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Spatial distribution and vertical profile of polybrominated diphenyl ethers and hexabromocyclododecanes in sediment core from Tokyo Bay, Japan

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Ubiquitous and historical contamination by brominated flame retardants in Tokyo Bay.

Abstract

Brominated flame retardants (BFRs), hexabromocyclododecanes (HBCDs) and polybrominated diethyl ethers (PBDEs) were detected in three sediment cores and six surface sediments of Tokyo Bay, Japan. HBCDs were detected for the first time in this region with concentrations ranging from 0.056 to 2.3 ng/g dry wt, implying their widespread contamination, even though their concentrations were lower than $\sum$PBDEs (di- to nona-BDEs) and BDE-209. Levels of these compounds were higher near to the highly populated industrial area of the bay implicating industrial and human activities as sources of these compounds. $\sum$PBDEs increased in the sediment layer up to the mid-1990s and decreased afterwards, whereas BDE-209 showed an increasing trend until now, following the usage of different commercial BDE mixtures. HBCDs first appeared in the mid-1970s and increased until today. The annual surficial flux of HBCDs (0.62–2.4 ng/cm^2/yr) is equal to $\sum$PBDEs (0.95–2.6 ng/cm^2/yr) but lower than that of BDE-209 (17–58 ng/cm^2/yr).

Keywords: Polybrominated diphenyl ethers (PBDEs); Hexabromocyclododecanes (HBCDs); Temporal trend; Sediment core; Tokyo Bay

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1. Introduction

In recent years, environmental contaminations by brominated flame retardants (BFRs), especially polybrominated diethyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) received increasing public attention due to their persistency, bioaccumulative feature, and possible adverse effects on human and wildlife. Both chemicals are used as additive flame retardants in a wide variety of commercial and household products such as plastics, textiles, and electronic appliances including computers, televisions, etc. Contamination by PBDEs is now ubiquitous; they can be found in air, water, fish, birds, marine mammals and humans all over the world (Hites, 2004).

Statistical data demonstrated that Asian countries shared about 40% (approximately 25,000 tons) of the global PBDE consumption in 2001. Among Asian countries, Japan could be one of the major consumers. In Japan, consumption of tetra-BDE (comparable to penta-BDE mixture), octa-BDE and deca-BDE commercial mixtures increased rapidly up to 1990, and then decreased gradually (Watanabe and Sakai,

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2003). Several studies showed ubiquitous distribution of PBDEs in the environment including air (Hayakawa et al., 2004), sediment (Choi et al., 2003a), fish (Ohta et al., 2002a; Akutsu et al., 2001) and humans (Choi et al., 2003b; Akutsu et al., 2003) from Japan. Studies examining temporal trend of PBDEs contamination in Japan revealed apparent increase of such contamination during the past 30 years since 1970. For instance, Choi et al. (2003b) estimated that PBDEs in Japanese human breast milk increased 44 times from 1970 to 2000. Kajiwara et al. (2004) found that PBDEs contamination in the northern fur seals peaked in around 1990–1991, followed by a decreasing trend towards 1998. However, in such studies, BDE-209 could not be detected probably due to its low bioavailability.

Technical mixture of HBCDs, which is used as flame retardants in extruded and expanded polystyrene for thermal insulation in buildings, consists of several isomers. Worldwide production of HBCDs was 16,700 tons in 2001 (Law et al., 2005). Residues of HBCDs were first reported in river sediments and fish in Sweden in the mid-1990s (Sellström et al., 1998). Since then, HBCDs have been repeatedly detected in many locations in Europe (Law et al., 2006), and also in remote areas such as the Arctic (de Wit et al., 2004). A review paper on the environmental fate of HBCDs has recently been published (Covaci et al., 2006). Although concern about this compound has grown, information on possible toxicological effects of HBCDs on humans and wildlife are limited. Recent studies suggested that HBCDs may have the same effect on humans like DDTs and PCBs by inducing genetic recombination that may provoke a number of diseases including cancer (Helleday et al., 1999). Neonatal exposure to HBCDs may cause developmental neurotoxic effects such as aberrations in spontaneous behavior and learning and memory function (Eriksson et al., 2002, 2004). A study on temporal trend of HBCDs in guillemot egg from the Baltic Sea (Sellström et al., 2003) revealed peak concentrations of HBCDs in the mid-1970s, followed by a decrease. The concentrations then increased again during the latter part of the 1980s and remained constant and high compared to those in the 1970s. In Japan, consumption of HBCDs increased continuously from around 600 tons in 1986 to 2200 tons in 2001 (Watanabe and Sakai, 2003). Despite this fact, comprehensive data on its contamination levels in environment, human and wildlife are not available for adequate risk assessment and management.

Bottom sediment is an important sink and reservoir of anthropogenic pollutants and has large impact on their distribution, transport, and fate in aquatic environment. Furthermore, vertical profile in dated sediment core can be used to estimate historical depositions of persistent organic pollutants into aquatic environments (Covaci et al., 2005; Song et al., 2004). In this study, surface and core sediments were collected from Tokyo Bay, situated near one of the most populous areas in the world, for determining contamination status of PBDEs and HBCDs. Temporal trend and flux of PBDEs and HBCDs to the bottom sediment were also investigated. To our knowledge, this is the first study to investigate temporal trend on HBCDs using dated sediment cores in Japan.

