Published in final edited form as:

Environ Sci Technol. 2006 September 15; 40(18): 5629–5635.

Synthetic Musk Fragrances in Lake Erie and Lake Ontario Sediment Cores

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Abstract

Two sediment cores collected from Lake Ontario and Lake Erie were sectioned, dated, and analyzed for five polycyclic musk fragrances and two nitro musk fragrances. The polycyclic musk fragrances were HHCB (Galaxolide), AHTN (Tonalide), ATII (Traseolide), ADBI (Celestolide), and AHMI (Phantolide). The nitro musk fragrances were musk ketone and musk xylene. Chemical analysis was performed by gas chromatography/mass spectrometry (GC/MS) and results from Lake Erie were confirmed using gas chromatography/triple-quadrupole mass spectrometry (GC/MS/MS). The chemical signals observed at the two sampling locations were different from each other due primarily to large differences in the sedimentation rates at the two sampling locations. HHCB was detected in the Lake Erie core while six compounds were detected in the Lake Ontario core. Using measured fragrance and ²¹⁰Pb activity, the burden of synthetic musk fragrances estimated from these sediment cores is 1900 kg in Lake Erie and 18000 kg in Lake Ontario. The input of these compounds to the lakes is increasing. The HHCB accumulation rates in Lake Erie for 1979-2003 and 1990-2003 correspond to doubling times of 16 ± 4 yr and 8 ± 2 yr, respectively. The results reflect current U.S. production trends for the sum of all fragrance compounds.

Introduction

Synthetic musk fragrances are found in many common household detergents, soaps, perfumes, shampoos, air fresheners, and cosmetics (1,2). Originally introduced as more economical substitutes for natural musk fragrances obtained from the musk deer and musk ox (3), synthetic musk fragrance usage increased throughout the 20th century and was estimated to be 8000 t/year in 1996 (4). In Europe in 1995 the combined usage rate of the two most commonly used synthetic musk compounds, HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran) and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene), was about 15.5 mg/day (5). Additionally, the U.S. Environmental Protection Agency lists HHCB as a high production volume chemical (more than 1 million pounds produced or imported into the United States each year) (6).

The estimated consumption of fragrance chemicals in the United States, including synthetic musk fragrances, benzenoids, terpenes, and other fragrance compounds, has more than doubled

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Brief Synthetic musk fragrances accumulate in Great Lakes sediment and the concentration of the most prevalent, HHCB, has roughly tripled over the past two decades.

Supporting Information Tables containing structures, tradenames, and selected physical-chemical properties of the synthetic musk fragrances are provided in the Supporting Information. Additional information about the sediment subcores and methods are also presented.

since 1990 (7). The consumption of synthetic musk fragrances in the United States increased by 25% between 1996 and 2000, going from an estimated 5200 metric tons to 6500 metric tons over this time (7). The growth in synthetic musk fragrance consumption in the United States between 1996 and 2000 was larger than the 15% growth in total fragrance chemicals during these years (7). It is clear that the use of synthetic musk fragrances in the United States has been increasing and it is likely that the rate of increase of the synthetic musk fragrances is larger than for total fragrance chemicals, for which a longer history of use is available.

Synthetic musk fragrances (musk xylene and musk ketone) were first detected in the aquatic environment in the Tama River near Tokyo, Japan in 1981 (8). Since the initial discovery of synthetic musk fragrances in the environment, they have been detected in water (2,3,9-14), air (15-17), biota (2-4,18-23), sewage influent and effluent (2,9,14,24,25), and sorbed to suspended particulate matter (10,26), sediment (3,18,27), and sewage sludge (28-30). Environmental concentrations of synthetic musk fragrances in the United States have been limited to only a few studies (11,15,24,25). At the time of this study, there were no published lacustrine sediment concentrations for synthetic musk fragrances in the United States. There has been one report of HHCB and AHTN in dated sediment cores from riparian wetland sediments of the Lippe River in Germany (27).

The lack of data for the United States is significant because the distribution of musk usage in the United States is believed to be different from usage in Europe and Japan where considerably more work has been done. Japan banned the use of musk xylene in the 1980s, and the German cosmetic and detergent industry agreed upon a voluntary partial phase-out of musk xylene in 1993 (2). As a result of the recent bans and reductions, the environmental concentrations of the nitro musks are decreasing in samples from Europe and Japan. While the total synthetic musk usage in Japanese and European markets is not decreasing, the markets are shifting from nitro musks in favor of polycyclic musks. The same shift is not believed to be occurring in North America (23). Because of probable differences in usage among the individual synthetic musk compounds in the United States and abroad, measurement of these compounds in environmental compartments in the United States is essential to properly assess environmental fate and exposure.

