MASS BALANCE ASSESSMENT OF POLYCYCLIC MUSKS IN WASTEWATER TREATMENT PLANTS IN KENTUCKY AND GEORGIA, USA

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Abstract

Wastewater treatment plants (WWTPs) are a source of polycyclic musks in the aquatic environment. In this study, contamination profiles and mass flow of polycyclic musks, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta [γ]-2-benzopyran (HHCB), 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN), and HHCB-lactone (oxidation product of HHCB), in two WWTPs, one located in Kentucky (Plant A, rural area) and the other in Georgia (Plant B, urban), USA, were determined. HHCB, AHTN and HHCB-lactone were detected in the influent, effluent, and sludge samples analyzed. Based on the daily flow rates and mean concentrations of polycyclic musks, the estimated discharge of total polycyclic musks to the rivers was 21 g/day from Plant A and 31 g/day from Plant B. Mass balance analysis suggested that only 30% of HHCB and AHTN entering the plants was accounted for in the effluent and the sludge. Removal efficiencies of HHCB and AHTN in the two WWTPs ranged from 72 to 98%. HHCB-lactone concentrations increased following the treatment. Concentrations of polycyclic musks in sludge were on the order of several parts per million. Incineration of sludge significantly reduced the concentration of polycyclic musks.

Introduction

HHCB, AHTN, and HHCB-lactone are found in many consumer products [1]. There is a great potential for the polycyclic musks to go down the drain, subsequently reaching wastewater treatment plants (WWTPs). The musks that enter WWTPs through the sewer system can be released into surface water, such as rivers, lakes, and estuaries. Thus, release through WWTPs is a pathway for the contamination of aquatic environment and the exposure of aquatic biota to polycyclic musks. HHCB and AHTN have been shown to accumulate in biota, including fish, marine mammals, human adipose tissues and breast milk due to lipophilicity of polycyclic musks (log K_{ow}: 5.4-6.3) [2-5]. These studies suggest widespread occurrence of HHCB and AHTN in wildlife and human tissues. Several studies have reported the occurrence of synthetic musks in WWTPs [6, 7]. HHCB and AHTN were the predominant polycyclic musks found in wastewater. Due to the efficient adsorption of HHCB and AHTN to particles, concentrations of HHCB and AHTN were found to be high in sewage sludge. While most of the earlier studies have reported concentrations of HHCB and AHTN in effluent from WWTPs, reports of concentrations of the polycyclic musks at various stages of wastewater treatment including sludge removal and disposal are limited. Concentrations of HHCB and AHTN can vary widely, depending on the size of the treatment plant, the size of the population served, the types of waste (domestic, industrial, and/or commercial), and the treatment methods employed. Variations in the concentrations of polycyclic musks in WWTPs from urban and rural areas as well as seasonal variations in loadings have not been reported. In this study, concentrations of HHCB, AHTN, and HHCB-lactone were determined in aqueous and solid matrices at various stages of treatment in two WWTPs during different seasons. One of the WWTPs selected for this study is located in Kentucky (Plant A; rural area) and the other in Georgia (Plant B; urban area), USA. Because Plant B sewage sludge is treated by incineration, sludge collected both before and after incineration was analyzed for this plant. We calculated mass flows of HHCB, AHTN, and HHCB-lactone and removal efficiencies of polycyclic musks in the two WWTPs. The overall goal was to assess the behavior and fate of HHCB, AHTN, and HHCB-lactone within the wastewater treatment processes.

Materials and Methods

Samples. Grab samples were collected during winter, spring, summer, and fall of 2005 at Plant A in Kentucky, and during spring, summer, and fall at Plant B in Georgia (No winter samples at Plant B). Plant A serves a population of 15,000 and receives 16.0 million litters of sewage per day. Plant B serves a population of

130,000 and receives 68.4 million liters of sewage per day. These two WWTPs treat primarily domestic and commercial wastewaters, and both plants employ an activated sludge treatment process. In Plant A, influent, before chlorination water (BCW), effluent, oxidation ditch sludge (OD), reactivated sludge (RAS), sludge compressed cake (CC) and final solid waste in dry pond (DP) were collected. In Plant B, influent, primary, effluent, ash basin water (ABW), aeration- mixed liquid suspension solids (MLSS), RAS, CC, and burnt sludge compressed cake (BCC) were collected.

