

Investigation of dietary exposure to PCDDs, PCDFs, and dioxin-like PCBs in Kyusyu district, Japan

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Introduction

Food intake has been considered to be the major source of exposure to PCDDs and their related compounds. Therefore, estimated dietary intake of these chemicals, based on the average Japanese living environment and dietary habits, could approximate total exposure. In some countries, dietary exposure levels have been evaluated by measuring the concentrations of these contaminants in major foodstuffs and taking account of the average food consumption data. On the other hand, in Japan, information regarding human exposure to such chemicals was limited until the Japanese government proposed a tolerable daily intake (TDI), in 1996, at 10 pg TEQ/kg body weight/day¹. The Ministry of Health and Welfare of Japan has conducted a full-scale investigation based on market basket procedure since 1996. The latest survey estimated the Japanese average dietary intake at 121 pg TEQ/person/day by combined analysis for 17 congeners of PCDDs/DFs and 3 of non-*ortho* coplanar PCBs with the TEFs proposed by NATO (1988) and WHO (1994)². Allowing for the new TEFs advanced by WHO in 1997, the present phases require further investigation. The present study was undertaken with the intention of updating the average Japanese dietary exposure level to PCDDs, PCDFs, and dioxin-like PCBs using WHO-TEFs (1997). Concentrations of 31 compounds were determined in total diet study (TDS) samples, then human exposure level to the chemicals was calculated and discussed.

Materials and Methods

We collected 124 common retail foods in Kyusyu district, western Japan, in 1997, selected according to the results of National Nutrition Research (the Ministry of Health and Welfare, Japan; 1993). Eventually, 13 TDS samples were prepared from these food items. Each sample (100g) was spiked with 17 kinds of ¹³C₁₂-labeled PCDDs/DFs and 14 kinds of ¹³C₁₂-labeled PCBs as an internal quantification standard. After digestion with 1N KOH/ethanol solution, the alkaline hydrolysate was extracted twice with n-hexane. After treatment with concentrated sulfuric acid, the crude extract was spiked with ³⁷Cl₄-labeled 2,3,7,8-TeCDD for column recovery verification, and further purified on an Ag-silica gel column first, and then on a charcoal column. On the later column, mono- and di-*ortho* PCBs were eluted with 10% (v/v) dichloromethane/n-hexane, then non-*ortho* PCBs and PCDDs /DFs were isolated with toluene. Each fraction was concentrated, and the second fraction was fortified with ¹³C₁₂-labeled 1,2,3,4-TeCDD as an internal recovery standard prior to an instrumental analysis. Analyses were performed by a HP 5890 series II gas chromatograph coupled to a Finnigan MAT-95 mass spectrometer. MS resolution was set to 10000 at 10% valley.

Results and Discussion

Estimations of dietary intake of 2,3,7,8-chlorine substituted PCDDs and PCDFs, respectively, for the 13 different food groups are listed in Table 1. The calculated total intake of PCDDs was 29pg TEQ/person/day, and that of PCDFs was 22 pg TEQ/person/day. Large amounts of PCDDs and of PCDFs were found in fatty food groups, such as fish, dairy products, and meat. In past studies in Japan¹⁾²⁾, the most prominent source for PCDDs/DFs was attributed to fish; their contribution to total toxicity of PCDDs/DFs was calculated to be 44% in this study. On the other hand, small amounts of these contaminants were found in the group of rice and rice products, a staple of Japanese diet, which was estimated to represent an intake of 0.13 pg TEQ/person/day.

