POLYBROMINATED DIOXINS (PBDDs/DFs) AND POLYBROMINATED DIPHENYL ETHERS(PBDEs) IN HOUSE DUST IN ORDINARY HOMES

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Abstruct
For the purpose of grasping the pollution tendency by polybrominated dibenzo-p-dioxins/dibenzofurans (PBDDs/DFs) and polybrominated diphenyl ethers (PBDEs) in ordinary homes, we analyzed PBDDs/DFs and PBDEs in house dusts gathered from several points in the houses.
PBDDs/DFs were detected in all investigated samples, and the range of concentration was 840 pg/g-69,000 pg/g. Most of detected compounds were PBDFs, and highly brominated compounds (hexa-, hepta-, octa-) were detected mainly. PBDEs were also detected in all samples, and the range of concentration was 130-8,100 ng/g. Except for one exception, congener composition of PBDEs had the highest percentage of DeBDE.
By this investigation, it seemed there was clear correlation between the concentration of PBDDs/DFs and PBDEs.

Introduction
It has been suggested that monitoring studies on PBDDs/DFs are required to understand the contamination and distribution in the environment by the Japanese government.
It is pointed out that PBDDs/DFs have toxic consequences equivalent of polychlororinated dizenzo-p-dioxins/dizenzofurans(PCDDs/DFs)[1)]. Brominated flame retardants such as PBDEs cause generation of PBDDs/DFs are widely used for something which constitutes indoor environment such as household electrical appliances, furniture, building materials to improve incombustibility. There is the report these compounds were detected in house dusts collected in ordinary homes [2)], however there is still a few information about brominated compounds in indoor environment. We examined PBDDs/DFs and PBDEs in house dust samples collected in ordinary homes, in order to analyze detail of the levels and congener compositions. PCDDs/DFs were also analyzed using the same sample for reference.

Materials and Methods
House dust samples: A total of 13 house dust samples were collected from 9 homes of Tama-city, Tokyo, Japan. They were gathered from around the television, the fluorescent lamp cover upper part, the air-conditioner filter, the pack of the vacuum cleaner inside, the washing machine outskirts, the fan heater filter, and the floor top. Because the enough amount of sample couldn't be gathered, 3 samples were mixed them gathered from 2 homes. The samples summary are shown in Table-1. The samples were stored at less than 5 °C until analysis. Further, for analysis of PBDDs/DFs and PBDEs, brown glassware equipments were used for shading, the filters which cuts ultraviolet rays in the fluorescent lamps in the laboratory were loaded.

Table-1 The samples summary

Sampling Point	Television			fluorescent lamp cover upper part				air-conditio-ner filter		washing machine outskirts	pack of the vacuum cleaner inside	fan heater filter	floor top
Home No.	1	3, 5	6	4	5	6	7, 8	2	9	4	5	5,8	3,8
Sample No.	1)	2)	3)	4)	5)	6)	7)	8)	9)	10)	11)	12)	13)

PBDDs/DFs standards: 12 unlabeled 2,3,7,8-substituted congeners (2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, OBDD, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF,

1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and OBDF) and 10 $^{13}C_{12}$-labeled(2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, OBDD, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF) congeners were obtained from Cambridge Isotope Laboratories.**PBDEs standards:** 27 unlabeled (#3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209) congeners and 12 $^{13}C_{12}$-labeled (#3, 15, 28, 47, 99, 138, 153, 154, 183, 197, 207, 209) congeners were also obtained from Wellington Laboratories.

PBDDs/DFs analyses: PBDDs/DFs, PBDEs and PCDDs/DFs were extracted from the samples(1-3 g) by soxhlet extraction with toluene over 16 hours. For the analyses of PBDDs/DFs, the requirements were taken from the soxhlet extracts. The extracts were spiked with $^{13}C_{12}$-labeled internal standards and were treated with concentrated sulfuric acid. Then the extracts were purified by a silica gel, a Florisil and an activated carbon column chromatography. The column chromatography effluents were spiked with $^{13}C_{12}$-labeled recovery standards, and subjected to HRGC/HRMS.

PBDE analyses: For the analyses of PBDEs, the requirements were taken from the above-mentioned extracts. The extracts were spiked with $^{13}C_{12}$-labeled internal standards and were treated with concentrated sulfuric acid. Then the extracts were purified by a silver nitrate/silica gel column chromatogurapy and subjected to a gel-permeation column chromatography(GPC). The column chromatography effluents were spiked with $^{13}C_{12}$-labeled recovery standards, and subjected to HRGC/HRMS.

PCDDs/DFs analyses: For the analyses fo PCDDs/DFs, requirements were taken from the above-mentioned extracts. PCDDs/DFs were prepared and analyzed in accordance with an analysis manual in Japan[3].

