CONTAMINATION LEVELS OF PBDEs, TBBPA, PCDDs/DFs, PBDDs/DFs AND PXDDs/DFs IN THE ENVIRONMENT OF JAPAN

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Introduction

Polybrominated diphenyl ethers (PBDEs) and Tetrabromobisphenol A (TBBPA) are used in large quantities as brominated flame-retardants (BFRs) for many applications such as television sets, computers, paints, and textiles etc. In Japan, the annual consumption of DecaBDE and TBBPA in 2000 was 2,800 and 32,300 tons, respectively. As a result, there is growing evidence that the large amounts of PBDEs or TBBPA in the environment are due to released during the manufacturing of these chemicals or consumer products containing these chemicals[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 (PBDDs) and –furans (PBDFs) [3].. These chemicals, as well as the BFRs, have been found to occur throughout the environment. And the intake of these contaminants from food, air and water is suspected to be the primary route of human.

At present, little is known about environmental pollution of the above brominated compounds in Japan[4, 5]. In this study, we describe the PBDEs and TBBPA contamination in the atmosphere and sediments from Osaka district as second big city in Japan. Then, to clear whether the above BFRs released to the environment are influenced to generate PBDDs/DFs and the mixed bromine/chlorine-substituted dibenzo-*p*-dioxins (PXDDs) and -furans (PXDFs) or not, it was also investigated the contamination level in the atmosphere and sediments at same sampling points. Finally, we estimated the contamination pathway and sources of such brominated pollutants.

Materials and Methods

Samples

The surface sediment samples (A - F; shown in Fig.1) were collected from 6 points around the coastal area of Osaka Bay in 1999. Flue gas samples (No.1&2 shown in Table 1) were sampled according to the JIS Z 8808 in 2000. By use of high-volume air sampler, the samples were collected at athletic field of Setsunan University in 2001. All samples were collected from Osaka district in Japan.

Analytical method

For the analysis of PBDEs, the quantification of PBDE congeners was performed by the method of relative calibration curves using seven different $^{13}C_{12}$-labelled BDE isomers (#28, 47, 99, 154, 183, 209) and thirty-one unlabelled native standards (TriBDEs; #17, 25, 28, 30, 32, 33, 35, 37, TeBDEs; #47, 49, 66, 71, 75, 77, PeBDEs; #85, 99, 100, 105, 116, 119, 126, HxBDEs; #138, 140, 153, 154, 155, 166, HpBDEs; #181, 183, 190,DeBDE; #209) purchased from Cambridge Isotope Laboratories (MA, USA). Other analytical conditions were performed according to our previous paper[5]. With respect to the quantification of PCDD/DF, PBDD/DF and PXDD/DF congeners (shown in Table1), the purified method was multi-layer silica-gel column chromatography, with an eluent of n-hexane and CH_2Cl_2:n-

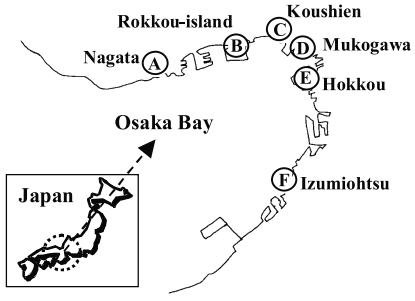

Fig. 1 Sampling points of sediment A~F

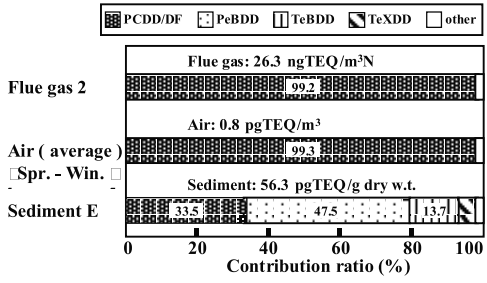

Fig. 2 Contribution ratio (%) to total TEQ by PCDD/DF PeBDD,TeBDD and TeXDD isomers

Table 1 Levels of TBBPA・PBDE in the Air and Sediment of Osaka district

	Air (pg/m^3)				Sediments[a)] (pg/g dry w.t.)					
	Spr.	Sum.	Aut.	Win.	A	B	C	D	E	F
TBBPA	-	-	-	-	3100	12000	680	940	2000	1700
TriBDE	0.75	1.1	0.030	1.7	440	68	250	170	360	2.6
TeBDE	1.2	2.2	0.41	2.0	150	52	44	190	320	350
PeBDE	0.17	0.55	0.55	0.44	150	40	23	78	310	550
HxBDE	0.49	0.70	0.16	1.1	190	20	34	64	550	36
HpBDE	1.3	0.57	0.81	1.4	150	53	200	270	450	320
DeBDE	100	330	200	340	55000	7800	20000	76000	350000	83000
Total PBDE	104	335	202	347	56100	8030	20600	76800	352000	84300

a) Sediment sample A~F (sampling points shown in Fig.1) were collected from the coastal area of Osaka Bay.