Table 2 shows the results for dioxin-like PCBs. Among 14 kinds of PCBs analyzed, concentrations for 12 kinds of non- and mono-*ortho* PCBs listed in WHO-TEFs (1997) were converted to the TEQ, although di-*ortho* PCBs (IUPAC #170, #180) were excluded from the toxic evaluation. However, it is worth noting the estimated dietary intake of PCB#170 was 21 ng/person/day while that of PCB#180 was 61 ng/person/day. Consequently, total intake of dioxin-like PCBs was estimated to be 82 pg TEQ/person/day, and PCB#126 showed the highest TEQ value at 57 pg TEQ/person/day. In this study, one of our interests was the amount of daily intake of mono-*ortho* PCBs and their toxic contributions; no data on this has been shown in previous Japanese studies¹⁾²⁾. Our results indicate that the dietary intake of mono-*ortho* PCBs is 24 pg TEQ/person/day, which is nearly equal to the 30% toxic contribution of dioxin-like PCBs to total intake. Overall, the average dietary exposure to PCDDs and their related compounds determined by our study was 134 pg TEQ/person/day, corresponding to 2.7 pg TEQ/kg body weight/day for a 50kg adult. This value is about 70% lower than the TDI proposed by the Ministry of Health and Welfare of Japan in 1996, and it is within the limits of TDI re-evaluated by WHO in 1998 (range of 1 to 4 pg/kg body weight/day). We remark that dioxin-like PCBs make a larger contribution than PCDDs and/or PCDFs to the total dietary risk. In addition, the toxic contribution is remarkable in the food group of fish and shellfish, while it is minor in other food groups. A similar trend of total planar PCBs dominating the total toxicity is observed in serum specimens from Japanese normal subjects³⁾. Accordingly, from the viewpoint of human contamination, the dietary exposure level of dioxin-like PCBs should hereafter be watched as well as that of PCDDs and PCDFs. Significantly, our results indicate that mono-*ortho* PCBs, which were not included in the past Japanese estimation¹⁾²⁾, demonstrate an approximate 20% contribution to the total dietary risk established by WHO-TEFs (1997).

Acknowledgement

A part of this work was supported by a grant from the Ministry of Health and Welfare, Japan.

References

- 1) K. Takayama, H. Miyata, O. Aozasa, M. Mimura and T. Kashimoto, J. Food Hyg. Soc. Japan, 32, 525-532 (1991) in Japanese.
- 2) M. Toyoda, H. Uchibe, T. Yanagi, Y. Kono, T. Hori and T. Iida, J. Food Hyg. Soc. Japan, 40, 98-110 (1999) in Japanese.
- 3) Y. Masuda, Chemosphere, 32, 583-594 (1996).

Table 1. Dietary intake (pg TEQ/person/day) of 2,3,7,8-chlorine substituted PCDDs and PCDFs in Kyusyu district, Japan

Compounds	TEFs	Number of food groups*												
		1	2	3	4	5	6	7	8	9	10	11	12	13
TCDD	1	-	1.1	-	0.18	-	0.89	0.53	1.2	-	3.8	1.8	1.6	0.23
8-PeCDD	1	-	0.85	-	0.16	-	-	-	-	-	6.6	3.3	3.6	-
7,8-HxCDD	0.1	-	-	-	-	-	-	-	-	-	-	-	0.20	-
7,8-HxCDD	0.1	-	-	-	-	-	-	-	0.23	-	-	-	0.68	-
8,9-HxCDD	0.1	-	0.095	-	-	-	-	-	-	-	-	0.47	0.26	-
6,7,8-HpCDD	0.01	0.096	0.038	0.006	0.042	0.041	0.015	0.030	0.11	0.013	0.036	0.44	0.17	0.009
	0.0001	0.004	0.003	0.002	0.007	0.003	< 0.001	0.002	0.001	< 0.001	0.002	0.021	0.004	< 0.001
CDDs		0.099	2.1	0.008	0.39	0.044	0.91	0.56	1.5	0.013	10	6.0	6.5	0.24
TCDF	0.1	-	0.11	0.018	0.062	-	-	-	-	-	3.2	0.12	-	0.009
8-PeCDF	0.05	-	0.027	0.004	-	-	-	0.037	-	-	0.27	0.067	0.028	0.005
8-PeCDF	0.5	-	0.26	-	0.17	-	-	-	-	-	8.1	2.8	2.9	0.074
7,8-HxCDF	0.1	-	-	-	0.051	-	-	-	-	-	0.14	0.55	0.51	-
7,8-HxCDF	0.1	-	-	-	0.038	-	-	-	-	-	0.18	0.38	0.39	-
8,9-HxCDF	0.1	-	-	-	-	-	-	-	-	-	0.062	0.095	0.078	-
7,8-HxCDF	0.1	-	-	-	0.031	-	-	-	-	-	0.22	0.52	0.70	-
6,7,8-HpCDF	0.01	0.029	0.010	0.002	0.006	0.014	0.002	0.013	0.021	0.005	0.025	0.097	0.041	0.003
7,8,9-HpCDF	0.01	-	-	-	0.003	-	-	-	-	-	-	-	0.006	-
	0.0001	-	-	-	< 0.001	-	-	-	-	-	-	-	< 0.001	0.004
CDFs		0.029	0.41	0.025	0.36	0.014	0.002	0.050	0.021	0.005	12	4.6	4.7	0.094
CDDs and PCDFs		0.13	2.5	0.033	0.75	0.058	0.91	0.61	1.5	0.018	23	11	11	0.33

