BROMINATED DIOXINS AND PBDEs IN DIET SAMPLES COLLECTED FROM FY2002 TO FY2005 IN JAPAN

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Abstract
The investigations carried out in Japan about brominated dioxins and PBDEs in diet samples from FY2002 to FY2005 were summarized. The daily intakes of PBDD/Fs and MoBPCDD/Fs ranged from 0 to 0.46 pg-TEQ/kg/day with a mean value of 0.0107 pg-TEQ/kg/day, and the daily intakes of PBDEs ranged from 180 to 8000 pg /kg/day with a mean value of 1692 pg-TEQ/kg/day and a median value of 1100 pg/kg/day.

Introduction
In Japan, polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs), monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans (MoBPCDD/Fs), polybrominated diphenyl ethers (PBDEs) and dioxins (including DL-PCBs) in air, dust fall, soil, surface water, sediment, groundwater, diet, fish and shellfish, wild animals and house dust have been investigated from FY2000 and the results are on the Web*. In this study, the dietary survey data from FY2002 to FY2005 are introduced collectively, since the publications are the results only for each single year and are in Japanese.

Materials and Methods
Sampling of diet: All meals, snacks and drinks for consecutive three days of a participant were prepared with a double, and the foods for one person were mixed all as a diet sample. From FY2002 to FY2004, 12 samples were collected every year, and 9 samples were collected in FY2005.

PBDD/Fs and MoBPCDD/Fs analyses: The samples (1000 g) spiked with $^{13}C_{12}$-labelled internal standards were stirred with aqueous KOH and then kept for about 12 hr at room temperature. The alkaline hydrolysates were extracted with *n*-hexane. The extracts were treated with concentrated sulfuric acid, and then purified with four kinds of column chromatography of silica gel, florisil, alumina and active carbon. Measurement was conducted by an isotope dilution method using a high resolution gas chromatograph/ high resolution mass spectrometer (HRGC/HRMS). The analyte and their standard limits of detection (LOD) are listed in Table 1.

PBDEs analyses: The samples (80 g) spiked with $^{13}C_{12}$-labelled internal standards were extracted with aceton. The extracts were concentrated and stirred with ethanolic KOH, and then kept for about 1 hr at room temperature. The alkaline hydrolysates were extracted with *n*-hexane. The extracts were treated with concentrated sulfuric acid, and then purified on a silver nitrate/silica gel column followed by a gel permeation chromatography. Measurement was conducted by an isotope dilution method using a HRGC/HRMS (Table 1).

PCDD/Fs and DL-PCBs analyses: The samples (100 g) spiked with $^{13}C_{12}$-labelled internal standards were stirred with aqueous KOH and then kept for about 12 hr at room temperature. The alkaline hydrolysates were extracted with *n*-hexane. The extracts were treated with concentrated sulfuric acid, and then purified with three kinds of column chromatography of silver nitrate/silica gel, alumina and active carbon. Measurement was conducted by an isotope dilution method using a HRGC/HRMS.

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* Web addresses are following:

FY2000	http://www.env.go.jp/chemi/dioxin/report/h12-rep.pdf		
FY2001	http://www.env.go.jp/chemi/report/h14-02/all.pdf		
FY2002	http://www.env.go.jp/chemi/report/h15-03/mat_04-1.pdf	—	http://www.env.go.jp/chemi/report/h15-03/mat_04-2.pdf
FY2003	http://www.env.go.jp/chemi/report/h16-15/04-1.pdf	—	http://www.env.go.jp/chemi/report/h16-15/04-6.pdf
FY2004	http://www.env.go.jp/chemi/report/h17-22/4-1.pdf	—	http://www.env.go.jp/chemi/report/h17-22/4-7.pdf
FY2005	http://www.env.go.jp/chemi/report/h18-11/chpt4-1.pdf	—	http://www.env.go.jp/chemi/report/h18-11/chpt4-3.pdf

