

**LEVELS AND TEMPORAL TRENDS OF BROMINATED FLAME RETARDANTS
(PBDEs AND HBCDs) IN ASIAN WATERS USING ARCHIVED SAMPLES FROM *ES*-BANK,
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Abstract

Concern over environmental contamination by brominated flame retardants (BFRs), especially by polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), have increased in recent years due to their persistence, bioaccumulative nature, and possible adverse effects on humans and wildlife. In this study, we summarize temporal trends of BFRs in Asian waters using samples archived in our environmental specimen bank (*es*-BANK), Ehime University, Japan. In general, the results indicate that environmental levels of PBDEs and HBCDs have risen significantly during the last 30 years. In the samples from Japan, where usage of some commercial PBDE products was voluntary discontinued in the 1990s, environmental PBDE levels seem to be steady or slightly decreasing since then. However, in the same samples, concentrations of HBCDs exhibited continuous increasing trend and, in recent years, the contaminant levels appear to exceed those of PBDEs reflecting increasing usage of HBCDs over PBDEs in Japan. Increasing environmental contamination by PBDEs and HBCDs was also noticed in Chinese coastal waters, indicating that the contamination by BFRs has already become evident even in developing countries.

Introduction

The Environmental Specimen Bank (*es*-BANK) at Center for Marine Environmental Studies, Ehime University was established in the year 2002. The *es*-BANK has a wide variety of environmental and biological samples from marine, fresh water and terrestrial ecosystems as well as human samples collected from various parts of the world over a period of nearly forty years. As of today, our *es*-BANK has about 100 000 samples collected from about 1000 species. When looking for issues of future interest, our archive permits specimens to be retrieved for analysis at a later date as methods improve or as new chemicals of interest are discovered. One of the potentials of the *es*-BANK is the possibility to characterize temporal trends of pollutants in ecosystems. The primary objective of the studies summarized below was to assess temporal trends of BFRs such as PBDEs and HBCDs in Asian waters using samples archived in our *es*-BANK.

Materials and Methods

Samples

Archived fat tissue of four marine mammal species, including female northern fur seals (*Callorhinus ursinus*) collected off Sanriku, Japan during 1972-1998 ($n=35$), male melon-headed whales (*Peponocephala electra*) mass stranded along Japanese coast in 1982, 2001 and 2006 ($n=15$), male striped dolphins (*Stenella coeruleoalba*) stranded along Japanese coast during 1978-2003 ($n=20$), and male finless porpoises (*Neophocaena phocaenoides*) collected from coastal waters of South China Sea in 1990, 2000 and 2001 ($n=12$), and three sediment core samples collected from Tokyo Bay, Japan in 2002 were employed for chemical analysis.

Chemical Analysis

Fat samples were Soxhlet extracted with a mixture of diethyl ether and hexane. An aliquot of the extract was added to a gel permeation chromatography (GPC) column for lipid removal. The GPC fraction containing organohalogens was concentrated and subjected to an activated silica gel column (Wakogel DX) for further clean-up and fractionation. Detailed analytical procedure for analysis of PBDEs and HBCDs in blubber samples was described previously.^{1,2}

Sediment samples were extracted with acetone. The extract was washed with hexane-washed water several times to remove coextracted substances. After concentration, the extract was subjected to GPC and activated silica gel column for further clean-up and fractionation. Detailed analytical procedure for analysis of PBDEs and HBCDs in sediment samples was described previously.³

Identification and quantification of PBDEs was done using gas chromatography combined with mass spectrometry (GC-MS), while HBCD isomers were identified and quantified using liquid chromatography combined with tandem mass spectrometry (LC-MS-MS) in a multiple reaction monitoring (MRM) mode.

Results and Discussion

Time trends of PBDE and HBCD concentrations in marine mammals

Northern fur seals

A total of eight congeners from di- to hepta-BDEs were detected in northern fur seals. The lowest PBDE levels were in the fur seals collected in 1972 (mean: 0.34 ng/g lipid wt.), while peak concentrations were around 1991-1994. The average concentration of PBDEs increased to about 150 times between 1972 and 1994, and then the levels decreased to about 50% in 1998 (Table 1 and Fig. 1). The reduction in PBDE levels observed in this study was probably a result of a voluntary phasing out the use of PentaBDE products by related Japanese industries in 1990 and the same in other countries affecting the Asia-Pacific waters. Ratios of BDE-153, BDE-154, and BDE-183 to total PBDEs increased since 1972, while those of some lower brominated congeners decreased. Similar shift in PBDE congener profiles between 1970 and 2000 was observed in Japanese human adipose tissue.⁴ This result implies an increase in demand for PBDEs, particularly the higher brominated diphenyl ethers during 1972-1998.

Table 1. Concentrations of BFRs (ng/g lipid wt.) in blubber of marine mammals from Asian waters.

