# CHARACTERIZATION OF JAPANESE POLLUTION BY PBDEs, TBBPA, PCDDs/DFs, PBDDs/DFs AND PXDD/DFs OBSERVED IN THE LONG-TERM STOCK-FISHES AND SEDIMENTS

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## Introduction

Polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBPA) are used in large quantities as brominated flame-retardants (BFRs) to reduce the risk of fire in a wide range of manufactured products such as computers, furniture, textiles and automobiles. In Japan, the annual consumption of DecaBDE and TBBPA in 2002 were 2,200 and 31,000 tons, respectively. As a result, there is growing evidence that the large amount of PBDEs in the environment is due to release during the manufacturing of these chemicals or of consumer products containing them[1, 2]. In addition, there is sufficient evidence that the incineration of consumer products containing such flame retardant chemicals results in the formation of polybrominated dibenzo-p- dioxins/ furans (PBDD/DFs) and monobromo-polychlorinated dibenzo-p-dioxins/furans (PXDD/DFs)[3,4]. These chemicals, as well as the BFRs, have been found to occur throughout the environment, and intake of these contaminants from food, air and water is suspected to be the primary route of human exposure. However, little is known about environmental contamination of the above brominated compounds in Japan[5,6].

In this paper, we describe time-trend analysis of the levels of these brominated compounds in Japanese sea bass and grey mullet in long-term stock-fish samples from 1986 to 2000. These fish were sampled from Osaka Bay and the mouth of the Yamato River which flows into Osaka Bay. Then, we investigated the levels of these compounds in sediment collected from the coastal area of the Setouchi Sea, in western Japan. Finally, on the basis of pyrolysis and photolysis experiments, using five BFRs as precursors of PBDDs/DFs, we tried to classify all the sediment samples analyzed into two groups: PBDD- or PBDF-predominated sediment.

## Materials and Methods

### Samples

Japanese sea bass and grey mullet were collected from Osaka Bay and the mouth of the Yamato River, respectively (shown in Figure 1). After dissecting the edible filet tissue from the fish and freeze-drying, the samples were archived at −80 °C. The surface sediment samples were collected in 2003 from seventeen points (see Fig. 1) around the coastal area of the Setouchi Sea.

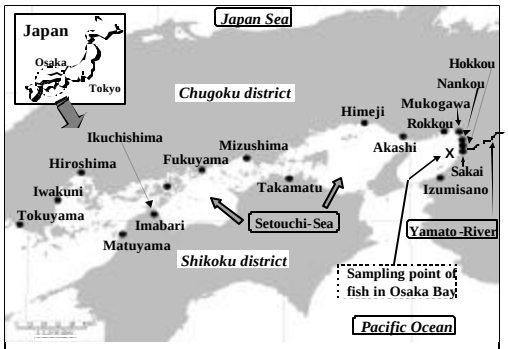


Fig. 1 Sampling map of sediments and long-term stock-fish (seabass)

### Analytical method

For the analysis of PBDEs, quantification of the PBDE congeners was achieved by the method of relative calibration curves using seven different $^{13}C_{12}$-labelled BDE isomers and thirty-one unlabelled native standards (TriBDEs; 8 kinds, TeBDEs; 6 kinds, PeBDEs; 7 kinds HxBDEs; 6 kinds, HpBDEs; 3 kinds, DeBDE) purchased from CIL (MA, USA). Other analytical methods were performed according to our previous paper[6]., The quantification of PCDD/DF (7/10 kinds), PBDD/DF (6/5 kinds) and PXDD/DF (5/3 kinds) congeners was similarily achieved using a multi-layer silica-gel column chromatography purification method, with an eluent of n-hexane and $CH_2Cl_2$:n-hexane (1:4). The eluate was concentrated and purified using an active carbon dispersed silica-gel column with eluent of n-hexane, $CH_2Cl_2$: n-hexane (1:3) and toluene. All purified samples were analyzed using HRGC-HRMS in EI-SIM mode. TBBPA was also determined by HRGC-HRMS using $^{13}C_{12}$-labelled internal standard. Further detailed methods can be found in our paper[7].