*The contents of each food groups are follows ; 1: Rice and rice products, 2 : Cereals, seeds and potatoes, 3 : Sugars and confectionaries, 4 : Fats and oils, 5 : Pulses, 6 : Fruits, 7 : Green vegetables, 8 : Other vegetables, mushrooms and seaweeds, 9 : Seasoning and beverages, 10 : Fish and shellfish, 11 : Meat and eggs, 12 : Milk and dairy products, 13 : Other foods (prepared foods)

- : It was not detected in the TDS sample, and so the daily intake was calculated as zero.

Table 2. Dietary intake (pg TEQ/person/day) of dioxin-like PCBs in Kyusyu district, Japan

pounds	TEFs	Number of food groups												
		1	2	3	4	5	6	7	8	9	10	11	12	13
-TeCB(#81)	0.0001	< 0.001	-	< 0.001	< 0.001	-	-	< 0.001	-	-	0.013	0.001	< 0.001	< 0.001
-TeCB(#77)	0.0001	0.003	0.003	< 0.001	< 0.001	0.001	< 0.001	0.002	0.001	< 0.001	0.21	0.010	0.001	< 0.001
1,5-PeCB(#126)	0.1	0.54	0.26	0.084	0.27	0.23	0.13	0.25	-	0.12	48	4.0	3.2	0.058
1,5,5'-HxCB(#169)	0.01	-	-	-	-	-	-	-	-	-	0.72	0.13	0.075	-
non-ortho PCBs		0.55	0.27	0.085	0.27	0.23	0.13	0.25	0.001	0.12	49	4.2	3.2	0.059
2,4'-PeCB(#105)	0.0001	-	0.004	0.002	0.004	0.001	-	0.003	-	-	1.8	0.14	0.022	0.001
1,5-PeCB(#114)	0.0005	-	-	-	-	-	-	-	-	-	2.1	0.14	-	< 0.001
1,5-PeCB(#118)	0.0001	-	0.018	0.007	0.017	0.005	0.004	0.009	0.008	0.006	7.5	0.61	0.10	0.006
1,5-PeCB(#123)	0.0001	-	0.016	0.003	0.001	0.008	0.006	-	-	0.007	6.1	0.068	0.008	0.004
2,4,5-HxCB(#156)	0.0005	-	-	0.004	0.007	-	-	-	-	-	3.8	0.25	0.056	0.004
2,4,5'-HxCB(#157)	0.0005	-	-	-	-	-	-	-	-	-	0.79	0.051	-	< 0.001
1,5,5'-HxCB(#167)	0.00001	-	-	< 0.001	< 0.001	-	-	-	-	-	0.038	0.002	< 0.001	< 0.001
2,4,5,5'-HpCB(#189)	0.0001	-	-	-	-	-	-	-	-	-	0.083	-	-	-
ortho PCBs		0	0.038	0.016	0.029	0.015	0.009	0.012	0.008	0.013	22	1.3	0.19	0.017
TCBs		0.55	0.31	0.10	0.30	0.24	0.14	0.27	0.009	0.13	71	5.4	3.4	0.076

