POLYBROMINATED DIPHENYL ETHERS (PBDES) IN MARINE SEDIMENTS FROM INDUSTRIALIZED BAYS OF KOREA

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Abstract

Concentrations of polybrominated diphenyl ethers (PBDEs) were determined in coastal sediments from heavily industrialized areas and major harbors in Korea. $\Sigma PBDE_{20}$ concentrations in sediments ranged from 2.03 to 2,253 ng/g dry weight. PBDE concentrations were higher at estuarine and inner bay locations close to industrial complexes and large harbors, indicating that the PBDE contamination in the sediments is due to local discharges from industrial complexes. Deca-BDE was the predominant congener and the concentrations were comparable to or higher than those reported from other countries. Non-parametric multidimensional scaling (MDS) ordination showed that deca-BDE technical mixture is the main source of PBDE contamination in Korean coastal waters, with minor contamination by octa-BDE product. This result is consistent with the consumption pattern of brominated flame-retardants (BFRs) in Korea. Significant correlations existed among BDEs 28, 47, 99, 100, 153, and 154; however, BDEs 183 and 209 showed little correlation with less highly brominated congeners.

Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used, in large quantities, as flame retardants for many applications.[1] PBDEs have the potential for endocrine disruption, bioaccumulation, and long-range transport.[2] The consumption of BFRs in Korea in 2002 was 49,050 tons.[3] Deca-brominated diphenyl ether (deca-BDE) accounted for a major proportion (25%; 12,324 tons), while penta-BDEs and octa-BDEs together accounted for a minor proportion (0.2%; 84 tons) of the total flame retardant market.[3] Despite reports of worldwide contamination by PBDEs, and despite the extensive use of PBDEs in Korea, there is only one report that document PBDE contamination in mussels and sediments from Korean coasts. [4] To date, no intensive surveys of PBDE contamination in Korean coastal waters, in particular at locations adjacent to industrial areas. The objective of this study was to describe the concentrations and congener patterns of PBDEs in coastal sediments and to evaluate the sources of contamination by PBDEs in industrialized regions of Korea.

Materials and Methods

Surface sediments (at a depth of 0−4 cm) were sampled at 111 locations representing three industrialized bays (Ulsan Bay, Busan Bay, and Jinhae Bay), from February 2003 to March 2004. Surface marine sediments were collected using a box-corer deployed from a research vessel. Detailed descriptions of preparation procedures and instrumental analysis have been presented elsewhere.[4,5] Briefly, 20 g of sediment samples were extracted in a Soxhlet apparatus using 200 mL of 10% of acetone in toluene for 24 h after spiking with $^{13}C_{12}$-labelled BDE congeners as internal standards (MBDE-MXC and MBDE-139-IS; Wellington Laboratories, Canada). The extracts of marine sediment were cleaned by passage through a multi-layer silica gel (neutral; 7734; 70–230 mesh; Merck) column with successive eluants of 120 mL of hexane and 100 mL of 10% methylene chloride in hexane. The eluants were concentrated to approximately 1 mL, and were then evaporated at room temperature to 100 µL for instrumental analysis. Quantitation of PBDEs was performed by a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC/HRMS; JMS 700D, JEOL) using relative response factors (RRF) of individual congeners. The capillary column used was a DB5-MS (30 m, 0.25 mm, 0.1 µm, J&W) for the separation of mono- to hepta-BDE congeners and a DB5-MS (15 m, 0.25 mm, 0.1 µm, J&W) for deca-BDE.

Results and Discussion

Spatial distribution of PBDEs

Twenty PBDE congeners were detected in all of the sediment samples from every bay sampled, indicating that PBDEs are widespread contaminants in Korean coastal waters. The $\sum PBDE_{20}$ (sum of 20 PBDE congeners) concentrations in sediments from the three industrial bays ranged from 2.03 to 2,253 ng/g dry wt. The deca-BDE concentrations ranged from 2.0 to 2,248 ng/g dry wt, which were one to three orders of magnitude higher than the sum of the concentrations of mono- to hepta-BDEs. In Ulsan Bay and Onsan Bay, $\sum PBDE_{20}$ concentrations ranged from 3.97 to 290 ng/g dry wt and deca-BDE concentrations ranged from 3.42 to 286 ng/g dry wt. PBDEs in sediments from Ulsan Bay and Onsan Bay were concentrated in inland rivers or streams and at inner locations of the bay, such as the Gosa Stream and the Woihwang River, indicating that contamination sources of PBDEs are located in rivers and the inner regions of the bays. Sediments from Busan Bay contained the highest PBDE concentrations among the bays studied here. $\sum PBDE_{20}$ concentrations ranged from 14.4 to 2,253 ng/g dry wt. Deca-BDE concentrations in Busan Bay sediments ranged from 14.0 to 2,248 ng/g dry wt. The overall concentrations of PBDEs in sediments from Busan Bay were higher at the inner locations close to harbors, such as Busan North Harbor and South Harbor, than at the outer locations. This result strongly suggests that harbor and shipyard activities are closely associated with PBDE contamination in coastal waters. Concentrations of PBDE in sediments from Jinhae Bay were the lowest among the bays investigated in this study. Sediment from most locations in this bay contained PBDE concentrations less than 50 ng/g dry weight, with exception of

Stations M1 and M2. $\sum PBDE_{20}$ concentrations varied from 2.03 to 151 ng/g dry wt and Deca-BDE concentrations ranged from 2.0 to 145 ng/g dry wt. High PBDE contamination in Jinhae Bay sediments was mostly concentrated in Masan Bay, which is a semi-closed system.