2. Materials and methods

2.1. Sampling site and sample collection

Tokyo Bay is a eutrophic coastal region with a surface area of 960 km^2 and water volume of 14.4×10^9 m^3, with an average depth of 15 m. The flow rate from rivers into Tokyo Bay is 2.1×10^7 m^3/d (Isobe et al., 2006). Three sediment cores and six surface sediments collected from Tokyo Bay (Fig. 1) were analyzed in this study. Detailed information on sampling survey, which was conducted by Japan Coast Guard in 2002, was described elsewhere (Shimizu et al., 2005). The sediment cores were collected from five locations in Tokyo Bay using a gravity corer (TP-1, TP-4, TP-5, TP-7, and TP-8; Fig. 1). Only the surface layer was analyzed for TP-7 and TP-8 in this study. Cores were sliced at 5 cm intervals onboard. Dating of sediment cores was performed using ^{210}Pb dating; details of the method and dating results are described in Shimizu et al. (2005). Sedimentation rate was calculated from excess ^{210}Pb (dpm) in each layer and cumulative weight (g/cm^2) in core. Average sedimentation rates of dry matter in three cores were calculated to be 0.15, 0.20, and 0.17 g/cm^2/yr, for TP-1, TP-4, and TP-5, respectively. Further, surface sediments were sampled from four locations with a Smith–MacIntyre grab sampler (T-2, T-3, T-4, and T-5 in Fig. 1). The top 5 cm of the sediment was taken from the sampler. All the samples were transported at −40 °C and stored in amber glass bottles at −20 °C until analysis.

2.2. Analytical methods

Sediment samples were extracted following the method described by Minh et al. (in press) with some modifications. Approximately 20 g of wet sediment sample was placed in a conical flask and spiked with surrogates including each 5 ng of ^{13}C-BDEs ($^{13}C_{12}$-BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, BDE-197, BDE-207 and BDE-209), and 10 ng of ^{13}C-HBCD (α-, β- and γ-$^{13}C_{12}$-HBCD). One hundred milliliter acetone was added to the flask and shaken vigorously for 60 min using an electric shaker (SR-2W model, TAITEC, Japan). The soil solution was filtered into a separating funnel containing 600 ml hexane-washed water and 100 ml hexane. The funnel was shaken vigorously for 15 min and then kept for at least 8 h to separate entirely the aqueous and the hexane layers. The aqueous layer was discarded and hexane layer was washed three times with 100 ml hexane-washed water. The extract was concentrated to about 10 ml by a rotary evaporator and further to 5 ml under gentle nitrogen stream. The hexane solution was diluted with 5 ml dichloromethane and subjected to gel permeation chromatography (GPC) for cleanup. The GPC fraction containing organohalogens was concentrated and passed through a column packed with 1.5 g of activated silica gel (Wako gel S-1, Wako Pure Chemicals, Japan) for further cleanup and fractionation. The fraction containing PBDEs was eluted by 80 ml of 5% dichloromethane in hexane (v/v) and the fraction containing HBCDs was eluted by 100 ml of 20% dichloromethane in hexane (v/v). The fraction of PBDEs was concentrated to 5 ml and treated with concentrated H_2SO_4 and activated copper strings. $^{13}C_{12}$-BDE-139 was added to PBDEs fraction as an internal standard and concentrated prior to GC–MS analysis (Kajiwara et al., 2004; Ueno et al., 2004). Concentrations of all the targeted BDEs congeners including di- to nona-BDE congeners were summed to obtain the total concentration of $\sum$PBDEs.

The HBCDs fraction was evaporated, transferred and spiked with 10 ng of HBCD-d_{18} (α-, β- and γ-HBCD-d_{18}) as an internal standard prior to LC–MS–MS analysis. The diastereomeric analysis of HBCDs was performed on the basis of an analytical method reported by Tomy et al. (2004). Sample extract was analyzed with Quattro Micro API triple-quadrupole mass spectrometer (Waters/Micromass, Tokyo, Japan) equipped with Alliance 2795 LC separation module (Waters, Tokyo, Japan). LC separation of three isomers (α-, β- and γ-) of HBCDs was achieved with an Extend-C18 column (2.1 mm i.d. × 150 mm, 5 μm). The mobile phase consisted of water/acetonitrile/methanol (20:30:50) at 0.2 ml/min in initial condition for 2 min and ramped to acetonitrile/methanol (30:70) 5 min and kept for 6 min. An MS–MS analysis, which was operated in negative mode of electrospray ionization (ESI), was performed in multiple reaction monitoring mode (MRM). Quantification of native HBCDs was achieved from mean value of the response of two MRM

