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Synthetic Musk Fragrances in a Conventional Drinking Water Treatment Plant with Lime Softening

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Abstract

Synthetic musk fragrances are common personal care product additives and wastewater contaminants that are routinely detected in the environment. This study examines the presence eight synthetic musk fragrances (AHTN, HHCB, ATII, ADBI, AHMI, musk xylene, and musk ketone) in source water and the removal of these compounds as they flow through a Midwestern conventional drinking water plant with lime softening. The compounds were measured in water, waste sludge, and air throughout the plant. HHCB and AHTN were detected in 100% of the samples and at the highest concentrations. A mass balance on HHCB and AHTN was performed under warm and cold weather conditions. The total removal efficiency for HHCB and AHTN, which averaged between 67% to 89%, is dominated by adsorption to water softener sludge and its consequent removal by sludge wasting and media filtration. Volatilization, chlorine disinfection, and the disposal of backwash water play a minor role in the removal of both compounds. As a result of inefficient overall removal, HHCB and AHTN are a constant presence at low levels in finished drinking water.

Keywords

polycyclic musk fragrances; PPCPs; persistent organic pollutants

Introduction

Synthetic musk fragrances are common additives in personal care products such as soaps, lotions, deodorants, and detergents (1). Their presence was first detected in the environment in 1981 (2) and they have since been detected in nearly all environmental compartments including water (2–6,7,8,9), air (10–12), sediment (4,6,13,14), aquatic organisms (15–18), and humans (15,19,20). They are released into the environment almost entirely as a result of wastewater discharges (18,21–27).

The use of synthetic fragrances began in early 20th century with the production of nitro-musks (4). Toxicity data later revealed the carcinogenic potential of musk xylene and musk ketone (28,29), in addition to a correlation between musk xylene concentrations and miscarriage in women (30). This data led to a ban of the compounds in Japan and industry-wide prohibition within the European Union (31). Because of concerns about the toxicity of nitro-musks, polycyclic musk compounds have been increasing in use (32) although little is known about chemical-specific U.S. fragrance consumption. HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8-hexamethylcyclopenta- γ -2-benzopyran (CAS 1222-05-5; Galaxolide), is listed by the USEPA

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as a High Production Volume chemical indicating that more than 1 million pounds produced or imported into the United States each year (33).

Despite the widespread and frequent use of polycyclic musk fragrances, limited ecological and human toxicity data are available. HHCB and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene; CAS 21145-77-7; Tonalide) bioconcentrate in aquatic biota (4) and have been measured in human blood (19), adipose tissue (34), and breast milk (35) (15,34). HHCB and AHTN have both shown weak estrogenic activity in human cells (36,37). Other studies have reported exclusively on the environmental risk assessment for AHTN and HHCB ((38,39)). None of these studies suggest that chronic exposure to low levels of polycyclic musk fragrances are harmful to humans and there are no water quality standards or limits of exposures defined for these compounds.

Although the main human exposure route for fragrances appears to be through frequent use of scented products (19,20), other routes such as the consumption of contaminated drinking water are likely. The objectives of this study were to quantify the removal and partitioning of eight synthetic fragrance compounds during conventional drinking water treatment with lime softening. Samples of water, indoor air from within the treatment plant, and waste sludge were analyzed for the presence of synthetic musk fragrances. The data was then used to analyze removal mechanisms through the construction of a mass balance model of the system's performance.

Materials and Methods

University of Iowa Water Treatment Plant

The venue for this study was the University of Iowa Water Treatment Plant. The plant is typical of Midwestern drinking water plants: it utilizes the Iowa River as its main water source, but has the capacity to draw from a groundwater well during times of high nitrate concentrations in the river. The plant can operate up to 6 million gallons per day (MGD), but typically operates around 3 MGD ($11,000 \text{ m}^3 \text{ d}^{-1}$). The main treatment processes are sedimentation using ferric sulfate for coagulation, slaked lime water softening, chlorine gas disinfection, and gravity filtration using anthracite, sand, and dual media filters (Fig 1). Table 1 expresses the hydraulic retention times for each of the individual treatment processes and the entire treatment process at various flow conditions.

