Distribution of Hexabromocyclododecane in Detroit River Suspended Sediments

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Introduction

Hexabromocyclododecane (HBCD, $C_{12}H_{18}Br_6$) is a brominated alicyclic hydrocarbon and is the principal flame retardant in polystyrene foams and is used as thermal insulation in the building industry. Secondary applications of HBCD include use in residential and commercial upholstery, transportation upholstery, draperies, and wall coverings. HBCD is an additive flame retardant; therefore, HBCD may migrate out of products into the environment during use or after disposal. There are four grades of technical mixture produced by industry, each containing different percentages of the three isomers. Typically, the γ–isomer is predominant (>70%) followed by the α– and then the β-isomer. The physical/chemical properties of HBCD are similar to those of BDEs [1]. The estimated log K_{ow} of HBCD (5.6) makes it a candidate for bioaccumulation [2]. Much of the information regarding the environmental occurrence of HBCD is the result of studies conducted in Scandinavia; Remberger et al. [3] have reported the results of a screening level survey of HBCD in a variety of environmental matrices including air, water, soil, sediments, sludge, biota and foodstuffs. These data indicate that HBCD is persistent, bioaccumulative, and amenable to long-range atmospheric transport.

In this study, we have investigated the occurrence and spatial distribution of HBCD in suspended sediments from the Detroit River using a recently developed congener specific method based on a liquid chromatography tandem mass spectrometry (LC/MS/MS) method. Time-integrated suspended sediments were collected over one-month periods at stations in the Detroit River, and analyzed by LC/MS/MS for the relative distribution of α-, β-, and γ-HBCD. The results of this study were compared with previous studies to determine the distribution of new and emerging POPs characteristic of modern industrial/urban activities, in relation to legacy POPs such as PCBs.

Experimental

Suspended sediments were sampled monthly in the Detroit River. Individual isomers of HBCD (α, β, and γ) were obtained from Cambridge Isotope Laboratories Inc. All three native (α, β and γ), deuterated (d_{18}–γ–HBCD), and carbon–13 mass labeled ($^{13}C_{12}$–γ–HBCD) HBCD congeners (each >98% purity) were provided by Wellington Laboratories Inc. Sediment samples were extracted by Accelerated Solvent Extraction (ASE) on a Dionex 200 instrument. Column cleanup was performed on a 30 cm x 1 cm chromatography column packed with 8 g of 100% activated ultra-trace silica gel and

topped with 1 cm fired sodium sulphate. Two sequential fractions were obtained: Fraction A – eluted with 65 mL of hexane; Fraction B – eluted with 75 mL of DCM: hexane (1:1). Fraction B contained HBCD, and an aliquot of this fraction was solvent exchanged into acetonitrile for analysis.

Samples were analyzed on a Micromass Quattro Ultima triple quadrupole MS equipped with a Waters 2695 LC system. Separation of the HBCD isomers was achieved on a Vydac 218MS 5 µm particle size 15 cm x 2.1 mm i.d. polymeric reversed-phase HPLC column. The mobile phase consisted of acetonitrile:water (each with 10mM ammonium acetate):methanol (65:23:12) for 5 min at 150 µL/min, followed by 100% acetonitrile for 7 min at 200 uL/min. The mass spectrometer was operated in electrospray ionization (ESI) negative ion mode. For infusion experiments to optimize mass spectrometer conditions, a Harvard syringe pump with a flow rate at10 µL/min was used. Source parameters were as follows: cone -5V; capillary 3.2kV; hex1 15V; hex2 0.3V; source temperature 125° C; desolvation temperature 350°C; cone gas and desolvation gas flow 130 and 500 L/hr respectively. Nitrogen was provided by a nitrogen generator (Parker Hannifin, Tewksbury, MA). For MS acquisition, Q1 was operated with unit resolution with a scan time of 0.5 seconds. For MS/MS acquisition, argon was used as the collision gas; the collision energy was -50eV. MS/MS detection used multiple reaction monitoring (MRM) conditions for the *m/z* 640.6 ($[M - H]^-$) $\rightarrow$ Br^- reaction (both isotopes), utilizing unit resolution on the first and third quadrupoles and a 200 ms dwell time. Quantitation of the HBCD isomers was based on the ion signal from MRM of the *m/z* 640.6 $[M-H]^-$ to Br^- transition (*m/z* 79 and 81). A five-point calibration curve was obtained from a dilution series of standards prepared from individual isomers.

