

CONTAMINATION STATUS AND TEMPORAL TRENDS OF POLYBROMINATED DIOXINS IN SEDIMENTS FROM TOKYO BAY

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Introduction

Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are the well known impurities of the brominated flame retardant (BFRs) chemicals such as technical polybrominated diphenyl ethers (PBDEs) and unintentional combustion products of flame-resistant resins treated with BFRs^{1,2}. Since a large amount of technical PBDE mixtures have been used as additive BFRs in Japan, PBDD/Fs have become a matter of concern due to their spreading contamination in the environment and adverse effects to humans and wildlife.

Recently, it was revealed that some PBDD congeners possibly bio-synthesized by marine organisms such as marine algae and cyanobacteria were also detected in fish and shellfish living in coastal waters^{3,4}. Therefore, it is assumed that anthropogenic PBDD/Fs and also naturally-derived PBDDs exist in coastal environment, but their distribution, temporal trend and potential source remain to be elucidated.

In this study, to clarify the horizontal and vertical distribution profiles of PBDD/Fs and to estimate their source, we analyzed PBDD/Fs using HRGC-HRMS in marine surface sediments and sediment core samples collected from Tokyo Bay which is one of the highly contaminated marine areas over the world.

Materials and methods

Sample collection

Marine surface sediments and sediment cores were collected by Japan Coast Guard at 13 locations covering the whole area of the Tokyo Bay in 2002 (Figure 1). In addition, dating of sediment cores were also investigated using ²¹⁰Pb dating by Japan Coast Guard⁵. All the sediment samples were stored at -25°C in environmental Specimen Bank (*es*-BANK) of Ehime University until chemical analysis.

Chemical Analysis

Chemical analysis of PBDD/Fs was carried out following the procedures described in a previous study with slight modification⁶. Briefly, Approximately 100 g of wet sediment samples were freeze-dried and homogenized with excess anhydrous sodium sulphate (Na₂SO₄). Approximately 20 g of dried sediment samples were extracted with toluene, using a High Speed Solvent Extractor (SE-100, Mitsubishi Chemical Analytechs, Japan) at 80°C at a 6.0 ml min⁻¹ flow rate for 60 min. Similarly, the samples were extracted again with 50% acetone/*n*-hexane (1:1 v/v) at 35°C at a 10 ml min⁻¹ flow rate for 30 min and crude extracts were mixed. The mixed-crude extract was concentrated using a rotary evaporator, then the solution was diluted to 10 ml with *n*-hexane. 2.0 ml of the

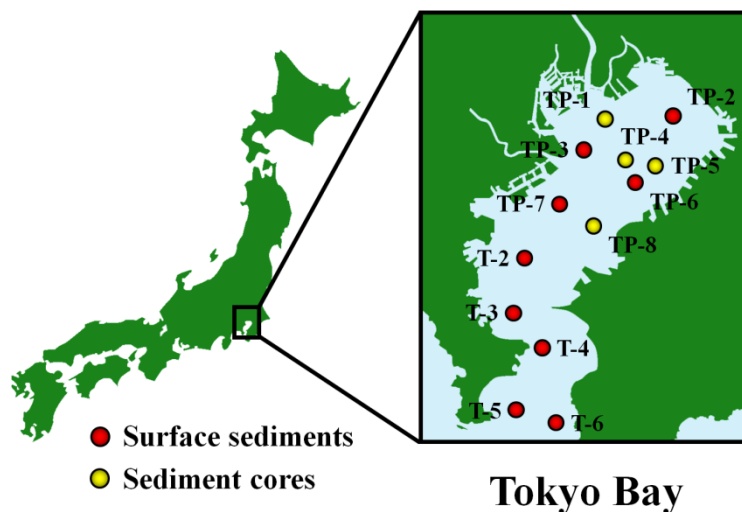


Figure 1. Sampling locations in Tokyo Bay, Japan.

extract (corresponds 4.0 g of dried sediment) was spiked with internal standards ($^{13}\text{C}_{12}$ -labeled PBDD/Fs) and fractionated by gel permeation chromatography (Bio-Beads S-X3, Bio-Rad Laboratories, USA, CA, 2 cm i.d. and 50 cm length). The PBDD/Fs fraction was concentrated and passed through multilayer silica gel packed in a glass column with 150 ml of 25% dichloromethane (DCM) /*n*-hexane (3:1 v/v). After concentration, the purified solution was added to activated carbon-dispersed silica-gel (Kanto Chemical Co. Inc., Japan) packed in a glass column. The first fraction was eluted with 30 ml of 25% DCM/*n*-hexane (3:1 v/v) and the second fraction with 80 ml of toluene. The second fraction (the PBDD/Fs fraction) was evaporated to dryness under a gentle stream of nitrogen and was spiked with internal standard (^{13}C -1,2,3,7,8-PeBDF). Identification and quantification of PBDD/Fs were performed using HRGC-HRMS (JEOL JMS-700D and JMS-800D, Japan).

