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TIME TRENDS AND FATE ANALYSIS OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN SEDIMENT CORES

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Introduction

Potential sources of polybrominated diphenyl ethers (PBDEs) to the atmosphere, soil, and water are principally manufacture of flame retardants and flame retardant products, atmospheric diffusion from the use of flame retardant products in homes and workplaces, dismantling and crushing in recycling plants, accidental fires, incineration of solid waste, and disposal in landfill sites. Although Sakai et al.[1)], Choi et al.[2)], and Ohta et al.[3)] have previously studied organic brominated compounds in sediments in Japan, information on PBDE sources is limited. This study analyzed time trends of organic brominated compounds in Hiroshima Bay and their spatial distribution in river sediments and developed PBDE emission models for estimating atmospheric and sediment concentrations. The simulated values were then compared with measured concentrations.

Materials and Methods

Sediment cores were collected in Hiroshima Bay in September 2002. The sediments were dated and PBDEs were analyzed using the same procedures described for a similar study of sediments in Osaka Bay[1)]. In addition, river sediments upstream and downstream of a flame retardant manufacturing plant were also collected and analyzed.

Using PBDE emissions data from European Union (EU) risk assessment reports[4, 5, 6)] as a reference, PBDE emissions for Japan were modeled. The three main flame retardants produced in Japan were T4BDE, O8BDE, D10BDE. Applications of T4BDE were assumed to have been the same in Japan as those of P5BDE in EU countries. On the basis of the amount of each PBDE product used in Japan and the homologue composition for each product, PBDE emissions at every stage from production to disposal were estimated for every homologue from T4BDE to D10BDE.

As no statistics on PBDE production prior to 1985 are available, it was assumed that manufacture of each PBDE flame retardant began in 1950 and that production volume increased exponentially through 1986.

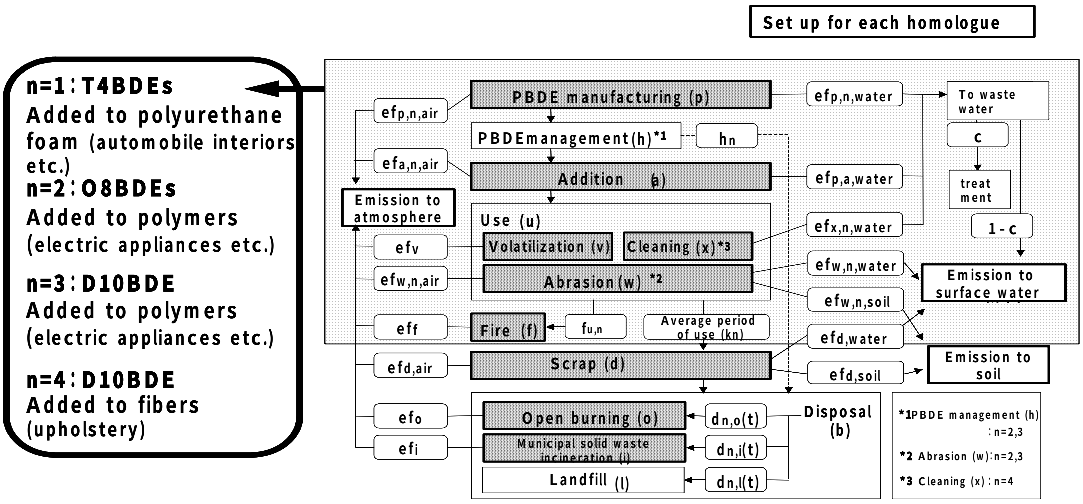

Figure 1 PBDE emission scenarios

Additionally, the actual composition of D10BDE was assumed to be D10BDE:N9BDE = 7:3. Figure 1 is a process flow diagram showing how PBDE emissions were estimated in this study. Because the EU risk assessment reports may have overestimated emissions in order to conservatively assess risk to humans, two model scenarios were devised. The low scenario set coefficient values to one-tenth those used by the mid scenario, including the coefficients for emissions from abrasion and washing of PBDE products, and emissions to water and soil that occurred when discarded products were scrapped. The concentrations in the environment were predicted by a multimedia environmental fate analysis using a level IV Mackay-type fugacity model to calculate the time transition of concentrations in each environmental media after the emission of the chemicals. The environmental media were specified as "atmosphere," "soil," "water," and "sediment." The melting point, vapor pressure, Henry's constant, solubility, and octanol–water partition coefficient values used for each PBDE were from Palm et al.7) and Tittlemier et al.8,9). Taking into account the different physicochemical properties of the different compounds, which cause higher brominated compounds to be photolyzed faster, the following half-life relationships were used: the half-life of each compound in water was set 10 times as long as that in the atmosphere, and the half-life in soil was set as 5 times that in water. The sediment half-life was set at 10 years.