The objectives of this study were to measure seven synthetic musk fragrances in sediments from Lake Erie and Lake Ontario and determine the temporal trend of their input into the lake systems. Five of the target compounds were polycyclic musk fragrances: HHCB, AHTN, ADBI (4-acetyl-1,1-dimethyl-6-tert-butylindan), AHMI (6-acetyl-1,1,2,3,3,5-hexamethylindan), (5-acetyl-1,1,2,6-tetramethyl-3-iso-propylindan), and ATII (5-acetyl-1,1,2,6-tetramethyl-3-iso-propylindan). Two of the compounds were nitro musk fragrances: musk xylene (1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene) and musk ketone (4-tert-butyl-3,5-dinitro-2,6-dimethylacetophenone). Additional information (including trade names, structures, and physical-chemical properties) about these compounds is provided in the Supporting Information. Patterns of synthetic musk fragrance accumulation in these sediments over time have been evaluated with ^{210}Pb sediment dating methods.

Methods

Chemicals

Pesticide grade solvents (hexane, acetone, dichloromethane, and methanol), sodium sulfate, 100-200 mesh silica gel, copper filings, and hydrochloric acid were obtained from Fisher Scientific (Fair Lawn, NJ). Pentachloronitrobenzene was obtained from Chem Service (West Chester, PA). HHCB, AHTN, ADBI, AHMI, and ATII were obtained from Promochem (Teddington, UK). Musk xylene and musk ketone were obtained from Sigma-Aldrich (St.

Louis, MO). The deuterated polycyclic aromatic hydrocarbon fluoranthene-*d*₁₀ was obtained from Cambridge Isotope Laboratories (Andover, MA).

Sediment Sample Collection

Sediment samples were collected from Lake Ontario and Lake Erie aboard the U.S. Environmental Protection Agency *R/V Lake Guardian* during August 7-12, 2003. The sediment sampling locations in each lake are shown in Figure 1. A 30 cm × 30 cm × 52 cm sediment box corer was used to bring undisturbed sediment from the lake bottom to the surface. Each box core was then sub-cored (31-34). Four to six polycarbonate tubes (7.6 cm diameter × 60 cm long) were inserted into the box core sediment and removed under vacuum to insure a solid, undisturbed column of sediment. Sections of ~2 cm thickness were collected as the sediment column was slowly extruded from the polycarbonate tube with a hydraulic press. Each sediment section was collected, stored, and transported in precleaned and weighed amber glass jars. The surrogate standard (100 µL of a 2.6 ng/µL fluoranthene-*d*₁₀ solution in hexane) was added to each sample prior to sample transport. The Lake Erie and Lake Ontario cores were divided into 37 and 23 sections, respectively. The water content, cumulative dry mass and other information for each sediment core section are listed in the Supporting Information.

Sediment Dating

Dating of the Lake Erie core has been published previously (35). The Lake Ontario core was dated by investigators at the University of Wisconsin-Milwaukee. The activity of ²¹⁰Po and ²⁰⁹Po was measured by alpha spectrometry and the activity of ²¹⁰Pb was calculated from these count rates. The sedimentation rate for each sediment core was then determined from the ²¹⁰Pb of the core sections using the rapid steady-state mixing model (31-34,36-38).

Sample Extraction and Preparation

All sediment samples were weighed and thoroughly mixed upon return from the sampling expedition. A ~4 g (wet weight) aliquot from each sample was dried at 105 °C for at least 24 hours to determine the dry weight of each sample. The sediment extraction method was based on a combination of extraction methods previously utilized in other studies (24,36). Glassware, glass wool, glass beads, and sodium sulfate used throughout the extraction procedure were combusted at 450 °C for a minimum of 4 hours. Using a solvent cleaned mortar and pestle, one-third to one-half of each sediment sample was mixed with sodium sulfate to remove water from the sediment sample. The dried mixture was transferred to a Soxhlet extractor lined with glass wool. The extract was collected in a 1000 mL round bottom flask containing glass beads and sodium sulfate. The dried sediment mixture was extracted for 24 hours with ~500 mL dichloromethane. The ~500 mL dichloromethane extract was reduced to ~2 mL and exchanged into hexane with successive 20-mL hexane additions using a rotary evaporator (Rotovap Model R-114, Büchi, Switzerland). Sulfur was removed from the resulting ~4 mL hexane extract with the addition of copper filings activated with concentrated hydrochloric acid. The extract with copper filings was capped and stored at -20 °C overnight.