Wastewater effluent is the primary source of fragrance compounds in surface water and the Iowa River is a recipient of treated wastewater. The National Pollution Discharge Elimination System (NPDES) permits upstream of Iowa City show that the Iowa River is subject to an average dry weather flow of 405 MGD and an average wet weather flow of 808 MGD of treated wastewater (40). At an average flow of 2,274 cfs, or 1470 MGD, the Iowa River is composed of approximately 30–55% treated wastewater (41). There are, however, no immediate sources of treated wastewater to the Iowa River directly upstream of the UI treatment plant.

Water, Air and Sludge Solids Sample Collection

Sample collection resulted in 14 water samples collected at each of 4 sampling points; 16 air samples collected throughout the plant; and 16 samples of solid sludge from the sedimentation and softening basins of the plant. Water samples were collected from the University of Iowa Water Treatment Plant in Iowa City, Iowa from October 2006 to June 2007 (Fig 1). Two 10 liter grab samples were collected of raw, sedimentation basin effluent, softener effluent, and finished drinking water on each sampling day. Passive air samplers equipped with polyurethane foam disk (PAS-PUF) were deployed in the interior of the water plant for 6–8 weeks from December 14 to February 5, 2007 and from May 26 to June 16, 2007. Polyurethane foam (PUF)

disks (Tisch Environmental TE-1014) were prepared for sampling by three 24-hour soxhlet extractions using hexane, acetone, and 1:1 acetone:hexane. We assumed air sampling rate of 2.5 m³/d as determined from previous studies in our laboratory (42). The PAS-PUF samplers were hung above major treatment processes (sedimentation basins, softeners, and gravity filters) approximately 3–6 m from the water surface depending on available anchors. The UI Water Plant produces two waste sludges as a part of the treatment process. Sedimentation sludge is a result of the coagulation, sedimentation, and settling processes and consists of matter settled from the raw river water. Softener sludge is a result of the water softening process and consists primarily of slaked lime. The softener sludge is also mixed with the clarified solids resulting from filter backwashes. Samples of the softener and sedimentation sludge were collected in combusted amber jars directly from the waste hauling truck immediately after it was loaded in order to measure synthetic fragrance content of the sludge immediately prior to leaving the water plant.

Sample Analysis

Once collected, water samples were immediately returned to the lab, spiked with 52 ng of surrogate standard, labeled musk xylene (D15), in 100 μ L acetone, and filtered using Whatman high-purity quartz microfiber filters. Sample extraction was performed using Waters Oasis® HLB 12cc 500 mg Solid Phase Extraction Cartridges. The samples were eluted with 10 mL acetone then 10 mL hexane, concentrated to approximately 0.75 mL using a Caliper LifeSciences TurboVap II Workstation Concentrator, and injected with 48 ng of the labeled internal standard AHTN (D3) in 100 μ L hexane.

PUFs from passive air samplers were extracted using an ASE Dionex 300 Accelerated Solvent Extractor. PUF disks were rolled, inserted into 100 mL sample cells, spiked with 52 ng of labeled surrogate standard musk xylene (D15), in 100 μ L acetone, and capped with fiber filters at each end. Extractions were made at 1500 PSI with a 1 cycle, 5-minute static extraction at 100 °C. Acetone:hexane (50:50, v:v) was used as the extraction solvent. Extracts of approximately 60 mL were collected and concentrated to approximately 0.75 mL.

The method used for sludge extraction has been described elsewhere (43,44). Briefly, each sample was weighed and dried at 100 °C for approximately 1–3 hours. A aliquot of 50 g solids mixed with combusted Ottawa sand was spiked with 52 ng of labeled musk xylene (D15) in 100 μ L acetone and extracted twice by accelerated solvent extraction (Dionex ASE-300) with a 1:1 isopropyl alcohol:water solution at 120 °C and with a 4:1 isopropyl alcohol:water solution at 200 °C. The collected extracts were then passed through a solid phase extraction cartridge (Waters Oasis® HLB 12cc 500 mg 6cc 1 g Florisil). Blanks were extracted simultaneously by loading cells with combusted Ottawa sand and spiking them with 52 ng of surrogate standard, musk xylene (D15), in 100 μ L acetone. All glassware used throughout collection and extraction procedures was combusted for a minimum of 4 hours at 450 °C prior to use.

