

ASSESSMENT OF BROMINATED FLAME RETARDANTS IN SEDIMENTS FROM ASIA: LEVELS, PROFILES AND TEMPORAL TRENDS

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Abstract

Spatial distribution and temporal trends of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) were evaluated in 119 surface sediment samples collected from several countries in Asia and 3 sediment cores from Tokyo Bay. The concentrations of BDE-209, total PBDEs (sum of mono- to deca-BDE congeners) and HBCDs ranged from <0.03-98 ng/g dry wt., nd-110 ng/g dry wt., and nd-59 ng/g dry wt., respectively. Elevated concentrations of BFRs were found in major urban areas with levels of BFRs at some locations in the range of those from polluted areas worldwide. Among the countries, higher concentrations of BFRs were found in sediments along coastal waters of Korea, indicating that Korea is one of the major consumers of BFRs in Asia. BDE-209 was the predominant PBDE congener in all the countries (up to 80-100%), whereas levels of penta- and octa-BDEs were much lower. Slightly different PBDE compositions were observed among samples collected from different locations, may be due to differences in degree of usage of commercial PBDEs and/or various environmental processes. Analyses of the sediment cores from Tokyo Bay showed that concentrations of BDE-209 and HBCDs rapidly increased in the upper layers which are coincident with the growing use of these commercial BFRs.

Introduction

Sediment is an important environmental matrix for monitoring of environmental contamination owing to its significance as a sink and reservoir for persistent pollutants and its potential impact on contaminants distribution, transport, and fate in the environment. Moreover, concern over sediment associated toxic chemicals is due to their ability to enter the aquatic food chain and elicit toxicity, particularly to sediment dwelling organisms.

Recently, there has been a growing concern over environmental pollution by brominated flame retardants (BFRs), a group of chemicals which are added to various consumer products, including electrical and electronic equipments, textiles, polymer materials etc., to prevent fire. These chemicals are similar in structure, properties and toxic potencies to some classical organochlorines (OCs), such as PCBs and dioxins which are well-known endocrine disrupters. Interestingly, levels of BFRs, especially polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), appear to be increasing in the environment and food chains, and thus are of concern for their effects on humans and wildlife. Asia has a high market demand for BFRs, particularly PBDEs; however, there is less information on their occurrence in Asia as compared to Europe and North America^{1,2}. The present study evaluated concentrations of PBDEs and HBCDs in sediments collected from various locations in Asian countries, including Japan, Korea, Vietnam, Laos, Malaysia and Indonesia to understand their contamination status, geographical variation, and temporal trends in the environment.

Materials and methods

Samples and study area

A total of 116 surface sediment samples from various locations in Asia, including Indonesia, Malaysia, Vietnam,

Thailand, Laos, Korea and Japan, (Figure 1) and three sediment cores from Tokyo Bay, Japan collected during 1998-2005 were used in this study. Results for some of the samples have been published elsewhere^{3,4}. Surface sediment samples were divided into two categories, namely samples collected from areas close to point sources in urban areas and samples from locations considered as unpolluted. The sediment cores were sliced into 5 layers and all the samples were stored in clean polyethylene bags and transported to laboratory in boxes packed with dry ice. In the laboratory (*es*-BANK, Environmental Specimen Bank for Global Monitoring at Ehime University) the sediment samples were kept at -20°C until chemical analysis⁵.