Column chromatography was used to remove interferences from the sediment extracts. The stationary phase consisted of an 18 cm column of 3% deactivated 100-200 mesh silica gel packed as a slurry in hexane. The silica gel was conditioned with 50 mL of hexane prior to addition of a sample extract. Three 50 mL eluent fractions were collected in series: hexane, dichloromethane, methanol. The dichloromethane fraction was reduced to ~100 µL using rotary evaporation and a nitrogen evaporation system (N-EVAP Model 111, Organomation Associates, Inc., Berlin, MA). The internal standard (100 µL of a 2.16 ng/µL solution of pentachloronitrobenzene in dichloromethane) was added and the resulting solution was transferred to a 200 µL glass insert contained within a 2 mL amber autosampler vial.

Sample Analysis by GC/MS and GC/MS/MS

All samples were analyzed by gas chromatography coupled to a mass spectrometer (GC/MS). Sediment core LE15M was analyzed with a ThermoFinnigan GCQ with electron ionization and an ion trap mass detector. Sediment core ON33M was analyzed with an HP6890GC/5973MSD with electron ionization and a quadrupole mass detector. A 30-m 5% phenyl methyl siloxane capillary column (HP-5MS; 0.25 mm I.D., 0.25 μ m film thickness) was used for all analyses. The same temperature program was used with both instruments. The initial oven temperature (90 °C) was held for 2 min. This was followed by a 10 °C/min ramp to 150 °C, then 1.5 °C/min to 170 °C, and finally 30 °C/min to 300 °C. The final temperature (300 °C) was held for 7 min (20 min with the ion trap instrument). A gas chromatography-triple quadrupole mass spectrometry (GC/MS/MS) method was developed and used to confirm the results for the Lake Erie sediment core. Methods for the synthetic musk fragrance analysis using ion trap MS/MS have been previously reported (28,39), however, this is the first report of a triple-quadrupole method for these compounds. A short discussion of this method is provided in the Supporting Information. The GC/MS/MS system consisted of an Agilent 6890 gas chromatograph and a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. The compounds, quantification ions, and transitions are listed in the Supporting Information.

Compounds were quantified using the internal standard method. Synthetic musk fragrance concentrations were corrected using the recovery of fluoranthene- d_{10} and the recovery of each musk compound from recovery experiments. The recovery of the individual musk compounds in recovery experiments ranged from 63% for HHCB to 86% for musk ketone. The fluoranthene- d_{10} recovery in samples was $62\% \pm 23\%$. Five sections from the Lake Erie core (19-22 and 37 in Table S4) have been excluded from further analysis due to low (1-2%) recoveries of fluoranthene- d_{10} .

The concentrations in Lake Erie core samples were blank corrected using the average mass of each compound found in 4 method blanks. The limits of detection (LOD) for the Lake Erie core were estimated from the standard deviation ($3 \times \text{SD}$) of these measured masses and the average dry sediment mass extracted (25 g). The LODs in the Lake Erie core ranged from 0.025 ng/g for ADBI to 0.15 ng/g for AHTN. The sediment in the lower eighteen sections of the Lake Ontario sediment should not have been exposed to ambient synthetic musk fragrances because they were deposited prior to the use of these compounds. The top five sections were blank corrected using the bottom 18 sections as matrix blanks. The LODs for this core were defined as $3 \times \text{SD}$ of the concentrations measured in these sections, or from the lowest calibration level and the average dry mass extracted for compounds not found in these lower sections (musk xylene, ATII, ADBI, and AHMI). The LODs for the Lake Ontario core ranged from 0.06 ng/g for ATII to 5.1 ng/g for HHCB. The determination of separate LODs for each core is warranted because the cores were processed at different times and with different laboratory personnel. In further analyses, compounds not detected are given a concentration of zero. The minimum sample to blank ratio for samples with concentrations above the LOD was 2.6 for HHCB.

Results and Discussion

Sedimentation Rate and Sediment Dating

The vertical profile of ^{210}Pb activity in the Lake Ontario sediment core is shown in the supporting information. The background (supported) ^{210}Pb activity was reached within the top 10 cm (3 g/cm^2) of the Lake Ontario core and was 0.99 pCi/g. The sedimentation rate (w) was determined from the unsupported ^{210}Pb activity [$A(z)$; the supported activity subtracted from the measured activity], in each core section with cumulative dry mass, z (g/cm^2), and

the ^{210}Pb decay constant [λ ; 0.0311 yr^{-1}] using Equation 1, where A_m is the activity at the sediment surface.

$$A(z) = A_m e^{-(\lambda z/w)} \quad \text{Equation 1}$$

The sedimentation rate in this core was $0.027 \text{ g/cm}^2\text{-yr}$.

