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Environnement Canada

Distribution of Hexabromocyclododecane in Detroit
River Suspended Sediments

By:

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Chris H. Marvin, Gregg T. Tomy, Mehran Alaei and Gordia MacInnis

Abstract

The distribution of hexabromocyclododecane (HBCD) isomers (α , β and γ) was determined in Detroit River suspended sediments using liquid chromatography tandem mass spectrometry (LC/MS/MS). Individual isomers of HBCD were measured at concentrations ranging from non-detect to 1.9 ng/g for the α -isomer, non-detect to 0.28 ng/g for the β -isomer, and non-detect to 2.3 ng/g for the γ -isomer. Concentrations of total HBCD ranged from non-detect to 3.7 ng/g. Roughly two-thirds of HBCD profiles in suspended sediments were dominated by the γ -isomer, and were similar to profiles of commercial technical mixtures. Profiles in the remaining samples were dominated by the α -isomer. The β -isomer was consistently detected at substantially lower levels than the other isomers. The spatial distribution of HBCD in the Detroit River was similar to other persistent organic pollutants (e.g., PCBs), and showed a strong association with urban/industrial activities in the watershed. However, the highest HBCD concentrations (2.6 – 3.7 ng/g) were associated with areas of contemporary industrial activity, and were much lower than maximum concentrations of PCBs (2.2 μ g/g) found in areas of the Detroit River associated with historical industrial activity.

NWRI RESEARCH SUMMARY

Plain language title

Distribution of hexabromocyclododecane in Detroit River suspended sediments

What is the problem and what do scientists already know about it?

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. Little is known of the distribution and fate of this compound in the North American environment.

Why did NWRI do this study?

This study was undertaken to determine the distribution of a new and emerging persistent organic pollutant (POP) characteristic of modern industrial/urban activities, in relation to legacy POPs such as PCBs.

What were the results?

The distribution of HBCD in suspended sediments in the Detroit River appeared to be heavily influenced by shoreline-based contemporary urban and industrial activities, which stood in contrast to PCBs that were associated with areas of historical industrial activity. The widespread occurrence, but relatively low concentrations, of HBCD in suspended sediments suggest that large urban areas can act as diffuse sources of HBCD used in modern industrial applications. The lack of any definitive trends in the ratios of the two predominant isomers, α - and γ -HBCD, combined with the potential for multiple environmental transformation processes, confounded any attempts to attribute isomer profiles to specific sources.

How will these results be used?

Results will be used by stakeholders, including the Detroit and St. Clair River RAPs, for assessment of the importance of integrating monitoring strategies geared towards new POPs into existing research and monitoring programs.

Who were our main partners in the study?

Department of Fisheries and Oceans

Distribution de l'hexabromocyclododécane dans les sédiments en suspension de la rivière Détroit

Chris H. Marvin, Gregg T. Tomy, Mehran Alaei et Gordia MacInnis

Résumé

La distribution d'isomères (α , β et γ) de l'hexabromocyclododécane (HBCD) a été déterminée dans les sédiments en suspension de la rivière Détroit à l'aide de la chromatographie en phase liquide en tandem avec la spectrométrie de masse (LC/MS/MS). Des isomères individuels du HBCD ont été mesurés à des concentrations allant d'une valeur indétectable à 1,9 ng/g pour l'isomère α , d'une valeur indétectable à 0,28 ng/g pour l'isomère β , et d'une valeur indétectable à 2,3 ng/g pour l'isomère γ . Les concentrations de HBCD total allaient d'une valeur indétectable à 3,7 ng/g. Environ deux tiers des profils de HBCD dans les sédiments en suspension étaient dominés par l'isomère γ et étaient semblables aux profils de mélanges techniques commerciaux. Les profils des échantillons restants étaient dominés par l'isomère α . L'isomère β était toujours détecté à une concentration nettement inférieure à celles des autres isomères. La distribution spatiale du HBCD dans la rivière Détroit était semblable à celles d'autres polluants organiques persistants (p. ex., les BPC) et était fortement liée aux activités urbaines ou industrielles dans le bassin hydrologique. Cependant, les concentrations de HBCD les plus fortes (2,6–3,7 ng/g) étaient associées avec des zones d'activités industrielles contemporaines et étaient beaucoup plus basses que les concentrations maximales de BPC (2.2 μ g/g) mesurées dans les zones de la rivière Détroit associées à des activités industrielles passées.

