

Monitoring of polybrominated diphenyl ethers in marine sediments and bivalves from Korean coastal areas

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Introduction

PBDEs are flame-retardants, which are added to a variety of materials such as television sets, computers, radios, textiles, new synthetic building materials and automobiles.¹ There are large amounts of PBDEs in the environment, which was released from their manufacturing or operating processes into environment.^{2, 3} 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.⁴ Marine organisms may be exposed to toxic organic contaminants by contact with contaminated seawater, sediments and the ingestion of contaminated prey. Due to low water solubility and high octanol/water partition coefficients (K_{ow}) in seawater, these chemicals can retain and concentrate in fatty tissues of these marine organisms such as migrate into fish, shellfish and invertebrates. In aquatic systems, toxic organic pollutants tend to bioconcentrate from water to aquatic animal and then biomagnify up through the multistep food chain.^{5, 6} Therefore, these organisms reflect the pollution extent of persistent toxic organic pollutants and some species can be used as bio-indicators at different environmental conditions and foodweb⁶. In this study, we planned to monitor the contamination of PBDEs in sediments and bivalves from the marine environment of Korea.

Materials and Methods

Marine sediments (0-3 cm) and bivalves were sampled at 25 stations from the coastal areas of Korea during a period of February to May 2004 (Fig. 1). Surface sediments 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 9 species as internal standards (MBDE-MXC and MBDE-209, Wellington Laboratories). The extracts were reduced to 1-2 mL in a rotary evaporator and then were transferred to *n*-hexane. Bivalve samples (about 50 g) 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 standards. The digested samples were liquid-liquid extracted with twice using *n*-hexane 200 mL after the addition of water and 50 g of anhydrous Na₂SO₄.

Samples were cleaned up on a multi-layer silica-based adsorbents (70-230 mesh, Neutral, Merck) column with 150 mL of 10% methylene chloride in *n*-hexane. The purified 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 100 μ L of *n*-nonane and determined for PBDEs.

Target compounds of PBDEs used in this study were as follows; 4-MBDE (BDE #3), 2,4-DiBDE (BDE #7), 4,4'-DiBDE (BDE #15), 2,2',4-TrBDE (BDE #17), 2,4,4'-TrBDE (BDE #28), 2,2',4,4'-TeBDE (BDE #47), 2,2',4,5'-TeBDE (BDE #49), 2,3',4,4'-TeBDE (BDE #66), 2,3',4',6-TeBDE (BDE #71), 3,3',4,4'-TeBDE (BDE #77), 2,2',3,4,4'-PeBDE (BDE #85), 2,2',4,4',5-PeBDE (BDE #99), 2,2',4,4',6-PeBDE (BDE #100), 2,3',4,4',6-PeBDE (BDE #119), 3,3',4,4',5-PeBDE (BDE #126), 2,2',3,4,4',5-HxBDE (BDE #138), 2,2',4,4',5,5'-HxBDE (BDE #153), 2,2',4,4',5,6'-HxBDE (BDE #154), 2,2',3,4,4',5',6-HpBDE (BDE #183), Deca-BDE (BDE #209) (BDE-CVS-A, Wellington Laboratories). Isotope labelled compounds (¹³C₁₂-4-MBDE, ¹³C₁₂-4,4'-DiBDE, ¹³C₁₂-2,4,4'-TrBDE,

$^{13}\text{C}_{12}$ -2,2',4,4'-TeBDE, $^{13}\text{C}_{12}$ -2,2',4,4',5-PeBDE, $^{13}\text{C}_{12}$ -2,2',4,4',5,5'-HxBDE, $^{13}\text{C}_{12}$ -2,2',4,4',5,6'-HxBDE, $^{13}\text{C}_{12}$ -2,2',3,4,4',5',6-HpBDE, $^{13}\text{C}_{12}$ -DecaBDE) were used as internal standards. The quantifications of PBDEs were performed by HRGC/HRMS (JMS-700D, JEOL) with relative response factor (RRF) method. A DB-5MS (30 m, 0.25 mm i.d., 0.1 d.f., J&W Sci.) was used for the separation of mono- to hepta-BDE congeners. Deca-BDE was analyzed using a DB5-MS (15 m, 0.25 mm i.d., 0.1 d.f., J&W Sci.) capillary column.

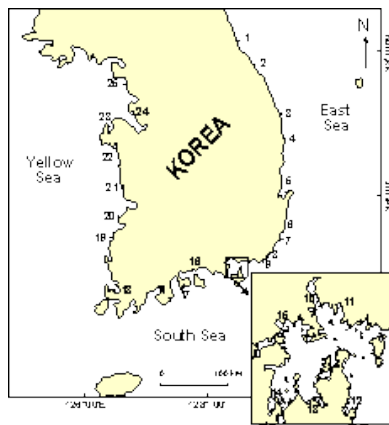


Fig. 1. Map showing sampling stations of marine sediments and bivalves from the coastal areas of Korea. The numbers indicate sampling stations.