The focusing factor (FF) is used to describe the enhanced or reduced sedimentation at a particular location relative to the lake wide average. A focusing factor greater than one indicates a location with greater than average sedimentation. The focusing factor was calculated with Equation 2 and was 1.7 for the Lake Ontario core.

$$FF = \frac{A_m w}{34.4 \lambda} \quad \text{Equation 2}$$

The sedimentation rate and focusing factor for the Lake Erie core were $0.73 \text{ g/cm}^2\text{-yr}$ and 7.9, respectively (35). The sedimentation rates and focusing factors for the two cores evaluated in this study are listed in Table 1 with values for other locations within Lake Erie and Lake Ontario from other reports. The sedimentation rate in the Lake Ontario sediment core reported here is slightly lower than reported for other locations in the lake, but both the sedimentation rate and focusing factor are comparable to previous studies. The sedimentation rate and focusing factor for the Lake Ontario core are considerably larger than reported for other locations in Lake Erie. Since the Lake Erie sediment was collected from a high deposition zone, a highly resolved temporal chemical signal was obtained in Lake Erie relative to the Lake Ontario sediment core.

From the sedimentation rates determined for each sediment core, the subcore sections were assigned dates based on the cumulative mass represented by each section. The Lake Erie core represented sediment deposited from 1974 at the bottom of the core to the sampling year (2003). Each sample from the Lake Erie core was a composite of sediment deposited over 0.7 ± 0.3 years. Because of more compaction at the bottom of the core, the bottom sections tended to have higher masses and consequently represented longer accumulation (~ 1 year) than sections toward the top of the core (~ 0.5 year). The Lake Ontario sediment core spanned a much larger time period. The top seven samples in this core covered sediment accumulation since 1895. Each sample represented 26 ± 7 years of sediment accumulation. The top sample covered about 9 years of accumulation.

Synthetic Musk Fragrance Concentrations

Only HHCB was found in Lake Erie sediment above the LOD while six compounds were detected in the Lake Ontario sediment. The HHCB concentrations in Lake Erie were about an order of magnitude lower than those found in Lake Ontario. HHCB was measured at concentrations at least an order of magnitude higher than all other compounds in Lake Ontario. Assuming that the relative abundance of the synthetic musk fragrances is consistent between the two sediment cores, the concentrations of all synthetic musk fragrances besides HHCB in the Lake Erie core are expected to be lower than the detection limits for this study.

The concentration profile for HHCB in Lake Erie is shown in Figure 2. It is evident by inspection of Figure 2 that the HHCB concentrations in this core track the U.S. consumption of fragrance materials over the past 2-3 decades. HHCB concentrations in Lake Erie ranged from 0.3 ng/g to 3.3 ng/g . These concentrations are considerably lower than those reported in suspended sediments from European rivers [80 ng/g - 14000 ng/g (10,26)] and a sewage pond sediment [75 ng/g – 160 ng/g (4)]. The Lake Erie concentrations are similar to the lower

concentrations measured in river sediment in Germany [$< \text{LOD}$ -3600 ng/g (3,10)]. The surficial concentration of HHCB was about an order of magnitude lower than the concentration of nonabrominated diphenyl ether (BDE-209) (39 ng/g) and similar to the sum of 12 other polybrominated diphenyl ethers (1.1 ng/g) in the surface sediment at this same location (35).

The concentration profile for each synthetic musk fragrance in Lake Ontario is shown in Figure 3 and the surface concentrations are listed in Table 2. The HHCB concentrations measured in Lake Ontario were higher than in Lake Erie, but were also similar to the lower concentrations measured in river sediments in Germany (3,10). Comparisons of the other compounds detected in the Lake Ontario core to these previous studies are similar. The decrease in sediment concentrations since 1980 of musk xylene and AHMI indicate a decrease in use of these compounds. This supports the hypothesis that nitro musk compounds are being phased out in favor of the polycyclic musk fragrances. Additionally, these data appear to indicate that there is also a shift away from the use of AHMI. Concentrations in the Lake Ontario core observed prior to 1945 may be due to sediment mixing, sampling artifacts, or laboratory contamination. The cause for the drop in the HHCB concentration at the top of the Lake Ontario core is unclear. Possible explanations include mixing at the sediment surface or differences in sediment properties at the sediment surface relative to the buried sediment. The surficial sediment had a larger moisture content than the underlying sediment.

The major source of synthetic musk fragrances to the Great Lakes is wastewater treatment plant effluent (15). Differences in concentration between the two sediment cores are likely due to differences in distance to sources — principally wastewater treatment plant outfalls. The Lake Ontario sediment was collected in close proximity to the Toronto metro area while large urban areas are further from the sampling location in Lake Erie. Other factors that could influence the sediment concentrations at the two locations include the total input of these compounds from wastewater treatment facilities to each lake and differences in loss processes including outflow, photolysis, volatilization, and sedimentation. These factors do not account for the observed concentration differences. For example, the Lake Erie drainage basin receives about 50% more wastewater treatment plant discharge than the Lake Ontario drainage basin ($\sim 120 \text{ m}^3/\text{s}$ and $\sim 80 \text{ m}^3/\text{s}$ for Lake Erie and Lake Ontario, respectively) (40); however, measured synthetic musk fragrance concentrations in the Lake Erie sediment core are lower than those found in the Lake Ontario sediment core. The difference may be due to the much higher biological productivity in Lake Erie and higher sediment accumulation.

