

## HISTORICAL TRENDS OF PBDD/Fs, PBDEs, PCDD/Fs AND DIOXIN-LIKE PCBs IN SEDIMENT CORES FROM TOKYO BAY

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### *Introduction*

Considering the increased use of brominated flame retardants (BFRs), temporal trends of their occurrence in the environment and their toxicological effects are of concern because of their high lipophilicity and persistent properties. In Japan, the domestic use of BFRs increased 3.4-fold from 20,000 tons in 1986 to 67,250 tons in 2000. Tetrabromobisphenol A (TBBPA) and polybrominated diphenyl ethers (PBDEs) are the main types of domestic BFRs. Hexabromocyclododecane (HBCD), tribromophenol (TriBP) and Bis (pentabromophenyl) ethane are also used as BFRs<sup>1</sup>. Heating PBDEs, TBBPA and other BFR-containing materials may lead to the formation of polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs)<sup>2</sup>. PBDD/F congeners have been identified during thermal degradation of BFRs<sup>3</sup> and BFR-containing materials<sup>4</sup> and are found in chimney depositions<sup>5</sup> from textile processing plants and vehicle exhaust<sup>6</sup>.

We reported the concentrations and trends of PBDE and PBDD/F congeners in fat tissue of Japanese<sup>7</sup>, but the data on the sources and detailed trends of PBDEs and PBDD/Fs in the environment were lacking. The temporal trends of the levels of PCDD/F and dioxin-like PCBs (DL-PCBs or Co-PCBs) in sediment cores from Tokyo Bay have been studied<sup>8,9</sup>. However, to date there are no sediment core data on PBDE and PBDD/F from Tokyo Bay which are needed to analyse temporal trends. In this study, we investigated the concentrations of PBDEs, PBDD/Fs, PCDD/Fs and dioxin-like PCBs in sediment cores from Tokyo Bay (1904-1999). As far as we know, this is the first report of PBDEs and PBDD/Fs in Tokyo Bay.

### *Materials and Methods*

On January 2001 sediment cores were taken from Tokyo Bay at a position of 35°34.063'N latitude and 139°54.319'E longitude. An acrylic pipe core sampler (diameter 10cm and length 100cm) was used to collect the sediment cores with 70cm depth were obtained. Sediment cores were sectioned in the laboratory into 2cm sections. All core sediments were stored frozen until dating and chemical analysis. Dating of the subsamples was based on the <sup>210</sup>Pb method. The average sedimentation rate was estimated to be 0.177g/cm<sup>2</sup>/yr and the average deposition rate was 1.207cm/yr considering the subsample conditions such as moisture content and density in a 2cm-section.

Analyses of PCDD/Fs and Co-PCBs in sediment cores were carried out using a manual for the analysis of sediments<sup>10</sup>. PBDEs and PBDD/Fs were analysed according to the combinations and modifications of previous methods<sup>11</sup> and guideline for PBDD/Fs<sup>12</sup>. Briefly, 10 grams of a dried sample was spiked with <sup>13</sup>C-labeled surrogate PCDD/Fs, Co-PCBs, PBDEs and PBDD/F standards and extracted in a Dean-Stark type Soxhlet extractor using toluene as solvent.

Extracts were subjected to a sequential cleanup using multi-layered silica (for Cl-compounds) or a modified silica column (for Br-compounds) followed by a Florisil (for Br-compounds) and an active carbon-impregnated silica column (for both compounds). Analysis by HRGC/HRMS was performed using SIM with a JEOL-700K HRMS equipped with a Hewlett-Packard 6890 GC and a CP-Sil 88 (50m, 0.25 mm i.d., 0.2  $\mu\text{m}$  stationary phase), DB-5 (30m, 0.25 mm i.d., 0.25  $\mu\text{m}$  stationary phase), CP-Sil 8CB (25m, , 0.25 mm i.d., 0.12  $\mu\text{m}$  stationary phase) and a DB-5HT (15m, 0.15 mm i.d., 0.1  $\mu\text{m}$  stationary phase). The HRMS was operated in electron impact (EI) ionization mode at a resolution of  $R > 10,000 \sim 12,000$  (10% valley). For identification of PBDFs, possible interference from PBDE fragments was checked for in the PBDD/F fraction. After injection, identification and quantification of target compounds were done by an isotope dilution method using an XMS data acquisition system and a DioK data processing system (JEOL, Japan).