hexane (1:4). The eluate was concentrated and purified by a active carbon dispersed silica-gel column with eluent of n-hexane, CH_2Cl_2: n-hexane (1:3) and toluene. All purified sample was analyzed by the use of HP6890 GC-JEOL JMS700 MS (HRGC-HRMS) at high-resolution condition (R=10,000) in EI-SIM mode. TBBPA was also determined by HRGC-HRMS in EI-SIM mode using $^{13}C_{12}$-labelled internal standard.

Results and Discussion

As shown in Table 1, the levels of TBBPA and PBDEs in the air and sediments collected from Osaka district of Japan was surveyed. With respect to the level of PBDEs in the air, it was observed with levels between 104 and 347 pg/m^3, showing higher levels of summer (July) and winter

(January). The PBDEs level in the sediment from Osaka Bay was 8 and 352 ng/g, high pollution was observed in the sample E (Hokkou), which was collected from the area of many chemical factories. The ratio of DeBDE for total concentration was over 96% in all samples. On the other hand, with respect to the level of TBBPA, the highest pollution was detected in the sample B (Rokkou-island), which was collected from the area of many harbor facilities. However, the whole level of TBBPA was comparatively low, showing the reverse phenomenon of the annual consumption of DeBDE and TBBPA in Japan. In addition, as interesting observation, when both compounds were photo-decomposed in organic solvents, it was recognized that high concentration of PBDF or Bisphenol A (BPA) was generated from PBDEs or TBBPA.

Table 2 compares the actual concentration of PCDDs/DFs (Table 2A), PBDDs/DFs (Table 2B), and PXDDs/DFs (Table 2C), in flue gas, air and sediments. When they were determined in the flue gas and air sample, almost was PCDDs/DFs, showing the levels of PCDDs/DFs > PXDDs/DFs > PBDDs/DFs,

Table 2A Levels of PCDD/DF in Flue gas, Air and Sediment

	Flue gas (ng/m^{3}N)		Air (fg/m^3)	Sediments[a] (pg/g dry w.t.)					
	FG 1[b]	FG 2[b]		A	B	C	D	E	F
2,3,7,8-TCDD	1.4	1.1	3.1	9.3	0.01	1.0	16	1.2	2.1
1,2,3,7,8-PeCDD	5.9	4.1	9.7	3.0	0.39	1.8	13	2.6	1.7
1,2,3,4,7,8-HxCDD	7.1	3.5	11	7.3	0.57	3.4	20	4.2	3.3
1,2,3,6,7,8-HxCDD	14	5.5	20	4.3	0.98	4.7	50	4.0	6.3
1,2,3,7,8,9-HxCDD	11	3.5	16	4.5	0.63	5.5	38	5.3	4.2
1,2,3,4,6,7,8-HpCDD	74	20	160	180	40	170	670	200	250
OCDD	61	21	230	5100	1900	5300	14000	6800	6200
Total PCDD	174	59	450	5310	1940	5490	14800	7020	6470
2,3,7,8-TCDF	7.9	7.3	21	13	0.6	5.6	37	2.3	1.8
1,2,3,7,8-PeCDF	19	11	45	14	0.98	9.1	95	8.2	7.4
2,3,4,7,8-PeCDF	20	11	45	10	0.63	5.1	50	6.2	6.4
1,2,3,4,7,8-HxCDF	19	7.0	59	14	1.1	9.9	130	10	8.9
1,2,3,6,7,8-HxCDF	12	5.8	48	11	0.65	6.9	73	9.9	6.7
1,2,3,7,8,9-HxCDF	1.6	0.26	12	N.D.	0.10	N.D.	4.3	0.26	0.35
2,3,4,6,7,8-HxCDF	22	7.0	115	13	1.2	9.2	95	16	15
1,2,3,4,6,7,8-HpCDF	37	17	290	81	13	70	500	110	94
1,2,3,4,7,8,9-HpCDF	14	1.3	80	3.7	1.1	5.1	77	10	8.2
OCDF	37	2.6	300	190	25	130	1500	260	270
Total PCDF	190	70	1020	350	44	251	2560	433	420
Total PCDD/DF	364	129	1470	5660	1980	5740	17400	7450	6890

b) FG 1 and 2 indicate the municipal solid and industrial waste incinerator, respectively.