Sommaire des recherches de l'INRE

Titre en langage clair

Distribution de l'hexabromocyclododécane dans les sédiments en suspension de la rivière Détroit.

Quel est le problème et que savent les chercheurs à ce sujet?

L'hexabromocyclododécane (HBCD, $C_{12}H_{18}Br_6$), un hydrocarbure alicyclique bromé, est le principal agent ignifugeant dans les mousses de polystyrène; il est utilisé comme isolant thermique dans l'industrie de la construction. Ses applications secondaires sont, entre autres, son utilisation dans les rembourrages résidentiels et commerciaux, le rembourrage dans les moyens de transport, les tentures et les revêtements muraux. C'est un additif ignifugeant; par conséquent, il peut être transféré dans l'environnement par des produits durant leur utilisation ou après leur élimination. On connaît peu de choses sur la distribution et le devenir de ce composé dans l'environnement nord-américain.

Pourquoi l'INRE a-t-il effectué cette étude?

Cette étude a été entreprise dans le but de déterminer la distribution d'un nouveau polluant organique persistant (POP) émergent qui est caractéristique des activités industrielles et urbaines modernes, par rapport aux anciens POP comme les BPC.

Quels sont les résultats?

La distribution du HBCD dans les sédiments en suspension de la rivière Détroit semble dépendre fortement d'activités urbaines et industrielles contemporaines sur le rivage, ce qui contraste avec les BPC, lesquels sont associés à des zones d'anciennes activités industrielles. La distribution étendue, mais à des concentrations relativement faibles, du HBCD dans les sédiments en suspension porte à croire que de grandes zones urbaines peuvent se comporter comme des sources diffuses du HBCD utilisé dans les application industrielles modernes. L'absence de tendances bien établies dans les rapports des deux isomères prédominants, α - et γ -HBCD, ajoutée à la possibilité d'une multitude de processus de transformation dans l'environnement, a embrouillé les tentatives faites pour attribuer des profils isomériques à des sources particulières.

Comment ces résultats seront-ils utilisés?

Les résultats seront utilisés par les intervenants, dont les PA des rivières Détroit et St. Clair, pour évaluer l'importance d'intégrer aux programmes de recherche et de surveillance actuels des stratégies de surveillance visant les nouveaux POP.

Quels étaient nos principaux partenaires dans cette étude?

Ministère des Pêches et des Océans.

Distribution of Hexabromocyclododecane in Detroit River Suspended Sediments

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Abstract

The distribution of hexabromocyclododecane (HBCD) isomers (α , β and γ) was determined in Detroit River suspended sediments using liquid chromatography tandem mass spectrometry (LC/MS/MS). Individual isomers of HBCD were measured at concentrations ranging from non-detect to 1.9 ng/g for the α -isomer, non-detect to 0.28 ng/g for the β -isomer, and non-detect to 2.3 ng/g for the γ -isomer. Concentrations of total HBCD ranged from non-detect to 3.7 ng/g. Roughly two-thirds of HBCD profiles in suspended sediments were dominated by the γ -isomer, and were similar to profiles of commercial technical mixtures. Profiles in the remaining samples were dominated by the α -isomer. The β -isomer was consistently detected at substantially lower levels than the other isomers. The spatial distribution of HBCD in the Detroit River was similar to other persistent organic pollutants (e.g., PCBs), and showed a strong association with

urban/industrial activities in the watershed. However, the highest HBCD concentrations (2.6 – 3.7 ng/g) were associated with areas of contemporary industrial activity, and were much lower than maximum concentrations of PCBs (2.2 µg/g) found in areas of the Detroit River associated with historical industrial activity.

Keywords: HBCD; Flame retardant; PCBs; Detroit River; Suspended sediment; Environmental concentration

1. Introduction

Flame retardants are substances added or applied to combustible materials to increase fire resistance (Alaee et al., 2003). Brominated flame retardants (BFRs) are either aromatic, aliphatic, or cycloaliphatic compounds containing between 50 to 85% bromine by weight (Younes, 2001). These compounds are a structurally diverse group that is incorporated into a variety of consumer and industrial products to increase their flame-resistance. Estimates suggest that global demand for BFRs is on the rise; from 1990 to 2000 usage increased from approximately 145 to 310 kilotons (Arias, 2002). BFRs have recently become a matter of concern due to increasing levels found in the environment. (Noren and Meironyté, 2000; Betts, 2002).

