

# POLYBROMINATED FLAMES RETARDANTS

## CONTAMINATIONS OF POLYBROMINATED DIPHENYL ETHERS IN MARINE SEDIMENTS FROM THE SOUTHEASTERN COASTAL AREAS OF KOREA

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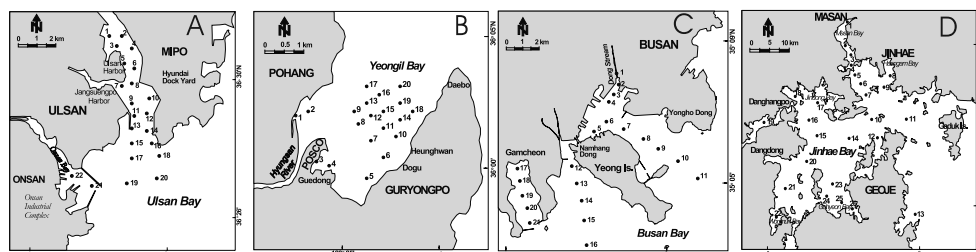
### Introduction

Polybrominated diphenylethers (PBDEs) have been widely used in large quantities as flame-retardant additives for many applications such as television sets, computers, radios, textiles, new synthetic building materials and automobiles.<sup>1</sup> They are a class of dicyclic aromatic compounds substituted with one to ten bromine atoms, result in 209 possible congeners depending on the numbers and positions of the bromine atoms and have similar properties with highly lipophilic and hydrophobic characters.<sup>2</sup> In addition, based on its chemical structure and biological experiments, it is concerned that PBDE may have endocrine disrupting effects.<sup>3,4</sup>

Because the use of flame-retardants is increasing on a global scale, there are large amounts of PBDEs in environment, which was released from their manufacturing or operating processes into environment.<sup>5,6</sup> Considering now a world-wide important environmental problems reaching even remote areas, it is surprising that there is no report on concentrations of PBDEs in environment including biological samples in Korea. Thus, prior to risk assessment of PBDEs, PBDEs contamination in marine environment of Korea needs to be investigated. The objective of this study is to investigate the levels and patterns of PBDEs in marine sediments from the southeastern coastal areas of Korea.

### Materials and Methods

Marine sediments (0-5 cm) were sampled at 89 stations from Pohang, Ulsan and Jinhae coasts, which were located in the southeastern parts of Korea, in November 2000 (Fig. 1).



**Figure 1.** Map showing sampling stations of marine sediments from the southeastern coastal areas of Korea. A: Pohang coast, B: Ulsan coast, C: Busan coast and D: Jinhae coast. The numbers indicate the sampling stations for each coast.

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Twenty grams of sediments were extracted in a Soxhlet apparatus with 200 mL of toluene for 24 hours, after being spiking with five 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. Samples were cleaned up on a multi-layer silica-based adsorbents (70-230 mesh, Neutral, Merck) column chromatography with 160 mL of *n*-hexane. 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 ( $^{13}\text{C}_{12}$ -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, and  $^{13}\text{C}_{12}$ -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.<sup>7</sup> All the spiked isotope compounds were detected with no interfering peak. The average recoveries were in the range of 89±7%. The calculated detection limit (S/N ratio=3) for individual PBDE in sediment was estimated at 0.01 ng/g dry weight.

## Results and Discussion

### *PBDEs in marine sediments*

The summary of PBDE concentrations in marine sediments from the southeastern coastal areas of Korea showed in Table 1. The highest level of total PBDEs was found in Station U2 from Ulsan coast and the lowest level was Station B3 from Busan coast. Total levels in sediments from Pohang coast ranged from 1.1 to 33.8 ng/g dry weight with a mean concentration of 5.3 ng/g dry weight. Total PBDEs concentrations in sediments from Ulsan coast were in the range of 1.6-36.4 ng/g dry weight and a mean concentration was 5.9 ng/g dry weight. In Busan coastal areas, total concentrations of PBDEs ranged between 0.56 and 17.8 ng/g dry weight with a mean concentration of 3.8 ng/g dry weight. Jinhae Bay showed the range of 0.5-8.2 ng/g dry weight with a mean 1.8 ng/g dry weight.