Results and Discussion

The information on study participants and their diets are summarized in Table 2. The participants were 30 women and 15 men, from 28 to 77 years old at the investigation. The quantity of a diet for three days in total was at a range of 11501g from 4463g. Their dietary intakes of dioxins (including DL-PCBs) ranged from 0.185 to 6.51 pg-TEQ/kg/day with a mean value of 1.12 pg-TEQ/kg/day and a median value of 0.697 pg-TEQ/kg/day, which were calculated assuming that the non-detected isomers are equal to zero. However, the daily intakes of dioxins by this investigation were almost agreed with that of national average of 1.20 ± 0.66 pg-TEQ/kg/day in Japan in FY2005[1], the intake of one participant exceeded the tolerable daily intake (TDI) of dioxins (4 pg-TEQ/kg/day).

The concentrations and daily intakes of PBDD/Fs, MoBPCDD/Fs, PBDEs and PCDD/Fs in diet samples are summarized in Table 3. The polybrominated dioxins were detected by a range of 0.01-0.97 pg/g (mean 0.083 pg/g, median 0.057 pg/g) in Σ(PBDD/Fs). As for the congener, TeBDDs, TeBDFs and PeBDFs were detected mainly, and PeBDDs, HxBDDs, HpBDDs, OBDD and OBDF were not detected. However, the ratio of Σ(PBDD/Fs) of detected for Σ(PCDD/Fs) were about 1/48 to 4.6 times, only three samples surpassed 1/3 in the ratio.

The monobrominated-polychlorinated dioxins were detected by a range of LLD-0.017 pg/g (mean 0.0028 pg/g, median detected 0.004 pg/g) in Σ(MoBPCDD/Fs). The ratio of Σ(MoBPCDD/Fs) of detected for Σ(PCDD/Fs) were about 1/230 to 1/57.

The daily intakes of PBDD/Fs and MoBPCDD/Fs ranged from 0 to 0.46 pg-TEQ/kg/day with a mean value of 0.0107 pg-TEQ/kg/day, which were calculated assuming that the non-detected isomers are equal to zero and also assuming that the toxicity of the corresponding isomer of PBDD/Fs and MoBPCDD/Fs are nearly equal to that of PCDD/Fs. The ratio of the daily intakes of PBDD/Fs and MoBPCDD/Fs of detected for those of PCDD/Fs and DL-PCBs were about 1/200 to 1/1.28.

The ΣPBDEs were detected by a range of 7.7-150 pg/g (mean 34 pg/g, median 28 pg/g). In the congener patterns of most samples, DeBDE was high relatively (more than 50 %), and TeBDEs was high next. The daily intakes of PBDEs ranged from 180 to 8000 pg/kg/day with a mean value of 1692 pg-TEQ/kg/day and a median value of 1100 pg/kg/day, which were calculated assuming that the non-detected isomers are equal to zero.

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References

1. http://www.mhlw.go.jp/topics/bukyoku/iyaku/syoku-anzen/dioxin/sessyu05/index.html

Table 1 The List of Investigated Brominated Compounds and Standard Limits of Detection (pg/g)