Species/Location	Year	n	PBDEs	HBCDs
Northern fur seal/ off Sanriku, Japan	1972	3	0.34 (0.33-0.34)	<0.1
	1976	3	4.3 (2.0-8.7)	2.4 (0.69-5.1)
	1980	2	8.5 (8.1-8.9)	0.77 (0.56-0.99)
	1982	3	29 (22-37)	6.5 (0.84-16)
	1985	2	15 (12-18)	1.6 (0.46-2.7)
	1988	2	47 (22-66)	3.6 (2.3-5.0)
	1991	5	49 (35-66)	15 (10-19)
	1994	5	53 (24-100)	33 (21-55)
	1997	5	28 (21-40)	33 (13-67)
Striped dolphin/ Pacific coast, Japan	1978	2	13 (13-13)	12 (12-13)
	1979	3	18 (13-21)	13 (10-16)
	1986	3	230 (190-270)	30 (26-36)
	1992	7	550 (420-660)	230 (140-320)
	2003	5	640 (530-850)	710 (580-940)
Melon-headed whale/ the Pacific coast, Japan	1982	5	26 (23-32)	7.0 (2.7-9.7)
	2001	5	320 (300-340)	390 (330-460)
	2006	5	300 (190-510)	430 (310-650)
Finless porpoise/ South China	1990	7	110 (84-170)	18 (4.7-37)
	2000-2001	5	710 (230-980)	35 (21-55)

*figures in parentheses indicate the range

Concentrations of HBCDs in northern fur seals ranged from <0.1 ng/g lipid wt. in 1972 to 67 ng/g lipid wt. in 1997 (Table 1). Retrospective analysis of fur seals blubber demonstrated that HBCD residues increased from 1972 to mid-1990s, and then slightly decreased in 1998 to about 70 % of its peak values (Fig. 1). Fur seals collected prior to 1991 accumulated HBCDs at levels apparently lower than PBDEs, whereas in the late 1990s the levels of these BFRs were comparable (Table 1). Annual consumption of HBCDs in Japan was about 2000 tons in the year 2000, while the use of TetraBDE and OctaBDE were voluntarily withdrawn from the Japanese market in 1991 and 2000, respectively.⁵ The occurrence of the peak contamination by HBCDs in fur seals later than PBDEs may be related to the relative production and use of HBCDs compared to PBDEs in Japan. The predominant isomer was α -HBCD which contributed more than 95% of the total HBCDs in all the samples analyzed. Although γ -HBCD was detected in the fur seals collected after 1990, isomeric composition did not change temporally, implying that the commercial mixtures of the same composition have been used around the Pacific during 1972-1998.

Striped dolphins

Mean concentrations of PBDEs in striped dolphins increased dramatically from 13 ng/g lipid wt. in 1978 to 640 ng/g lipid wt. in 2003 (Table 1 and Fig. 1). The concentrations increased rapidly until 1992 and since then tended to be steady until 2003. Of the fourteen PBDE congeners analyzed, a total of thirteen congeners from di- to deca-BDE were identified. Contributions of BDE-154 and BDE-153 to total PBDEs were higher than those

generally reported in biological samples. It might be due to the fact that OctaBDE mixture was used more extensively than TetraBDE mixture in Japan.

Continuous increasing trend was noticed for HBCD concentrations during the same period, from 12 ng/g lipid wt. in 1978 to 710 ng/g lipid wt. in 2003. When recent data for HBCDs were compared, the levels in the striped dolphins were higher than those in cetaceans from other regions of Asia-Pacific, probably due to intensive usage in recent years and high consumption of HBCDs in Japan among Asian countries.

Melon-headed whales

In melon-headed whales, PBDE levels in 2006 were significantly higher than 1982, showing about 10 times increase in the past 20 years (Table 1). When we compared PBDE congener patterns, higher contributions of hexa-BDEs were observed in melon-headed whales collected in 2006 than those in 1982. This is similar to the trend found in northern fur seals from the Pacific coast of Japan indicating a possible change in the source products.

Similarly, HBCD levels in 2006 were significantly higher than 1982, showing about fifty times increase (Table 1). Among the three isomers identified, α -HBCD was the only isomer detected in the whales in 1982, while in 2001, small quantities of β - and γ -isomers were also detected. In the specimens collected in 1982, HBCD levels were one order of magnitude lower than PBDEs, while in 2001 and 2006, HBCD levels exceeded PBDEs, showing a similar pattern as observed in the northern fur seals and striped dolphins.

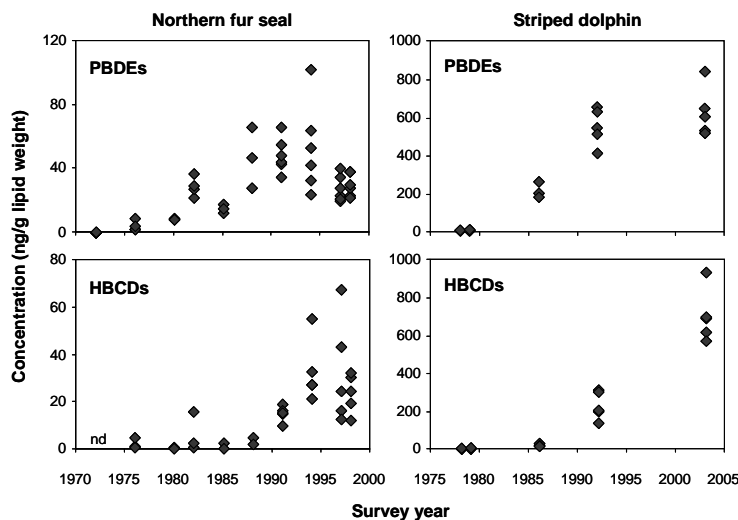


Fig. 1. Temporal trends of PBDEs and HBCDs in northern fur seals and striped dolphins.