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 (American Chemistry Council). Secondary applications of HBCD include use in residential and commercial upholstery, transportation upholstery, draperies, and wall coverings (de Wit, 2002, American Chemistry Council). In 1999, the global demand for HBCD (approximately 16 kilotons) was more than double that of the penta-bromodiphenyl ether mixture (approximately 8.5

kilotons, de Wit, 2002). Of the estimated world market demand for HBCD in 1999 of 15,900 metric tons, 3,100 was consumed in North America (de Wit, 2002). Similar to the brominated diphenyl ethers (BDEs), HBCD is an additive flame retardant. Therefore, HBCD is not covalently bonded to the material and may migrate out of products into the environment during use or after disposal. With implementation of mandatory (EU), or voluntary (Japan), restrictions on the production of some brominated flame retardants, use of HBCD as a replacement product is expected to increase (Kemmlein et al., 2003).

Technical HBCD is produced industrially by addition of bromine to *cis-trans-trans*-1,5,9-cyclododecatriene (American Chemistry Council; Reyes et al., 1997). The technical mixture contains three diastereoisomers (α , β and γ , Figure 1) and tetrabromocyclododecene as an impurity (<2%). There are four grades of the technical mixture produced by industry, each containing different percentages of the three isomers (Peled et al., 1995). Typically, the γ -isomer is the most dominant (>70%) followed by the α - and then the β -isomer. The physical/chemical properties of HBCD are similar to those of BDEs (Tittlemier et al., 2002). The estimated log K_{ow} of HBCD (5.6) makes it a candidate for bioaccumulation (MacGregor and Nixon, 1997).

Despite its global use, there is relatively little known about the fate and environmental levels of HBCD. The physical properties of low volatility and low water solubility result in HBCD having an affinity for adsorption on sediments. Watanabe and Sakai (2003) reported that higher brominated compounds are less mobile in the environment and tend to accumulate in sediments near primary sources. Sellström et al. (1998) calculated the bioavailability of HBCD (15) to be similar to BDE-47 (6.6–19) and BDE-99 (17). Reports of HBCD in aquatic biota include detection of HBCD in mussel

tissues downstream of a flame-retardant production plant (van Leeuwen, 2002), in guillemot eggs from the Baltic (Lundstedt-Enkel et al., 2001), and in fish from the River Viskan (Sellström et al., 1998). In North America, Tomy et al. (2004) recently studied the biomagnification of the α - and γ - isomers of HBCD in Lake Ontario food web samples. High levels of HBCD (mg/kg) have also been measured in dust samples from indoor air (Bergman et al., 1997; Leonards et al., 2001). Much of the information regarding the environmental occurrence of HBCD is the result of studies conducted in Scandinavia; Remberger et al. (2004) 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.

Toxicological studies of HBCD have also indicated the potential for deleterious health effects due to exposure. Sublethal effects of HBCD have been reported in juvenile rainbow trout (*Oncorhynchus mykiss*, Ronisz et al., 2001). After 5 days, HBCD was found to induce catalase activity, an increase in liver somatic index, and an antagonistic effect on CYP1A. In an *in vitro* study using mammalian cells, HBCD was linked to carcinogenesis through induction of genetic recombination (Helleday et al., 1999).

The Detroit River is one of the four major connecting channels of the Great Lakes, and provides the link between western Lake Erie and Lake St. Clair. The Detroit River also serves as the border between Canada and the United States; its binational watershed includes the metropolitan areas of Detroit, Michigan and Windsor, Ontario, with an associated combined population of roughly three and a half million people. The watershed is highly urbanized and industrialized and provides a variety of sources of

chemical contamination to the river, including urban runoff, sewage treatment plants, combined sewer overflows and industrial wastes. High concentrations of persistent organic pollutants (POPs) including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) have been detected in Detroit River sediments (Furlong et al., 1988; Kaiser et al., 1985; Hamdy and Post, 1985; Thornley and Hamdy, 1984; Marvin et al., 2002). The river has been designated as an Area of Concern (AOC) by the International Joint Commission (IJC) due to environmental impairments, many of which are related to POPs contamination of both biotic and abiotic matrices.