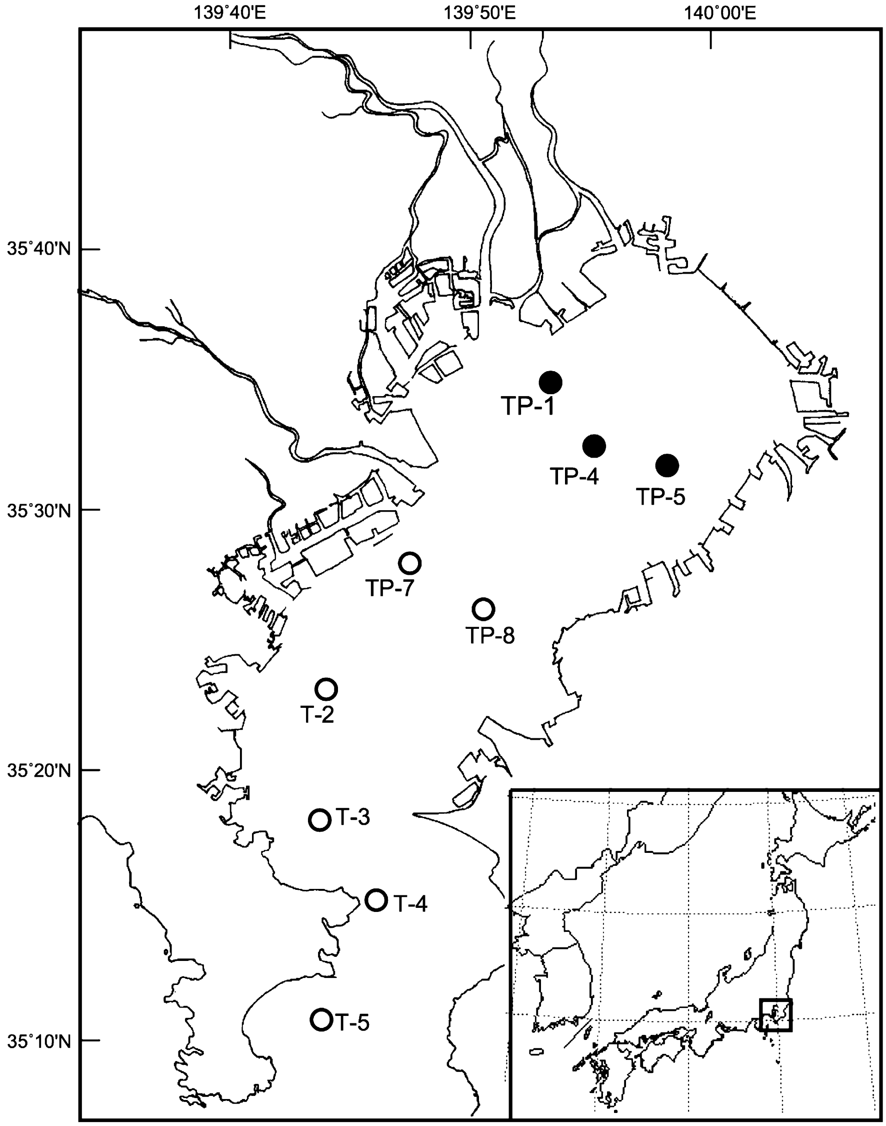

Fig. 1. Sampling locations in Tokyo Bay, Japan. Closed circle, sediment core; open circle, surface sediment.

transitions (i.e., m/z 640 > 81, m/z 642 > 81) corrected with response of $^{13}C_{12}$-HBCDs (i.e., m/z 652 > 81 MRM transition).

We defined the method detection limit (MDL) as the concentrations corresponding to those exhibiting a signal to noise ratio of 10 on the chromatogram of standard solution. MDL for each HBCD isomer was calculated to be 0.01 ng/g in dry sediment. Recoveries of $^{13}C_{12}$-HBCDs spiked to the sample extracts were always in the range of 70–120%. Organic carbon content in sediment samples was approximated by ignition loss, defined as the loss in weight of dried sediment during ignition at 600 °C for 2 h. A procedural blank was analyzed every seven samples to check for interferences and contamination. Concentrations of $\sum$PBDEs, BDE-209 and HBCDs were expressed in ng/g dry wt unless stated otherwise.

3. Results and discussion

3.1. Spatial distribution

Concentrations of $\sum$PBDEs (sum of di- to nona-BDEs) and BDE-209 ranged from 0.051 to 3.6 ng/g dry wt and from 0.89 to 85 ng/g dry wt, respectively (Table 1). A concentration gradient was observed, showing decreasing $\sum$PBDEs and BDE-209 levels towards the mouth of the bay. Particularly, concentrations of $\sum$PBDEs and BDE-209 decreased from TP-1, TP-4 and TP-5 (near Tokyo municipal areas) to TP-7 and TP-8 (in the middle of the bay), and further decreased in stations T-2–T-5. These concentration gradients clearly demonstrated that populated areas such as Tokyo and Yokohama cities are major emission sources of PBDEs to the bay. This trend was also observed for other contaminants, e.g., estradiol and related compounds (Isobe et al., 2006). Discharge of municipal sewages and atmospheric deposition of fine particles could be the transport pathway of PBDEs to the aquatic environment. In geographical comparison, $\sum$PBDEs in Tokyo Bay were comparable to those in Osaka Bay (0.23–1.9 ng/dry wt; Ohta et al., 2002b) and those from some other industrialized areas in Japan (0.013–2.4 ng/dry wt; Choi et al., 2003a). However, concentrations of BDE-209 were lower in the present study compared to those in the Osaka Bay (78–350 ng/dry wt; Ohta et al., 2002b). This

Table 1
Sampling location and concentrations of $\sum$PBDEs, BDE-209 and HBCDs in surface sediment