*The contents of each food groups are follows ; 1: Rice and rice products, 2 : Cereals, seeds and potatoes, 3 : Sugars and confectionaries, 4 : Fats and oils, 5 : Pulses, 6 : Fruits, 7 : Green vegetables, 8 : Other vegetables, mushrooms and seaweeds, 9 : Seasoning and beverages, 10 : Fish and shellfish, 11 : Meat and eggs, 12 : Milk and dairy products, 13 : Other foods (prepared foods)

- : It was not detected in the TDS sample, and so the daily intake was calculated as zero.

Table 1. Dietary intake (pg TEQ/person/day) of 2,3,7,8-chlorine substituted PCDDs and PCDFs in Kyusyu district, Japan

Compounds	TEFs	Number of food groups*												
		1	2	3	4	5	6	7	8	9	10	11	12	13
2,3,7,8-TeCDD	1	-	1.1	-	0.18	-	0.89	0.53	1.2	-	3.8	1.8	1.6	0.23
1,2,3,7,8-PeCDD	1	-	0.85	-	0.16	-	-	-	-	-	6.6	3.3	3.6	-
1,2,3,4,7,8-HxCDD	0.1	-	-	-	-	-	-	-	-	-	-	-	0.20	-
1,2,3,6,7,8-HxCDD	0.1	-	-	-	-	-	-	-	0.23	-	-	-	0.68	-
1,2,3,7,8,9-HxCDD	0.1	-	0.095	-	-	-	-	-	-	-	-	0.47	0.26	-
1,2,3,4,6,7,8-HpCDD	0.01	0.096	0.038	0.006	0.042	0.041	0.015	0.030	0.11	0.013	0.036	0.44	0.17	0.009
OCDD	0.0001	0.004	0.003	0.002	0.007	0.003	<0.001	0.002	0.001	<0.001	0.002	0.021	0.004	<0.001
Total PCDDs		0.099	2.1	0.008	0.39	0.044	0.91	0.56	1.5	0.013	10	6.0	6.5	0.24
2,3,7,8-TeCDF	0.1	-	0.11	0.018	0.062	-	-	-	-	-	3.2	0.12	-	0.009
1,2,3,7,8-PeCDF	0.05	-	0.027	0.004	-	-	-	0.037	-	-	0.27	0.067	0.028	0.005
2,3,4,7,8-PeCDF	0.5	-	0.26	-	0.17	-	-	-	-	-	8.1	2.8	2.9	0.074
1,2,3,4,7,8-HxCDF	0.1	-	-	-	0.051	-	-	-	-	-	0.14	0.55	0.51	-
1,2,3,6,7,8-HxCDF	0.1	-	-	-	0.038	-	-	-	-	-	0.18	0.38	0.39	-
1,2,3,7,8,9-HxCDF	0.1	-	-	-	-	-	-	-	-	-	0.062	0.095	0.078	-
2,3,4,6,7,8-HxCDF	0.1	-	-	-	0.031	-	-	-	-	-	0.22	0.52	0.70	-
1,2,3,4,6,7,8-HpCDF	0.01	0.029	0.010	0.002	0.006	0.014	0.002	0.013	0.021	0.005	0.025	0.097	0.041	0.003
1,2,3,4,7,8,9-HpCDF	0.01	-	-	-	0.003	-	-	-	-	-	-	-	0.006	-
OCDF	0.0001	-	-	-	<0.001	-	-	-	-	-	-	-	<0.001	0.004
Total PCDFs		0.029	0.41	0.025	0.36	0.014	0.002	0.050	0.021	0.005	12	4.6	4.7	0.094
Total PCDDs and PCDFs		0.13	2.5	0.033	0.75	0.058	0.91	0.61	1.5	0.018	23	11	11	0.33