### **Results and Discussion**

**PCDD/Fs** The results in pg/g dry wt of sediment cores are summarized in Table 1 and Figure 1. PCDD/F concentrations increased from the 1950s to the late 1970s, and then generally leveled off. The increases of PCDD/Fs were due to the high levels of HpCDD and OCDD, and the major contributor to these congeners was pentachlorophenol (PCP) as an impurity. For instance, due to the increased use of PCP during 1957~67<sup>9</sup>, the ratio of PCDDs to PCDFs rapidly changed from 3~4 before its use (see 1904~1948 slices) to 6~7 after its use (see 1953~1973 slices). Furthermore, due to the input of chloronitrofen (CNP) from the middle 60s, the ratio increased again during 1971-1982 because it contained 1368- and 1379-TeCDD as impurities. These temporal trends of PCDD/Fs are similar to previous results<sup>9</sup>. Considering the decrease in dioxin inventories from 7.4~7.6kg-TEQ in 1997 to 1.7kg-TEQ in 2001<sup>13</sup>, decreasing trends for chlorinated dioxins are expected in the future.

**Co-PCBs** The Co-PCB levels increased from 1946-48 to 1971-73, with a drastic increase from the middle of the 1950s. During 1977 to 1982, Co-PCB concentrations decreased to 8,000 pg/g and then generally leveled off. Since the major source of Co-PCBs is PCB formulations (particularly KC-300 and 400), there were no significant changes in the congener profiles from TeCBs to HpCB (Fig. 1). However, banned-PCB formulations in closed systems which are still operating should be observed to assess temporal trends or accidental exposures.

**PBDEs** Background levels of PBDEs were found during 1904-1941 (DeBDE was not analysed). The concentrations increased rapidly from 1946-48 to the surface layers in 1998-1999 and peaked in 1992-93 (78 ng/g, dry wt). The major congener during the whole period was DeBDE (BDE-209). BDE-47, a persistent congener in human fat tissue (35.6%)<sup>7</sup> contributed only <0.2 % in the cores during 1980-1999. Congener profiles of PBDEs, particularly Tri-HpBDEs, changed from low to high during the whole period. Therefore, it seems that sediment cores strongly reflect the profiles of PBDEs produced in the market. In Japan, DeBDE use increased rapidly from 1986 (3,000 t), peaked in 1990 (10,000 t) and then decreased in 2000 (2,800 t). Comparing the historical use and the temporal trends of PBDEs in the sediment cores, the results indicate a lag of ~10 years between peak use and deposition in the sediments. The levels in surface layers and temporal trends of PBDEs were similar to those in sediment cores from Osaka Bay<sup>14</sup>.

**PBDD/Fs** For PBDD/Fs, congeners having no specifications were included as possible brominated dioxins and furans. The PBDD/F congeners, TeBDD, Te~HxBDF. PeBDD and HxBDD were below the detection limits or were interfered with by high backgrounds on the chromatograms during the whole period. The levels of PBDD/F increased significantly from late 1960s to the mid-1990s, and then generally leveled off (Table 1). The historical trends of

PBDD/Fs were similar to those of PBDEs. The concentrations were found in the order : HxBDF> TeBDFs > PeBDFs > TeBDDs. We do not have explanations for the potential sources of PBDD/Fs found in the sediment samples. No significant correlations between PBDF and PBDE levels were observed. Investigations of the potential contribution of other BFRs to the depositions are needed in the future.

