caged at the same time and locations, as well as the concentrations of pharmaceuticals and personal care products in water at the caging sites estimated from residues accumulated in passive samplers. Here, we report the concentrations of HHCB and AHTN accumulated in the caged fish and we estimate BCFs along a 9.9 km concentration gradient in the NSR using the previously reported estimates of the time weighted average (TWA) concentrations of these compounds in water. The fate of these polycyclic musk compounds in the NSR over the concentration gradient in the NSR was also modeled using the Quantitative Water Air Sediment Interaction (QWASI) model developed by the Canadian Environmental Modeling Centre (CEMC, 2005). From this model, we predicted which processes were most important in describing the attenuation of HHCB and AHTN in the river, including the processes of transport in water, volatilization, transformation and sedimentation.

2. Materials and methods

2.1. Fish caging

The caging sites were located upstream and downstream of the effluent discharge from the Gold Bar wastewater treatment plant (GBWWTP) that serves the city of Edmonton, AB, Canada. The WWTP serves approximately 730,000 people and has an average daily flow of 255 ML/d. The plant has 8 anaerobic digesters for secondary treatment, and tertiary treatment for biological nutrient removal and UV disinfection.

Fathead minnows (FHM) with mean weights of 1.76 ± 0.09 g were caged in the NSR at sites upstream and downstream of the discharge from the GBWWTP according to methods described by Jasinska et al. (2015). Briefly, native FHMs were harvested from a pond in the watershed of the North Saskatchewan River and maintained at 12 °C in the aquatic facility at the University of Alberta (Edmonton, AB, Canada) for two weeks prior to deployment. Fish were caged in the NSR over four weeks from September 13 to October 13, 2011 at 6 sites in the river (Fig. 1). The two upstream sites (i.e. NSR 1 and NSR 2) were, respectively 1.25 km and 1.10 km upstream on the south bank of the river relative to the discharge on the south side of the river from the GBWWTP. Fish were also caged at four downstream sites (i.e. NSR 3, 4, 5 and 6), which were, respectively, 0.15, 1, 2.5, and 9.9 km downstream of the GBWWTP discharge at depths of 40–70 cm in the wastewater plume along the south bank of the river (Fig. 1). FHMs were deployed in 4 Frabill© bait buckets (25 fish per bucket) placed within perforated Rubbermaid© containers and the fish were fed weekly with trout pellets that contained no detectable quantities of HHCB and AHTN. The caging experiment was conducted according to an approved University of Alberta Animal Use Committee Protocol #753. At the termination of the experiment, 10 to 12 fish were selected at random from each caging site, euthanized and sent frozen on dry ice to the University of Ottawa (Ottawa, ON, Canada). The fish samples were kept at −80 °C prior to preparation for analysis of musks.

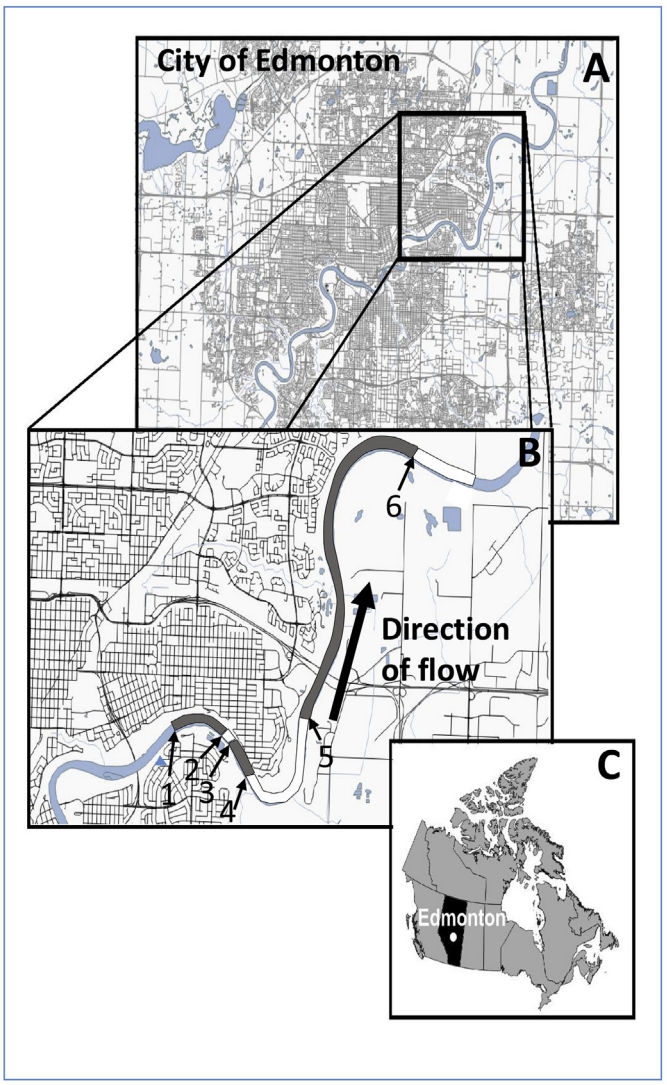

Fig. 1. Location of study sites in the City of Edmonton (A), along the North Saskatchewan River (B). Reference site (1) is located 1.25 km upstream of the GBWWTP. Site 2 is at the GBWWTP effluent (10977, 50th Street, Edmmonton, AB). Sites 3, 4, 5 and 6 are respectively 0.150, 1, 2.5 and 9.9 km downstream. Numbers denote the location of the study sites on the river, and the downstream sections represent the six respective river compartments used in our models (details for these river sections are in Table S4). Inset C shows the location of Edmonton in Canada, with the Province of Alberta highlighted.

2.2. Chemicals

Analytical grade HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyrane) and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-tetrahydronaphtalene in 2,2,4−trimethylpentane) at 98% purity was supplied by Ultra

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