Results and Discussion

PBDDs/DFs: The results of analysis of PBDDs/DFs were indicated in Table-2 and the congener compositions were indicated in Figure-1. PBDDs/DFs was detected in all investigated samples, and the range of concentration was 840 pg/g-69,000 pg/g. Sample No.2 and 11 had high concentration with 69,000 and 64,000 pg/g respectively. Most of detected compounds were PBDFs, and highly brominated compounds were detected mainly. The range of concentration of PBDDs/DFs was 660 pg/g-76,000 pg/g, according to the finging of the house dust samples which were gathered in the ordinary homes by the Ministry of the Environment from 2003 to 2005[4]. For the differences in the respective detection limit, so it couldn't be compared simply, but there were no differences so much with the finding by the Ministry of the Environment for this finding. PBDFs were also detected maily in the Ministry of the Environment investigation[4]. There was a little difference in the ratio of OBDF because of difference in the detection limit, the congener compositions were similar for the most part.

PBDEs: The results of analysis of PBDEs were indicated in Table-3 and the congener compositions were indicated in Figure-2. PBDEs were also detected in all samples, and the range of concentration was 130-8,100 ng/g. Sample No.9 had very high concentration with 8,100 ng/g. These results were equal to the finding by the Ministry of the Environment described first mostly, the range of concentration of PBDEs was 120-7,900 ng/g. There were also similar level mostly more than the overseas example of report[5]. As for a congener composition, DeBDE occupied much percentage except for sample No.9. There was a group ranked high of NoBDEs and OBDEs following DeBDE, there was also a group ranked high of PeBDEs and TeBDEs on the other hand. DeBDE,PeBDEs and TeBDEs accounted for 90 % of the whole according to an overseas report[5]. The congener composition of sample No.9 was quite different from other samples, but the reason was unclear.

PCDDs/DFs: PCDDs/DFs were also detected in all samples, and the range of concentration was 360-27,000 pg/g. The level of PCDFs were higher than that of PCDDs. Sample No.9 had extremly high concentration with 27,000 pg/g, but the reason was also unclear.

Table-2 Concentrations of PBDDs/DFs in house dust samples

PBDDS/DFs	Sample No.												(pg/g)
	1)	2)	3)	4)	5)	6)	7)	8)	9)	10)	11)	12)	13)
2,3,7,8-TeBDD	<30	<6	<9	<8	<8	<6	<8	<7	<6	<8	<8	<10	<7
ΣTeBDDs	40	5,000	92	240	360	320	230	1,300	1,100	52	42	200	49
1,2,3,7,8-PeBDD	<20	4	<6	<5	<5	<4	<5	<4	<4	<5	<5	<7	<5
ΣPeBDDs	<20	16	<6	<5	20	<4	<5	<4	33	<5	<5	<7	<5
1,2,3,4,7,8/1,2,3,6,7,8-HxBDD	<200	<60	<80	<70	<70	<50	<70	<60	<50	<80	<80	<100	<70
1,2,3,7,8,9-HxBDD	<100	<30	<40	<30	<30	<20	<30	<30	<20	<30	<40	<50	<30
ΣHxBDDs	0	<60	<80	<70	<70	<50	<70	<60	<50	<80	<80	<100	<70
ΣHpBDDs	<100	470	<40	<40	<40	<30	<40	<30	180	<40	<40	<50	<30
OBDD	<200	240	<70	<70	<70	<50	<70	<60	60	<70	<70	<90	<60
2,3,7,8-TeBDF	<7	5	<2	<2	23	4	<2	6	41	<2	<2	<3	<2
ΣTeBDFs	89	460	100	310	6,000	880	810	2,000	3,400	110	84	540	160
1,2,3,7,8-PeBDF	<40	30	<10	<10	30	<8	10	<10	22	<10	<10	<20	<10
2,3,4,7,8-PeBDF	<20	30	<8	<7	22	11	21	<6	23	<7	<8	<10	<7
ΣPeBDFs	100	1,900	130	200	5,900	950	1,000	840	2,500	240	130	1200	300
1,2,3,4,7,8-HxBDF	<60	540	<20	<20	210	80	180	50	110	260	20	<30	90
ΣHxBDFs	220	11,000	230	340	3600	1,800	1,900	940	1,700	3,600	300	2,700	1,300
1,2,3,4,6,7,8-HpBDF	400	20,000	360	260	1,500	2,300	1,800	1,400	930	15,000	280	1,500	3,500
ΣHpBDFs	400	24,000	360	260	1,600	2,400	1,800	1,600	1,100	17,000	280	1,700	4,000
OBDF	<2000	26,000	<700	<70	<700	2,200	<700	1,700	<500	43,000	<700	<1000	3,000
ΣPBDDs/DFs	850	69,000	910	1,400	17,000	8,600	5,700	8,400	10,000	64,000	840	6,300	8,800

