POLYBROMINATED DIPHENYLS IN MARINE SEDIMENTS AND BIVALVES FROM THE COASTAL AREAS OF KOREA

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Introduction

PBDEs are flame-retardants, which are added to a variety of materials. These compounds are widely used in television sets, computers, radios, textiles, new synthetic building materials and automobiles.[1] The annual global production of PBDEs in 1992 was 40,000 tons including 30,000 tons of the decabromodiphenyl ether (DeBDE), and it continues to grow.[2] Hence, there are large amounts of PBDEs in environment, which was released from their manufacturing or operating processes into environment.[3, 4] PBDEs derived from a large number of sources are mainly transported to the sea by atmospheric deposition and river input. Since hydrophobic organic contaminants including PBDEs tend to be strongly associated with particulate matter, their final sink is thought to be the bottom sediments.[5] Therefore, sediment is a deposition place that provides a valuable record of the recent input of contaminants to the marine environment. Aquatic organism may bioaccumulate and bioconcentrate environmental contaminants to more than 1,000,000 times of the concentrations detected in the water column. International monitoring programs for marine pollutants are carried out using bioindicators such as shellfish, particularly mussels (*Mytilus edulis*) and oysters (*Crassostrea gigas*).[6, 7] These bivalves are an effective trapping mechanism for many environmental pollutants because of their wide distribution, abundance, sedentary behavior, and pronounced ability to accumulate organic compounds at proportions that correspond to concentrations in their surroundings. Therefore, this survey was concentrated to investigate the contamination levels and patterns of PBDEs in sediments and bivalves from the coastal areas of Korea.

Materials and Methods

Marine sediments (0-5 cm) were sampled at 20 stations from the coastal areas of Korea during a period of February to May 2000. Bivalve samples collected at the same stations with sediments in May to July 2001 (Fig. 1). Sediment samples were collected with a box-core sampler. Mussel (*Mytilus coruscus and M. edulis*) and oyster (*Crassostrea gigas*), which were located on piers, rocks or buoys in the seawater column, were scraped with a rake.

Twenty grams of sediments were extracted in a Soxhlet apparatus with 200 mL of toluene for 24 hours, after being spiking with 5 species as internal standards (MBDE-MXA and MBDE-MXB, Wellington Laboratories). The extracts were reduced to 1-2 mL in a rotary evaporator and then were transferred to *n*-hexane. Fifty grams (basis of wet weight) of bivalve samples were homogenized with a ultra-disperser. Homogenized samples were decomposed in 200 mL of 1 N KOH ethanolic solution for 2 hours by mechanical shaking after the spike of internal standard. The digested samples were liquid-liquid extracted with twice using n-hexane 100 mL after the addition of water and 50 g of anhydrous Na_2SO_4.

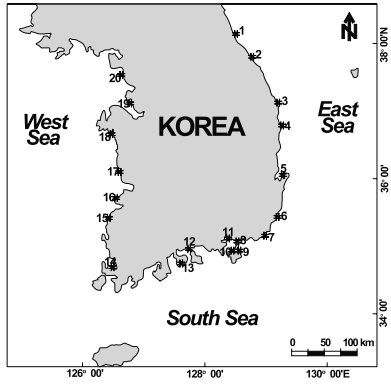

Figure 1. Map showing sampling stations of marine sediments and bivalves from the coastal areas of Korea. The numbers indicate sampling stations.

Samples were cleaned up on a multi-layer silica-based adsorbents (70-230 mesh, Neutral, Merck) column with 160 mL of *n*-hexane. The purified sediment and bivalve samples were concentrated to less than 1 mL, and left at a room temperature for one or two days to evaporate to dryness. The residues were dissolved with 30 μL of *n*-nonane and determined for PBDEs.

Target compounds of PBDEs used in this study were as follows; 2,4,4'-TrBDE (BDE #28), 2,2',4,4'-TeBDE (BDE #47), 2,2',4,4',5-PeBDE (BDE #99), 2,2',4,4',5,5'-HxBDE (BDE #153) and 2,2',4,4',5,6-HxBDE (BDE #154) (Wellington Laboratories). Isotope labelled compounds ($^{13}C_{12}$-2,4,4'-TrBDE, $^{13}C_{12}$-2,2',4,4'-TeBDE, $^{13}C_{12}$-2,2',4,4',5-PeBDE, $^{13}C_{12}$-2,2',4,4',5,5'-HxBDE, and $^{13}C_{12}$-2,2',4,4',5,6-HxBDE, Wellington Laboratories) were used as internal standards. Quantification was performed by the method of relative calibration curves using both native and internal standards. The GC/MSD (5973N, Agilent) was used for the determinations of PBDEs under the selective ion monitoring (SIM) method using tow ion molecular ions for each degree of bromination with the positive electron impact (PEI) mode. Further details of analytical methods and instrumental analysis procedures were based on previously used methods.[8] All the spiked isotope compounds were detected with no interfering peak. The recovery tests of both sediment and bivalve samples were acceptable. The calculated detection limit (S/N ratio=3) for individual PBDE was estimated at 0.01 ng/g dry weight for sediment and at 0.01 ng/g wet weight for bivalve.

Results and Discussion

PBDEs in marine sediments and bivalves

De Boer et al.[4] reported that PBBs and PBDEs are present in sperm whales (Physeter macrocephalus), which normally stay and feed in deep water, indicating that these compounds have reached deep ocean waters. In this study, five congeners of PBDEs were detected in most of sediment and organism samples, indicating that there was widespread contamination of PBDEs in Korean marine ecosystem.

