POLYBROMINATED FLAMES RETARDANTS

TIME TRENDS AND HORIZONTAL DISTRIBUTION OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN SEDIMENT CORES FROM OSAKA BAY, JAPAN

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Introduction

Attention was attracted to polybrominated diphenyl ethers (PBDEs) by the reports of Norén and Meironyé[1,2]. Although many recent studies of PBDEs, including their toxicity, their concentration in environmental media and in ocean mammals, and sources and exposure, are available, and research programs on fish, shellfish, human mother's milk, and blood has been actively developed, comparative information on concentrations of PBDEs in environmental media and on sources and transport routes are limited.

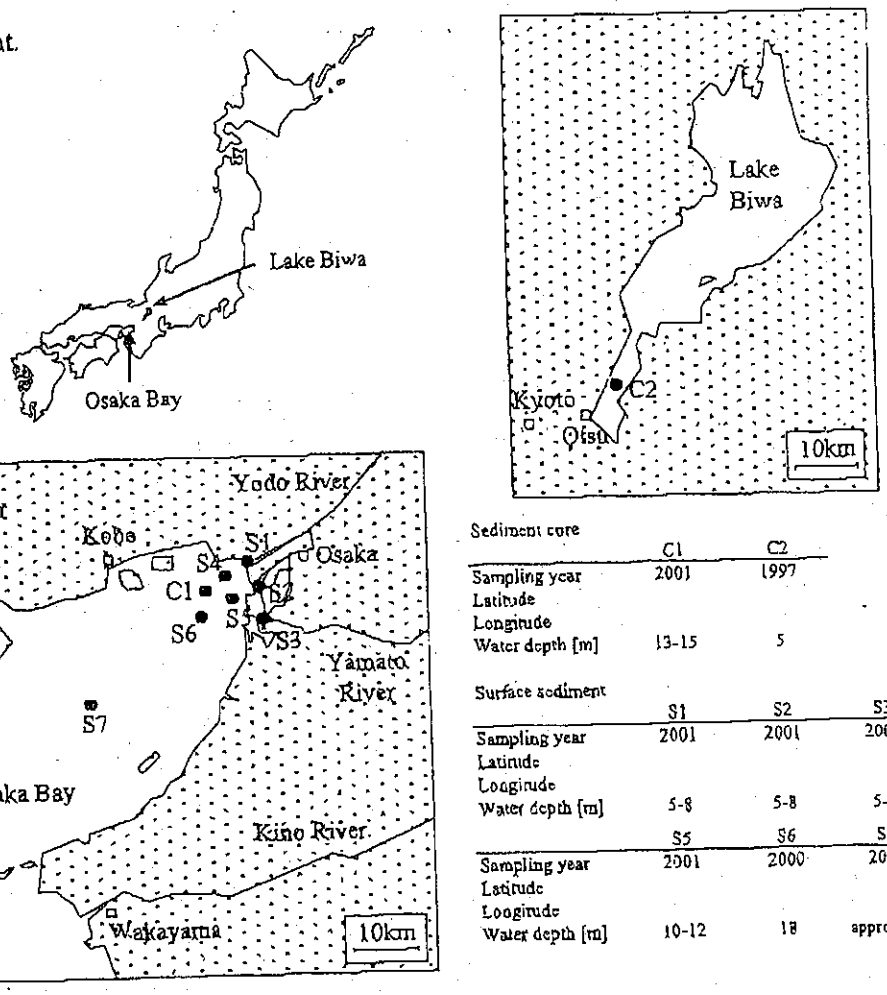
This study analyzed concentrations of PBDEs in sediment core samples from Osaka Bay and Lake Biwa and investigated their vertical distribution profiles in those samples. PBDE concentrations in the surface layer of sediments collected in the mouth, coastal area, and center of Osaka Bay were also analyzed to investigate the horizontal distribution profile of PBDEs in surface layer sediments.

