DIETARY INTAKE OF DIOXINS AND THEIR DAILY VARIATIONS ESTIMATED BY DUPLICATE DIET STUDY

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Introduction

The latest results from investigations in several countries agree that the mean dietary intake of dioxins is less than the Tolerable Daily Intake (TDI) proposed by the WHO and that dioxin intake has declined during the last several decades[1)-3)]. Such trends have also been recognized in some surveys performed in Japan[4)-6)]. Prospective development in this field aims to provide reliable estimations of human exposure along with time trends.

In 1999, we reported on dietary intake of 29 kinds of dioxins based on a total diet study (TDS) in the Kyushu region of Japan[4)]. A duplicate diet study (DDS) was performed subsequently to obtain details and updates regarding the dietary intake in the same region. We collected DDS samples on seven successive days from adult volunteers, then evaluated the volunteers' actual daily intake of dioxins and variations in that intake. The data estimated from the DDS were compared with those previously obtained from the TDS.

Materials and Methods

From September to December 2000, we collected two series of individual DDS samples for seven consecutive days from different adult volunteers living in Fukuoka prefecture in the Kyushu region of Japan. The composition of each DDS sample was examined through a questionnaire collected from each volunteer.

We were concerned about arriving at an unjustifiable estimation caused by large numbers of 'non-detects'. Therefore, we aimed for about 10 times the lower limit of detection (LOD) that we used in our routine analysis for individual farm products, which meant that our sample size had to be increased. Therefore, to attain the desired LOD, we asked the volunteers to collect duplicate of their meals by dividing them into solid foods (including fluid fatty foods such as milk) and fluid foods (tea and other beverages).

Each homogenized solid sample (300 g) was spiked with 29 kinds of $^{13}C_{12}$-labeled dioxins as an internal quantification standard. The sample was digested with 1 N potassium hydroxide/ethanol for 2 hours with stirring, and then extracted twice with n-hexane. On the other hand, the fluid sample corresponding to the weighed solid sample (ranging from 84 g to 180 g) was also measured and subsequently extracted twice with n-hexane. Then both extracts were evaporated and mixed prior to a clean-up step. The clean-up conditions were those summarized in a previous report[4)]. Analyses were performed using an HP 6890 Plus gas chromatograph (Hewlett-Packard, USA) coupled to an AutoSpec ULTIMA mass spectrometer (Micromass, UK). The combination of capillary columns used in this study was as follows: an SP-2331 (0.32 mm x 60 m, Supelco, USA) to determine tetra-, penta-, and hexa-CDD/Fs; a BPX-5 (0.25 mm x 60 m, SGE, Australia) to determine hepta- and octa-CDD/Fs as well as non-ortho PCBs; and an HT-8 (0.32 mm x 50 m, SGE, Australia) to determine mono-ortho PCBs.

The LOD for each congener was decided according to the guidelines for food analysis of dioxins issued by the Ministry of Health and Welfare of Japan (1999). Consequently, the LODs shown in Table 1 were attained, and 53 non-detects were found within the total of 406 congeners analyzed. The non-detect congeners were principally treated with their intake as zero (ND = 0) in order to coordinate the data with our previous results from the TDS. Replacement by half of the LOD (ND = LOD/2) was also evaluated for reference.

Results and Discussion

Figure 1 shows changes in dietary intake of dioxins during the seven days, as estimated by an analysis of DDS samples; Table 2 summarizes the changes. For volunteer A (male, 32 years, 84.5 kg), the average total intake of dioxins was calculated to be 119 pg TEQ/day (ranging from 28.3 pg TEQ/day to 318 pg TEQ/day). This corresponded to 1.41 pg TEQ/kg body weight/day. For volunteer B (female, 52 years, 55.5 kg), the average dietary intake was calculated to be 84.9 pg TEQ/day (ranging from 9.89 pg TEQ/day to 131 pg TEQ/day). This corresponded to 0.87 pg TEQ/kg body weight/day. These values, based on each volunteer's body weight, were lower than the mean dietary intake estimated by our previous investigation, based on TDS: at 2.67 pg TEQ/kg body weight/day for a 50 kg adult[4]. In addition, as all the non-detects were substituted for LOD/2, the average total intake for the week was increased by 8.4% for volunteer A and by 14% for volunteer B (Table 2).