Chemical analysis. Liquid-liquid extraction was performed on wastewater samples. Mixed wastewater samples (100 mL), with particles, were taken in a 250 mL glass separatory funnel, and were spiked with 50 µL of the internal standard d_3-AHTN (1 µg/mL in acetone) before extraction. Fifty milliliters of hexane were added to the 250 mL separatory funnel, and the sample was shaken for 5 min. After shaking, the hexane layer was transferred to a clean flask. The aqueous layer was extracted again with 50 mL of dichloromethane, and the organic layer was combined with hexane. For removal of moisture, the extract was passed through a glass funnel packed with 30 g of anhydrous sodium sulfate, and was concentrated to 1 mL using a rotary evaporator and a nitrogen-purge concentrator. Sludge samples (1 to 5 g) were spiked with 100 ng of d_3-AHTN before extraction. Moisture was removed from the samples by homogenization of each sample with approximately 75 g of anhydrous sodium sulfate. The samples were Soxhlet-extracted using a 400 mL mixture of hexane and dichloromethane (1:3, v/v) for 16 h. The extracts were concentrated to 1 mL.

The concentration of each of the three polycyclic musks was determined by use of a gas chromatograph interfaced with a mass spectrometric detector (Agilent 6890 GC and 5973 MSD; Agilent Technologies). Gas chromatographic separation was carried out using a 30 m Rxi-5ms fused silica column (0.25 mm i.d., 0.25 µm film thickness, Restek Corp.). Two microliters of the extract was injected in splitless mode at 230°C. The column oven temperature was programmed from 120°C (2 min) to 160°C at a rate of 10°C/min (3 min), and then at 2.5°C/min to 250°C, which was held for 2 min. The ions were monitored at m/z 243, 258, and 213 for HHCB; m/z 243, 258, and 159 for AHTN; m/z 257 and 272 for HHCB-lactone; and m/z 246 and 261 for d_3-AHTN. Limit of quantification (LOQ) was 10 ng/L for aqueous samples. The LOQs for sludge samples were 20 ng/g dw for HHCB and AHTN and 50 ng/g dw for HHCB-lactone; the LOQ was set to be 5 times that of procedure blank levels. Recoveries of d_3-AHTN in samples were 96±33%. Details of the analytical procedure and the instrumental conditions have been described previously [1, 7].

Results and Discussion

Wastewater. Concentrations of HHCB, AHTN, and HHCB-lactone in wastewater influent, primary (or BCW), and effluent from both WWTPs are shown in Table 1. The concentrations in the samples varied widely ranging from 10 to 7030 ng/L, 13 to 5400 ng/L, and 66 to 790 ng/L, for HHCB, AHTN, and HHCB-lactone, respectively. The highest concentrations of HHCB and AHTN were measured in the influent of Plant A, and the highest concentration of HHCB-lactone was measured in ABW of Plant B. Concentrations of HHCB and AHTN in influent from both WWTPs were 3 to 60 times higher than those in effluent. Distribution of HHCB-lactone was similar in both plants, with concentrations ranging from 214 to 232 ng/L in Plant A and 237 to 378 ng/L in Plant B. Mean concentrations of HHCB and AHTN in influent of Plant A were 5 times higher than the mean concentrations for Plant B. However, concentrations of HHCB and AHTN in effluents from Plants A and B were similar. No significant difference in the concentrations of polycyclic musks was found between rural Plant A and urban Plant B ($p>0.05$). Concentrations of polycyclic musks in samples collected during various seasons were examined. In Plant A, concentrations of HHCB and AHTN in influent were higher in warm seasons (summer and fall, 235-7030 ng/L) than in cold seasons (winter and spring, 43 and 112 ng/L). In Plant B, the concentrations in influent were slightly higher in fall than in the other two seasons for which samples existed. Overall, there was no significant difference in HHCB and AHTN concentrations in influent samples between warm and cold seasons ($p>0.05$).

The HHCB/AHTN ratios in influent from Plants A and B were 1.2±0.7 and 1.2±0.5, respectively. Earlier studies have reported HHCB/AHTN ratios to be 4.5 to 6, reflecting the greater production and usage of HHCB compared with ATHN [7, 8]. There was significant correlation between HHCB and AHTN in wastewater samples ($p<0.0001$). In contrast, there was a lack of significant relationship between the concentrations of HHCB and HHCB-lactone in wastewater samples. The wide range of concentrations in influent samples can be caused by daily variations in composition of wastewater (domestic or industrial) and local sources. This can influence the ratios of HHCB and AHTN in influent samples.

Table 1. Concentrations (ng/L) of polycyclic musks in wastewater collected in 2005 from two wastewater treatment plants, Plant A in Kentucky and Plant B in Georgia.