Table 2B Levels of PBDD/DF in Flue gas, Air and Sediment

	Flue gas (pg/m^{3}N)		Air (fg/m^3)	Sediments[a] (pg/g dry w.t.)					
	FG 1[b]	FG 2[b]		A	B	C	D	E	F
2,3,7,8-TBDD	N.D.	N.D.	N.D.	0.71	2.7	2.5	3.5	6.7	4.0
1,2,3,7,8-PeBDD	N.D.	N.D.	N.D.	2.7	6.0	12	16	23	19
1,2,3,4,7,8-HxBDD / 1,2,3,6,7,8-HxBDD	1.9	1.6	0.065	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,2,3,7,8,9-HxBDD	N.D.	0.48	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
OBDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Total PBDD	1.9	2.1	0.065	3.4	8.7	15	20	30	23
2,3,7,8-TBDF	1.8	2.8	1.3	0.19	0.30	0.5	1.1	1.5	0.52
1,2,3,7,8-PeBDF	0.86	0.25	0.090	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2,3,4,7,8-PeBDF	1.4	2.0	0.090	N.D.	N.D.	N.D.	N.D	N.D.	N.D.
1,2,3,4,7,8-HxBDF	0.90	0.81	35	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,2,3,4,6,7,8-HpBDF	N.D.	N.D.	N.D.	0.51	N.D.	0.32	6.9	45	7.6
Total PBDF	5.0	5.9	36	0.7	0.30	0.82	8.0	47	8.1
Total PBDD/DF	6.9	8.0	36	4.1	9.0	16	28	77	31

and their congener pattern in both samples was also similar. Whereas it could be find the extremely interesting phenomenon in the marine sediments analyzed.. Thus, high concentrations of TBDD, PeBDD and TXDD as 2,3,7,8-substituted isomer were detected. Although the reason is presently unclear, it may be attributed to other BFRs like Tribromophenol or Hexabromobenzene etc. as precursor for formation of PBDDs/DFs and PXDDs/DFs. Mason and Safe evaluated the toxicity of PBDDs/DFs and PXDDs/DFs, comparing that of 2,3,7,8-TCDD, it was observed that such isomers exhibited the activity higher than 2,3,7,8-TCDD with AHH induction or Thymus shrink potency in

Table 2C Levels of PXDD/DF in Flue gas, Air and Sediment

	Flue gas (pg/m^{3}N)		Air (fg/m^3)	Sediments [a] (pg/g dry w.t.)					
	FG 1[b]	FG 2[b]		A	B	C	D	E	F
2-Br-3,7,8-Cl-DD	40	8.6	0.35	5.0	0.84	6.5	4.9	1.9	1.1
2,3-Br-7,8-Cl-DD	43	2.8	0.31	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1-Br-2,3,7,8-Cl-DD	88	14	0.065	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2-Br-3,6,7,8,9-Cl-DD	5.1	N.D.	0.39	N.D.	N.D.	N.D.	N.D.	0. 32	N.D.
1-Br-2,3,6,7,8,9-Cl-DD	150	7.6	0.35	0.25	0.092	0.63	0.73	0.75	0. 12
1-Br-2,3,4,6,7,8,9-Cl-DD	140	16	0.50	2.3	2.0	3.0	5.0	2.7	5.3
Total PXDD	470	49	2.0	7.6	2.9	10	11	5.7	6.5
3-Br-2,7,8-Cl-DF	110	16	0.075	N.D.	N.D.	N.D.	2.0	N.D.	N.D.
1-Br-2,3,7,8-Cl-DF	N.D.	7.0	0.20	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Total PXDF	110	23	0.28	N.D.	N.D.	N.D.	2.0	N.D.	N.D.
Total PXDD/DF	580	72	2.3	7.6	2.9	10	13	5.7	6.5

Wister rat[6, 7]. Therefore, it can be considered that the toxicity of same congener of PBDDs/DFs or PXDDs/DFs is nearly equal to that of PCDDs/DFs. On the basis of this assumption, the contribution ratio to total TEQ by PCDDs/DFs, PBDDs/DFs and PXDDs/DFs was calculated by using 2,3,7,8-TCDD equivalent factors (Fig. 2). With respect to the flue gas and air, the contribution to total TEQ is almost PCDDs/DFs, while in the case of sediment, the four or five bromine/chlorine-substituted dibenzo-*p*-dioxins and -furans like TBDD, PBDD and TXDD was occupied. Further study is needed to clarify the sources and the formation mechanism of PBDDs/DFs and PXDDs/DFs in the water environment.

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