BROMINATED DIOXINS	FY2002	FY2003	FY2004	FY2005
2,3,7,8-TeBDD	0.004	0.004	0.002	0.002
∑TeBDDs	0.004	0.004	0.002	0.002
1,2,3,7,8-PeBDD	0.008	0.008	0.001	0.001
∑PeBDDs	0.008	0.008	0.001	0.001
1,2,3,4,7,8-/ 1,2,3,6,7,8-HxBDD	0.04	0.04	0.02	0.02
1,2,3,7,8,9-HxBDD	0.04	0.04	0.008	0.01
∑HxBDDs	0.04	0.04	0.02	0.02
∑HpBDDs	—	0.08	0.01	0.009
OBDD	—	0.2	0.01	0.02
2,3,7,8-TeBDF	0.004	0.004	0.0007	0.0009
∑TeBDFs	0.004	0.004	0.0007	0.0009
1,2,3,7,8-PeBDF	0.008	0.008	0.002	0.002
2,3,4,7,8-PeBDF	0.008	0.008	0.002	0.003
∑PeBDFs	0.008	0.008	0.002	0.003
1,2,3,4,7,8-HxBDF	0.04	0.04	0.005	0.007
∑HxBDFs	0.04	0.04	0.005	0.007
1,2,3,4,7,8,9-HpBDF	—	0.08	0.01	0.009
∑HpBDFs	—	0.08	0.01	0.009
OBDF	—	0.2	0.1	0.1
2 - MoB - 3,7,8-TrCDD	0.004	0.004	0.003	0.001
∑MoB-TrCDDs	0.004	0.004	0.003	0.001
1 - MoB - 2,3,7,8-TeCDD	0.004	0.004	0.002	0.002
∑MoB-TeCDDs	0.004	0.004	0.002	0.002
2 - MoB - 3,6,7,8,9-PeCDD	0.008	0.008	0.003	0.002
∑MoB-PeCDDs	0.008	0.008	0.003	0.002
1 - MoB - 2,3,6,7,8,9-HxCDD	0.02	0.02	0.009	0.007
∑MoB-HxCDDs	0.02	0.02	0.009	0.007
1 - MoB - 2,3,4,6,7,8,9-HpCDD	0.04	0.04	0.02	0.008
∑MoB-HpCDDs	0.04	0.04	0.02	0.008
3 - MoB - 2,7,8-TrCDF	0.004	0.004	0.003	0.001
∑MoB-TrCDFs	0.004	0.004	0.003	0.001
1 - MoB - 2,3,7,8-TeCDF	0.004	0.004	0.003	0.001
∑MoB-TeCDFs	0.004	0.004	0.003	0.001
∑MoB-PeCDFs	0.008	0.008	0.003	0.002
∑MoB-HxCDFs	0.02	0.02	0.009	0.007
∑MoB-HpCDFs	0.04	0.04	0.02	0.008

PBDEs	FY2002	FY2003	FY2004	FY2005
4-MoBDE(#3)	—	3	0.6	0.6
∑MoBDEs	—	3	0.6	0.6
2,4-DiBDE(#7)	—	1	0.2	0.3
4,4'-DiBDE(#15)	—	1	0.1	0.3
∑DiBDEs	—	1	0.2	0.3
2,2',4-TrBDE(#17)	—	1	0.2	0.4
2,4,4'-TrBDE(#28)	0.2	1	0.2	0.2
∑TrBDEs	—	1	0.2	0.4
2,2',4,5'-TeBDE(#49)	—	1	0.2	0.3
2,3',4',6-TeBDE(#71)	—	1	0.1	0.2
2,2',4,4'-TeBDE(#47)	0.2	1	0.2	0.4
2,3',4,4'-TeBDE(#66)	—	1	0.1	0.4
3,3',4,4'-TeBDE(#77)	—	1	0.1	0.2
∑TeBDEs	—	1	0.2	0.4
2,2',4,4',6-PeBDE(#100)	0.2	1	0.1	0.5
2,3',4,4',6-PeBDE(#119)	—	1	0.1	0.4
2,2',4,4',5-PeBDE(#99)	0.2	1	0.1	0.4
2,2',3,4,4'-PeBDE(#85)	—	1	0.2	0.3
3,3',4,4',5-PeBDE(#126)	—	1	0.4	0.7
∑PeBDEs	—	1	0.4	0.7
2,2',4,4',5,6'-HxBDE(#154)	0.5	3	0.3	0.5
2,2',4,4',5,5'-HxBDE(#153)	0.5	3	0.3	0.5
2,2',3,4,4',5'-HxBDE(#138)	—	3	0.4	0.6
2,3,3',4,4',5'-HxBDE(#156)	—	3	0.2	0.3
∑HxBDEs	—	3	0.4	0.6
2,2',3,4,4',6,6'-HpBDE(#184)	—	3	0.4	0.8
2,2',3,4,4',5',6-HpBDE(#183)	0.5	3	0.3	1
2,3,3',4,4',5',6-HpBDE(#191)	—	3	0.3	0.8
∑HpBDEs	—	3	0.4	1
2,2',3,3',4,4',6,6'-OcBDE(#197)	—	3	0.2	0.5
2,2',3,4,4',5,5',6-OcBDE(#203)	1	3	0.6	0.5
2,2',3,3',4,4',5,6-OcBDE(#196)	—	3	0.6	0.5
2,3,3',4,4',5,5',6-OcBDE(#205)	1	3	0.6	0.5
∑OcBDEs	—	3	0.6	0.5
NoBDE(#207)	—	3	0.9	1
NoBDE(#206)	—	3	1	1
∑NoBDEs	—	3	1	1
DeBDE(#209)	2	5	2	2