Sampling location			Water depth (m)	Ignition loss (%)[a]	Concentration (ng/g dry wt)		
Station	Latitude	Longitude			$\sum$PBDEs[b]	BDE-209	HBCDs[c]
Core sediment							
TP-1	35°35.2′N	139°52.7′E	13	12	3.6	85	2.1
TP-4	35°32.7′N	139°54.8′E	20	14	2.2	46	2.0
TP-5	35°31.7′N	139°58.7′E	19	12	1.1	20	0.73
Surface sediment							
TP-7	35°27.8′N	139°46.9′E	33	12	0.78	18	1.2
TP-8	35°25.7′N	139°50.7′E	25	10	0.48	9.2	0.33
T-2	35°23.3′N	139°43.6′E	19	3.9	0.06	1.5	0.056
T-3	35°18.3′N	139°43.1′E	45	5.3	0.08	2.3	0.18
T-4	35°14.9′N	139°45.4′E	31	5.1	0.05	0.89	0.11
T-5	35°09.0′N	139°43.0′E	185	6.8	0.13	1.9	0.13

[a] Ignition loss, loss in weight of dried sediment during ignition at 600 °C for 2 h.
[b] $\sum$PBDEs, sum of di- to nona-BDE congeners.
[c] HBCDs, sum of α-, β- and γ-HBCD isomers.

phenomenon may be due to the fact that sampling stations in Osaka Bay were very near to the coast, which could be strongly affected by municipal and industrial wastewaters containing high levels of anthropogenic pollutants such as PBDEs. On the other hand, sampling stations in the present study were relatively far from the coastal areas. In Korea, concentrations of $\sum$PBDEs ranged from 0.05 to 6.37 and from 1.1 to 33.8 ng/dry wt in two studies along the coastal areas (Moon et al., 2002a,b). In the Pearl River Delta of China, $\sum$PBDEs ranged from 0.04 to 94.7 ng/g dry wt, and BDE-209 from 0.4 to 7340 ng/g dry wt. In North America, concentrations of $\sum$PBDEs and BDE-209 among the Great Lakes ranged from 0.49 to 6.33 ng/dry wt and from 4.3 to 211.2 ng/g dry wt, respectively (Song et al., 2004, 2005a,b) with concentrations comparable to those in the present study. In Europe, $\sum$PBDEs and BDE-209 in several rivers of UK ranged from 0.46 to 17 ng/g dry wt and from 0.57 to 119 ng/g dry wt, respectively (Allchin and de Boer, 2001). In Sweden, very high levels of $\sum$PBDEs and BDE-209 (8–50 and 68–7100 ng/g dry wt, respectively) were found in rivers (Sellström et al., 1998). In general, $\sum$PBDEs and BDE-209 in the surface sediments from Tokyo Bay varied within the common range observed for riverine and coastal sediments around the world.

HBCDs were detected in all the surface sediments, proving widespread presence of this contaminant in the aquatic environment. Concentrations of HBCDs in the surface sediments ranged from 0.056 to 2.3 ng/g dry wt, which is in the same range of reported values (Covaci et al., 2006) and is comparable to those of $\sum$PBDEs. To our knowledge, this is the first study showing HBCDs in the environmental media in Japan indicating that more attention should be paid to this contaminant. Recent studies in Europe showed that HBCDs are bioaccumulative and can be transferred from sediment via invertebrates and predatory fish to higher trophic levels such as fish-eating birds and seals (Morris et al., 2004; Leonards et al., 2004). In this context, more studies should be carried out with other environmental matrices and biota including humans for evaluating biomagnification and risk assessment of these contaminants in Japan. Similar to PBDEs, a decreasing trend of HBCDs from northwestern part to mouth of the bay was also observed. This result supports the hypothesis that municipal and industrialized area in Tokyo metropolitan and Kanagawa prefecture are emission sources of PBDEs and HBCDs to Tokyo Bay. Besides, levels of HBCDs in all sediments collected in relatively far away sites of Tokyo Bay also suggest that HBCDs undergo long-range atmospheric transport (Remberger et al., 2004; de Wit et al., 2004).

Data on HBCDs contamination in Japan are scarce. In the present study, concentrations of HBCDs in the surface sediments collected in Tokyo Bay ranged from 0.056 to 2.3 ng/g dry wt, comparable to a general worldwide range. For example, HBCDs in the estuarine and riverine sediments of the Netherlands ranged from <0.8 to 9.9 ng/g dry wt (Morris et al., 2004). HBCDs in sediments from the Dublin Bay, Ireland and Drammens River and Drammens Fjord, Norway were in the range of <1.7–12, <0.12–4.1 and 0.2–14.14 ng/g dry wt, respectively (Morris et al., 2004). HBCDs in suspended sediments from Detroit River, Canada were found at levels from <0.075 to 3.7 ng/g dry wt (Marvin et al., 2006). Some sediments from particular areas may contain very high levels of HBCDs such as those from the vicinity of a site of BFRs manufacture at Newton Aycliffe, UK that contained HBCDs at 1680 ng/g dry wt (Morris et al., 2004).