## Results and Discussion

Figure 2 shows the time-dependent variation of PBDE and TBBPA contamination in Japanese sea bass. A remarkable contamination was observed in the samples of 1988 and 1989, showing over 400 ng/g fat for the lower-BDEs. However, it was found that such contamination levels gradually decreased after 1990, and the accumulation level in the 1999 sample

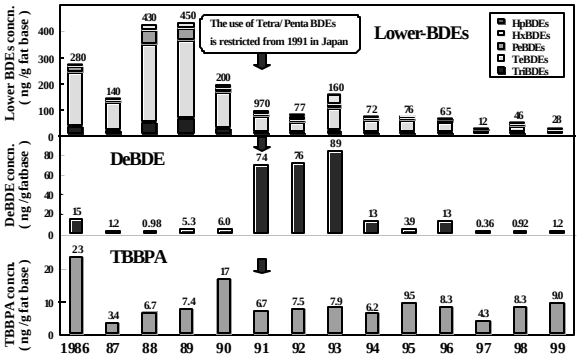


Fig. 2 Time trend analysis of Lower-BDEs, DeBDE and TBBPA in the seabass (1986-1999) captured from Osaka Bay

was only ~5 %, of the maximum (1989) level. This phenomenon was very particular and might be due to the demand and usage of PBDEs in Japan; 6,000 tons in 1986, increasing to 12,000 tons by 1990. In 1991 there was a voluntary restriction on the use of pentaBDEs and octaBDEs, causing the trend to reverse and resulting in an increase in the relative proportion of the deca isomer being used In 2002 the demand for DecaBDE was only 2200 tons.

Then, the contribution ratio of the PBDE isomers to the total concentration in Japanese seabass (1989 vs. 1999) was compared. In the 1989 sample, the isomer ratios were : 2,2',4, 4'-TeBDE (51.8%), 2,4,4'/2',3,4-TriBDE (10.8%), 2,3',4',6-TeBDE (7.8%), 2,3',4,4'-TeBDE (6.9%) and 2,2',4,4',5-PeBDE(6.1%), whereas the order in the 1999 samples were 2,2',4,4'-TeBDE (34.9%), 2,2',3,4,4',5,6'-HpBDE(15.9%), 2,2',4,4',5,6'-HxBDE(10.5%), 2,4,4'/2',3,4-TriBDE (5.6%) and 2,2',4,4',6,6'-HxBDE (5.2%). It was clear that the isomer ratios of Hx- or HpBDE congeners (decomposition products of DeBDE) were increasing with time. The above observation reflects the restricted usage of pentaBDEs and octaBDEs products as BFRs since 1991 in Japan. Similar phenomena were also recognized in comparative studies of grey mullet sampled in 1987 and 1999 (data not shown). On the other hand, it was observed that the accumulation levels of TBBPA in Japanese sea-bass were relatively low and unrelated to the increase in its demand.

As shown in Figure 3, levels of lower-BDEs (Tri- to HpBDEs), DeBDE and TBBPA in the sediments collected were surveyed. The levels of lower-BDEs and DeBDE in the seventeen sediment samples were 0.16 - 26.0 ng/g and 1.3- 710 ng/g d.w., respectively. In contrast, those of TBBPA was 0.08 –5.0 ng/g d.w. High levels of DeBDE were observed in the samples from Sakai, Nankou, Hokkou and Rokkou, which were collected from an area containing many chemical factories, and the proportion of DeBDE in the total concentration was over 90% in most samples. With respect to the level of TBBPA, high pollution levels were similarily detected in the samples from Nankou, Hokkou and Tokuyama. However, the total concentrations of TBBPA were comparatively low, showing a reverse trend from