Results and Discussion

PBDEs in marine sediments and bivalves

Twenty congeners of PBDEs were detected in all of sediment and organism samples, indicating that there was widespread contamination of PBDEs in the Korean marine ecosystem. De Boer et al.³ reported that 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. The concentrations of total PBDEs in marine sediments and bivalves from Korean coastal areas were presented in Fig. 2. In general, the most contaminated areas with PBDEs were concentrated at southeastern part of Korea as an aspect of sediment and bivalve accumulation status. This result was in accordance with that of other toxic organic contaminants such as PCDDs/DFs, dioxin-like PCBs and PAHs.^{7,8,9} Total concentrations of PBDE in the marine sediments from Korea varied from 0.45 to 494 ng/g dry weight with a mean concentration of 27.7 ng/g dry weight. The highest level of total PBDEs was found at Station 8 from Busan coast, which is the largest harbor with various industrial complex in Korea. PBDEs from the sediments at Stations 6 (Ulsan) and 7 (Onsan) revealed relatively higher contamination than those of other locations. These stations are located at near the largest petrochemical industrial facilities in Korea. In particular, Stations 1, 2, 3, 4 and 5 collected from East Sea were characterized by primarily sand (84-98% sand fraction) and PBDE levels showed the lowest values (0.45-2.79 ng/g dry weight). This result can be indicated that sediment grain-size distribution is also one of important factors governing PBDEs accumulation and has to be considered. Indeed, fine grain-size sediments have been shown to accumulate hydrophobic organic contaminants at greater concentrations than coarse sands.¹⁰

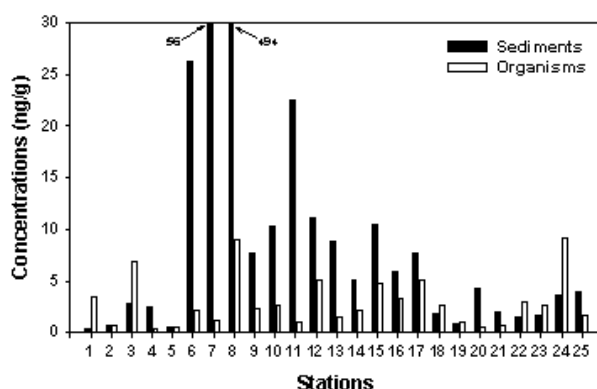


Fig. 2. Concentrations of total PBDEs in marine sediments and bivalves from Korean coastal areas. Sediments were in the basis of ng/g dry weight and bivalves were in the basis of ng/g wet weight.

Total concentrations of 20 PBDEs in bivalves varied from 0.38 to 9.19 ng/g wet weight with a mean concentration of 2.94 ng/g wet weight. In general, there were no significant differences of PBDEs accumulation in marine organisms among the sampling stations. Relatively higher level of total PBDEs was found at Station 24 from Asan coast, while the bivalves from Station 4 (Hupo coast) revealed the lowest values.

PBDEs compositions in sediments and bivalves

To compare PBDE congener patterns in the marine sediments and bivalves, all data were normalized to the total sum of 20 PBDE species. The congener compositions of PBDEs in marine sediments and bivalves were presented in Fig. 3. Deca-BDE (#209) is the main component of PBDE congeners in all samples of marine sediments and bivalves. Deca-BDE in sediments occupied over 90% and that in bivalves showed the proportion of about 60%. This result indicates that the input of Deca-BDE is the main source of PBDE contamination in the Korean marine environments. Exception of Deca-BDE, the predominant contributors of PBDE congeners in sediments and bivalves were in the order of BDE #47, BDE #99, BDE #100 and BDE #183. In general, the lower brominated compounds in marine organisms such as BDE #47 and BDE #99 are highly available.^{11, 12}

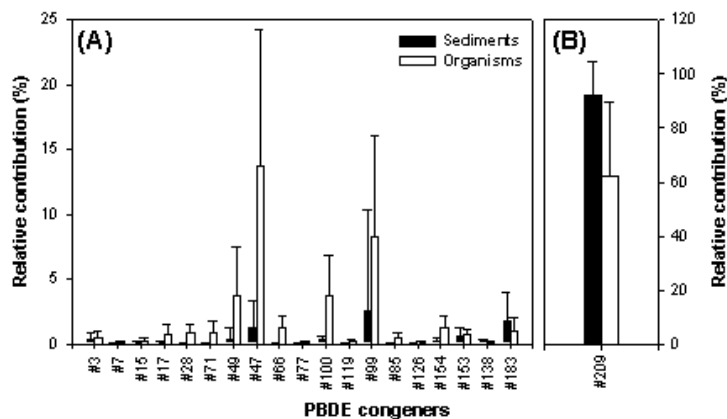


Fig. 3. Compositions of PBDE congeners in marine sediments and bivalves from Korean coastal areas. (A) is the composition of 19 PBDE congeners and (B) is the contribution of Deca-BDE.

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