3.2. Vertical profiles

Distribution of $\sum$PBDEs and BDE-209 at different depths in each core is shown in Fig. 2. In the sediment core TP-1, levels of $\sum$PBDEs and BDE-209 mostly increased from the depth 15–20 cm to the top layer. Sediment dating data suggested rapid increase of PBDEs in this core from the late 1960s to the late 1990s. Concentrations of $\sum$PBDEs and BDE-209 in the surface layer of TP-1 were about 10 times higher than those in the segment 15–20 cm, where they first appeared. Low residue of PBDEs observed in the segment 35–40 cm (~1915), before the commercialization of PBDE

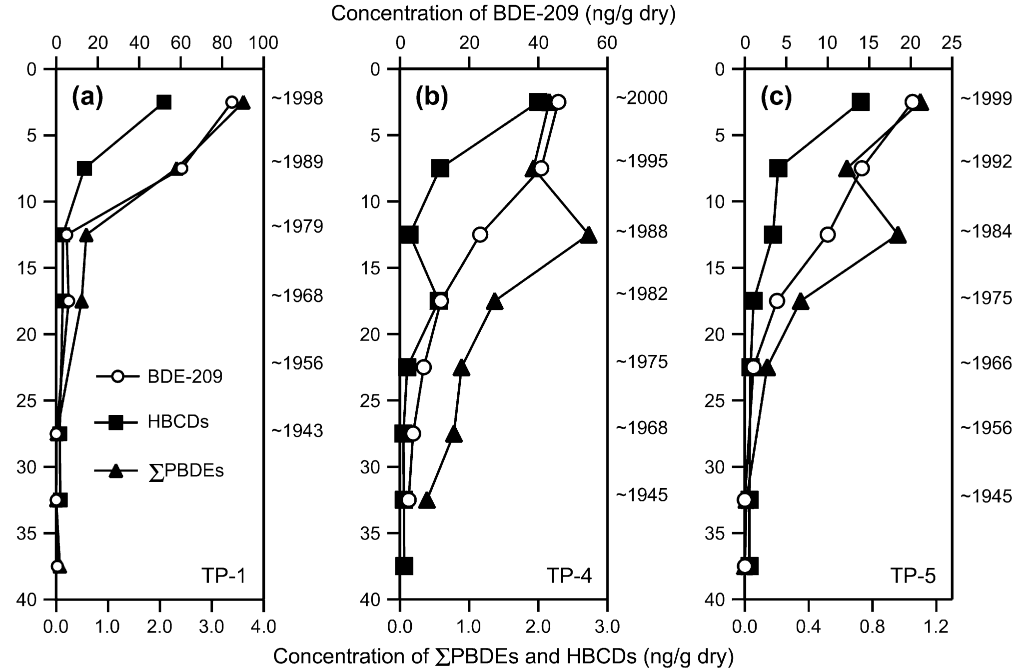

Fig. 2. Vertical profiles of concentrations of ∑PBDEs, BDE-209, and HBCDs in the sediment cores taken from (a) TP-1; (b) TP-4; and (c) TP-5. (Value in right side indicates estimated year of sedimentation.) ∑PBDEs, sum of di- to nona-BDE congeners; HBCDs, sum of α-, β- and γ-HBCD isomers.

products, might be due to vertical mixing in the surface of the sediment. In the core TP-4, ∑PBDEs consistently increased from the segment 30–35 cm (~1945) to the segment 10–15 cm (~1988), followed by slight decrease to the top layer (~2000). On the other hand, BDE-209 consistently increased from the segment 30–35 cm to the top layer. In core TP-5, ∑PBDEs increased from the segment 20–25 cm (~1966) to 10–15 cm (~1986), followed by slight decrease in 5–10 cm (~1992). Concentration of BDE-209 in TP-5 increased from the segment 20–25 cm to the surface with similar pattern comparable to the other cores. Although the segmentation of three sediment cores might be rather large (5 cm interval), the retrospective analysis of these BFRs in Tokyo Bay was achieved by this study.

Consumption of deca-BDE and octa-BDE technical mixtures increased until 1990 and 1991, followed by consistent decrease in Japan (Watanabe and Sakai, 2003). On the other hand, consumption of tetra-BDE mixture, which was similar to the penta-BDE commercial mixture, was voluntarily phased out in 1990. In the present study, a slight decrease of ∑PBDEs concentration was found in the mid-1990s in two cores TP-4 and TP-5 (Fig. 2). This phenomenon might be the reflection of the phase-out and reduction of tetra- and octa-BDE mixtures in the early 1990s. Temporal trend of PBDEs in archived northern fur seal samples collected around Japan (Kajiwara et al., 2004) was similar to the present study with ∑PBDEs peaking around 1991–1994, followed by a decrease until 1998. Another study examining sediment cores from Tokyo Bay reported similar increasing trend of ∑PBDEs until the mid-1990s, followed by slight decline up to year 2000 (Choi et al., 2003c). Alternatively, temporal trend of BDE-209 in this study is relatively consistent in all the three cores, showing an increase in BDE-209 levels until recent years. Similar temporal trend was also observed in the core sediment from Osaka Bay and Tokyo Bay, Japan (Choi et al., 2003c,d). The temporal trend of BDE-209 in the core sediments is different from consumption rate of deca-BDE mixture in Japan (Watanabe and Sakai, 2003), showing that demand for consumption has decreased since 1990. This result suggests a time gap between consumption and emission of deca-BDE indicating that the level of such compounds should be further monitored in future. When compared to other studies on sediment cores around the world, the temporal trends of PBDEs in this study are mostly similar to those observed in a sediment core collected in the Pearl River Delta (Mai et al., 2005) and several cores collected in the Great Lakes (Song et al., 2004, 2005a,b), which reported the highest concentration in the top layers. However, the depth profile of PBDEs in the present study is somewhat different compared to those reported by Zegers et al. (2003), which demonstrated decreasing trend of most BDE congeners including BDE-209 in sediment cores from Western Europe.