The largest TEQ contributions to the total dietary intake of dioxins during a week were exhibited by 3,3',4,4',5-penta CB (PCB 126) for both the volunteers. The contributions reached about half of the total intake for volunteer A and 40% of that for volunteer B. This trend was similar to the results from the TDS: In that analysis, PCB 126 occupied 43% of the total intake. Furthermore, for both the volunteers, dioxin-like PCBs made a larger TEQ contribution than PCDDs or PCDFs in the total intake: a 60% contribution for A and 47% for B. This tendency was also in agreement with the TDS results. In view of the TDS results, contributions of dioxin-like PCBs originated mainly from animal foods, especially fish and shellfish. In fact, we found a correspondence between the daily intake of dioxins and that of fish for volunteer A (Figure 1).

In our previous results from the TDS, the secondary contributor to the total intake of dioxins was PCDFs. However, for volunteer B, it was PCDDs. This difference might be relevant to the amount of meat eaten ('M') against the amount of fish eaten ('F'); the weight-ratio of 'M' to 'F' was calculated as 5.4 for volunteer B but only 0.45 for volunteer A.

It is worth noting that dioxin-like PCBs had larger daily variations than either PCDDs or PCDFs had (Figure 1). Therefore, it can be said that the levels of dietary intake of dioxin-like PCBs may be the main factor not only of weight but also of fluctuations in the daily exposure to dioxins. As shown in Figure 2, there are positive linear relationships of congener patterns for daily intake between TDS and DDS. Therefore, it is considered that the DDS samples from the volunteers generally reflected an average characteristic of food contamination by dioxins in the Kyushu region of Japan. We have reported here results from only two series of DDS samples. It is necessary now to obtain the results of additional examinations on DDS samples collected from other volunteers, in order to further our understanding of the general situation of dietary exposure to dioxins in the region.

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Table 1. Limit of detection (LOD) for dioxin-isomers (pg/g wet basis).

	Tetra- and Penta-DD/Fs	Hexa- and Hepta-DD/Fs	Octa DD/F	Non-ortho PCBs	Mono-ortho PCBs
For individual food	0.01	0.02	0.05	0.1	1
For DDS samples	0.001	0.002	0.05	0.01	1

Table 2. Estimated dietary intake of dioxins of two volunteers during the seven concecutive days (pg TEQ/day)*.

Congeners	Volunteer A			Volunteer B		
	Mean	Min	Max	Mean	Min	Max
2,3,7,8-TetraCDD	**4.49**	0	10.72	**1.98**	0	5.10
1,2,3,7,8-PentaCDD	**12.21**	3.71	25.89	**8.72**	1.68	24.10
1,2,3,4,7,8-HexaCDD	**0.30**	0.00	0.59	**1.66**	0.00	8.45
1,2,3,6,7,8-HexaCDD	**1.13**	0.85	1.40	**1.37**	0.36	2.82
1,2,3,7,8,9-HexaCDD	**0.44**	0	0.89	**0.42**	0	1.03
1,2,3,4,6,7,8-HeptaCDD	**0.37**	0.24	0.58	**0.76**	0.17	2.00
OctaCDD	**0.03**	0.01	0.05	**0.04**	0.01	0.09
Total PCDDs	**18.96**	6.52	38.97	**14.95**	2.72	41.09
2,3,7,8-TetraCDF	**5.50**	0.52	14.78	**1.33**	0.16	4.72
1,2,3,7,8-PentaCDF	**0.77**	0.27	2.21	**0.67**	0.09	3.49
2,3,4,7,8-PentaCDF	**19.12**	3.55	56.76	**6.71**	1.60	23.64
1,2,3,4,7,8-HexaCDF	**0.74**	0.48	1.17	**0.72**	0	2.00
1,2,3,6,7,8-HexaCDF	**0.79**	0.50	1.25	**0.70**	0	2.79
1,2,3,7,8,9-HexaCDF	**0.00**	0	0.00	**0.04**	0	0.31
2,3,4,6,7,8-HexaCDF	**0.83**	0	1.68	**0.37**	0	1.54
1,2,3,4,6,7,8-HeptaCDF	**0.12**	0.09	0.16	**0.20**	0.04	0.53
1,2,3,4,7,8,9-HeptaCDF	**0**	0	0	**0.01**	0	0.04
OctaCDF	**0**	0	0	**0**	0	0
Total PCDFs	**27.88**	6.92	77.94	**10.76**	1.96	38.47
3,4,4',5-TetraCB(#81)	**0.02**	0.02	0.03	**0.02**	0.02	0.03
3,3',4,4'-TetraCB(#77)	**0.13**	0.02	0.47	**0.07**	0.01	0.29
3,3',4,4',5-PentaCB(#126)	**59.12**	5.85	171.45	**17.91**	2.42	65.51
3,3',4,4',5,5'-HexaCB(#169)	**1.39**	0	5.44	**0.47**	0	1.48
2,3,3',4,4'-PentaCB(#105)	**1.74**	0.19	4.34	**0.67**	0.09	2.57
2,3,4,4',5-PentaCB(#114)	**0.63**	0	1.52	**0.22**	0.04	0.75
2,3',4,4',5-PentaCB(#118)	**5.28**	0.57	13.47	**1.95**	0.28	7.31
2',3,4,4',5-PentaCB(#123)	**0.10**	0	0.29	**0.04**	0.01	0.15
2,3,3',4,4',5-HexaCB(#156)	**3.14**	0.30	7.55	**1.12**	0.18	3.49
2,3,3',4,4',5'-HexaCB(#157)	**0.85**	0.07	1.90	**0.30**	0.04	1.06
2,3',4,4',5,5'-HexaCB(#167)	**0.05**	0	0.12	**0.01**	0	0.05
2,3,3',4,4',5,5'-HeptaCB(#189)	**0.06**	0.01	0.13	**0.02**	0	0.09
Total dioxin-like PCBs	**72.51**	7.12	200.73	**22.81**	3.11	82.77
Total Dioxins	**119.35**	28.32	317.64	**84.90**	9.89	130.82
Total Dioxins (ND=1/2LOD)	**129.40**	36.66	326.79	**97.07**	17.99	132.37