The average HHCB/AHTN ratio in the top two subcores of the Lake Ontario sediment was ~ 28 . This ratio is higher than what is typically released from U.S. wastewater treatment plants (~ 1.4) (24,25). The HHCB/AHTN ratio has been shown to increase in natural systems due mainly to the faster photolysis rate of AHTN relative to HHCB (14). For example, the dissolved phase HHCB/AHTN ratio in Lake Michigan was ~ 5 (15). The larger ratio in Lake Ontario sediment than in Lake Michigan water is due, in part, to a faster lakewide photolysis rate in Lake Ontario than Lake Michigan due to the differences in depths between the two lakes [Lake Michigan 176 m; Lake Ontario 74 m (41)] and the relatively higher affinity of HHCB for sediment.

HHCB Accumulation Rate and Doubling Time

The accumulation rate (k , yr^{-1}) of contaminants in sediment can be determined from the concentration (C) of the contaminant over time (t) using Equation 3, where the accumulation rate and initial concentration (C_0) are fit parameters.

$$C = C_0 e^{kt} \quad \text{Equation 3}$$

The doubling time (t_2) can then be determined from the accumulation rate using Equation 4.

$$t_2 = \frac{0.693}{k}$$
Equation 4

The determination of the accumulation rate of HHCb in the Lake Erie sediment core is illustrated in Figure 4 for the periods 1979-2003, 1979-1990, and 1990-2003. The r^2 for these regressions range from 0.31 to 0.47 and are statistically significant ($p < 0.01$). From 1979-2003, the accumulation rate ($k \pm$ standard error) for HHCb in Lake Erie sediments was $0.042 \pm 0.011 \text{ yr}^{-1}$. The accumulation rates were $-0.064 \pm 0.019 \text{ yr}^{-1}$ and $0.084 \pm 0.025 \text{ yr}^{-1}$, for the periods 1979-1990 and 1990-2003, respectively. The accumulation rates for 1979-2003 and 1990-2003 correspond to doubling times of $16 \pm 4 \text{ yr}$ and $8 \pm 2 \text{ yr}$, respectively. Since the sedimentation rate at this location was constant over this time period, these doubling times are likely due to increased inputs of these compounds to the lake system. A similar analysis of the U.S. production data shown in Figure 2 reveal a doubling time of $15 \pm 3 \text{ yr}$ for the period 1990-2004. The HHCb concentration doubling time over this period is faster than the U.S. production for all fragrance compounds. This supports the hypothesis that the use of synthetic musk fragrances in the U.S. has increased faster than that indicated from total fragrance chemical production.

Due to the low sedimentation rate for the Lake Ontario core, interpretation of the chemical signal is more limited than the Lake Erie core. There are only four sediment sections representing the period since 1950, the onset of widespread synthetic musk fragrance use. This core can be used to estimate sediment fluxes, loadings, inventories, and burdens.

Sediment Fluxes, Loadings, Inventories, and Burdens

The inventory (I) of each compound in each core was determined from the concentration in each sediment section (C_i), the density of each section (ρ_i), depth of each section (d_i) and focusing factor (FF) using Equation 5.

$$I = \frac{\sum C_i \rho_i d_i}{FF}$$
Equation 5

From the inventory and lake areas [A ; Lake Erie $25,700 \text{ km}^2$ and Lake Ontario $18,960 \text{ km}^2$ (41)], the full lake burden (B) can be estimated using Equation 6.

$$B = I \times A$$
Equation 6

The flux of contaminants entering the lake sediments can be determined from the surface sediment concentration (C_s), the sedimentation rate (w) and the focusing factor (FF).

$$F = \frac{C_s w}{FF}$$
Equation 7

From the flux and lake area (A), the yearly loadings to the lake sediment can be estimated using Equation 8.