Chemicals analysis

Analysis of BFRs was carried out according to the method described elsewhere³, with slight modifications. Fourteen PBDE congeners (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-206, BDE-207, BDE-209) and HBCDs (α -, β - and γ -HBCD) were analyzed. Briefly, 20 g of wet sediment samples were spiked with $^{13}\text{C}_{12}$ -labeled PBDEs ($^{13}\text{C}_{12}$ -BDE-3, -15, -28, -47, -99, -153, -154, -183, -197, -207, -209) and $^{13}\text{C}_{12}$ -HBCDs ($^{13}\text{C}_{12}$ - α -, β - and γ -HBCDs), and extracted using liquid-liquid extraction. The extract was then subjected to gel permeation chromatography (GPC). The GPC extract was further purified and fractionated by silica gel chromatography. The fraction containing PBDEs was treated with concentrated H_2SO_4 and activated copper for sulfur removal. Prior to quantification and identification, the fractions containing PBDEs and HBCDs were spiked with $^{13}\text{C}_{12}$ -BDE-139 and deuterized HBCDs (α -, β - and γ -HBCD- d_{18}) as internal standards. Quantification of PBDEs was carried out using a gas chromatograph with a mass spectrometry detector (GC-MS) in the negative chemical ionization mode, and a liquid chromatograph equipped with tandem mass spectrometry detector (LC-MS-MS) using electrospray ionization for the isomeric composition of HBCDs.

Results and discussion

Levels and geographical distribution

PBDEs and HBCDs were widely detected in sediments from various locations in Asian countries (Table 1), indicating their ubiquitous usage in Asia. Levels of PBDEs were found to be relatively higher than those of HBCDs in almost all the locations, and this is concomitant with the difference in historical usage between these two BFRs. Concentrations of BDE-209, Σ PBDEs (sum from mono- to deca-BDE) and Σ HBCDs in surface sediments of the present study varied widely depending on the background locations, ranging between <0.03-98 ng/g dry wt., nd-110 ng/g dry wt., and nd-59 ng/g lipid wt., respectively (Table 1). Figure 2 shows the distribution of Σ PBDEs and Σ HBCDs in sediments from all the locations investigated. Among the Asian countries studied, higher concentrations of BFRs were found in sediments from Korea and the levels were in the range of those in sediments from polluted areas worldwide^{1,2}, suggesting that Korea could be one of the major consumers of these compounds in Asia. Similar distribution pattern was also found in a monitoring study of these compounds using mussel as a bioindicator⁶. In all the countries, higher concentrations of BFRs were found at locations close to human activities such as canals, harbors and industrial sites, indicating that such localized sources of these compounds and urban areas are major sources of BFRs to aquatic environment. Interestingly, residue levels of BFRs, particularly PBDEs in major urban areas of Asian developing countries such as Vientiane (Laos), Jakarta and Surabaya (Indonesia), Port Dickson and Port Klang (Malaysia) were in the range of values found in developed countries like Korea and Japan (Figure 2), indicating developing nations may also have pollution sources of BFRs. On the other hand, concentrations of BFRs

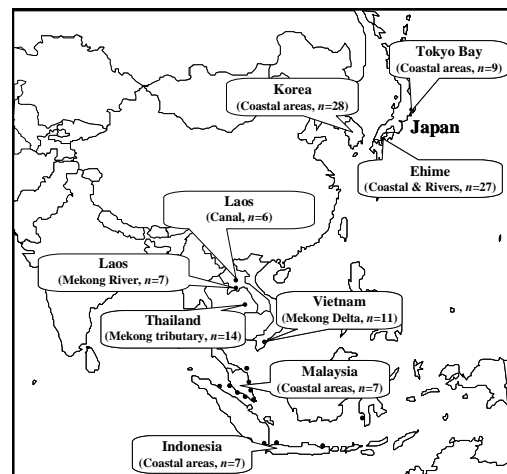


Figure 1. Map showing sampling locations.

at locations without known sources were lower or below detection limits. The contamination by BFRs at these sites is probably due to diffuse sources and long-range atmospheric transport.

Table 1. Residue levels of BFRs (ng/g dry wt.) in surface sediments from some countries in Asia.