In the present study, concentrations of HBCDs increased from segment 20–25 cm to the top layer of all sediment cores. HBCDs were detected first in sediment segments dated the late 1960s and the early 1970s (Fig. 2c). Concentrations of HBCDs in the top layer of TP-1 and TP-4 were roughly same and about four times higher than those in TP-5. Data on HBCDs in sediment cores in Japan and other locations in the world are not yet available for comparison. To our knowledge, this is the first report in which the temporal trend of HBCDs was investigated using sediment cores, showing its increasing concentration since the late 1960s. Watanabe and Sakai (2003) showed that consumption of HBCDs in Japan increased from 600 tons in 1986 to 2200 tons in 2001 and so its emission to the environment may probably increase in future.

Based on the other studies on sediment cores from Tokyo Bay, most anthropogenic pollutants, such as heavy metals, PCBs, LABs (linear alkylbenzenes), and NP (nonylphenol) showed peak concentrations in the subsurface layer deposited in the mid-1970s with a decreasing trend towards surface (Matsumoto, 1983; Sanada et al., 1999; Isobe et al., 2001). This phenomenon is probably a result of the ban on PCB production, regulations on industrial wastewater and development of municipal sewer systems. On the other hand, PBDEs and HBCDs, analytes of this study, showed an increasing trend in sediment cores, which might be due to their use as flame retardants until now. Anticipating the environmental risk of these compounds, continuous monitoring studies are necessary to evaluate the temporal trend of BFRs pollution in Tokyo Bay.

3.3. Inventory and fluxes

Inventory of the contaminants represent the total integrated mass of analytes per unit area, indicating the sum of historical load of contaminants to a particular location. The inventory of ∑PBDEs, BDE-209 and HBCDs in the three cores from Tokyo Bay was estimated using Eq. (1) suggested by Song et al. (2004)

$$\text{Inventory} = \sum C_i \rho_b d_i \qquad (1)$$

where C_i is the concentration in segment i (ng/g dry wt); ρ_b is the dry mass bulk density (g/cm^3) and d_i is the thickness of the segment i (cm).

Inventories of ∑PBDEs and BDE-209 in the three cores were 38–120 ng/cm^2 and 590–1700 ng/cm^2, respectively (Table 2). The lowest inventories of ∑PBDEs and BDE-209 were recorded in the core TP-5. In the Great Lakes, the inventories of ∑PBDEs and BDE-209 were 0.15–7.75 ng/cm^2 and 3.1–140.8 ng/cm^2, respectively (Song et al., 2004, 2005a,b), which were one to two orders of magnitude lower than those in the present study. The concentrations of ∑PBDEs and BDE-209 in the surface sediments of this study were lower than those in the Great Lakes; the higher inventories in Tokyo Bay might be due to higher sedimentation rates (0.69–1.2 g/cm^2/yr; Table 2) compared to those in the Great Lakes (0.0108–0.371 g/cm^2/yr). The inventory of HBCDs was 13–38 ng/cm^2 (Table 2). The range of HBCDs inventory was slightly lower than that of ∑PBDEs and about 50-fold lower than those of BDE-209.

Total loads of analytes in the sediment of Tokyo Bay with a water surface area of 1000 km^2 were calculated to be 380–1200, 5900–17,000, and 130–380 kg for ∑PBDEs, BDE-209, and HBCDs, respectively. Though these values are possibly overestimated because the three cores we analyzed were taken from northern part of the bay, the most extreme case of contamination can be estimated. The total load of ∑PBDEs and BDE-209 in Tokyo Bay was in the same range of those in each lake of the Great Lakes (130–2400 kg for ∑PBDEs and 2500–47,000 kg for BDE-209; Song et al., 2004, 2005a,b). Interestingly, though the total load of these chemicals was roughly the same in Tokyo Bay and in the Great Lakes, inventories were much higher in Tokyo Bay than in the Great Lakes, which is probably due to difference in water surface area and sedimentation rate.

The surficial flux of PBDEs and HBCDs into bottom sediment in recent years was estimated by Eq. (2), in which R is sedimentation rate (g/cm^2/yr)

$$\text{Flux}_s = C_s R_s \qquad (2)$$

The surficial flux of ∑PBDEs and BDE-209 in Tokyo Bay was found to be 0.95–2.6 and 17–58 ng/cm^2/yr, respectively. The lowest flux was found in the core TP-5, which is consistent with the observation of the inventories. In comparison to the surficial flux of ∑PBDEs and BDE-209 in the Great Lakes (0.008–0.315 and 0.1–8.93 ng/cm^2/yr, respectively), the values in Tokyo Bay were higher. As Tokyo Bay is a small and shallow embayment, surficial fluxes in Tokyo Bay were higher than those in the Great Lakes whereas total loads were similar. The surficial flux of HBCDs ranged from 0.62 to 2.4 ng/cm^2/yr, which is comparable to ∑PBDEs. This result clearly indicates the increasing input of HBCDs into Tokyo Bay in recent years. It is noteworthy that HBCDs can be transferred from sediment via invertebrates and predator fish to higher trophic levels such as fish-eating birds and seals (Morris et al., 2004; Leonards et al., 2004). Therefore, continuous increasing input of HBCDs into Tokyo Bay in recent years should be of concern for further biological studies.