Finless porpoises

PBDE concentrations in finless porpoises from South China Sea increased significantly (six fold) from 84 ng/g lipid wt. in 1990 to 980 ng/g lipid wt. in 2001. The significant increase of PBDE levels in finless porpoises suggests that PBDEs have been used more extensively in recent years. The study area located in the Pearl River Delta has numerous electronic and telecommunication industries. In China, the domestic production of BFRs was 10 000 tons in the year 2000 and the demand for BFRs increases at a rate of 8% per year.⁶ The proportion of BDE-47 and BDE-100 was smaller during 1990 than in 2000/01, and the opposite was true for BDE-153 and BDE-154, which may suggest the continuous or increasing usage of PentaBDE mixture in this region, when compared to OctaBDE mixture.⁷

HBCDs were detected in all the finless porpoises from South China Sea coast (Table 1), indicating that the contamination by HBCD has already become evident even in developing countries. Mean concentrations of total HBCDs in finless porpoises increased two fold from 1990 to 2000/01. Unlike the case of northern fur seals, striped dolphins and melon-headed whales collected around Japan, HBCD concentrations in finless porpoises from South China Sea in 2000/01 were still much lower than PBDEs, approximately twenty times lower. These results may indicate that demand for HBCDs, as an alternative for PBDE formulations, is not increasing rapidly in South China.

Time trends of PBDE and HBCD concentrations in sediment cores

Vertical profiles of Σ PBDEs (sum of di- to nona-BDE congeners), BDE-209 and HBCDs are shown in Figure 2. In all the sediment cores, the highest concentrations of Σ PBDEs, BDE-209 and HBCDs were observed

in surface layers of each core. PBDEs appeared in the layer dated to the mid 1940s, while HBCDs were not detected until the layer of early 1970s. This probably reflects difference in onset of commercial usage of these BFRs. There was a slight decreasing or steady trend of Σ PBDEs in the mid 1990s in the cores TP-4 and TP-5 in accordance with discontinued usage of tetra- and octa-BDE technical mixtures in Japan. Furthermore, the relative composition of PBDE congeners demonstrated declining inputs of tetra- and octa-BDE mixtures. Temporal trend of PBDEs in northern fur seals was similar to that in the sediment cores with PBDEs peaking around the early 1990s, followed by a decrease until 1998. On the other hand, input of deca-BDE mixture constantly increased during this period and BDE-209 contributed nearly 100% of PBDE input to the sediments in the year 2000.

The present study underlines the utility of specimen banks in understanding historical loading of environmental contaminants and forecasting their future trends. Specimen banking is also a valuable tool to evaluate the success of policy measures to control the pollution by persistent chemicals. Our investigation also highlights the need for environmental monitoring of PBDEs and HBCDs, which is especially important in the case of HBCDs as they are being used as a replacement for PBDEs.

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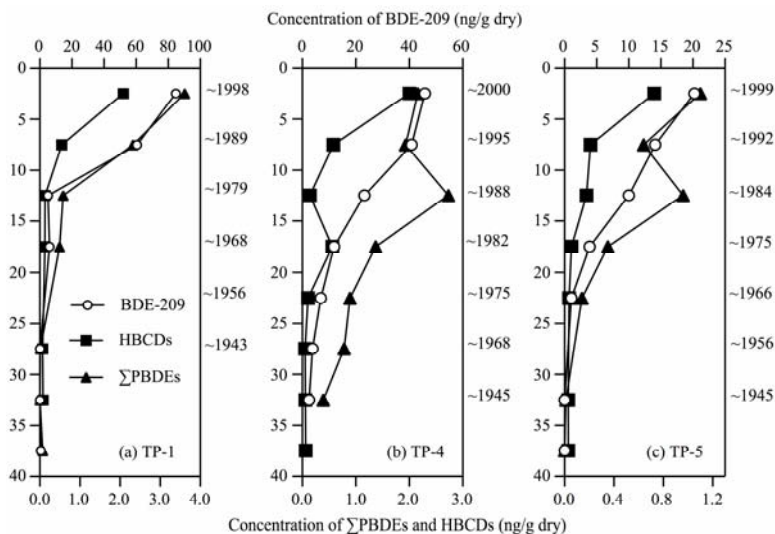


Fig. 2. Vertical profiles of Σ PBDE (di- to nona-BDEs), BDE-209 and HBCDs concentrations in sediment cores from Tokyo Bay, Japan (a) TP-1, (b) TP-4, (c) TP-5. Value on the right side indicates estimated year of sedimentation.