*The isomers of non-detect were treated their intake as zero.

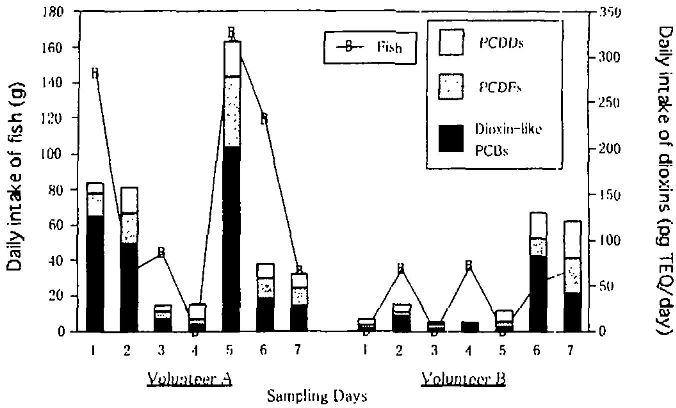

Figure 1. Daily dietary intake of dioxins for two volunteers.

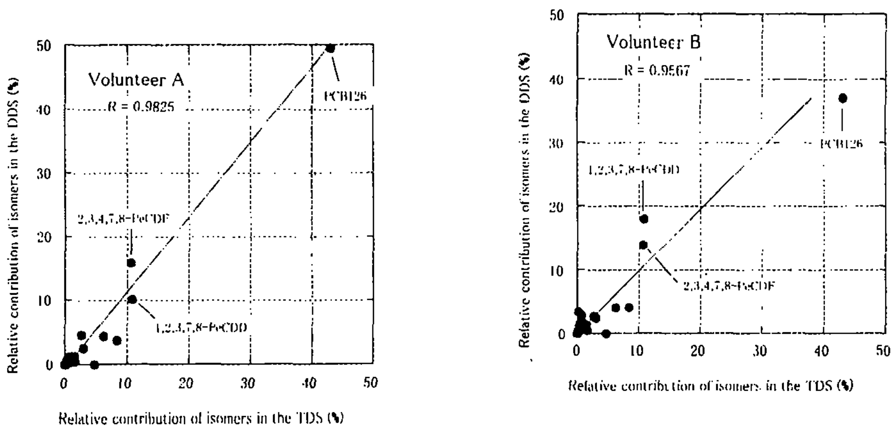

Figure 2. Relationship between relative contributions of dioxin-isomers estimated in the TDS and those of the DDS.

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