Locations	Year	M (%)	TOC (%)	Mono- to Nona-BDE	BDE-209	ΣPBDEs	ΣHBCDs
Indonesia (Coastal, n=7)	1998	59 (31-78)	1.2 (0.24-2.8)	0.38 (nd-1.7)	9.9 (0.031-54)	10 (0.032-57)	0.40 (nd-0.96)
Malaysia (Coastal, n=7)	1998	30 (17-40)	na	0.027 (nd-0.086)	8.3 (0.16-29)	8.8 (0.19-30)	0.050 (nd-0.24)
Vietnam (Delta Mekong River, n=11)	2003	48 (18-89)	1.2 (0.55-1.8)	0.075 (nd-0.31)	0.60 (<0.030-3.1)	0.075 (nd-0.31)	0.13 (nd-0.52)
Laos (Vientiane Canal, n=6)	2005	54 (37-67)	3.2 (0.18-5.0)	2.2 (0.33-4.8)	8.2 (0.91-20)	10 (1.3-25)	13 (0.080-37)
Laos (Middle Mekong River, n=7)	2005	55 (29-98)	0.48 (0.34-0.61)	0.15 (nd-0.71)	0.22 (<0.030-1.3)	0.40 (nd-1.5)	0.0041 (<0.01-0.01)
Thailand (Mekong tributary, n=14)	2005	48 (18-89)	0.94 (0.15-2.4)	0.044 (nd-0.32)	0.29 (<0.030-1.6)	0.33 (0.040-1.9)	0.53 (<0.01-1.4)
Japan (Tokyo Bay, n=9)	2003-2004	9.0 (3.9-14)	na	0.94 (0.050-3.6)	20 (0.89-85)	21 (0.94-89)	0.76 (0.056-2.1)
Japan (Coastal & Rivers Ehime, n=27)	2005-2006	53 (30-99)	na	0.11 (nd-0.52)	2.3 (nd-18)	2.4 (nd-19)	0.62 (0.01-5.0)
Korea (Coastal, n=28)	2005	28-71	0.37-5.5	3.7 (0.44-32)	18 (0.35-98)	21 (0.40-110)	11 (0.39-59)

Note: M= moisture content, TOC= total organic carbon, na= not available, nd= not detected.

Congener and isomer profiles

Among the PBDE congeners analyzed in this study, BDE-209 was the most predominant congener contributing up to 80-100% of the total (Figure 3, Table 1) and the profiles corresponded to the general pattern observed in sediments worldwide¹. The relatively high proportion of BDE-209 in sediments is probably due to the fact that deca-BDE accounts for most of the worldwide total formulation of PBDEs, including Asia¹. Moreover, this compound is very hydrophobic ($K_{ow} \sim 10$), which may cause it to partition to the sinking sediment particles. The other abundant congeners after BDE-209 were BDE-47, -99, -183, -206, and -207 (Figure 3), indicating other commercial mixtures (penta- and octa-BDE) also influenced the profile observed. The availability of octa- to nona-BDE congeners, including BDE-196, -206, and -207 in some sediments of the present study may be due to the fact that these congeners are also present in the commercial formulation of octa- and deca-BDE as impurities⁷ and/or as a result of photolytic and microbial degradation/debromination of BDE-209^{8,9}. The variation of PBDE congener profiles may also indicate the divergence in the degree of usage of different commercial PBDE mixtures in different locations/countries.