**Table 1.** Summary of PBDE congener concentrations (mean ± standard deviation, ng/g dry weight) in marine sediments from the southeastern coastal areas of Korea

	POHANG	ULSAN	BUSAN	JINHAE
BDE #28	1.16 ± 0.34	0.97 ± 0.96	0.11 ± 0.07	0.12 ± 0.19
BDE #47	1.96 ± 3.95	1.60 ± 2.34	1.00 ± 1.61	0.54 ± 0.49
BDE #99	1.25 ± 1.89	1.82 ± 3.50	1.96 ± 2.73	0.71 ± 0.55
BDE #153	0.47 ± 0.59	0.74 ± 0.80	0.32 ± 0.45	0.20 ± 0.30
BDE #154	0.47 ± 0.50	0.76 ± 0.68	0.36 ± 0.50	0.21 ± 0.39
SUM	5.31 ± 7.96	5.88 ± 7.91	3.75 ± 4.78	1.77 ± 1.65

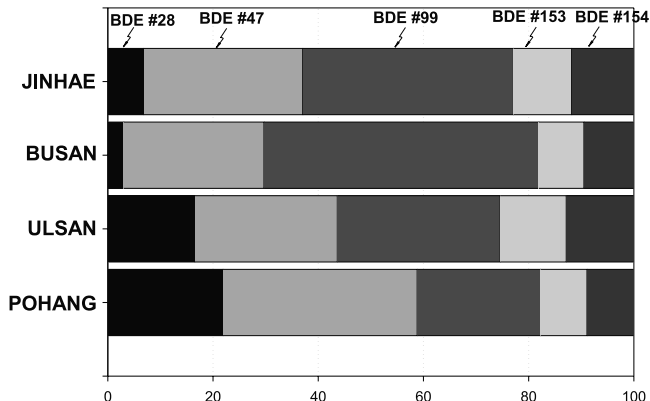
Until recent, most survey on PBDEs distribution were focused on the compounds of 2,2',4,4'-TeBDE (BDE #47) and 2,2',4,4',5-PeBDE (BDE #99). In this study, the mean levels of 2,2',4,4'-TeBDE (BDE #47) and 2,2',4,4',5-PeBDE (BDE #99) in marine sediments from the southeastern coasts of Korea were in the range of 1.0-2.0 ng/g dry weight and 0.9-2.2 ng/g dry weight, respectively.

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These results were comparable to the PBDE levels in sediments from River Nith and Avonmouth.<sup>8</sup> PBDE levels in sediment from Drammenfjord, Western Wadden Sea and Lake Woserin<sup>9</sup> showed the lower values than those in this investigation. However, PBDE levels in sediments collected from Haringvliet-east, River Meuse, Waal<sup>10</sup>, Humber, Tees estuary, and River Skerne, which were located near suspected sources including a manufacturers of PeBDE and OcBDE, several industries using PeBDE, several landfill receiving wastewaters suspected to contain PBDEs<sup>8</sup>, revealed an order of about 10-50 fold greater than those reported here. Consequently, it means that PBDEs contamination in surface sediments from several southeastern coasts of Korea, which are surrounded by industrial complex such as Pohang, Ulsan, Busan and Masan cities, was relatively moderate in comparison to other marine environment in the world.

## *PBDE compositions*

To compare PBDE congener patterns of each coast, all data were normalized to the total sum of five PBDE species (Fig. 2). The 2,2',4,4'-TeBDE and 2,2',4,4',5-PeBDE were predominant congeners in sediments collected from Pohang, Ulsan, Busan and Jinhae coasts. Allchin et al.<sup>8</sup> investigated the compositions 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. From these results, the tetra-, penta- and deca-BDE were detected in most sediment samples and 2,2',4,4',5-PeBDE generally occurred at a higher concentrations than TeBDE in sediments from downstream in the UK. In this study, preliminary contributors in sediment were 2,2',4,4'-TeBDE (BDE #47) and 2,2',4,4',5-PeBDE (BDE #99), showing similar findings to Allchin et al.<sup>8</sup>



**Figure 2.** Average normalized compositions of PBDE congeners in marine sediments from the southeastern coastal areas of Korea.

The main source of tetra- and penta-BDE in the marine environment was known as the debromination by photo- and bio-degradation of DeBDE which occupies approximately 75% of PBDE congeners used as flame-retardants. On the basis of chemical structure, DeBDE is fully brominated and there is only one congener. Commercial DeBDE is typically composed of 97-98% DeBDE.<sup>11</sup> Despite DeBDE having the highest consumption, the majority of the PBDEs found in the environment are

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lower brominated compounds. This discrepancy can be explained if the higher compounds degrade to tetra, penta and hexa congeners.<sup>12</sup> Indeed, DeBDE has been identified as serious pollutants in river sediments from Osaka in Japan, which was located near manufacturing factories of flame-retardants. However, DeBDE were not detected in marine sediments from Osaka Bay, Japan.<sup>13</sup> It indicates that DeBDE was metabolized toward lower brominated compounds such as tetra, penta and hexa congeners.<sup>14</sup> Therefore, TeBDE and PeBDE were likely to be dominant congeners in marine ecosystem.

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