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 developed by Budakowski and Tomy (2003). 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.

2. Experimental

2.1 Sample collection and preparation

Suspended sediments were sampled monthly in the Detroit River in 2001, as previously described by Marvin et al. (2002). Briefly, single-point sediment trap moorings were deployed from May to November at nine stations in the Detroit River ranging from the mouth at the outflow to western Lake Erie to the head in southern Lake

St. Clair. Each sediment trap mooring consisted of six individual 1-metre length sections of core tubing (7 cm internal diameter) affixed to a steel rack and anchored using a railway wheel in order to maintain the stability of the mooring in strong current regimes. A removable cup of high-density polypropylene was fitted to the bottom of each tube to provide a receptacle for sediment accumulation. The moorings were refurbished monthly and the accumulated material deposited in the traps was removed, refrigerated at 4°C and transported to the laboratory. For the analysis of HBCD, each sample was homogenized, and a 5-gram aliquot was air dried in a fume hood. Samples were also subjected to a thorough physical characterization, including particle size analysis and total organic carbon (TOC) as detailed in Marvin et al. (2002).

2.2 Chemicals

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. (Guelph, ON, Canada). Pesticide grade dichloromethane, hexane, isooctane, and HPLC grade acetonitrile, methanol and water were obtained from Caledon Laboratories (Georgetown, ON, Canada). Ultra-trace silica gel and sodium sulphate were also obtained from Caledon Laboratories.

2.3 Sample Extraction and Cleanup

Sediment samples were extracted by Accelerated Solvent Extraction (ASE) on a Dionex 200 instrument (Dionex, Mississauga, ON, Canada). The sediments were transferred to a 22 mL capacity stainless steel cell and the void space filled with Ottawa Sand (Fisher Scientific, Fairlawn, NJ). The cells were heated to 100°C for 5 minutes and extracted with DCM at 2000 psi. The flush volume was 75% over 3 static cycles. Extracts

were collected in 40 mL amber vials and concentrated to 1mL in isooctane. 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). Each fraction was concentrated to 1 mL in isooctane. 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 (Micromass, Manchester, UK) equipped with a Waters 2695 LC system. Separation of the HBCD isomers was achieved on a Vydac 218MS 5 μ m particle size 15 cm x 2.1 mm i.d. polymeric reversed-phase HPLC column (Mandel Scientific, Guelph, ON). The mobile phase consisted of acetonitrile:water (each with 10mM ammonium acetate):methanol (65:23:12) for 5 min at 150 μ L/min, followed by 100% acetonitrile for 7 min at 200 μ L/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 (Harvard Apparatus, Holliston, MA) with a flow rate at 10 μ L/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; collision energy was -50eV. MS/MS detection used multiple

reaction monitoring (MRM) conditions for the m/z 640.6 $[\text{M} - \text{H}]^- \rightarrow \text{Br}^-$ 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 $[\text{M} - \text{H}]^-$ to Br^- transition (m/z 79); confirmation was done on the $[\text{M} - \text{H}]^-$ to m/z 81 transition. A six-point calibration curve was obtained from a dilution series of standards prepared from individual isomers.

2.4 Quality Control

Spiked method blanks and spiked standard reference materials (SRMs) were run with each set of six samples. Recoveries were determined by addition of $\text{d}_{18}\text{-}\gamma\text{-HBCD}$ prior to sample extraction; quantitative data was not corrected for recovery. MS/MS detection of $\text{d}_{18}\text{-}\gamma\text{-HBCD}$ and $^{13}\text{C}_{12}\text{-}\gamma\text{-HBCD}$ was based on the analogous $[\text{M} - \text{H}]^- \rightarrow \text{Br}^-$ reaction monitored for the native HBCD (m/z d_{18} : 657.6 and ^{13}C : 652.4 $[\text{M} - \text{H}]^-$). Duplicate samples were used to verify repeatability of the analytical method. Method detection limits (MDLs) were determined by spiking $\alpha\text{-HBCD}$ and $\gamma\text{-HBCD}$ into an ASE cell packed with 10 g of Ottawa Sand and cleaned up in the same manner as samples. The MDLs were estimated at 10 pg on-column for individual HBCD isomers. The linear dynamic range of the method was estimated to be 40 pg to 5 ng injected on-column ($r^2 = 0.9985$). Relative response factors (RRFs) calculated using native and ^{13}C -HBCD isomer ratios were 1.06 ± 0.56 , 1.04 ± 0.26 , and 1.02 ± 0.12 for the alpha, beta, and gamma isomers, respectively.

