ATMOSPHERIC DEPOSITION OF POLYBROMINATED DIPHENYLETHERS (PBDEs) IN COASTAL AREAS IN KOREA

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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[2,3]; they are, therefore, recognized as an emerging group of persistent organic pollutants (POPs).[4]

In Korea, the use of flame retardants has been steadily increasing, by approximately 10% per year during the last decade.[5] Total consumption of brominated flame retardants (BFRs), within the total flame retardant market, was approximately 56%.[5] The consumption of BFRs in Korea in 2002 was 49,050 tons.[6] 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.[6]

PBDEs are reported to be transported over long distances and are introduced into the terrestrial and aquatic systems through wet and dry deposition. Therefore, atmospheric transport and deposition constitute the primary distribution pathway moving PBDEs from their sources. Despite this, there is still little information on atmospheric depositional fluxes of PBDEs and their seasonal variability, on either the local or the global scale. The objective of this study was to determine atmospheric depositional fluxes and seasonal variations in concentrations of PBDEs in some coastal locations in Korea.

Materials and Methods

Atmospheric deposition samples were collected at Daeyeon-dong (urban site) and Gijang-gun (suburban site) in Busan, at Wolpo-dong (urban site) in Masan, and at Haengam-dong (rural site) in Jinhae, Korea. These areas are located along the southern coast of Korea, within 1 km of the coast line. Bulk atmospheric deposition samples were collected monthly during January−December 2004. The samplers were made up of stainless steel pots with an inner diameter of 50 cm and a height of 50 cm and were covered by steel net with small mesh (0.5 cm × 0.5 cm) to avoid damage caused by birds and animals. Sampling procedures have been described in detail elsewhere.[7] In brief, atmospheric deposition samples were separated into particulate and liquid phases. Particle

samples were isolated by filtration of water through glass fiber filters. The liquid phase was extracted using solid phase extraction (SPE) disks (ENVI-18 DISK, 47 mm, Supelco). The GFFs, SPE disks, and glass wool were extracted with 200 mL of toluene for 5 h under reflux after spiking with internal standards. The extracts were filtered through glass wool and were concentrated to 1–2 mL using a rotary evaporator. The solvent was transferred to hexane and adjusted to a volume of 10 mL. The extracts were cleaned by passage through a multi-layer silica column containing $AgNO_3$-silica gel, H_2SO_4-silica gel, and KOH-silica gel, 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 evaporated at room temperature to 50–100 µL. In this study, twenty mono- to deca-BDE congeners were analyzed in bulk deposition samples. 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

Depositional fluxes of PBDEs

All of the PBDE congeners were detected in bulk deposition samples, indicating that PBDEs are distributed in the region through atmospheric deposition. Atmospheric depositional flux of ∑PBDE (sum of 20 PBDE congeners) in all coastal locations varied from 10.1 to 89.0 µg/m^2/year. The average depositional fluxes of sum mono- to hepta-BDE congeners were: 1.74 µg/m^2/year for Daeyeon, 2.16 µg/m^2/year for Gijang, 1.88 µg/m^2/year for Wolpo, and 0.55 µg/m^2/year for Haengam. The average depositional fluxes of deca-BDE (BDE 209) were several-fold higher than those of mono- to hepta-BDEs and were 48.1, 20.1, 33, and 16.9 µg/m^2/year for Daeyeon, Gijang, Wolpo, and Haengam, respectively. The depositional fluxes of PBDEs measured in our study were higher than those reported for Sweden[8], but lower than Japan.[9] The atmospheric depositional fluxes of ∑PBDE were significantly different among the sampling locations (ANOVA, $p < 0.05$) and the average deposition fluxes were in the order, Daeyeon (urban) > Wolpo (urban) > Gijang (suburban) > Haengam (rural). This indicates a strong urban−rural gradient in PBDEs fluxes. The difference in PBDE depositional fluxes between the two urban areas,

Seasonal variation in PBDEs

Monthly variations in the levels of particles and PBDE fluxes in the four coastal locations are presented in Figure 1. The particulate depositional fluxes were high in winter (<10°C, November–March) and low in summer (>20°C, June–September), consistent with the seasonal trends in atmospheric suspended particle concentrations. The monthly depositional fluxes of PBDEs showed a high variation in the urban locations (Daeyeon and Wolpo).