Results and Discussion

Time trends in sediment cores of Hiroshima Bay

The vertical distribution profile for total PBDEs in sediment cores of Hiroshima Bay was compared with that for total PCBs (Figure 2). The total PBDEs concentration increased from 0.066 ng/g at 60–62 cm depth below the sea floor to 2.3 ng/g at 4–6 cm depth, where the concentration was highest. Although concentrations were lower above 4 cm depth, the PBDE load to sediment may not have been decreasing because sediments near the surface may have been mixed. The total PBDEs concentration in the surface layers in Hiroshima Bay was relatively small compared with the total PBDEs concentration of 90 ng/g measured in the upper layers of sediment cores in Osaka Bay in 2001. The low values near the surface in Hiroshima Bay sediments may reflect the fact that the Hiroshima population is relatively low compared with Osaka and probably fewer sources such as

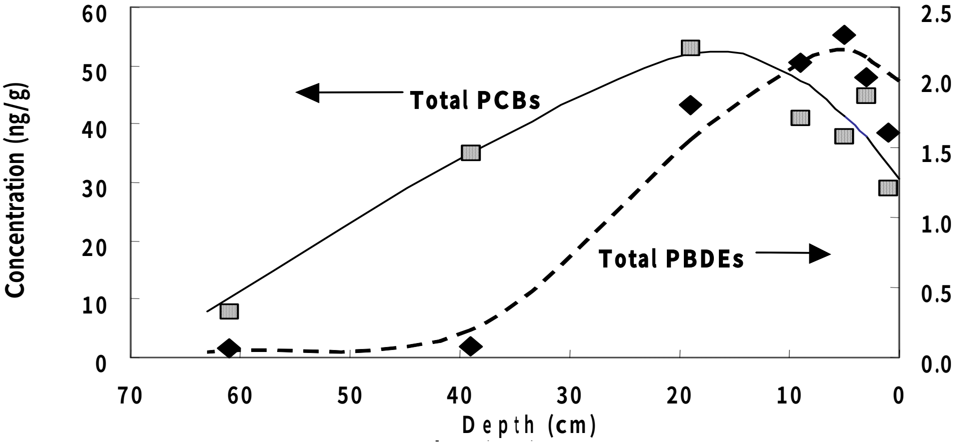

Figure 2 PBDEs trend in sediments of Hiroshima Bay

plastic molding plants are located there. Furthermore, the D10BDE and N9BDE homologues of PBDE are more abundant in layers above 20 cm depth.

Horizontal PBDE distribution along Isumi River

PBDE concentrations were also measured in sediments of Isumi River, Chiba Prefecture (Figure 3).