$$L = F \times A$$
Equation 8

The sediment fluxes, loadings, inventories, and burdens are listed in Table 2 for all compounds detected in each core. The HHCB inventory in Lake Erie was 7.5 ng/cm² with an estimated total lake burden of 1900 kg. From the flux of HHCB (0.29 ng/cm²-yr), an additional 75 kg are deposited yearly to the Lake Erie sediment. The total yearly loading of HHCB to Lake Erie calculated from a typical concentration of HHCB in wastewater [1640 ng/L (24,25)] and the estimated volume of wastewater entering the Lake Erie drainage basin [120 m³/s; (40)] is 6200 kg/yr. The estimated HHCB sediment burden and loading are reasonable relative to the total yearly input of HHCB to the Lake Erie system. In Lake Ontario, the total synthetic musk fragrance (ΣSMF) inventory was 96 ng/cm², with a majority being HHCB (86 ng/cm²). The estimated HHCB and total synthetic musk fragrance lake wide sediment burden are 16000 kg and 18000 kg, respectively. The flux and loading estimates for HHCB in Lake Ontario are 0.26 ng/cm²-yr and 49 kg/yr. HHCB accounts for the majority of the total synthetic musk fragrance loading of 53 kg/yr. The total yearly loading of HHCB to Lake Ontario calculated as above [the estimated wastewater input into Lake Ontario is 79 m³/s; (40)] is 4100 kg/yr. The sediment loading estimates for Lake Ontario also appear reasonable based on the total lake loading. The hydraulic residence times for Lake Erie and Lake Ontario are 3 yr and 8 yr, respectively (41). These residence times are both short relative to other Great Lakes and they closely match the temporal resolution of the Lake Erie and Lake Ontario sediment cores. For these reasons, the interpretation of these annual deposition rates are not significantly affected by the hydraulic residence times.

The inventory and burden estimates for Lake Erie likely underestimate the actual totals because the cores only date to ~1980, while these compounds were in use for 20-30 years prior to 1980. Additionally, while the focusing factor corrects for lake wide sedimentation differences, sediment synthetic musk fragrance concentrations likely vary across the lake. The differences in concentration between the Lake Erie and Lake Ontario cores may point to the importance of local sources (i.e. wastewater treatment outfalls) on sediment concentrations. For this reason it is possible that the inventories and fluxes estimated for Lake Ontario may overestimate the actual values due to the proximity of this sampling location to Toronto.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank the captain and crew of the *R/V Lake Guardian* for their help with sample collection and the U.S. EPA Great Lakes National Program Office for arranging ship time for this study. We appreciate assistance with sediment dating from Ron Hites at Indiana University and Patrick Anderson and Val Klump at the Great Lakes WATER Institute, University of Wisconsin- Milwaukee. Collin Just and Carolyn Persoon contributed to development of the GC/MS/MS method. The Environmental Health Sciences Research Center (NIH P30 ES05605) and the Center for Global and Regional Environmental Research at the University of Iowa provided funding for this work.

References

- (1). Rimkus GG. Polycyclic musk fragrances in the aquatic environment. *Toxicol. Lett* 1999;111:37–56. [PubMed: 10630702]
- (2). Rimkus GG, Gatermann R, Huhnerfuss H. Musk xylene and musk ketone amino metabolites in the aquatic environment. *Toxicol. Lett* 1999;111:5–15. [PubMed: 10630699]
- (3). Fromme H, Otto T, Pilz K. Polycyclic musk fragrances in different environmental compartments in Berlin (Germany). *Wat. Res* 2001;35:121–128.
- (4). Gatermann R, Biselli S, Huhnerfuss H, Rimkus GG, Hecker M, Karbe L. Synthetic musks in the environment. Part 1: Species-dependent bioaccumulation of polycyclic and nitro musk fragrances in freshwater fish and mussels. *Arch. Environ. Contam. Toxicol* 2002;42:437–446. [PubMed: 11994785]