Table 2 Information on Study Participants and Their Diets

Code of Participants in FY2002	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3
Age/Male or Female	40M	39F	77M	34F	31M	58F	49F	58F	35F	37F	33F	35F
Weight(kg)	72	52	65	50	70	66	62	58	54	52	55	52
Total Dietary Intakes for 3 Days(g)	5158	7514	6143	7799	9367	7493	9314	8544	7521	6755	5852	6870
TEQ[1](pg-TEQ/g)	0.012	0.052	0.032	0.038	0.014	0.016	0.13	0.023	0.01	0.028	0.023	0.0093
Daily Intakes of TEQ[1](pg-TEQ/kg/day)	0.287	2.505	1.008	1.976	0.624	0.605	6.51	1.129	0.464	1.212	0.816	0.410
Ratio to TDI[2](%)	7.2	63	25	49	16	15	163	28	12	30	20	10
Code of Participants in FY2003	E1	E2	E3	F1	F2	F3	G1	G2	G3	H1	H2	H3
Age/Male or Female	28F	50F	44F	58F	54F	31F	38F	61F	64F	65M	66M	47F
Weight(kg)	50	49	43	56	53	45	50	52	51	53	70	53
Total Dietary Intakes for 3 Days(g)	4463	7267	6831	6166	7321	5112	4779	6937	8208	7220	6623	4765
TEQ[1](pg-TEQ/g)	0.012	0.039	0.011	0.019	0.013	0.012	0.0058	0.018	0.061	0.066	0.024	0.086
Daily Intakes of TEQ[1](pg-TEQ/kg/day)	0.357	1.928	0.582	0.697	0.599	0.454	0.185	0.800	3.272	2.997	0.757	2.577
Ratio to TDI[2](%)	8.9	48	15	17	15	11	4.6	20	82	75	19	64
Code of Participants in FY2004	I1	I2	I3	J1	J2	J3	K1	K2	K3	L1	L2	L3
Age/Male or Female	41M	51F	39F	37M	51F	63M	44M	29F	58F	70F	53F	37M
Weight(kg)	84	54	59	90	50	44	62	55	56	46	53	60
Total Dietary Intakes for 3 Days(g)	7950	6364	6553	7623	5529	7983	6911	6524	6925	11501	6116	7188
TEQ[1](pg-TEQ/g)	0.021	0.02	0.012	0.039	0.0057	0.013	0.0068	0.036	0.049	0.024	0.022	0.0097
Daily Intakes of TEQ[1](pg-TEQ/kg/day)	0.663	0.786	0.444	1.101	0.210	0.786	0.253	1.423	2.020	2.000	0.846	0.387
Ratio to TDI[2](%)	17	20	11	28	5.3	20	6.3	36	50	50	21	9.7
Code of Participants in FY2005	M1	M2	M3	N1	N2	N3	O1	O2	O3			
Age/Male or Female	29M	53F	44M	28M	48F	50F	47M	32F	65M			
Weight(kg)	63	50	59	64	48	60	64	65	60			
Total Dietary Intakes for 3 Days(g)	10804	5663	5050	7423	7989	6434	7327	6036	7578			
TEQ[1](pg-TEQ/g)	0.0064	0.0096	0.053	0.0068	0.041	0.0075	0.013	0.016	0.014			
Daily Intakes of TEQ[1](pg-TEQ/kg/day)	0.366	0.362	1.512	0.263	2.275	0.268	0.496	0.495	0.589			
Ratio to TDI[2](%)	9.1	9.1	38	6.6	57	6.7	12	12	15			