All sample extracts were analyzed on an Agilent Technologies 6890N Network GC system with a Hewlett Packard 5973 Mass Selective Detector using selected ion monitoring (SIM) and electron impact mode. For HHCB and AHTN, ions 243 and 258 (m/z) were used for quantification and confirmation, respectively. Further details can be found in Peck and Hornbuckle (3).

All solvents used were Fisher Scientific Pesticide Grade (Fair Lawn, NJ). Standards for the synthetic musks were purchased from Promochem (Teddington, UK): HHCB; AHTN; 4-acetyl-1,1-dimethyl-6-tert-butylindane (ADBI), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI; CAS 15323-35-0; Phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-iso-propylindane (ATII; CAS 68857-95-4 ; Traseolide), 6,7-dihydro-1,1,2,3,3-pentamethyl-4-(5H)-indanone (DPMI; CAS 33704-61-9; Cashmeran), 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (musk

xylene; CAS 81-15-2) and 4-tert-butyl-3,5-dinitro-2,6-dimethylacetophenone (musk ketone; CAS 81-14-1). Labeled compounds, AHTN (D3) and musk xylene (D15) were also obtained from Promochem.

Results

Quality Control

Surrogate standard spikes were used to monitor extraction efficiencies and consistent laboratory practices. The average recoveries for musk xylene (D3) for cold weather water samples, warm weather water samples, passive air samples, sedimentation sludge samples, and lime sludge samples were $64 \pm 5\%$, $81 \pm 8\%$, $49 \pm 7\%$, $49 \pm 13\%$, and $55 \pm 8\%$, respectively. Method blanks exhibited low amounts of the fragrance compounds, relative to that in the samples. Average sample mass to blank ratios ranged from 19:1 for the river water samples to 4:1 for the Clearwell water samples. There were no significant blank contaminations except for DPMT, which contaminated the plastic tubing of 100% of samples and was excluded from further analysis. Additionally, a recovery test was conducted for each musk in the study by spiking a standard solution directly onto the SPE media. With the exception of DPMT, no recoveries were less than 90% (45). A breakthrough test was also conducted of the SPE media and showed no detectable breakthrough ((45).

Method detection limits (MDLs) were calculated using a series of 15 diluted samples to determine the minimum limit to which the compounds could be accurately quantified. A t-test value of 2.145 was used, which represented 14 degrees of freedom and 97.5% confidence. MDLs were different for each compound but all below 0.25 ng/L.

Concentrations in Water, Air and Settling Solids

Water samples were collected during October and November 2006, February 2007, and during May and June 2007. The concentrations in the raw Iowa River water ranged from 1 to 20 ng L⁻¹ for HHCB and 0.5 to 10 ng L⁻¹ for AHTN. Concentrations for the other polycyclic musks were more than an order of magnitude lower (Table 2). All reported water concentrations reflect dissolved phase concentrations. We observed significant variability in the concentration of fragrance compounds in the influent water, with higher concentration of fragrances in the influent river water during cold weather. Although the data is sparse, the elevated concentrations appear related to periods of heavy precipitation which may have caused overflow of untreated sewage or reduction in pollutant treatment upstream. In any case, the concentrations we report are lower than values reported for more populated river watersheds (8,9,46,47).