3. Results and Discussion

3.1 Occurrence of HBCD in Detroit River Suspended Sediments

Spatial trends of HBCD in Detroit River suspended sediments exhibited a strong association with urban and industrial activities in the watershed. These spatial trends were similar to those observed for other POPs including polychlorinated naphthalenes, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, and tetrabromobisphenol-A (Marvin et al., 2002; Quade et al., 2003), in that the highest concentrations were detected in suspended sediments sampled near, or downstream of, areas of intensive urbanization/industrialization. The spatial distribution of total HBCD (sum of the 3 individual isomers) in suspended sediments in the Detroit River, expressed as the annual mean concentration (\pm standard deviation), is shown in Figure 2. The distribution of total PCBs are also shown for comparison.

The highest individual monthly concentrations of total 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 (Figure 2). 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 total 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).

Although there is a general similarity in the distribution of HBCD compared to PCBs (Figure 2), there are some distinct differences that may reflect a difference in primary source area. 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 (Marvin et al., 2002). This area is bordered by the Michigan mainland to the west and Grosse Ile to the east, and has been identified as containing the majority of contaminated sediment within the Detroit River (Michigan Department of Environmental Quality, 1987). The PCB contamination in the Trenton Channel 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. Although, like PCBs, relatively greater concentrations of total HBCD in suspended sediments were detected on the American side of the river, stations exhibiting the highest levels were more upstream in the middle and upper reaches. Station 1168 is located downstream of the outflow of the Rouge River into the Detroit River. The Rouge

River watershed is highly industrialized, and also receives the effluent from the Detroit River wastewater treatment plant.

Although the combination of the spatial distribution of HBCD, and the upstream/downstream and east-to-west comparisons, provide evidence that the metropolitan Detroit area of the watershed constitutes a source of HBCD, absolute concentrations must be considered in assessing significance. The 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). It is widely acknowledged that 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 (International Joint Commission, 1997). 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. These results are similar to those of Remberger et al. (2004), who found elevated levels of HBCD in air and sediments in urban areas as a potential result of diffuse emission from common-use products including building materials and car interiors.

3.2 Variation of HBCD Isomers in Detroit River Suspended Sediments

Total HBCD concentrations were based on the sum of the three individual isomers. The HBCD concentrations in all Detroit River suspended sediment samples collected in 2001 are listed in Table 1. 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 (Table 1). Selected LC/MS/MS chromatograms for station 1169 (October) and station 1168 (August) are shown in Figure 3. The β -isomer was typically found at relatively lower concentrations, compared to the other two isomers (Table 1), and was only detected in roughly a quarter of the samples. The HBCD profile exhibited by the chromatogram for station 1168 in August (Figure 3B) is representative of approximately two-thirds of the samples where HBCD was detected in that the γ -isomer was predominant. This profile has similarities to a HBCD technical mixture (Marvin et al. 2003), and has also been reported to be typical of profiles in bottom sediments (Allchin and Morris 2003). The other samples (roughly one-third) in which HBCD was detected exhibited relatively higher concentrations of the α -isomer. The HBCD profile for station 1169 in October (Figure 3A) is more typical of profiles in aquatic biota (Tomy et al., 2004).

Variation in HBCD concentrations and profiles of the individual isomers in extracts of suspended sediments at two sites (station 1169 and station 1161) on a monthly basis are shown in Figure 4. We were unable to distinguish any definitive trends in the HBCD profiles on a seasonal basis. However, the profile shown in Figure 3B in which the γ -isomer dominates appears to be more typical of samples collected in spring and early summer (Table 1), while the α -isomer is more abundant in some of the fall months (September and October). 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 (Reyes et al., 1997; Peled et al., 1995), differences in physical properties including

variations in K_{ow} , among individual isomers (Tomy et al., 2004), 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.