Materials and Methods

Sampling points for sediment cores were specified by using a Global Positioning System (GPS). (Fig. 1). Sediment core samples were taken with an acrylic pipe (length: 1.2 m; inside diameter: 10 cm), which was vertically inserted into the sediments and pulled out with the sediments inside. Five sediment core samples were taken at each point. Core samples were sliced into 2-cm-thick samples, and parts that had been in contact with the pipe lining were disposed of. All 5 sediment cores were treated in the same way, and samples from the same vertical level were mixed. Three surface sediment samples were also taken at each point with a Smith & Macintyre bottom sampler. These samples were also mixed. After air drying, the samples were crushed and stored in an airtight container. The surface sediment samples (depth: 0~2 cm) from Osaka Bay collected in September 2000 at location S6 were analyzed. The sediment samples taken from Lake Biwa at location C2 in July 1997 were used[3]. Other samples were taken in September 2001.

The analytical method used was based mainly on JIS K 0312[4] and internal standards of polychlorinated biphenyls (PCBs) and PBDEs congeners were added. For the clean-up spike, 10 labeled $^{13}C_{12}$ PCB congeners (one each of mono- to deca-chlorinated compounds) and one labeled $^{13}C_{12}$ T4BDE congener and one H6BDE congener were used for quantitative analysis. Sediment core samples were Soxhlet extracted with toluene and then cleaned up by using multilayer silica gel column chromatography. Samples used for polychlorinated dioxins/furans (PCDD/Fs) analysis were additionally fractionated by using alumina column chromatography. Cleaned-up samples were concentrated and the extracts analyzed with high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Because PBDEs are decomposed by ultraviolet rays, we used brown glass vitrics for analysis and tried to cover other equipment with aluminum foil as much as possible to

block the light.



Sediment core	C1	C2
Sampling year	2001	1997
Latitude		
Longitude		
Water depth [m]	13-15	5

Surface sediment	S1	S2	S3	S4
Sampling year	2001	2001	2001	2001
Latitude				
Longitude				
Water depth [m]	5-8	5-8	5-8	10-12

	S5	S6	S7
Sampling year	2001	2000	2001
Latitude			
Longitude			
Water depth [m]	10-12	18	approx. 36

Figure 1. Sediment sampling points

Results and Discussion

Time trends in sediment cores of Osaka Bay

Vertical Time trends of PBDEs, PCBs, and PCDD/Fs in Osaka Bay sediment core samples (C1) are shown in Figure 2. The concentrations of PBDEs and PCBs shown are the sums of mono- to deca-brominated and -chlorinated homologues, respectively. The values for PCDD/Fs shown are toxic equivalent (TEQ) values from WHO-TEF (1997). PBDEs were not detected in layers older than 1957 and were found more in layers deposited after 1984. The concentration increased consistently toward the upper layers. In the top layer, the concentration was the same as that of PCBs. The percentage of D10BDE was high in all layers. PCDD/F concentrations were about 20 pgTEQ/g in the decades from 1960 through 1990 and decreased in the upper layers. The levels of PCBs were very low in the older layers. They were highest in the layer deposited in 1957 (349 ng/g) and constant at about 100 ng/g after 1980.

Many studies have investigated time trends in PCB distributions in sediment cores from Japan[5], Europe[6,7], and North America[8,9]. Those studies have shown that the concentrations were low before PCB production and use (the first half of the 20th century) and highest in the layers deposited during the

1970s at the peak of PCB production and use. They again became lower in the layers deposited after the 1970s. This study found the same trend.

In the case of PBDEs, the peak was observed in the upper layers, after the PCB peak. This might reflect a time lag caused by the demand peak of PBDEs being later than that of PCBs. PBDEs are still manufactured and used, although with lower demand, and products containing PBDEs manufactured in the past may be disposed of in the future.