- (5). van de Plassche, EJ.; Balk, F. Environmental risk assessment of the polycyclic musks AHTN and HHCB according to the EU-TGD. RIVM; 1997.
- (6). U.S.EPA. 2003.
- (7). Somogyi, LP.; Kishi, A. Aroma Chemicals and the Flavor and Fragrance Industry. SRI International; 2001.
- (8). Yamagishi T, Miyazaki T, Horii S, Kaneko S. Identification of musk xylene and musk ketone in freshwater fish collected from the Tama River, (Tokyo). Bull. Environ. Contam. Toxicol 1981;26:656–662. [PubMed: 7260436]
- (9). Gatermann R, Huhnerfuss H, Rimkus G, Attar A, Kettrup A. Occurrence of musk xylene and musk ketone metabolites in the aquatic environment. Chemosphere 1998;36:2535–2547.
- (10). Dsikowitzky L, Schwarzbauer J, Littke R. Distribution of polycyclic musks in water and particulate matter of the Lippe River (Germany). Org. Geochem 2002;33:1747–1758.
- (11). Osemwengie LI, Steinberg S. On-site solid-phase extraction and laboratory analysis of ultra-trace synthetic musks in municipal sewage effluent using gas chromatography-mass spectrometry in the full-scan mode. J. Chromatogr. A 2001;932:107–118. [PubMed: 11695855]
- (12). Winkler M, Headley JV, Peru KM. Optimization of solid-phase microextraction for the gas chromatographic-mass spectrometric determination of synthetic musk fragrances in water samples. J. Chromatogr. A 2000;903:203–210. [PubMed: 11153942]
- (13). Garcia-Jares C, Llompart M, Polo M, Salgado C, Macias S, Cela R. Optimization of a solid-phase microextraction method for synthetic musk compounds in water. J Chromatogr A 2002;963:137–148. [PubMed: 12187964]
- (14). Buerge IJ, Buser HR, Muller MD, Poiger T. Behavior of the polycyclic musks HHCB and AHTN in lakes, two potential anthropogenic markers for domestic wastewater in surface waters. Environ. Sci. Technol 2003;37:5636–5644. [PubMed: 14717174]
- (15). Peck AM, Hornbuckle KC. Synthetic musk fragrances in Lake Michigan. Environ. Sci. Technol 2004;38:367–372. [PubMed: 14750709]
- (16). Kallenborn R, Gatermann R, Planting S, Rimkus GG, Lund M, Schlabach M, Burkow IC. Gas chromatographic determination of synthetic musk compounds in Norwegian air samples. J. Chromatogr. A 1999;846:295–306.
- (17). Kallenborn, R.; Gatermann, R. Synthetic musks in ambient and indoor air. In: Rimkus, GG., editor. Synthetic Musk Fragrances in the Environment. Springer; Berlin: 2004.
- (18). Fromme H, Otto T, Pilz K, Neugebauer F. Levels of synthetic musks; Bromocyclene and PCBs in eel (*Anguilla anguilla*) and PCBs in sediment samples from some waters of Berlin/Germany. Chemosphere 1999;39:1723–1735. [PubMed: 10520489]
- (19). Bester K, Huhnerfuss H, Lange W, Rimkus GG, Theobald N. Results of non target screening of lipophilic organic pollutants in the German Bight II: polycyclic musk fragrances. Wat. Res 1998;32:1857–1863.
- (20). Draisci R, C M, Ferretti E, Palleschi L, Catellani G, A A. Evaluation of musk contamination of freshwater fish in Italy by accelerated solvent extraction and gas chromatography with mass spectrometric detection. J. Chromatogr. A 1998;814:187–197. [PubMed: 9718694]
- (21). Draisci R, Marchiafava C, Palleschi L, Ferretti E, Anastasio A, Visciano P. Determination of musk compounds in freshwater fish samples collected in Italy. Ind Aliment-Italy 1999;38:374–376.
- (22). Franke S, Meyer C, Heinzel N, Gatermann R, Huhnerfuss H, Rimkus G, Konig WA, Francke W. Enantiomeric composition of the polycyclic musks HHCB and AHTN in different aquatic species. Chirality 1999;11:795–801. [PubMed: 10561711]
- (23). Gatermann R, Hellou J, Huhnerfuss H, Rimkus G, Zitko V. Polycyclic and nitro musks in the environment: A comparison between Canadian and European aquatic biota. Chemosphere 1999;38:3431–3441.
- (24). Simonich SL, Begley WM, Debaere G, Eckhoff WS. Trace analysis of fragrance materials in wastewater and treated wastewater. Environ. Sci. Technol 2000;34:959–965.
- (25). Simonich SL, Federle TW, Eckhoff WS, Rottiers A, Webb S, Sabaliunas D, De Wolf W. Removal of fragrance materials during US and European wastewater treatment. Environ. Sci. Technol 2002;36:2839–2847. [PubMed: 12144256]