Results and discussion

Horizontal distribution

PBDD/Fs were detected in all the sediment samples analyzed in this study. The total PBDF levels were the highest at TP-1 in surface sediments (196 pg g^{-1} dry wt.) and the levels decreased from the closed-off section (TP-1~TP-8; $36\text{-}196 \text{ pg g}^{-1}$ dry wt.) to the mouth of Tokyo Bay (T-2~T-6; $7.1\text{-}44 \text{ pg g}^{-1}$ dry wt.) (Figure 2). The PBDFs horizontal distribution was similar to profile of PBDEs reported previously⁷. Furthermore, 1,2,3,4,6,7,8-heptaBDF, a known impurity in the technical DecaBDE mixture⁸, was detected in surface sediments as a major congener and the concentrations of 1,2,3,4,6,7,8-heptaBDF and BDE-209 were strongly correlated ($R^2=0.73$, $p < 0.005$), suggesting that the emission source of PBDFs were technical PBDE mixture used in industrial application, especially DecaBDE. In contrast, total PBDD levels were the highest at T-6 (22 pg g^{-1} dry wt.) located at the mouth of the bay and the distribution pattern was distinctly different from the profile of PBDFs (Figure 2). Moreover, PBDD congeners mostly contained 2,7-/2,8-diBDD (30-40%) and 1,3,7-/1,3,8-triBDD (60-70%), which can be expected to be synthesized by marine organisms such as algae and cyanobacteria^{3,4}, indicating that almost all the PBDD detected in surface sediments were derived from natural origin.

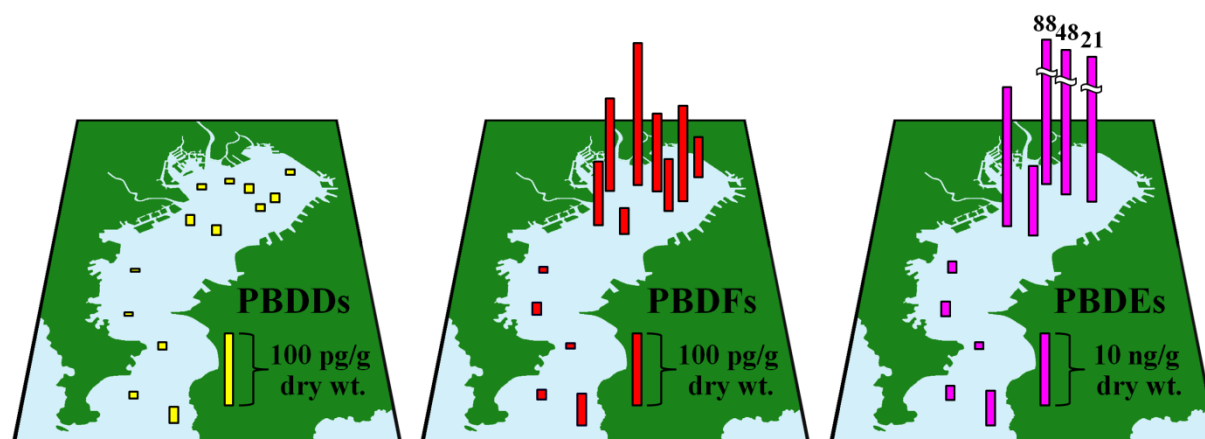
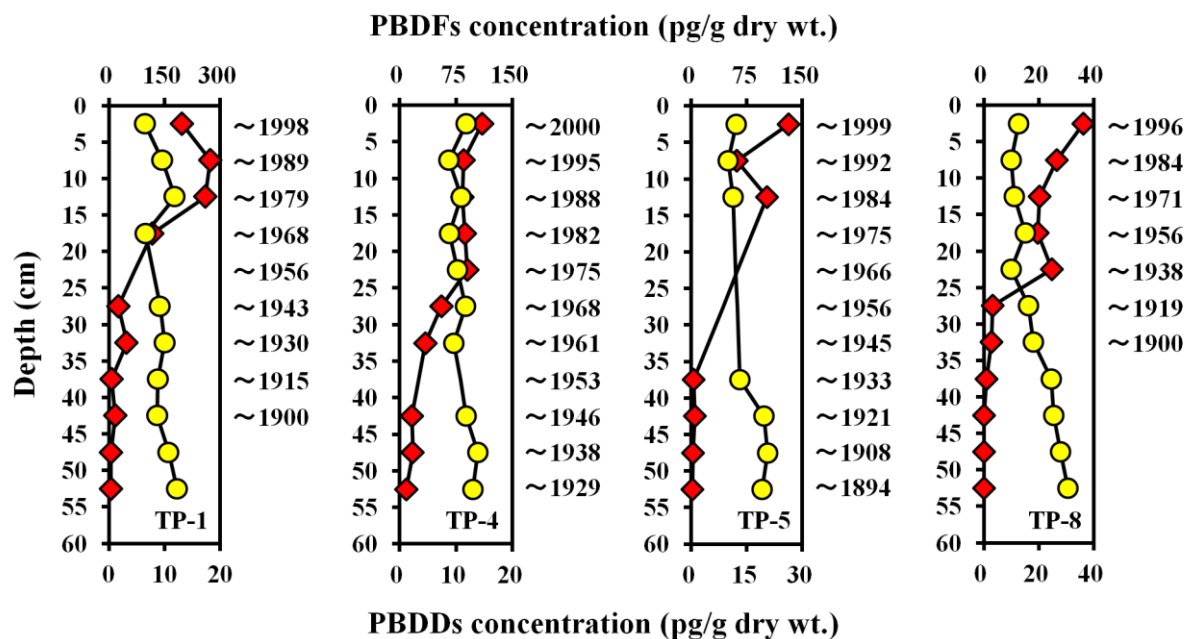