*The contents of each food groups are follows ; 1: Rice and rice products, 2 : Cereals, seeds and potatoes, 3 : Sugars and confectionaries, 4 : Fats and oils, 5 : Pulses, 6 : Fruits, 7 : Green vegetables, 8 : Other vegetables, mushrooms and seaweeds, 9 : Seasoning and beverages, 10 : Fish and shellfish, 11 : Meat and eggs, 12 : Milk and dairy products, 13 : Other foods (prepared foods)

- : It was not detected in the TDS sample, and so the daily intake was calculated as zero.

Table 2. Dietary intake (pg TEQ/person/day) of dioxin-like PCBs in Kyusyu district, Japan

Compounds	TEFs	Number of food groups												
		1	2	3	4	5	6	7	8	9	10	11	12	13
3,4,4',5'-TeCB(#81)	0.0001	< 0.001	-	< 0.001	< 0.001	-	-	< 0.001	-	-	0.013	0.001	< 0.001	< 0.001
3,3',4,4'-TeCB(#77)	0.0001	0.003	0.003	< 0.001	< 0.001	0.001	< 0.001	0.002	0.001	< 0.001	0.21	0.010	0.001	< 0.001
3,3',4,4',5'-PeCB(#126)	0.1	0.54	0.26	0.084	0.27	0.23	0.13	0.25	-	0.12	48	4.0	3.2	0.058
3,3',4,4',5,5'-HxCB(#169)	0.01	-	-	-	-	-	-	-	-	-	0.72	0.13	0.075	-
Total non- <i>ortho</i> PCBs		0.55	0.27	0.085	0.27	0.23	0.13	0.25	0.001	0.12	49	4.2	3.2	0.059
2,3,3',4,4'-PeCB(#105)	0.0001	-	0.004	0.002	0.004	0.001	-	0.003	-	-	1.8	0.14	0.022	0.001
2,3,4,4',5'-PeCB(#114)	0.0005	-	-	-	-	-	-	-	-	-	2.1	0.14	-	< 0.001
2,3',4,4',5'-PeCB(#118)	0.0001	-	0.018	0.007	0.017	0.005	0.004	0.009	0.008	0.006	7.5	0.61	0.10	0.006
2',3,4,4',5'-PeCB(#123)	0.0001	-	0.016	0.003	0.001	0.008	0.006	-	-	0.007	6.1	0.068	0.008	0.004
2,3,3',4,4',5'-HxCB(#156)	0.0005	-	-	0.004	0.007	-	-	-	-	-	3.8	0.25	0.056	0.004
2,3,3',4,4',5'-HxCB(#157)	0.0005	-	-	-	-	-	-	-	-	-	0.79	0.051	-	< 0.001
2,3',4,4',5,5'-HxCB(#167)	0.00001	-	-	< 0.001	< 0.001	-	-	-	-	-	0.038	0.002	< 0.001	< 0.001
2,3,3',4,4',5,5'-HpCB(#189)	0.0001	-	-	-	-	-	-	-	-	-	0.083	-	-	-
Total mono- <i>ortho</i> PCBs		0	0.038	0.016	0.029	0.015	0.009	0.012	0.008	0.013	22	1.3	0.19	0.017
Total PCBs		0.55	0.31	0.10	0.30	0.24	0.14	0.27	0.009	0.13	71	5.4	3.4	0.076

*The contents of each food groups are follows ; 1: Rice and rice products, 2 : Cereals, seeds and potatoes, 3 : Sugars and confectionaries, 4 : Fats and oils, 5 : Pulses, 6 : Fruits, 7 : Green vegetables, 8 : Other vegetables, mushrooms and seaweeds, 9 : Seasoning and beverages, 10 : Fish and shellfish, 11 : Meat and eggs, 12 : Milk and dairy products, 13 : Other foods (prepared foods)

- : It was not detected in the TDS sample, and so the daily intake was calculated as zero.