1) The TEQ concentrations of PCDD/Fs and DL-PCBs were calculated using the WHO-TEF(1997), and assuming that the non-detected isomers are equal to zero.
2) TDI= 4 pg-TEQ/kg/day

Table 3 Concentrations (pg/g) and Daily Intakes of Brominated Dioxins, PBDEs and PCDD/Fs in Diet Samples

	FY2002(n=12)		FY2003(n=12)		FY2004(n=12)		FY2005(n=9)	
	Median	Range	Median	Range	Median	Range	Median	Range
ΣTeBDDs	0.0235	0.013-0.077	0.053	0.007-0.12	0.034	0.004-0.086	0.037	0.010-0.10
ΣPeBDDs		LLD		LLD		LLD		LLD
ΣHxBDDs		LLD		LLD		LLD		LLD
ΣHpBDDs		NT		LLD		LLD		LLD
OBDD		NT		LLD		LLD		LLD
ΣTeBDFs	0.0125	0.007-0.057	0.014	0.003-0.095(11)[1]	0.00765	0.005-0.070	0.023	0.0078-0.080
ΣPeBDFs	0.014	0.011-0.017(3)[1]		0.014(1)[1]	0.005	0.002-0.018(7)[1]	0.005	0.003-0.26(7)[1]
ΣHxBDFs		LLD		LLD	0.013	0.001-0.016(2)[1]		0.52(1)[1]
ΣHpBDFs		NT		LLD		0.01(3)[1]	0.0385	0.012-0.065(2)[1]
OBDF		NT		LLD		LLD		LLD
Σ(PBDD/Fs)	0.043	0.021-0.15	0.0745	0.021-0.14	0.052	0.010-0.20	0.078	0.018-0.97
ΣMoB-TrCDDs		LLD	0.0105	0.004-0.017(2)[1]		LLD	0.0025	0.002-0.003(2)[1]
ΣMoB-TeCDDs		LLD		LLD		LLD		LLD
ΣMoB-PeCDDs		LLD		LLD		LLD		0.003(1)[1]
ΣMoB-HxCDDs		LLD		LLD		LLD		LLD
ΣMoB-HpCDDs		LLD		LLD		LLD		LLD
ΣMoB-TrCDFs		LLD		LLD		LLD		0.004(1)[1]
ΣMoB-TeCDFs		LLD		LLD		LLD		LLD
ΣMoB-PeCDFs		LLD		LLD		LLD		LLD
ΣMoB-HxCDFs		LLD		LLD		LLD		LLD
ΣMoB-HpCDFs		LLD		LLD		LLD		LLD
Σ(MoBPCDD/Fs)		LLD	0.0105	0.004-0.017(2)[1]		LLD	0.003	0.002-0.007(3)[1]
TEQ(PBDD/Fs)[2] (pg-TEQ/g)		0		0.0007(1)[1]		0.0001(3)[1]	0.000215	0.0001-0.011(4)[1]
TEQ(MoBPCDD/Fs)[2] (pg-TEQ/g)		0		0		0		0
TEQ(PBDD/Fs+MoBPCDD/Fs)[2] (pg-TEQ/g)		0		0.0007(1)[1]		0.0001(3)[1]	0.000215	0.0001-0.011(4)[1]
Daily Intakes of TEQ(PBDD/Fs+ MoBPCDD/Fs)[2] (pg-TEQ/kg/day)		0		0.022(1)[1]	0.0037	0.0032-0.0040(3)[1]	0.0079	0.0037-0.46(4)[1]
ΣMoBDEs		NT		LLD		LLD		LLD
ΣDiBDEs		NT		LLD	0.095	0.09-0.1(2)[1]		0.6(1)[1]
ΣTrBDEs		NT	3	1-5(7)[1]	0.6	0.20-1.5(6)[1]	0.3	0.2-7.6(7)[1]
ΣTeBDEs		NT	16.5	5-87	4.35	1.5-20	3.9	1.6-41
ΣPeBDEs		NT	7.5	4-30	3.7	1.7-7.1	2.6	0.9-23