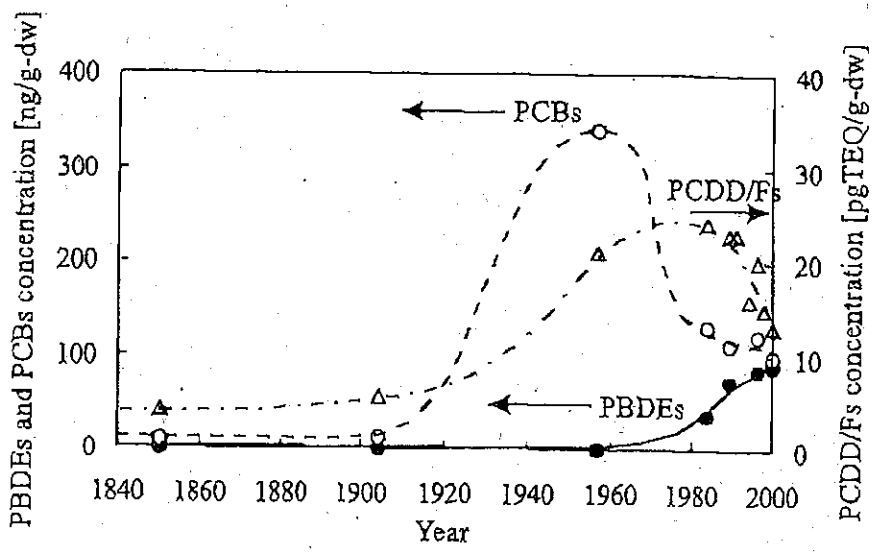


Figure 2. Time trends of PBDEs, PCBs, and PCDD/Fs in sediment cores from Osaka Bay

Horizontal PBDE distribution

Measurements of PBDEs in the upper layers of sediments are shown in Figure 3, in which the values indicated are the sums of nona- to deca-BDEs, hepta- to octa-BDEs, and tri- to hexa-BDEs and their homologues. Levels of D10BDE, a PBDE homologue, were high in all samples from the upper sediment layer. They were between 910 and 120 ng/g in mouths of rivers (S1~S3), but lower at offshore sites, and were not detected at S7, the sampling point farthest from any river mouth (detection limit: 6 ng/g). PBDE homologues other than D10BDE were detected only in the mouths of rivers (S1~S3).

Ohta[10] reported PBDE concentrations in surface sediment samples collected at 9 locations in Osaka Bay. The total concentrations of T3BDEs~H6BDEs in the surface layers were between 0.179 and 1.62 ng/g-dw (dry weight). Higher concentrations, at the levels of 1.62 ng/g-dw and 1.52 ng/g-dw were detected at Amagasaki and Osaka Nanko, respectively, which are densely populated and heavily industrialized areas. In this study, tri- to hexa-BDEs in 3 samples (S1~S3) from the mouths of rivers were detected at levels between 0.20 and 1.4 ng/g. Those measured levels are close to those reported by Ohta.

Acknowledgments

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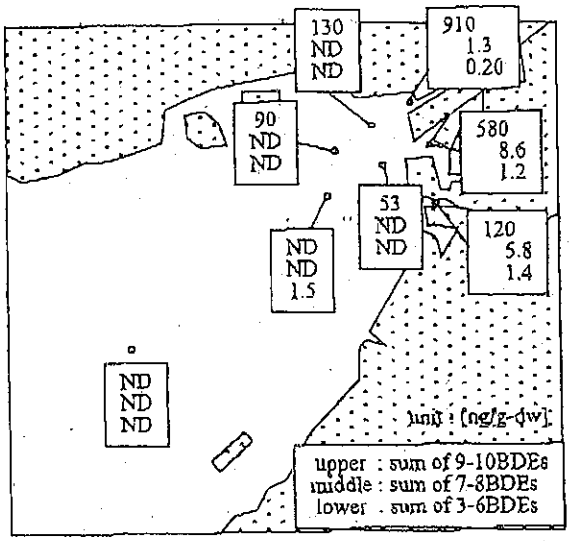

Figure 3. PBDE concentrations in surface sediment samples

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