4. Conclusions

The distribution of HBCD in suspended sediments in the Detroit River appeared to be heavily influenced by shoreline-based contemporary urban and industrial activities, which stood in contrast to PCBs that were associated with areas of historical industrial activity. The widespread occurrence, but relatively low concentrations, of HBCD in suspended sediments suggest that large urban areas can act as diffuse sources of HBCD used in modern industrial applications. The lack of any definitive trends in the ratios of the two predominant isomers, α - and γ -HBCD, combined with the potential for multiple environmental transformation processes, confounded any attempts to attribute isomer profiles to specific sources.

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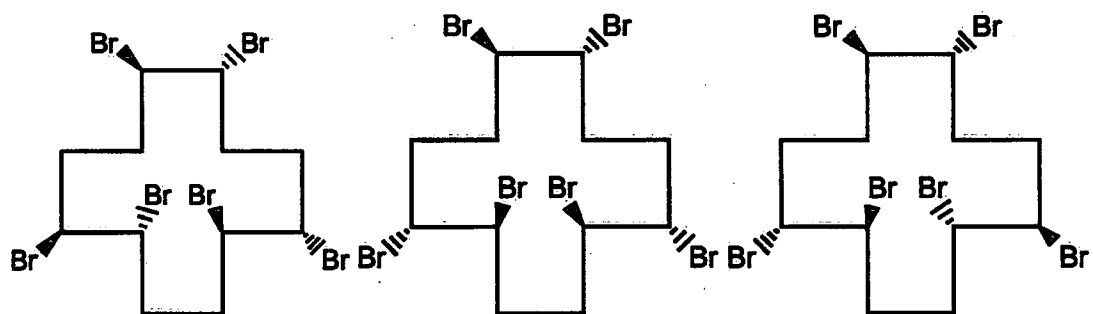
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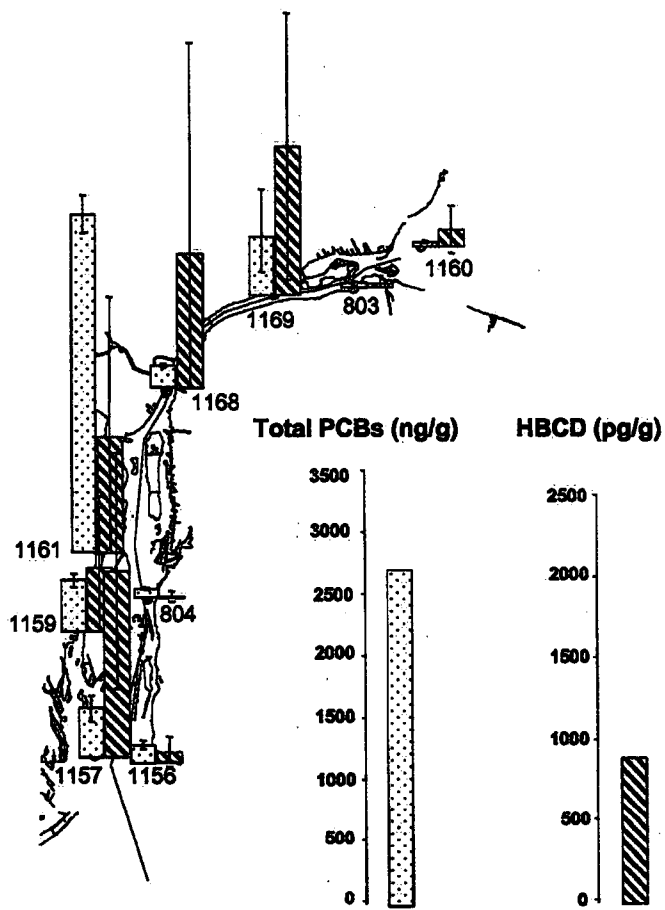
Figure 1. Structures of α -, RR SR RS (left), β -, RR RS RS (middle) and γ -, RS SS SR, (right) hexabromocyclododecane.