ΣHxBDEs		NT	7	2-14(6)[1]	1.1	0.3-5.1(11)[1]	1.6	0.5-6.6(6)[1]
ΣHpBDEs		NT		LLD		1.1(1)[1]		1(1)[1]
ΣOcBDEs		NT		3(1)[1]		0.6(1)[1]	0.75	0.6-0.9(2)[1]
ΣNoBDEs		NT	2.5	2-16(6)[1]	2	1-3(3)[1]	3	1-5(7)[1]
DeBDE		NT	18.5	15-56	10	3-35	12	5-27
ΣPBDEs	17[3]	7.7-62[3]	49	34-150	25	8.2-65	24	7.7-89
Daily Intakes of ΣPBDEs[4] (pg/kg/day)	775	180-3100	2000	1100-8000	1000	480-1900	910	440-3700
ΣTeCDDs	0.155	0.026-0.43	0.195	0.047-1.2	0.17	0.028-0.57	0.068	0.031-0.17
ΣPeCDDs	0.0145	0.009-0.040(10)[1]	0.019	0.006-0.067(10)[1]	0.012	0.003-0.041	0.011	0.003-0.018(8)[1]
ΣHxCDDs	0.015	0.008-0.027(7)[1]	0.019	0.004-0.034(11)[1]	0.011	0.001-0.034(11)[1]	0.014	0.006-0.022
ΣHpCDDs	0.030	0.007-0.068(11)[1]	0.029	0.013-0.063	0.017	0.011-0.040	0.020	0.011-0.046
OCDD	0.135	0.050-0.43	0.135	0.070-0.38	0.089	0.058-0.16	0.096	0.037-0.16
ΣPCDDs	0.354	0.083-0.993	0.372	0.169-1.475	0.318	0.151-0.822	0.262	0.096-0.342
ΣTeCDFs	0.050	0.006-0.24(10)[1]	0.0565	0.015-0.35	0.0325	0.010-0.15	0.044	0.022-0.080
ΣPeCDFs	0.018	0.007-0.088(11)[1]	0.026	0.011-0.13(9)[1]	0.011	0.002-0.052(11)[1]	0.017	0.003-0.032
ΣHxCDFs	0.0195	0.009-0.12(4)[1]	0.011	0.004-0.027(3)[1]	0.004	0.002-0.020(10)[1]	0.003	0.002-0.006(5)[1]
ΣHpCDFs	0.010	0.007-0.082(5)[1]		0.006(2)[1]	0.0045	0.003-0.005(4)[1]	0.003	0.002-0.005(8)[1]
OCDF		0.03(1)[1]		LLD		0.007(3)[1]		LLD
ΣPCDFs	0.070	0.007-0.366	0.087	0.015-0.513	0.055	0.011-0.227	0.064	0.025-0.109
Σ(PCDD/Fs)	0.435	0.10-1.3	0.51	0.19-1.6	0.375	0.19-1.0	0.32	0.12-0.45

LLD & NT = Less than LOD and Not Tested

1) The value in the bracket indicate number of samples detected.

2) The TEQ for PBDD/Fs and MoBPCDD/Fs were calculated with measured isomers only, and calculated assuming that the toxicity of the correponding isomer of PBDD/Fs and MoBPCDD/Fs are nearly equal to that of PCDD/Fs(WHO-TEF(1997)), and also assuming that the non-detected isomers are equal to

3) The sum of ten congeners (see Table 1).

4) The dietary intakes of ΣPBDEs were calculated assuming that the non-detected isomers are equal to zero.