Table-3 Concentrations of PBDEs in house dust samples

PBDEs	Sample No.												(ng/g)
	1)	2)	3)	4)	5)	6)	7)	8)	9)	10)	11)	12)	13)
4-MoBDE(#3)	<2	<0.5	<0.3	<0.09	<0.03	<0.1	<0.6	<0.3	<0.2	<0.2	<0.1	<0.9	<0.6
ΣMoBDEs	<2	<0.5	<0.3	<0.09	<0.03	<0.1	<0.6	<0.3	<0.2	<0.2	<0.1	<0.9	<0.6
2,4-DiBDE(#7)	<2	<0.4	<0.3	<0.07	<0.03	<0.09	<0.5	<0.2	<0.2	<0.2	<0.08	<0.7	<0.5
4,4'-DiBDE(#15)	<1	<0.3	0.5	0.08	<0.02	0.96	<0.4	<0.2	6.0	<0.1	0.15	0.5	<0.3
ΣDiBDEs	<2	<0.4	0.9	0.08	<0.03	1.1	<0.5	<0.2	7.8	<0.2	0.15	0.5	<0.5
2,2',4-TrBDE(#17)	<3	<0.7	0.7	<0.1	<0.4	0.9	1.5	<0.4	77	<0.3	<0.1	<1	<0.8
2,4,4'-TrBDE(#28)	<5	<1	6.4	0.4	0.8	6.3	10	0.8	550	<0.4	0.4	3	<1
ΣTrBDEs	<5	<1	14	0.4	0.8	14	18	0.8	950	<0.4	0.4	3	<1
2,3',4',6-TeBDE(#71)	<2	<0.4	11	0.61	1.1	11	8.9	2.7	580	<0.2	0.58	3.5	0.6
2,2',4,5'-TeBDE(#49)	<2	<0.5	1.0	0.36	<0.3	1.1	0.7	1.2	42	<0.2	<0.09	<0.9	<0.6
2,2',4,4'-TeBDE(#47)	<2	<0.6	25	2.9	6.3	27	31	14	2,800	0.8	6.9	11	6.2
2,3',4,4'-TeBDE(#66)	<3	<0.8	17	0.4	1.5	17	7	3.2	610	<0.3	0.6	3	<0.9
3,3',4,4'-TeBDE(#77)	<3	<0.7	1.3	<0.1	<0.4	1.3	<0.8	0.3	33	<0.2	<0.1	<1	<0.8
ΣTeBDEs	49	13	61	5.2	9.6	65	52	25	4,300	0.8	8.4	19	0.68
2,2',4,4',6-PeBDE(#100)	<3	1	1.2	0.8	0.6	1.4	2	3.5	260	<0.3	1.9	<2	<1
2,3',4,4',6-PeBDE(#119)	<4	<1	<0.6	<0.2	<0.6	0.7	<1	0.6	24	<0.3	<0.2	<2	<1
2,2',4,4',5-PeBDE(#99)	<4	5	22	4.2	3.8	22	14	22	1,700	1.2	9.2	7	4
2,2',3,4,4'-PeBDE(#85)	<5	<1	1.7	0.2	<0.8	1.2	<2	1.1	75	<0.5	0.5	<2	<2
3,3',4,4',5-PeBDE(#126)	<9	<2	<1	<0.4	<1	<0.4	<3	<1	<1	<0.8	<0.4	<4	<3
ΣPeBDEs	57	6	37	6.7	6.4	38	16	48	2,400	1.2	12	7	4
2,2',4,4',5,6'-HxBDE(#154)	<6	<2	1	0.5	1.1	0.8	<2	2.1	84	<0.6	0.8	<3	<2
2,2',4,4',5,5'-HxBDE(#153)	<6	2	4	0.7	1.8	2.0	2	4.2	150	<0.6	1.2	<3	<2
2,2',3,4,4',5'-HxBDE(#138)	<10	<3	<2	<0.5	<2	<0.6	<4	<2	10	<1	<0.6	<5	<3
2,3,3',4,4',5'-HxBDE(#156)	<8	<2	<1	<0.4	<1	<0.4	<3	<1	<0.9	<0.7	<0.4	<4	<2
ΣHxBDEs	43	2	5	1.2	2.9	2.8	2	8.3	270	<1	2.0	<5	<3
2,2',3,4,4',6,6'-HpBDE(#184)	<5	<1	<0.8	<0.2	<0.8	<0.3	<2	<0.7	<0.6	<0.5	<0.2	<2	<1
2,2',3,4,4',5',6-HpBDE(#183)	<7	10	<1	0.6	6	1.8	6	3	16	3.1	1.0	3	5
2,3,3',4,4',5',6-HpBDE(#191)	<5	<1	<0.9	<0.2	<0.9	<0.3	<2	<0.7	<0.6	<0.5	<0.3	<2	<2
ΣHpBDEs	<7	14	<1	1.0	6	1.8	6	3	16	5.2	1.3	8	5
2,2',3,3',4,4',6,6'-OBDE(#197)	<5	17	<0.8	0.8	5.1	1.0	10	1.5	4.9	12	0.7	3	5
2,2',3,3',4,4',5,6'-OBDE(#196)	<3	55	<0.4	1.7	5.2	0.9	9.4	4.9	2.6	48	0.9	5	10
ΣOcBDEs	<5	150	<0.8	5.2	24	41	43	14	11	120	3.2	21	25
2,2',3,3',4,4',5,6,6'-NoBDE(#207)	<10	180	3	4.7	6	6.6	35	14	9	180	3.5	9	39
2,2',3,3',4,4',5,5',6-NoBDE(#206)	<7	330	3	5.7	6	7.5	16	19	11	330	4.2	12	57
ΣNoBDEs	<10	630	9	13	16	19	69	42	25	620	9.9	28	120
DeBDE	90	3,200	88	100	100	14	130	160	160	2,800	97	110	540
ΣPBDEs	240	4,000	210	130	170	290	340	300	8,100	3,500	130	200	700