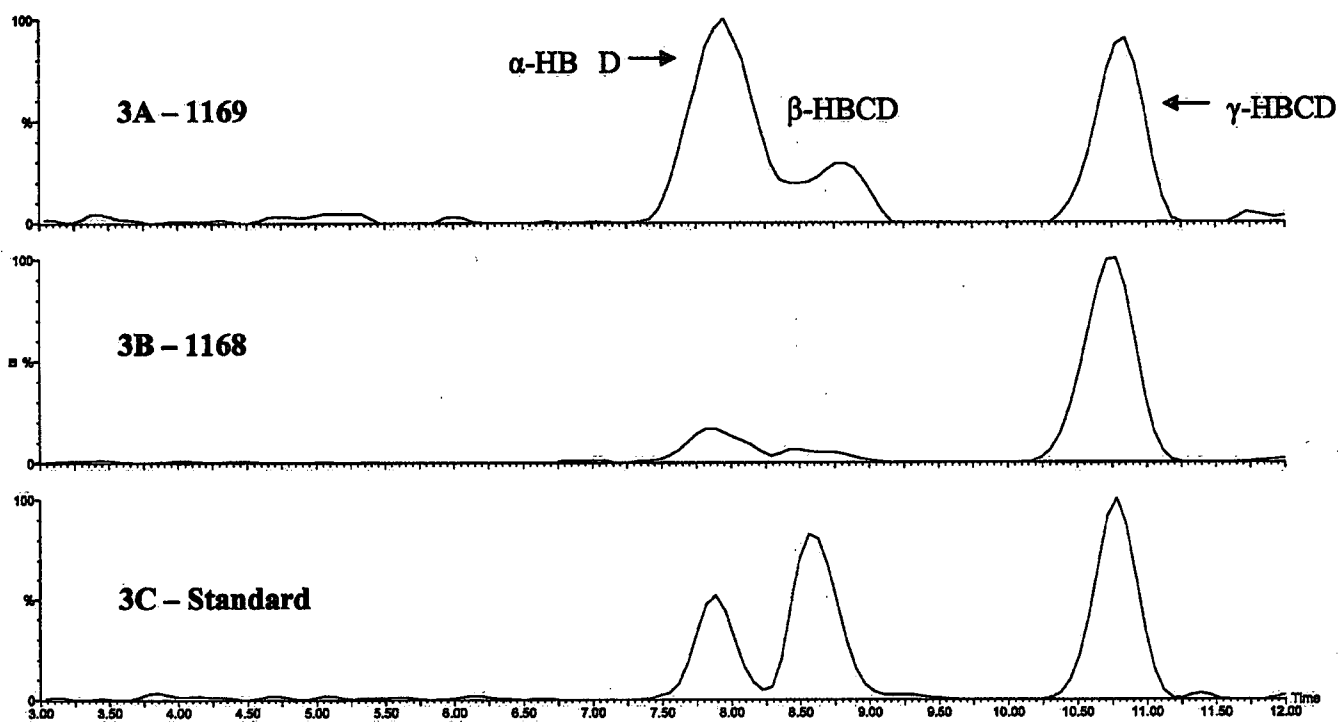
Figure 2. Spatial distribution of total HBCD (pg/g) and PCBs ($\mu\text{g/g}$) in Detroit River suspended sediments expressed as the annual mean concentration. PCB data taken from Heidtke et al. 2003.

Figure 3. LC/MS/MS chromatograms showing the m/z 640.6 - 81 transition for the α -, β -, and γ -HBCD isomers in a standard solution (bottom panel) and Detroit River suspended sediments from station 1169 (top panel) and station 1168 (middle panel).

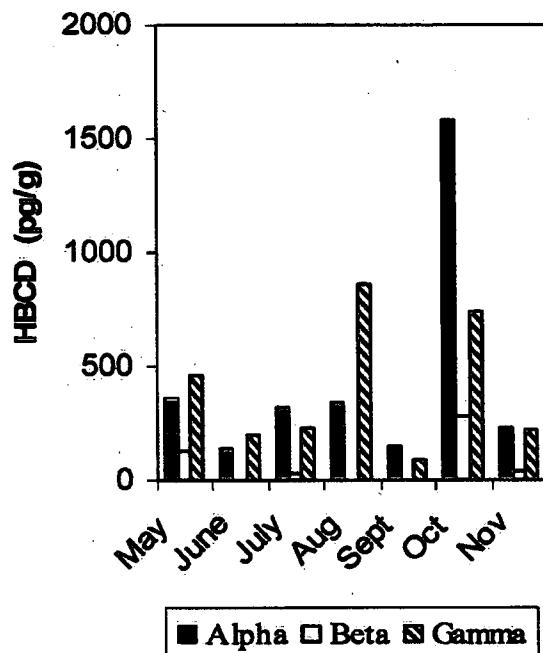
Figure 4. Monthly variation of α -, β -, and γ -HBCD isomers in Detroit River suspended sediments from stations 1169 and 1161.