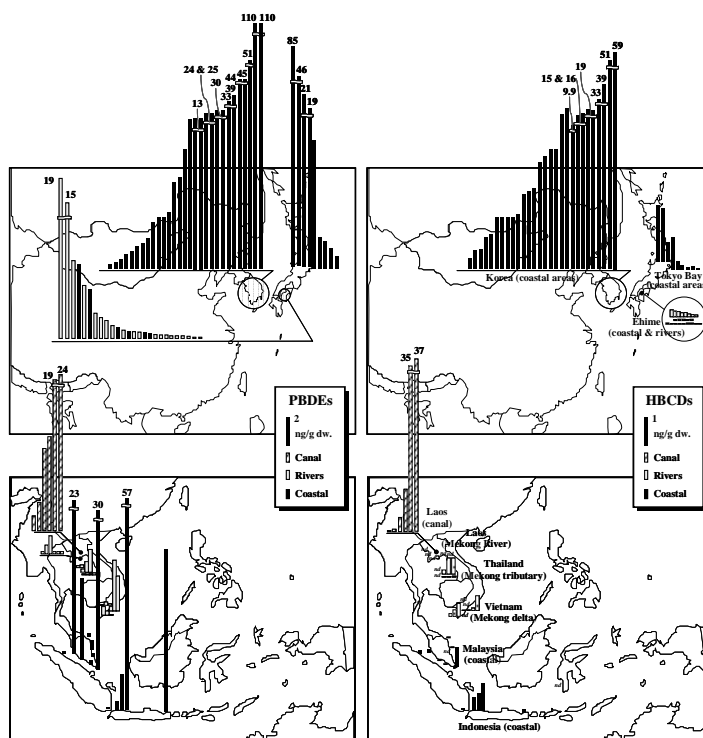


Figure 2. Distribution of BFRs in sediments from Asia.

HBCD isomer profiles in most sediment samples were found to be similar to that of commercial HBCD formulations, with γ -HBCD being the most abundant isomer². However at some locations (Figure 3), the contribution of α -HBCD and β -HBCD were also significant. The reason for the difference in the composition of the HBCD stereoisomers

between some sediments and technical HBCD is not clear, probably due to thermal isomerization during the processing of HBCDs and/or by stereoisomer-specific processes in the environment². Further studies are needed to clarify this point.

Temporal trend

Analysis of PBDEs and HBCDs in sediment cores taken from three locations in Tokyo Bay showed the highest concentrations of BFRs in the top layers, particularly for BDE-209 and HBCDs³ (data not shown), indicating continuous input of these compounds into the environment. PBDEs appeared first in the layer dated to the mid-1940s, whereas HBCDs in the middle of 1970s, concurrent to the time difference in introduction of these two BFR products into the market. There was a slight decreasing or steady trend of PBDEs in the mid-1990s in two cores, and this was in accordance with discontinued usage of tetra- and octa-BDE commercial mixtures in Japan¹⁰, whereas BDE-209 and HBCDs continuously increased until 2000. As the consumption of deca-BDE commercial mixture has decreased since early 1990s¹⁰, the environmental levels of BDE-209 in sediment would be expected to be lower in future. The opposite situation may be expected for HBCDs which is in growing demand as a replacement for PBDEs. Further studies are needed to ascertain spatial trends of BFRs in Asia and to define future contamination trends, especially in developing countries as many of them are sites for e-waste recycling.

Acknowledgements

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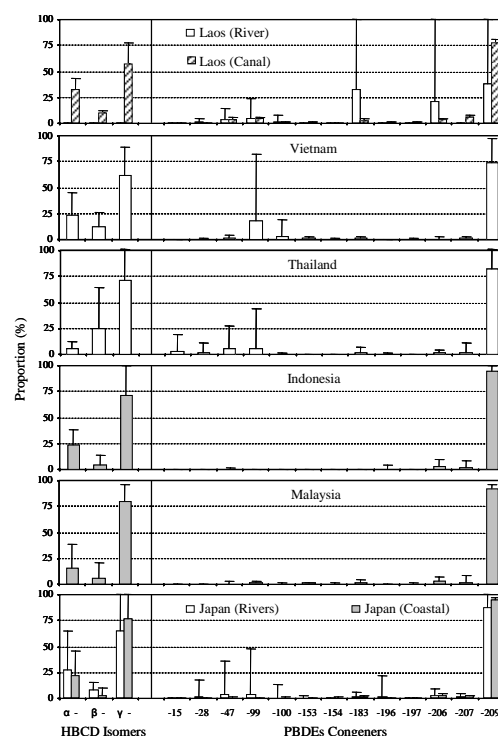


Figure 3. Congener and isomer profiles.