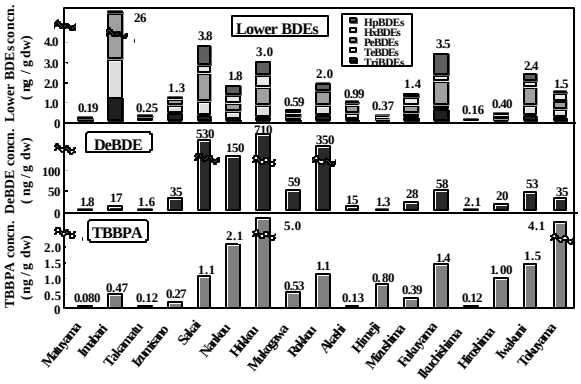


**Fig. 3 Levels of Lower-BDEs, DeBDE and TBBPA in the sediments collected from the coastal area of Setouchi-Sea in Japan**

the annual demand for DeBDE and TBBPA in Japan.

As shown in Figure 4, the levels of PCDDs/DFs, PXDDs /DFs and PBDDs/DFs in the sediments from the Setouchi Sea were compared. Most were PCDDs/DFs, with the levels of PCDDs/DFs (1.3 - 13 ng/gd.w.) > PBDDs/DFs (15 - 16,000 pg/g d.w.) > PXDDs/DFs (1.0 - 90 pg/g d.w.). Especially high pollution by PBDDs/DFs was observed in the sample from Mizushima, and high concentrations of TeBDD/DF, PeBDD and HxBDD as the 2,3,7,8-substituted isomer were detected.

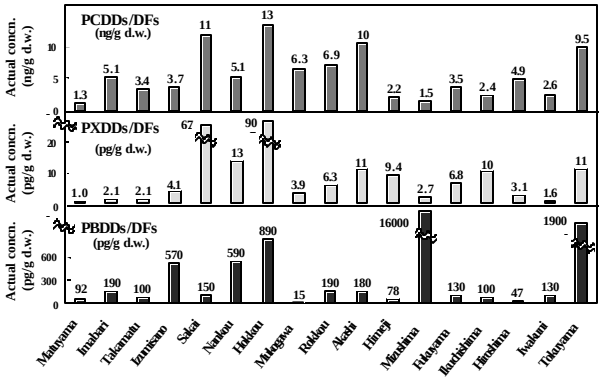


Fig. 4 Levels of PCDDs/DFs, PXDDs/DFs and PBDDs/DFs in the sediments collected from the coastal area of Setouchi-Sea in Japan

Figure 5 compares the patterns of PBDDs/DFs congeners in the samples of sediments and pyrolysis (300 °C, 60 min) of five kinds of BFRs. Detailed analysis of the data from the seventeen sediment samples, indicated they could be classified as either PBDDs-predominated sediment (eight samples) or PBDFs-predominated sediment (nine samples). Next, to clarify the different types of contamination, the congener pattern of PBDDs/DFs formed by pyrolysis of BFRs was investigated. Interestingly, it was observed that PBDD congeners were exclusively formed from TBBPA and TBP, whereas PBDF congeners were formed from HBB and DeBDE. Therefore, we believe the differences in the two types of sediments may be attributed to the differences in the BFRs used in the manufacturing, plastic or other chemical factories in the area surrounding each sampling point.

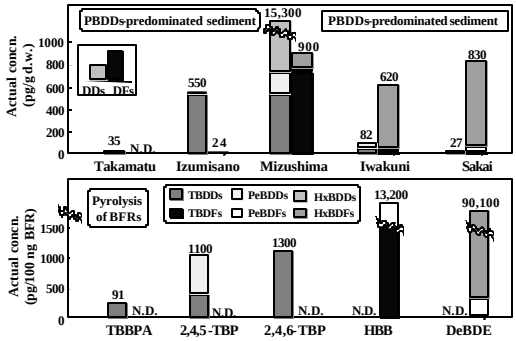


Fig. 5 Comparison of the patterns of PBDDs/DFs congener in the samples of sediments and pyrolysis of five kinds of BFRs

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