1169



1161

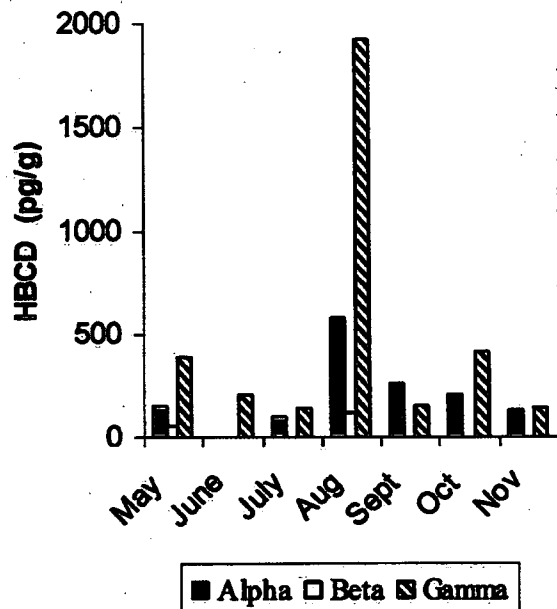


Table 1. Concentrations of individual HBCD isomers and total HBCD in monthly suspended sediment samples from the Detroit River. "nd" denotes not detected.

	Station	1160	803	1169	1168	1161	1159	804	1157	1156
May	α -HBCD	45	nd	361	nd	153	nd	nd	1850	nd
	β -HBCD	nd	nd	131	Nd	54	nd	nd	237	nd
	γ -HBCD	232	136	456	119	395	137	nd	190	163
	Total HBCD	277	136	948	119	602	137	nd	2280	163
June	α -HBCD	nd	nd	138	Nd	nd	135	nd	667	nd
	β -HBCD	nd	nd	nd	Nd	nd	35	nd	214	nd
	γ -HBCD	59	nd	202	52	202	167	nd	1050	nd
	Total HBCD	59	nd	340	52	202	337	nd	1930	nd
July	α -HBCD	nd	nd	318	Nd	101	nd	nd	474	nd
	β -HBCD	nd	nd	28	Nd	nd	nd	nd	95	nd
	γ -HBCD	347	nd	228	Nd	137	58	nd	209	nd
	Total HBCD	347	nd	575	Nd	238	58	nd	778	nd
Aug	α -HBCD	nd	nd	338	1130	580	200	nd	334	nd
	β -HBCD	nd	nd	nd	246	120	nd	nd	46	nd
	γ -HBCD	57	nd	862	2270	1930	574	85	313	nd
	Total HBCD	57	nd	1200	3650	2630	774	85	694	nd
Sept	α -HBCD	nd	nd	152	786	266	nd	nd	153	nd
	β -HBCD	nd	nd	nd	70	nd	nd	nd	Nd	nd
	γ -HBCD	nd	nd	88	116	157	nd	nd	154	nd
	Total HBCD	nd	nd	241	973	423	nd	nd	307	nd
Oct	α -HBCD	nd	nd	1580	233	208	812	nd	311	nd
	β -HBCD	nd	nd	283	nd	nd	141	nd	99	nd
	γ -HBCD	nd	nd	738	179	418	258	nd	333	83
	Total HBCD	nd	nd	2600	625	625	1211	nd	743	83
Nov	α -HBCD	nd	nd	227	158	132	124	nd	532	163
	β -HBCD	nd	nd	38	nd	nd	nd	nd	nd	nd
	γ -HBCD	nd	nd	215	189	141	113	nd	720	55
	Total HBCD	nd	nd	480	347	273	237	nd	1252	218

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