	HHCB				AHTN				HHCB-lactone			
Plant A	Influent	BCW	Effluent		Influent	BCW	Effluent		Influent	BCW	Effluent	
Winter (Feb 9)	43	22	67		112	99	133		255	177	467	
Spring (May 26)	NA	NA	10		NA	NA	13		NA	NA	73	
Summer (Aug 8)	7032	24	53		5396	184	150		300	343	288	
Fall (Sep 9)	423	17	46		235	155	225		140	122	86	
Mean	2499	21	44		1914	146	130		232	214	229	
Plant B	Influent	Primary	Effluent	ABW	Influent	Primary	Effluent	ABW	Influent	Primary	Effluent	ABW
Spring (Apr 29)	455	51	28	66	257	108	38	77	766	66	322	787
Summer (Aug 8)	284	99	98	28	334	127	192	223	107	195	267	356
Fall (Sep 26)	522	418	39	87	572	286	187	316	238	451	545	584
Mean	420	189	55	60	388	173	139	205	371	237	378	576

NA; not available, BCW; before chlorination water, ABW; ash basin water

Sludge. HHCB, AHTN, and HHCB-lactone were detected in all of the sewage sludge samples analyzed from Plants A and B, except for sludge collected after incineration in Plant B (Table 2). The HHCB, AHTN, and HHCB-lactone concentrations in sludge were in the ranges of <0.02 to 36 µg/g, <0.02 to 7.2 µg/g, and <0.05 to 17 µg/g, respectively. The mean concentrations HHCB, AHTN, and HHCB-lactone found in sludge from Plant A were significantly lower than those for Plant B ($p<0.05$). This pattern is different from that found in influent samples, in which concentrations in Plant A were higher than those in Plant B. Although both WWTPs employ an activated sludge treatment process, treatment efficiency, types of microorganisms involved, and suspended particle concentrations can contribute to the differences in the concentrations between influent and sludge samples. The concentrations of HHCB and AHTN in sludge in this study were slightly lower than those from New York State (HHCB; 7.2-108 µg/g and AHTN; 0.81-14 µg/g)[7], and were similar to the concentrations found in Switzerland (HHCB; 7.4-36 µg/g and AHTN; 2.5-11 µg/g)[9]. In Plants A and B in the present study, concentrations of HHCB-lactone were three times lower than those from New York State (3.7-22 µg/g)[7].

A significant positive correlation coefficient existed between HHCB and AHTN concentrations measured in sludge samples from both Plants A and B ($p<0.0001$). The ratios of HHCB/AHTN concentrations in sludge from Plants A and B were 3.7±1.2 and 4.9±0.5, respectively. Despite the lack of significant correlation between HHCB and HHCB-lactone in wastewater, a significant positive correlation was found for these compounds in sludge samples. This indicates that influent is not a direct source of HHCB-lactone in WWTPs; rather, HHCB-lactone is generated by oxidation of HHCB during the activated sludge process. The burning of dewatered sludge, employed by Plant B, efficiently removed all of the polycyclic musks that we analyzed. Overall, adsorption and deposition of polycyclic musks to sludge can constitute a major removal mechanism for polycyclic musks in WWTPs. Incineration of sludge is an efficient treatment process by which to reduce the discharge of polycyclic musks to the terrestrial environment.

Table 2. Concentrations (µg/g dry weight) of polycyclic musks in sludge collected in 2005 from two wastewater treatment plants, Plant A in Kentucky and Plant B in Georgia.

	HHCB				AHTN				HHCB-lactone			
Plant A	OD	RAS	CC	DP	OD	RAS	CC	DP	OD	RAS	CC	DP
Winter (Feb 9)	9.8	11	NA	2.0	3.1	2.8	NA	1.2	5.5	4.9	NA	5.6
Spring (May 26)	7.7	6.9	NA	NA	1.8	1.4	NA	NA	3.4	2.6	NA	NA
Summer (Aug 8)	6.7	2.9	7.5	5.4	1.4	0.53	1.7	1.6	4.0	1.3	3.6	5.8
Fall (Sep 9)	2.9	3.0	NA	21	1.2	1.0	NA	6.7	1.0	0.89	NA	10
Mean	6.8	6.0	7.5	9.5	1.9	1.4	1.7	3.1	3.5	2.4	3.6	7.2
Plant B	MLSS	RAS	CC	BCC	MLSS	RAS	CC	BCC	MLSS	RAS	CC	BCC
Spring (Apr 29)	18	26	36	NA	3.6	5.6	7.2	NA	7.0	7.0	17	NA
Summer (Aug 8)	22	21	2.1	<0.02	4.5	4.1	0.36	<0.02	7.3	5.9	0.81	<0.05
Fall (Sep 26)	19	11	2.8	<0.02	3.7	2.7	0.62	0.021	7.8	4.0	0.67	<0.05
Mean	20	19	14	<0.02	4.0	4.1	2.7	0.021	7.4	5.6	6.3	<0.05