3.4. Composition of congeners and isomers

Fig. 3 shows temporal trend in the composition of important BDE congeners including three representative congeners in tetra-BDE mixture (BDE-47, BDE-99 and BDE-100; Fig. 3a), three in octa-BDE mixture (BDE-153, BDE-154 and BDE-183; Fig. 3b) and one in deca-BDE mixture (BDE-209; Fig. 3c).

Table 2
Inventory and surficial flux of ∑PBDEs, BDE-209 and HBCDs in sediment cores from Tokyo Bay

	Sedimentation rate (g/cm^2/yr)	∑PBDEs[a]		BDE-209		HBCDs[b]	
		Inventory (ng/cm^2)	Surficial flux (ng/cm^2/yr)	Inventory (ng/cm^2)	Surficial flux (ng/cm^2/yr)	Inventory (ng/cm^2)	Surficial flux (ng/cm^2/yr)
TP-1	0.69	76	2.5	1700	58	34	1.4
TP-4	1.2	120	2.6	1500	54	38	2.4
TP-5	0.86	38	0.95	590	17	13	0.62

[a] ∑PBDEs, sum of di- to nona-BDE congeners.

[b] HBCDs, sum of α-, β- and γ-HBCD isomers.

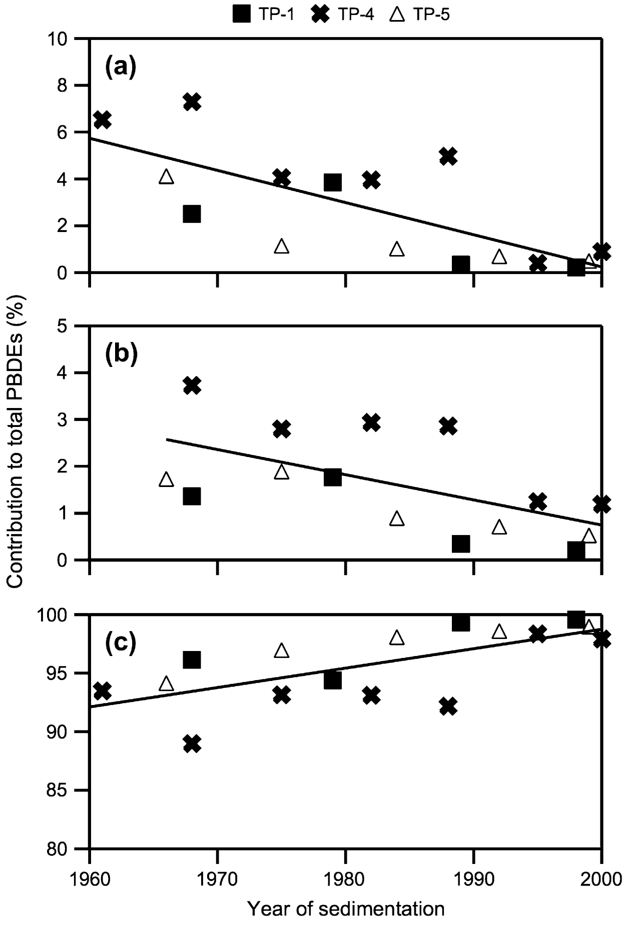

Fig. 3. Temporal trend of contributions of (a) tetra-BDE, (b) octa-BDE, and (c) deca-BDE, to total PBDEs in TP-1, TP-4, and TP-5.

Contributions of tetra-BDE and octa-BDE to the total significantly decreased from the early 1960s to 2000 ($p = 0.004$ and 0.015, respectively). On the other hand, contribution of deca-BDE increased during this period from about 90% in the early 1960s to nearly 100% in 2000 ($p = 0.006$). This fact suggests increasing input of deca-BDE mixture to the environment in recent years. This result agrees well with the fact that the contribution of deca-BDE mixture in the total domestic consumption of PBDEs in Japan increased from 67% in 1986 to 100% in 2000 (Watanabe and Sakai, 2003). Interestingly, contribution of tetra-BDE mixture seemed to decrease more dramatically than octa-BDE mixture around the early 1990s when the consumption of tetra-BDE was completely discontinued (Fig. 3a and b). Similar result was also observed in the northern fur seal samples collected in Japan during 1972–1998 (Kajiwara et al., 2004). Result of this study revealed faster decrease of tetra-BDE congeners (BDE-47, BDE-99 and BDE-100) compared to those of octa-BDE (BDE-153 and BDE-154).

Kajiwara et al. (2004) reported that contributions of BDE-153 and BDE-154 are particularly high in the seal samples from Japan compared to those from Europe and the US (Law et al., 2002; Ikonomou et al., 2002; She et al., 2002), suggesting different usage patterns of commercial PBDE products in Japan. Regarding this, Zegers et al. (2003) reported the absence of BDE-183, the marker for octa-BDE mixture, in all the sediment cores collected from Western Europe; this congener was detected in all the sediment cores in the present study also. This is probably due to the use of octa-BDE mixture more intensively in Japan rather than in Europe. Representative congeners in penta-BDE product such as BDE-47, BDE-99, BDE-100 reflected well in sediments from the Great Lakes and Pearl River Delta (Song et al., 2004; Mai et al., 2005). In contrast, sediments from Tokyo Bay revealed somewhat different composition, with absence of BDE-100, suggesting the use of different types of PBDE products in Japan. The tetra-BDE mixture used in Japan probably contained lesser proportion of BDE-100 compared to commercial penta-BDE mixture used in Europe and the US. Accurate data on the composition of tetra-BDE used in Japan are not yet available for further discussion.