- (26). Winkler M, Kopf G, Hauptvogel C, Neu T. Fate of artificial musk fragrances associated with suspended particulate matter (SPM) from the river Elbe (Germany) in comparison to other organic contaminants. *Chemosphere* 1998;37:1139–1156.
- (27). Heim S, Schwarzbauer J, Kronimus A, Littke R, Woda C, Mangini A. Geochronology of anthropogenic pollutants in riparian wetland sediments of the Lippe River (Germany). *Org. Geochem* 2004;35:1409–1425.
- (28). Herren D, Berset JD. Nitro musks, nitro musk amino metabolites and polycyclic musks in sewage sludges - Quantitative determination by HRGC-ion-trap-MS/MS and mass spectral characterization of the amino metabolites. *Chemosphere* 2000;40:565–574. [PubMed: 10665395]
- (29). Berset JD, Bigler P, Herren D. Analysis of nitro musk compounds and their amino metabolites in liquid sewage sludges using NMR and mass spectrometry. *Anal. Chem* 2000;72:2124–2131. [PubMed: 10815975]
- (30). Stevens JL, Northcott GL, Stern GA, Tomy GT, Jones KC. PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks, and polychlorinated n-alkanes in UK sewage sludge: Survey results and implications. *Environ. Sci. Technol* 2003;37:462–467. [PubMed: 12630459]
- (31). Simcik MF, Golden KA, Liu SP, Eisenreich SJ, Lipiatou E, Swackhamer DL, Long DT. Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments. *Environ. Sci. Technol* 1996;30:3039–3046.
- (32). Pearson RF, Swackhamer DL, Eisenreich SJ, Long DT. Concentrations, accumulations, and inventories of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments of the Great Lakes. *Environ. Sci. Technol* 1997;31:2903–2909.
- (33). Pearson RF, Swackhamer DL, Eisenreich SJ, Long DT. Concentrations, accumulations, and inventories of toxaphene in sediments of the Great Lakes. *Environ. Sci. Technol* 1997;31:3523–3529.
- (34). Eisenreich S, Capel P, Robbins J, Bourbonniere R. Accumulation and diagenesis of chlorinated hydrocarbons in Lacustrine sediments. *Environ. Sci. Technol* 1989;23:1116–1124.
- (35). Zhu LY, Hites RA. Brominated flame retardants in sediment cores from Lakes Michigan and Erie. *Environ. Sci. Technol* 2005;39:3488–3494. [PubMed: 15952352]
- (36). Simcik MF, Jeremiason JD, Lipiatou E, Eisenreich SJ. Enhanced removal of hydrophobic organic contaminants by settling sediments in western Lake Superior. *J. Great Lakes Res* 2003;29:41–53.
- (37). Robbins JA, Edgington DN. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. *Geochim. Cosmochim. Acta* 1975;38:285–304.
- (38). Robbins J, Krwzowski J, Mozley S. Radioactivity in Sediments of the Great Lakes: Post-Depositional redistribution by Deposit-Feeding Organisms. *Earth and Planetary Science Letters* 1977;36:325–333.
- (39). Eschke HD, Dibowski HJ, Traud J. Determination of polycyclic musk flavors in human fat and milk by using selective ion trap GC/MS/MS. *Deut Lebensm-Rundsch* 1995;91:375–379.
- (40). World Lakes Database. International Lake Environment Committee; [Accessed: April 5, 2006].
- (41). Quinn FH. Hydraulic residence times for the Laurentian Great Lakes. *J. Great Lakes Res* 1992;18:22–28.
- (42). Song WL, Ford JC, Li A, Sturchio NC, Rockne KJ, Buckley DR, Mills WJ. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie. *Environ. Sci. Technol* 2005;39:5600–5605. [PubMed: 16124292]

Figure 1.
Sediment sampling locations in Lake Erie and Lake Ontario.

Figure 2.
Trend of fragrance chemical consumption in the United States (7) and the HHCB concentration in Lake Erie sediment.

Figure 3.
Synthetic musk fragrance concentration profiles at Lake Ontario sampling location.

Figure 4.
Determination of HHCB input rates to Lake Erie.

Table 1**Sedimentation Rates and Focusing Factors**

	Location	Sedimentation Rate (g/cm ² -yr)	Focusing Factor	Reference
Lake Erie				
LE-15 (this study)	42° 31' N; 79° 53' W	0.73	7.9	(35)
LE-9	42° 32' N; 79° 37' W	0.37	1.61	(42)
LE-37	42° 07' N; 81° 34' W	0.11	1.25	(42)
Lake Ontario				
LO-33	43° 35' N; 78° 48' W	0.027	1.72	this study
LO-19	43° 22' N; 79° 21' W	0.030	1.07	(33)
LO-40	43° 35' N; 78° 00' W	0.064	1.71	(33)
LO-30	43° 32' N; 76° 54' W	0.067	2.04	(33)
LO-40	43° 35' N; 78° 00' W	0.033	1.15	(42)
LO-30	43° 32' N; 76° 54' W	0.035	1.13	(42)

Table 2

Synthetic Musk Fragrance Surface Concentrations, Inventories, Burdens, Fluxes, and Loadings in Lake Erie and Lake Ontario Sediment

	Dry Weight Surface Concentration (ng/g)	Inventory (ng/cm ²)	Burden (kg)	Flux (ng/cm ² -yr)	Loading (kg/yr)
Lake Erie					
HHCB	3.2	7.5	1900	0.29	75
Lake Ontario					
HHCB	16	86	16000	0.26	49
AHTN	0.96	5.2	990	0.015	2.9
ATTI	0.27	1.4	270	0.0043	0.81
AHMI	<0.049	0.34	65	<0.00077	<0.150
ADBI	0.10	0.40	75	0.0016	0.30
Musk Xylene	<0.068	2.6	500	<0.011	<2.0
ΣSMF	18	96	18000	0.28	53