The concentrations of the detected compounds decreased over the course of drinking water treatment (Table 2). However, the concentrations of ADBI, AHMI, MX, MK, and ATII were near the detection limit and highly variable and so we could not determine the removal efficiency. The concentrations of HHCB and AHTN were consistently above detection limits and so the plant performance was assessed for these two compounds (Fig 2). For the cold weather samples, calculated percent removals for AHTN and HHCB were 79% and 70%, respectively. In warm weather, we observed percent removals of 89% and 67% for AHTN and HHCB respectively (Table 3). The removal efficiency of AHTN at the Iowa plant is similar to the 71% reported by Stackelberg et al. (2007) for a drinking water plant in an urban watershed (47). The removal efficiency of HHCB at the Iowa plant was less than Stackelberg et al. reported. They found 100% average removal of HHCB.

Air samples were collected in warm and cold weather within the water plant to determine the potential for volatilization from the treatment processes. Many fragrances were not detected

in air during the cold weather sampling (Table 4). AHTN and HHCB were detected in every air sample collected during the warm weather sampling. ATII and MK were frequently detected during warm weather sampling. Sample mass to blank mass ratios for these samples ranged from 6.2 to 63. The air concentrations above the treatment processes appeared to correlate with water turbulence. The lowest concentrations were seen in the sedimentation basin (quiescent conditions) and the highest above water softeners (mixing hot slaked lime). Above the filters (quiescent conditions), the concentrations fell in the middle, perhaps as a result of the influence of volatilization occurring from the softeners in the same room.

AHTN and HHCB were detected in all 16 of the sedimentation and lime sludge solid samples at levels that exceeded method blanks by more than a factor of 3. In general, higher concentrations of both compounds were found in the sedimentation sludge than in sludge that resulted from lime softening (Table 5).

Discussion

Two steady-state mass balance model analyses were performed to assess the role of volatilization, adsorption, sedimentation, chlorine oxidation, and filtration in the removal of synthetic musk fragrances from finished drinking water under warm and cold weather conditions. Figure 3 shows the mass balance with respect to the treatment process and loss mechanisms. Photolysis and biodegradation were not considered significant under the residence time and environmental conditions present in the treatment plant.

The mass flow of fragrances entering (F_{in} , mg day⁻¹) and leaving the plant (F_{out} , mg day⁻¹), respectively, is a function of the flow in and out of the plant (Q_{in} and Q_{out} is 9000 and 11,000 m³ d⁻¹ for cold and warm weather, respectively), the concentration of the fragrances in the river (C_{river}) and the clearwell reservoir at the exit point of the plant ($C_{clearwell}$), and the flow used for two filter backwashes per day ($Q_s = 40,000$ gal/d).

$$F_{in} = Q_{in} C_{river} \quad \text{Equation 1}$$

$$F_{out} = (Q_{in} - Q_s) C_{clearwell} + Q_s C_{clearwell} = Q_{in} C_{clearwell} \quad \text{Equation 2}$$

The net volatilization flux of fragrances from the water ($J_{a/w}$, ng m⁻² day⁻¹) was calculated as a function of the overall mass transfer coefficient (k_{ol} , m d⁻¹), the average water-phase concentration (C_w , Table 2), the average gas-phase concentration (C_a , Table 4), and H is the dimensionless Henry's constant (3), and A is the surface area of the treatment process (Fig 3). The mass transfer coefficient, k_{ol} , was calculated as reported elsewhere and assumed 1 m s⁻¹ for the windspeed and 10 °C and 30 °C for cold and warm weather samples, respectively (48). The mass flow is equal to the net volatilization flux multiplied by the water surface area.

$$J_{a/w} = k_{ol} \left(C_w - \frac{C_a}{H} \right) A \quad \text{Equation 3}$$

The loss of fragrances due to sedimentation and sorption to waste sludge is a function of the volume of sludge leaving each day (V_{sludge}) and the fragrance concentration in the sedimentation or lime softening sludge (C_{sludge} , ng m⁻³). Each day approximately 10 m³ of

sedimentation and 45 m³ of lime softening sludge leave the University of Iowa Drinking Water Treatment Plant.

$$F_{sludge} = V_{sludge} C_{sludge} \quad \text{Equation 4}$$

Gibs et al. (2007) described the effect of chlorine residuals on the concentrations of AHTN where R represents the percent mass removed by chlorine residuals (49). As a result of these findings, we assumed that the effect of residual chlorine on the presence of HHCB and AHTN led to 10% mass removal of AHTN (R=0.10) and zero removal for HHCB (R= 0):

$$\text{Chlorine Rxtn} = Q_{in} C_{softener} R \quad \text{Equation 5}$$

where $C_{softener}$ is reported in Table 2.