NA; not available, OD; oxidation ditch, RAS; reactivated sludge, CC; sludge compressed cake, DP; final sludge in dry pond, MLSS; aeration- mix liquid suspension solid, BCC; burned sludge compressed cake

Mass flow in WWTPs. Mass loadings were calculated based on average concentrations of polycyclic musks with the average daily flow of influent, primary, effluent, and solid wastes produced at the WWTPs (Fig. 1).   The daily inflow of musks calculated for HHCB, AHTN, and HHCB-lactone in our study was 40 g/day, 31 g/day, and 3.7 g/day for Plant A, and it was 29 g/day, 27 g/day, and 25 g/day for Plant B.   The outflow through effluent discharge into rivers for HHCB, AHTN and HHCB-lactone was 0.67 g/day, 2.0 g/day, and 3.5 g/day for Plant A, and it was 2.9 g/day, 7.4 g/day, and 20 g/day for Plant B. Although the daily inflow of wastewater into Plant B was about four-fold greater than that in Plant A, the mass flow of HHCB and AHTN in Plant A was slightly higher than the mass flow in Plant B.   Based on the estimated daily mass loading, the removal efficiencies of HHCB and AHTN in the two WWTPs can be calculated to range from 72 to 98%.   The removal efficiencies of polycyclic musks in WWTPs are similar to those reported earlier for activated sludge treatment process, in which HHCB and AHTN reductions of 99% and 98%, respectively [8], were found. The mass flow of HHCB-lactone increased or remained constant through the different stages of treatment process (Fig.1).   The daily discharge of HHCB-lactone to the rivers was 3.5 g from Plant A and 20 g from Plant B.

A mass loss of 32 g/day for HHCB and 26 g/day for AHTN, on average, was found in Plant A.   In other words, more than 70% of HHCB and AHTN entering this WWTP
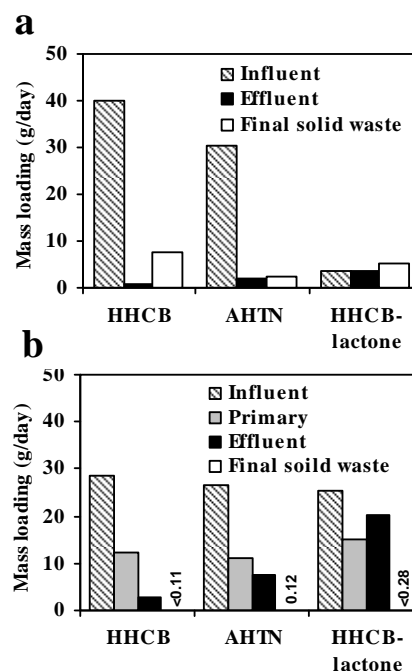

Fig. 1. Mass loading (g/day) of polycyclic musks in (a) Plant A and (b) Plant B.

were not detected downstream in effluent and sludge combined.   Biological and chemical transformation and volatilization are mechanisms of removal that can account for the loss of polycyclic musks in WWTPs.   We found a mass gain of 5.0 g/day for HHCB-lactone in Plant A.   HHCB-lactone could be produced by oxidation of HHCB in the treatment process.   However, the mass gain of HHCB-lactone in Plant A was only 16% of the mass loss of HHCB.   It is probable that HHCB is transformed into several breakdown products or conjugates in addition to HHCB-lactone.   Further studies are needed to elucidate mechanisms and pathways of transformation of polycyclic musks in WWTPs.   Volatilization can be a major mechanism of loss of polycyclic musks in WWTPs. The sludge is dewatered and burnt in Plant B. Concentrations of polycyclic musks decreased dramatically following incineration of sludge.   For Plant B, mass flow of total polycyclic musks from incinerated sludge was <0.5 g/day, a value was approximately 30 fold lower than that for Plant A (15 g/day in final solid). It has been recognized that disposal of sludge to the terrestrial environment through landfill and/or agricultural application can contribute to environmental release of polycyclic musks. The incineration of sludge substantially reduced the concentrations of polycyclic musks discharged to the terrestrial environment.

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