Total levels of five species PBDE in sediments from the Korean coastal areas varied from 0.05 to 6.37 ng/g dry weight with a mean concentration of 0.62 ng/g dry weight. The highest level of total PBDEs was found in Station 6 from Ulsan coast, which is located close to a large number of industrial complex producing petroleum, automobiles, ships and products in Korea. The concentrations of BDE #47 and BDE #99 were in the range of 0.01-4.03 ng/g dry weight (mean 0.30 ng/g dry weight) and

0.03-1.43 ng/g dry weight (mean 0.17 ng/g dry weight), respectively. However, BDE #28, BDE #153 and #154 congener concentrations were near detection limits (<0.01 ng/g dry weight) in the sediments. In particular, Stations 1, 2, 3, 4 and 5 collected from East Sea were characterized by primarily sand (94.2-99.4% sand fraction) and PBDE levels showed the lowest values (0.05-0.22 ng/g dry weight). This result can be indicated that sediment grain-size distribution is also one of important factors governing PBDEs contamination and has to be considered. Indeed, fine grain-size sediments have been shown to accumulate hydrophobic organic contaminants at greater concentrations than coarse sands.[9]

Total concentrations of five species PBDE in bivalves varied from 0.05 to 0.69 ng/g wet weight with a mean concentration of 0.19 ng/g wet weight. The highest level of total PBDEs was found in Station 15 from Gochang coast. The concentrations of BDE #47 and BDE #99 were in the ranges of 0.01-0.08 ng/g wet weight (mean 0.04 ng/g wet weight) and 0.02-0.37 ng/g wet weight (mean 0.09 ng/g wet weight), respectively. The concentrations of BDE #28, BDE #153 and BDE #154 congener were relatively low such as those of sediments.

PBDEs compositions in sediments and bivalves

To compare PBDE congener patterns of each coast, all data were normalized to the total sum of five PBDE species. The congener compositions of PBDEs in sediments and bivalves collected from each coast is illustrated in Fig. 2.

In sediments, BDE #47 (36.6±13.1%) and BDE #99 (35.2±12.8%) congeners usually present in the highest proportion, followed by BDE #154 (13.4±7.6%), BDE #153 (11.6±5.5%) and BDE #28 (9.4±4.0%). Allchin et al.[10] investigated the levels of PBDEs in sediments and biota samples collected from some locations in the UK where brominated flame-retardants are known to be manufactured or handled in large quantities. According to this study, the tetra-, penta- and deca-BDE were detected in most sediment samples from downstream in the UK and BDE #99 generally occurred at a higher concentrations than BDE #47. In this study, preliminary contributors in sediment were BDE #47 and BDE #99.

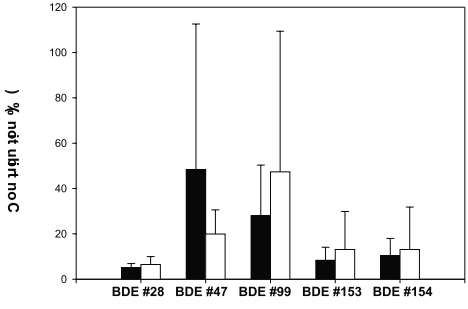

Figure 2. Comparison of average compositions of individual PBDE congeners to total concentrations of PBDEs in sediments and bivalves from Korean coast. Black box indicates the PBDE composition of marine sediments and white box indicates the PBDE composition of bivalves. Vertical lines represent standard deviations.

In bivalves, the predominant congener was BDE #99 (41.8±10.0%), followed by BDE #47 (25.4±9.8%), BDE #154 (12.0±4.5%), BDE #153 (12.0±3.6) and BDE #28 (8.8±4.2%).

In general, the PBDEs profiles in biota seem to resemble each other, though there are a few exception. The dominant species in biota was BDE #47, followed by BDE #99, BDE #153 and BDE #154. The lower brominated compounds such as BDE #47 and BDE #99 are highly available.[11, 12] However, this pattern was mostly fish profile but, in the case of shellfish, filter-feeding marine bivalves

such as oyster and mussels can be abosrbed xenobiotics adsorbed on a small grain-size fraction of particles through digestive system. PBDEs migrated with particle into bivalve are accumulated to a greater extent. Therefore, BDE #99 in shellfish matrix is thought to be a high proportion relative to low molecular BDE #47 unlike fish.

Correlation analysis

A regression analysis was carried out to investigate the relationship within individual PBDE compound (Table 1). In sediment samples, there was a highly positive correlation ($r=0.78$-0.97, $0.01<p<0.05$, $n=20$) between the concentrations of PBDE species. In the bivalve samples, there was no correlation within lower molecular weight PBDEs unlike marine sediments. However, the relationships within heavier molecular congeners such as BDE #99, BDE #153 and BDE #154 showed a significant correlation ($r=0.90$-0.96, $0.01<p<0.05$, $n=20$). This finding was thought to be relation with a metabolism of shellfish species. In the marine environment, the majority of heavier molecular weight PBDEs was strongly with particulate matter because of hydrophobic and persistent character of PBDEs. These compounds migrated with particles into bivalve are accumulated to a greater extent. Therefore, heavier molecular weight PBDEs in bivalve matrix is thought to be a high correlation relative to low molecular weight PBDEs.

Table 1. Correlation coefficients of PBDE congeners in marine sediments and bivalves from the coastal areas of Korea

		BDE #28	BDE #47	BDE #99	BDE #153	BDE #154	
				BIVALVE			
BDE #28	SEDIMENT		0.687**	0.213	0.307	0.302	BIVALVE
BDE #47		0.840***		0.275	0.340	0.227	
BDE #99		0.851***	0.974***		0.959***	0.904***	
BDE #153		0.916***	0.892***	0.945***		0.916***	
BDE #154		0.780***	0.867***	0.921***	0.913***		
				SEDIMENT			

*$0.014<p<0.05$, **$0.001<p<0.01$, ***$p<0.001$.

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