Filtration losses were calculated by measuring the presence of fragrances in backwash water and solids. Backwash solids are clarified and combined with softener solids prior to leaving to plant and are thus accounted for in measurements of exiting softener solids. Clarified backwash water is discharged directly into the Iowa River and is assumed to have the same concentration as its origin at the clearwell.

Mass Balance Results

The largest mass removal in warm weather is due to lime sludge removal, including adsorption to lime solids added for water softening and solids captured by the filter media and subsequently collected as backwash solids. Lime sludge removal accounts for 78% of the total HHCB removal and 58 % of the AHTN removal. It is a much larger loss mechanism than sedimentation because the mass of sludge produced. Three to six times as much sludge is produced from the softening and backwash processes than is produced by sedimentation. The importance of the softening and backwash solids removal is consistent with the largest reductions in the water concentrations observed between the water softener and filtration stages. It appears that HHCB and AHTN adsorb to softener solids during softening and are removed by the constant draw off of waste lime sludge and/or to the suspended solids during filtration. Because the filter media (sand and anthracite) is designed to remove particles through the physical process of straining rather than an adsorption process, the removal occurring in that process is likely a result of the removal of suspended sediment containing adsorbed synthetic fragrance compounds. After lime sludge removal, chlorination is an important removal mechanism for AHTN (~20% of the total removal) but is negligible for HHCB. Ferric sludge removal and volatilization is the next most important mechanism (~10% for both mechanisms and compounds). The practice of disposing of clarified backwash water has little effect on removal.

The calculated loss of HHCB and AHTN were compared to the overall loss determined from the measurements of the influent and effluent concentrations and water flow. During warm weather, the model accounted for approximately 77% and 49% of the respective mass of HHCB and AHTN lost between entering and leaving the plant. During cold weather, the model accounts for 67% and 57% of the HHCB and AHTN in the plant, respectively. A major reason for the discrepancy is that the concentrations and mass flow of fragrance compounds into the plant was not constant and we did not attempt to sample the same parcel of water as it moved through the plant. Other likely explanations include heterogeneity in the concentration of fragrances in the lime and ferric sludge solids, imprecision in the estimate of oxidation from chlorine, and underestimation of volatilization during turbulent conditions. Nevertheless, the model is helpful for understanding the relative importance of various processes for the removal

of polycyclic musk fragrances within a typical drinking water plant. Additional examination of the plant removal efficiencies should focus on how operations of the plant could be manipulated to improve overall removal of these compounds from finished drinking water. For example, our study has shown that sorption to particles associated with lime softening and filter backwash is more important than sorption to particles associated with sedimentation through addition of ferric salts. This may be a function of the relative magnitude of surface area in suspension or due to contact time. Examination of these operating parameters is needed to improve the removal efficiency of these compounds and other pharmaceuticals and personal care products from drinking water.

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Figure 1.
University of Iowa Water Treatment Plant diagram and water sampling locations (red circles)

Figure 2. Average concentrations of AHTN and HHCB measured at four locations in the drinking water plant. Each location was sampled fourteen times throughout the year ($n = 14$). The error bars represent the 95% confidence intervals.