For these urban locations, the PBDE depositional flux measured in winter (<10°C median: 49.5 μg/m2/year) was relatively higher than that measured in summer (>20°C median: 32.1 μg/m2/year). However, the suburban and rural locations (Gijang and Haengam) did not show any seasonal trend in PBDE concentrations, although there was a seasonal variability in particulate depositional fluxes. This lack of seasonal trend may be due to the release of PBDEs from secondary sources such as air-surface exchange in less populated suburban and rural areas.

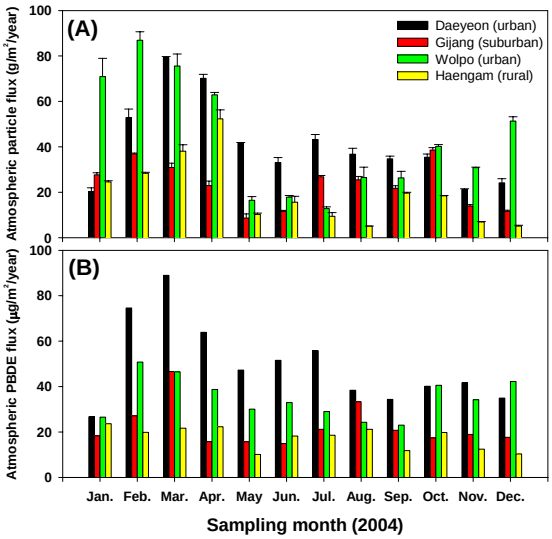

Figure 1. Monthly variation in depositional fluxes of atmospheric particles (A, g/m^2/year) and PBDEs (B, μg/m^2/year) from four coastal locations in Korea. Whiskers on the bars representing particulate depositional fluxes (A) denote standard deviations of mean values (n=3).

PBDE congener profiles

The relative contributions of 20 PBDE congeners in all monthly deposition samples from each of the four coastal locations in Korea are presented in Figure 2. BDE 209 was the predominant congener, accounting for over 93% to total PBDE concentrations in all of the sampling locations. Other major congeners in deposition samples were BDEs 99 and 47. This result is consistent with what was observed in Japan.[9] The BDEs 47 and 99 in air samples from Illinois and Michigan (USA) were the predominant congeners[10], although a recent study showed an increase in BDE 209 in the same two locations.[11] The difference of the profiles of PBDE congeners between Korea and USA indicats the usage patterns of PBDE mixtures between Korea and USA.

Relationship of PBDEs and meteorological parameters

Significant correlations existed among tetra-, penta-, and hexa-BDEs such as BDE 47, 99, 100, 153, and 154; however, BDEs 183 and 209 showed little correlation with less highly brominated congeners. This pattern suggests that the sources of lower-molecular-weight PBDEs are different from the sources of BDE 209 or BDE 183; additionally, it could imply differences in the partitioning behavior between the less highly and the more highly brominated congeners. BDE 209 showed relatively moderate correlations with other PBDE congeners,

except BDE 99. Some studies have reported the possibility of photolytic debromination of BDE-209, to produce less highly brominated congeners in the environment.[12] Relationships between individual PBDE congeners and meteorological parameters such as temperature and rainfall were investigated. Among PBDE congeners, BDEs 47, 100, and 154 showed a negative correlation with ambient temperature, whereas BDE 209 and ∑PBDE did not show any correlation. This pattern implies that high temperature is associated with increasing concentrations of lower-molecular-weight PBDEs. It has been suggested that tetra- and penta-BDEs originate from secondary sources such as air-surface exchange, while the deca-BDE originates from primary sources. No significant correlation was observed between individual PBDE congener and rainfall, in our study. This is because, most particles containing neutral, lipophilic contaminants are scavenged from the atmosphere at the beginning of the rain event.

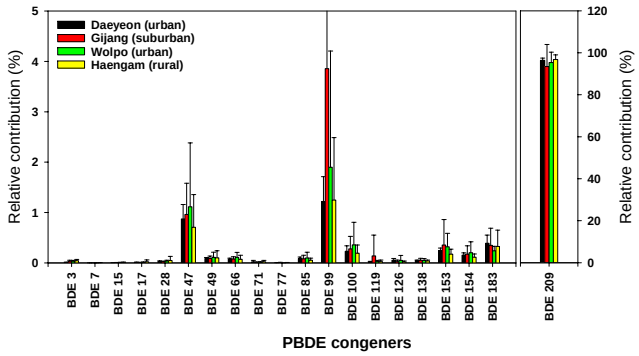

Figure 2. Relative contributions of 20 PBDE congeners to atmospheric depositional fluxes in four coastal locations in Korea. Whiskers on the bars represent standard deviations of each PBDE congener for monthly samples (n=12 for each sampling location).

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