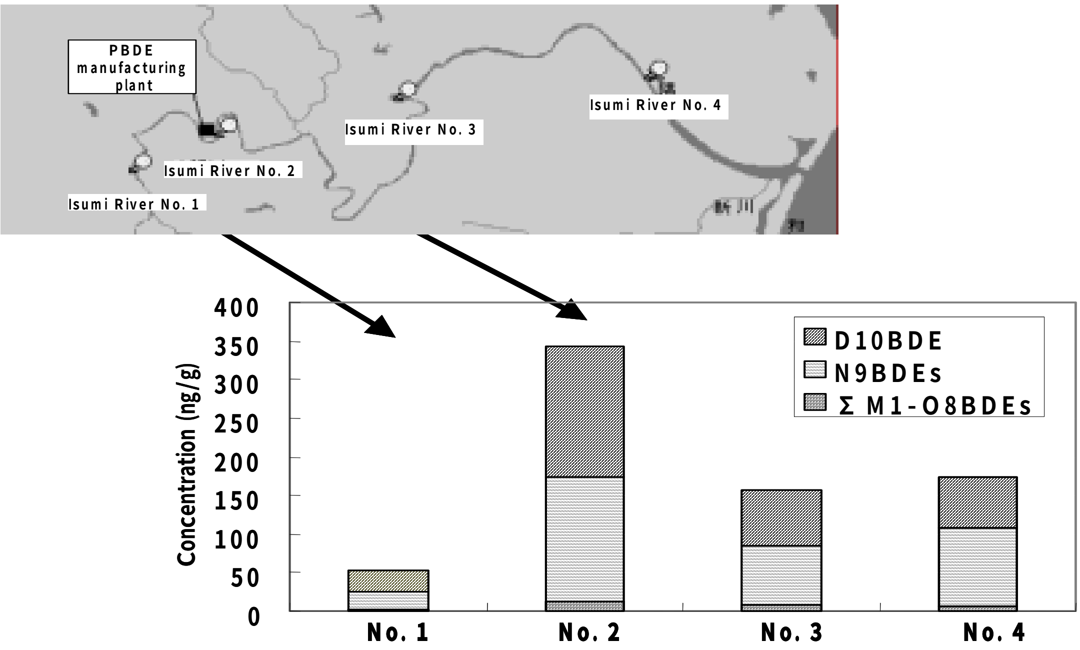

Figure 3 PBDEs distribution in sediments of Isumi River

The concentration of PBDEs was distinctly higher downstream (total PBDEs, 340 ng/g; Isumi River No. 2) of the manufacturing plants compared with upstream (53 ng/g; Isumi River No. 1). This manufacturing plant can thus be considered a source of PBDEs. The PBDE concentration decreased downstream from Isumi River No. 2 (Isumi River Nos. 3 and 4). D10BDE followed by O8BDE was the most abundant homologues in sediment samples. PBDE concentrations in the vicinity of manufacturing plants of flame retardants and of flame retardant products have been previously reported. Allchin et al.[10)] collected sediment samples and fish samples from several rivers and reported that concentrations of BDE-47, -99, PeBDE (DE-71), OcBDE (DE-79) were highest in the vicinity and downstream of plants that manufactured the flame retardants PeBDE and OcBDE, and Sellström et al.[11)] found higher concentrations of PBDEs in sediments downstream of plastic and textile factories.

Modeling emissions from PBDE sources and environmental transport

Measured atmospheric concentrations were obtained from data reported by Ohta et al.[3)] and Hayakawa et al.[12)]. For measured concentrations in sediments, the results reported in this paper and data reported by Sakai et al.[1)] and Ohta et al.[3)] were used. The predicted concentrations obtained by the low and mid PBDE emission scenarios were compared with these measured values (Figure 4).

Although few data are available for measured atmospheric concentrations, the T4BDE and P5BDE values predicted by the mid scenario were close to the median measured values.

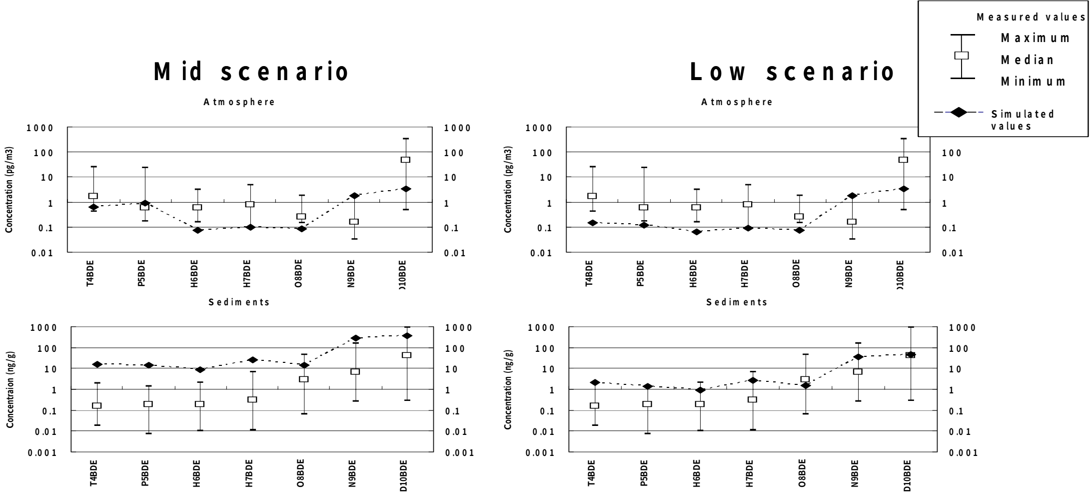

Figure 4 Comparison between predicted and measured concentrations of PBDEs (2001)

In contrast, the low scenario resulted in values smaller than the measured median value by about a factor of 10, except for N9BDE. In sediments, the low scenario estimated measured concentrations more accurately than the mid scenario.

Therefore, the actual amounts of PBDEs emitted to water are close to those estimated by the low scenario of this study. However, it is not enough to measure PBDE homologues in only the atmosphere and sediments, so further monitoring of environmental concentrations is essential.

Acknowledgments

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