Results and Discussion

Spatial trends of HBCD occurrence in Detroit River suspended sediments exhibited a strong association with urban and industrial activities. The spatial distribution of total HBCD, expressed as the annual mean concentration (± standard deviation), is shown in Figure 1. The distribution of total PCBs are also shown for comparison. Highest individual monthly concentrations of HBCD were detected in samples from station 1169 (2,600 pg/g in October) in the upper reaches of the river near Belle Isle, from station 1168 (3,650 pg/g in August) near the mouth of the Rouge River, and at station 1161 (2,600 pg/g in August) near the head of the Trenton Channel. The presence of sources of HBCD in urbanized/industrialized areas of the Detroit River are also evidenced by comparison of concentrations at the upstream station (station 1160, 106 pg/g annual mean) and the downstream station at the mouth of the river outflow to Lake Erie (station 1157, 1,140 pg/g annual mean). Levels of HBCD at station 1159 in the Trenton Channel (393 pg/g annual mean) were elevated compared to station 804 on the eastern side of the river near Fighting Island where HBCD was detected in trace amounts (12 pg/g annual mean). The influence of HBCD associated with suspended sediments being carried through the Trenton Channel was also evidenced by higher HBCD levels at station 1157 on the western side of the river at the outflow to Lake Erie (1,140 pg/g annual mean) compared to station 1156 at the same latitude, but on the Canadian side of the river, where HBCD was rarely detected (66 pg/g annual mean). Elevated concentrations of total HBCD were also found in the upper reaches of the river at station

1169 (910 pg/g annual mean), but HBCD was only rarely detected, and at relatively lower concentrations at station 803 (19 pg/g annual mean) and station 1160 in Lake St. Clair (106 pg/g annual mean).

The highest concentrations of PCBs in suspended sediments in the Detroit River are typically found in stations in the lower reaches of the river in the Trenton Channel, which can be primarily attributed to historical contamination by industries including steel manufacturing and chlor-alkali production. In contrast, HBCD is a current-use industrial chemical. Highest total HBCD concentrations in Detroit River suspended sediments were typically three orders of magnitude less (low ppb level) than PCB concentrations in the Trenton Channel (low ppm level). There are more significant environmental problems on the Michigan side of the river due to greater presence of industry and the larger population of the Detroit metropolitan area. Therefore, the distribution and occurrence of HBCD in Detroit River suspended sediments appear to be commensurate with land-use patterns, i.e., general urbanization and industrialization, and do not provide evidence of the presence of significant point sources.

Individual isomers of HBCD were found at maximum concentrations of 1,850 pg/g for the α-isomer, 283 pg/g for the β-isomer, and 2,300 pg/g for the γ-isomer. The γ-isomer was predominant in roughly two-thirds of the samples. The β-isomer was typically found at low concentrations, and was only detected in a quarter of the samples. Roughly one-third of the samples exhibited relatively higher concentrations of the α-isomer, which is more typical of profiles in aquatic biota [4]. The mechanisms responsible for the significant variation in the HBCD profiles remain unclear. Potential factors affecting the ratio of the individual isomers are numerous, and include the isomeric composition of the technical mixture which can be thermally rearranged during manufacture of the final product, differences in physical properties including variations in K_{ow}, among individual isomers, source, and metabolic and transformation processes. These factors will undoubtedly prove confounding in development of any methods to track sources of HBCD into the aquatic environment.

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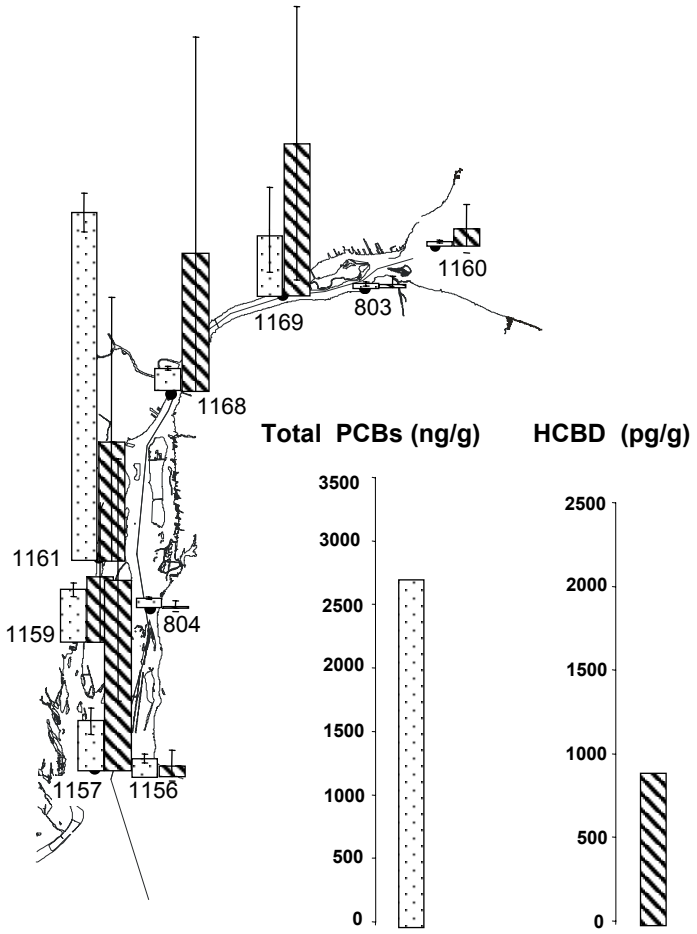
Figure 1. Spatial distribution of total HBCD (pg/g) and PCBs (µg/g) in Detroit River suspended sediments expressed as the annual mean concentration.