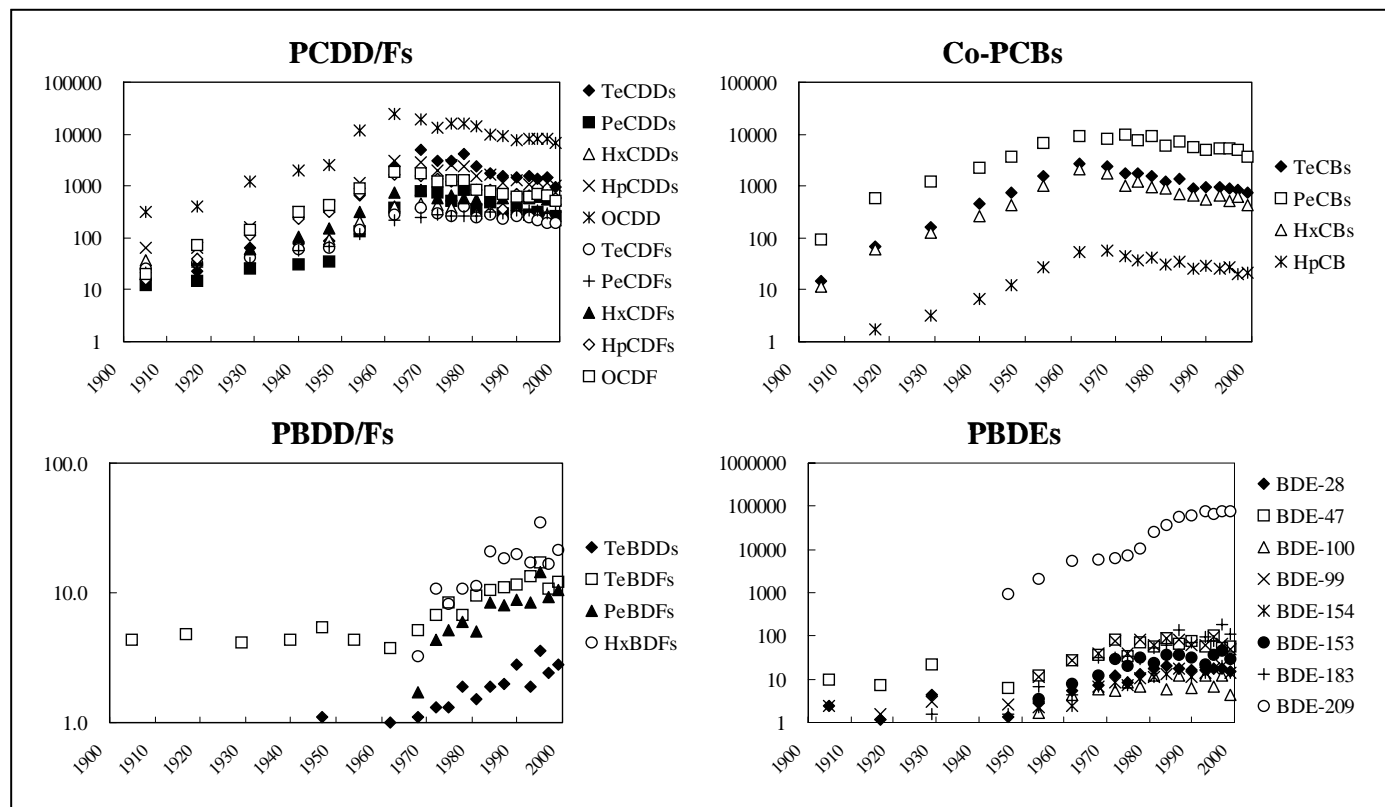
Table 1. Concentrations of PBDEs, PBDD/Fs, PCDD/Fs and Co-PCBs in the sediment cores from Tokyo Bay

Compounds	1904-06	1916-18	1928-30	1939-41	1946-48	1953-55	1961-63	1967-69	1971-73	1974-76
PBDEs	14	10	30	NA <sup>a</sup>	914	2203	5414	5840	6353	7281
PBDD/Fs <sup>b</sup>	5.7	6.3	5.3	5.2	7.0	5.6	5.2	11.2	23.1	23.2
PCDD/Fs	552	763	1948	3314	4139	15911	36250	33333	23422	26632
Co-PCBs	121	709	1522	2928	4839	9441	13866	12595	12646	10472
Compounds	1977-79	1980-82	1983-85	1986-88	1989-91	1992-93	1994-95	1996-97	1998-99	
PBDEs	11103	25299	37125	57194	59529	78050	68161	75039	76593	
PBDD/Fs <sup>b</sup>	25.5	27.5	41.9	39.6	43.1	40.9	70	39	46.9	
PCDD/Fs	27260	21230	16632	14933	13674	13688	13693	13845	11211	
Co-PCBs	11832	7998	9136	7207	6617	6856	6685	6601	4959	

<sup>a</sup> na : not analysed      <sup>b</sup> : congener(s) below the limit of quantification (LOQ), above the limit of detection (LOD) were included

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**Figure 1. Historical trends of PCDD/Fs, Co-PCBs, PBDD/Fs and PBDEs in the sediment cores from Tokyo Bay**