Fig. 4 shows the comparison of PBDEs including BDE-47, BDE-99, BDE-153 and BDE-183 in the surface sediments of this study with those in air, atmospheric deposition and soil samples collected from Kyoto city, Japan (Hayakawa et al., 2004). Proportion of lower brominated congeners such as BDE-47 and BDE-99 in the sediments was higher compared to the soils but lower than in atmospheric depositions. On the other hand, proportion of the higher brominated congener BDE-183, which has high affinity to particulates, is lower in the sediments compared to soils but higher compared to atmospheric depositions. This phenomenon probably suggests that the bottom sediment in Tokyo Bay was supplied by particulates from both atmospheric deposition and soil washout. Relatively high sedimentation rate in Tokyo Bay compared to those in the Great Lakes may also explain this phenomenon.

HBCDs diastereomeric composition in the surface sediments from Tokyo Bay demonstrated the predominance of γ-HBCD (60–100%), followed by α-HBCD (0–40%). β-HBCD was found only in the surface of TP-1 (about 7%), though it was found in more than half of sediment samples analyzed using LC–MS (Covaci et al., 2006). Compositions of α-HBCD in

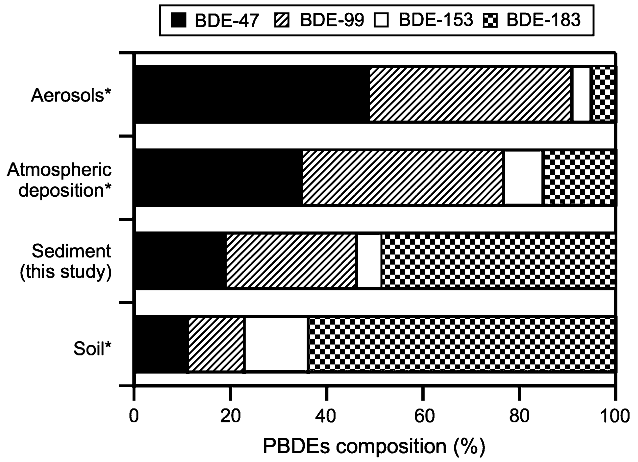

Fig. 4. Congener composition of BDE-47, BDE-99, BDE-153, and BDE-183 in aerosols, atmospheric deposition, sediment, and soil in Japan (*Hayakawa et al., 2004).

some samples are higher than those in commercial formulations (approximately 10%; Law et al., 2005). It is known that the thermal rearrangement of the HBCD diastereomers may occur at temperature above 160 °C, leading to conversion of γ-HBCD into α-HBCD. Higher percentage of α-HBCD in sediments from Tokyo Bay may indicate that its major source may be the heat-treated polymer materials or textiles, which are produced at temperature above 160 °C (Morris et al., 2004; Sellström et al., 1998). Vertical distribution of isomeric composition of HBCDs in the sediment cores TP-1, TP-4 and TP-5 demonstrates similar patterns with those in the surface sediments, showing more than 20% of α-HBCD in most of the segments, except in two segments in the core TP-4 that contained 100% of γ-HBCD (Fig. 5). This result suggests that major source of HBCDs could be the heat-treated polymers. However, it is not distinguishable whether the difference in the composition of the diastereomers is caused by thermal isomeric rearrangement of technical HBCDs mixture or by isomer-specific behavior in the environment (Covaci et al., 2006). Further study is necessary to evaluate the environmental fate and ecological risk of HBCDs.

4. Conclusions

BFRs were detected in all the surface sediment samples of Tokyo Bay, indicating ubiquitous contamination by these chemicals in this area. This is the first comprehensive monitoring research on HBCDs pollution in Japan. Concentrations of BFRs were higher in the northern part of the bay and showed a decreasing trend towards the mouth of the bay, indicating that municipal and industrial wastewaters are the possible sources of BFRs. Vertical profiles of PBDEs and HBCDs in the core sediments were also examined. Concentrations of ∑PBDEs increased until 1980s and remained constant up to the top layer. Probably ∑PBDEs concentrations may decrease in near future because their use has already been terminated. Concentrations of BDE-209 and HBCDs were found to be increasing. Especially, concentrations of HBCDs are expected to increase with its increasing usage. Therefore, widespread and continuous monitoring studies need to be done in Tokyo Bay to prevent serious environmental pollution and to manage environmental risks.

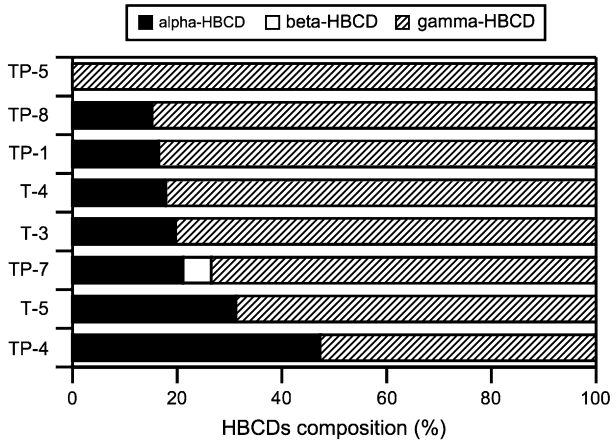

Fig. 5. Composition of HBCD isomers in surface sediment from Tokyo Bay.

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