Congener patterns and potential sources of PBDEs

Deca-BDE (BDE 209) accounted for over 95% of the total PBDE concentrations in all three bays. Next to BDE 209, the most abundant congeners in sediments were BDEs 183, 99, and 47. To further characterize the spatial variability in PBDE congeners, two-dimensional ordination by non-parametric multidimensional scaling (MDS) was performed using PRIMER for Windows (PRIMER Version 5.2.9, Plymouth, UK). The results of non-parametric MDS ordination of the 20 PBDE congeners for individual sampling locations, using the Bray-Curtis similarities calculated from square-root transformed data are shown in Fig. 1. Circles on the variable plot (Fig. 1a) were distinguished by two cluster groups of sampling locations. Locations close to terrestrial areas were discriminated from the locations on the outer parts of the bays. The first group (large circle) represented the locations in the inner part of South Harbor, North Harbor, the Woihwang River, and Onsan Bay. Sampling locations of this group corresponded to high concentrations of deca-BDE (Fig. 1b), suggesting that the deca-BDE technical mixture is the important product discriminating the PBDE contamination in Korean coastal waters and is associated with various industrial activities and heavy ship traffic. The second group comprised of locations such as Gosa Stream (G1−G2), corresponding to high concentrations of hepta-BDE (BDE 183) (Fig. 1c). Although the predominance of deca-BDE in the total PBDE concentrations was apparent, the sediments from stations G1 and G2 showed a relatively high contribution of BDE 183 (about 20−23%), compared to other PBDE congeners. BDE 183 accounted for 42% and 12.6% in DE-79 product and Bromkal 79-8DE product, respectively. [6] This suggests that stations, G1 and G2 were contaminated by such octa-BDE mixtures. Gosa Stream is located near factories in Ulsan City used for manufacturing building materials and automobile components.

Correlation among PBDE congeners and organic carbons

To investigate potential sources and distribution, Pearson correlation analyses were performed for the PBDE congeners in marine sediments. Highly significant correlations were found among the concentrations of tri-, tetra-, penta- and hexa-BDEs such as BDEs 28, 47, 99, 100, 153, and 154 (r = 0.689−0.971, $p < 0.001$). The BDE 183 showed relatively moderate correlation (r = 0.538−0.791, $p < 0.001$) with the lower brominated congeners, with the exception of BDE 99 (r = 0.253, $p = 0.007$). However, BDE 209 exhibited relatively low correlations (r = 0.139−0.443, $p = 0.001$−0.144) with other PBDE congeners. This indicates that the more highly brominated congeners have different sources and environmental behavior, compared with the less highly brominated congeners. The relationships between individual PBDE congeners and TOC in sediments were

investigated. Although PBDEs were expected to be associated mainly with organic carbon-rich particles, the correlations between PBDE congeners and TOC content in sediments were low (r = 0.164−0.297, p = 0.086−0.002), particularly for ∑PBDE or BDE 209 concentrations (r = 0.058−0.062). This may be attributed to the combined effect of local sources, transport, mixing, and deposition.

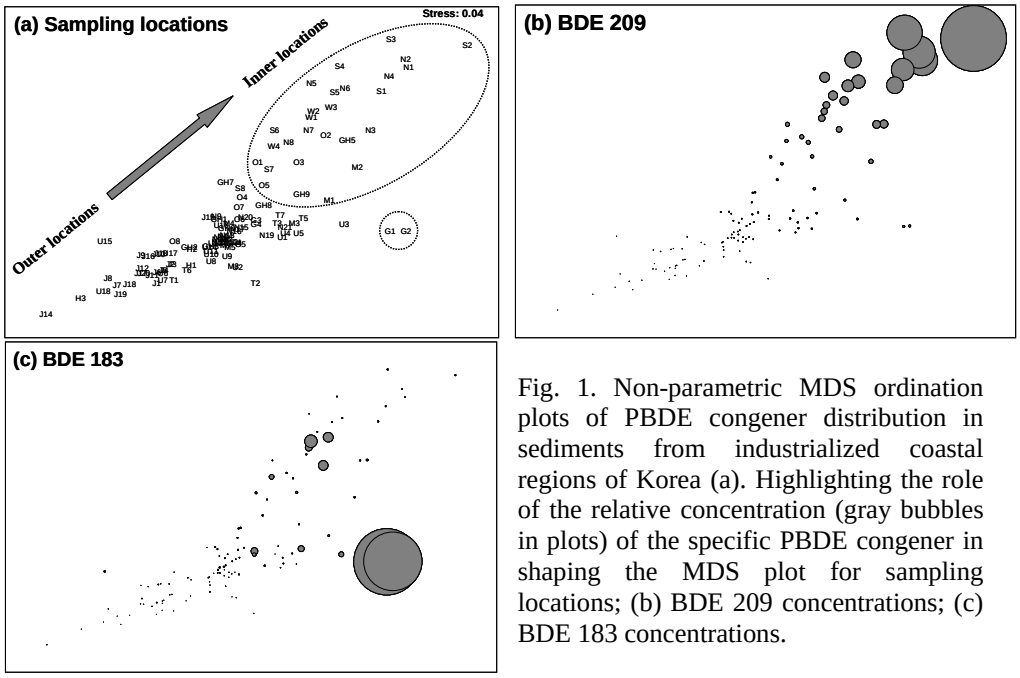

Fig. 1. Non-parametric MDS ordination plots of PBDE congener distribution in sediments from industrialized coastal regions of Korea (a). Highlighting the role of the relative concentration (gray bubbles in plots) of the specific PBDE congener in shaping the MDS plot for sampling locations; (b) BDE 209 concentrations; (c) BDE 183 concentrations.

References

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