Figure 3.
Water plant mass balance

Table 1

UI Water Plant process hydraulic retention times based on plant flow

		Hydraulic Retention Times (Hours)					
		2	2.5	3	3.5	4	4.25
Flow (MGD)							
Sedimentation Basin		5.7	4.6	3.8	3.3	2.8	2.7
Softener		3.2	2.6	2.1	1.8	1.6	1.5
Filter & Recarbonation Chamber		2.3	1.8	1.5	1.3	1.1	1.1
TOTAL		11.2	9	7.4	6.4	5.5	5.3

Table 2Aqueous phase concentrations of analytes (average $\pm 95\%$ confidence interval)

Compound	Aqueous Phase Concentration (C_w , ng L ⁻¹) N = 14			
	River (C_{river})	Sedimentation Basin (C_{sed})	Softener (C_{softener})	Clearwell ($C_{\text{clearwell}}$)
DPMI ^a	180 $\pm$ 80	71 $\pm$ 25	130 $\pm$ 71	9.9 $\pm$ 2.8
ADBI	ND	0.02 $\pm$ 0.03	ND	ND
AHMI	0.8 $\pm$ 1.4	0.71 $\pm$ 1.2	0.59 $\pm$ 1.0	0.06 $\pm$ 0.07
HHCB	7.3 $\pm$ 2.7	6.9 $\pm$ 2.5	4.6 $\pm$ 1.9	2.2 $\pm$ 0.72
MX	0.15 $\pm$ 0.11	0.07 $\pm$ 0.07	0.03 $\pm$ 0.04	ND
AHTN	2.8 $\pm$ 0.95	2.8 $\pm$ 0.87	2.7 $\pm$ 0.68	0.51 $\pm$ 0.20
MK	0.06 $\pm$ 0.07	0.06 $\pm$ 0.11	0.04 $\pm$ 0.08	ND
ATII	0.07 $\pm$ 0.14	ND	ND	ND

^aThe elevated concentrations of DPMI are due to contamination and do not represent concentrations present within the water plant.

Table 3

Comparison of AHTN and HHCB average total removal for warm and cold weather conditions

	Average Concentration (C_w , ng L ⁻¹)			
	Cold Weather Samples (n=9)		Warm Weather Samples (n=5)	
	AHTN	HHCB	AHTN	HHCB
Influent	3.0	8.0	2.5	5.7
Effluent	0.62	2.4	0.26	1.9
% Removal	79%	70%	89%	67%

Table 4

Warm weather passive air sample average concentrations and 95% confidence intervals

Compound	Gas phase concentrations above each process ($\mu\text{g m}^{-3}$)			
	Sedimentation Basins	Flocculation Basins	Water Softeners	Gravity Filters
ADBI	ND	ND	ND	ND
AHMI	ND	ND	ND	ND
HHCb	160 ± 30	220 ± 50	1200 ± 210	900 ± 210
MX	ND	ND	ND	ND
AHTN	70 ± 10	90 ± 20	480 ± 70	380 ± 100
MK	190 ± 380	180 ± 350	20 ± 30	160 ± 280
ATII	ND	ND	100 ± 60	30 ± 50

Table 5

Average concentration of dry sludge, including, 95% confidence intervals. The sludge samples were approximately 92% water by volume.

Compound	Sedimentation Sludge Average Concentration (ng/g d.w.)	Lime Sludge Average Concentration (ng/g d.w.)
HHCB	9.9 ± 4.2	4.8 ± 1.0
AHTN	3.5 ± 1.1	1.3 ± 0.26

Table 6

Mass balance results

	Warm Weather Model		Cold Weather Model	
	HHCB	AHTN	HHCB	AHTN
MASS IN (mg/d)				
Inflow	64 ± 14	28 ± 6.9	73 ± 36	27 ± 12
MASS OUT (mg/d)				
Effluent	20 ± 10.3	3.0 ± 0.4	21 ± 7.2	5.6 ± 2.5
Lime Sludge	27 ± 7.2	7.2 ± 1.7	27 ± 7.2	7.2 ± 1.7
Ferric Sludge	3.7 ± 0.4	1.3 ± 0.2	3.7 ± 0.4	1.3 ± 0.2
Volatilization	3.4	1.6	4.1	1.5
Chlorine Oxidation	0.0	2.1 ± 1.0	0.0	2.3 ± 0.8
Backwash water	0.3 ± 0.2	0.03 ± 0.0	0.4 ± 0.1	0.1 ± 0.04
Mass Out: Total	54 ± 14	15 ± 2.0	56 ± 14	18 ± 5.5