From our results, both PBDDs/DFs and PBDEs concentrations were various depend on sampling points, and the differences which were also slightly about congener compositions became clear. These cause was suggested with difference of source of brominated flame retardants, but the tendency by the sampling points couldn't be investigated by this investigation.
It was seemed that it was necessary to be further investigations as the indicator which estimates exposure in indoor environment. There was clear correlation between the concentration of PBDDs/DFs and PBDEs by excluding sample No.9.

References

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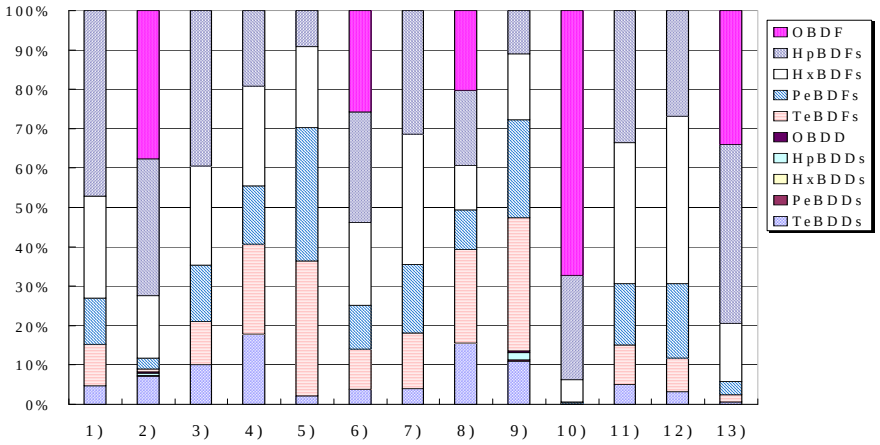

Figure-1 Congener compositions of PBDDs/DFs in house dust samples

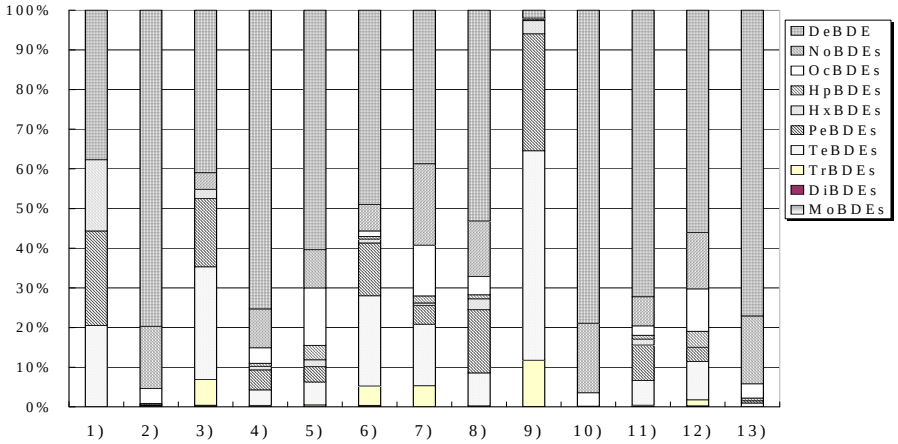

Figure-2 Congener compositions of PBDEs in house dust samples