Figure 2. Spatial distribution of PBDDs, PBDFs and PBDEs in surface sediments collected from Tokyo Bay. PBDEs data were cited from Minh *et al.*, (2007).

Vertical distribution

The present study also evaluated the vertical distribution profiles of PBDD/Fs in sediment cores collected from TP-1, TP-4, TP-5 and TP-8. As a result, total PBDF and PBDE levels gradually increased from deep layer to surface layer in the all sediment cores. In addition, there was a positive correlation between the concentrations of 1,2,3,4,6,7,8-heptaBDF and BDE-209 ($R^2=0.65$, $p<0.001$), indicating that contamination of PBDFs was derived from PBDEs and have become advanced over time (Figure 3 and 4). In contrast, PBDDs were detected in the sediment cores dating from early 1900s where PBDFs and PBDEs were not detected in these sedimentary layers



(Figure 3). Furthermore, these profiles were significantly different from PBDFs and PBDEs (Figure 3 and 4). This phenomenon strongly suggests that 2,7-/2,8-diBDD and 1,3,7-/1,3,8-triBDD were naturally occurring compounds.

Conclusion

In the present study, not only anthropogenic PBDD/Fs but also naturally-derived PBDDs were detected in the all the sediment samples from Tokyo Bay. Although almost all of PBDDs that were detected in the sediment cores dating from early 1900s were derived from natural origin, anthropogenic PBDF levels have rapidly increased after the 1950s, indicating that the recent contamination of PBDD/Fs in Tokyo Bay was mostly

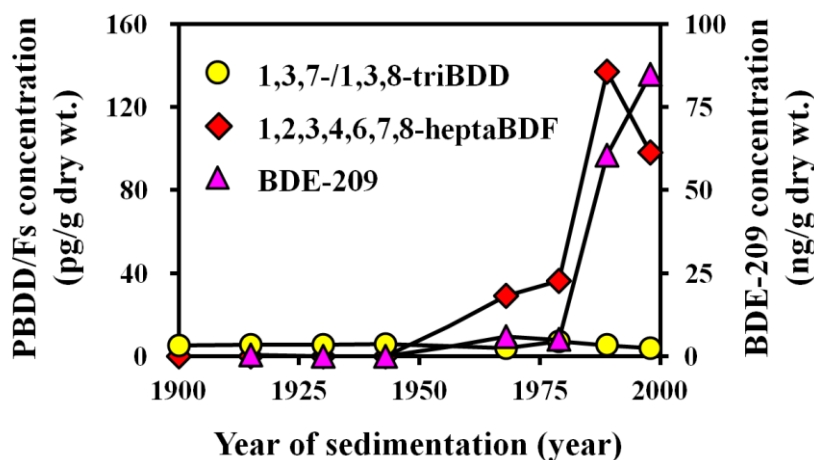


Figure 4. Temporal trends of concentrations of 1,3,7-/1,3,8-triBDD, 1,2,3,4,6,7,8-heptaBDF and BDE-209 in sediment core collected from TP-1.

Figure 3. Vertical profiles of PBDDs and PBDFs in sediment cores collected from TP-1, TP-4, TP-5, TP-8. Yellow circle: PBDDs; Red square: PBDFs.

dominated by anthropogenic PBDFs. In addition, there is the possibility that naturally-derived PBDD levels might change as a result of the destruction in marine ecosystem caused by human activity such as coastal development, global warming, eutrophication etc. Hence, it is necessary to conduct continuous monitoring and risk assessment of PBDD/Fs for human and wildlife.

Acknowledgements

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