ESTIMATION OF 1999-2005 DAILY DIETARY INTAKE OF DIOXINS BY TOTAL DIET STUDY IN TOKYO METROPOLITAN AREA

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Abstract
We estimated the daily dietary intake of dioxins, consisting of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) through foods retailed in the Tokyo metropolitan area from 1999 to 2005 by the total diet-market basket method. These amounts were less than half that of the tolerable daily intake (TDI) of 4 pg TEQ/kg/day for dioxins established in Japan. The dioxins taken daily through fish and shellfish (group 10) accounted for more than 70% of the total TEQs. In addition, more than 90% of the daily intake of dioxins was taken group 10, meat and eggs (group 11), and milk and dairy products (group 12). Also, this study showed that the ratio of dl-PCBs in the daily intake of dioxins is increasing yearly, because the reduction rate of dl-PCBs was lower than that of PCDDs and PCDFs in foods.

Introduction
Dioxins are residual organic pollutants with various types of toxicity. It has been reported that 95% or more of the total dioxin exposure in humans is diet-derived. [1, 2] In Japan, several studies on the daily intake of dioxins from food have been reported.[3, 4, 5, 6] However, little information is available on the daily intake of dioxins with continuous surveillance in the Tokyo metropolitan area. Tokyo is the capital of Japan with a population of 12 million. Various foods are collected and consumed there, not only from Japan but from every corner of the world. Therefore, an estimation of the daily dietary intake of dioxins is highly significant regarding risk evaluation. Here, we report the results of monitoring in the Tokyo metropolitan area that was carried out from 1999 to 2005 by a total diet study (TDS) method.

Materials and Methods
Samples
The planning of TDS samples was based on official food classification (14 groups) and the previous year's data on food consumption in the Tokyo region obtained from the Japanese Nutrition Survey, which was carried out by the Ministry of Health, Labor and Welfare of Japan (1998-2004). Table 1 shows the classification of 14 food groups and the contents of food stuff samples in 2004. Every year, more than 300 individual foods were bought from supermarkets, department stores, and retail stores in Tokyo and cooked or prepared by each group in ways typical for consumption. Especially, we prepared samples from over 50 species in group 10 (fish and shellfish). All group samples were adequately homogenized, and then frozen at –40 ^{o}C until analysis.
Materials
Native and ^{13}C-PCDDs, PCDFs, and dl-PCBs as authentic standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). The multi-layer silica gel column was a SUPELCO Multi-layer Dioxin Tube obtained from SIGMA-ALDRICH JAPAN (Tokyo, Japan). Active carbon-impregnated silica gel was purchased from Wako Pure Chemical Industries (Tokyo, Japan).
Extraction and cleanup
The samples were spiked with 17 kinds of ^{13}C-PCDDs and PCDFs, 4 kinds of ^{13}C-non-*ortho*-PCBs, and 8 kinds of ^{13}C-mono-*ortho*-PCBs before the initial extraction. Methods of extraction and cleanup in the samples were described previously in detail.[7]
HRGC-HRMS analysis
HRGC-HRMS was performed using a Micromass (Manchester, UK) Autospec Ultima coupled to a Hewlett Packard 6890 gas chromatograph (Palo Alto, CA, USA) and an HP 7683 auto injector. The measurement of PCDDs and PCDFs was performed using an SGE BPX-DXN capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness). A SUPELCO SP-2331 capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness) was used as a confirmation column for 2,3,7,8-PCDD/PCDF. The measurement of dl-PCBs was performed using an SGE

HT-8 capillary column (50 m × 0.22 mm i.d., 0.25 µm film thickness). The temperatures of the interface and ion source were both 270 ^{o}C, with an electron energy of 35eV and trap current of 500µA. The mass spectrometer was operated at a resolution of 10,000. Selected ion monitoring was employed using the two most intense ions from the molecular ion cluster for each homologue. Data processing was performed using standard VG OPUS software for automatic peak area measurement and to calculate the mass of each compound present. Calculation of the 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) of the dioxin analogues in analyzed samples was carried out on the basis of the toxicity equivalent factor (TEF) reported in 1998 and re-evaluated in 2005 by the WHO.

Table 1 The classification of 14 food groups and the contents of food stuff samples (2004)

No.	Food group	Number of Food stuffs	Examples
1	Rice and rice products	7	Rice, Glutious rice cake
2	Cereals, seeds and potatoes	27	Wheat flour, Bread, Potato
3	Sugars and confectioneries	28	Sugar, Honey, Cookies, Cake
4	Fats and oils	15	Butter, Mayonnaise, Soybean oil
5	Pulses	21	Tofu (Soybean curd), Miso
6	Fruits	19	Orange, Apple, Grape, Banana
7	Green vegetables	16	Tomato, Spinach, Carrot, Pumpkin
8	Other vegetables, mushrooms and seaweeds	35	Cabbage, Onion, Japanese radish
9	Seasoning and beverages	36	Soy sauce, Beer, Coffee, Green tea
10	Fish and shellfish	85	Sardine, Tuna, Eel, Mackerel, Shrimp
11	Meat and eggs	41	Beef, Pork, Chicken, Hen's egg
12	Milk and dairy products	19	Cow milk, Yogurt, Cheese
13	Other foods (prepared foods)	12	Curry powder
14	Drinking water	1	Tap water
	Total	362	

Results and Discussion

Figs 1 and 2 show the yearly change in the daily intake of dioxins. The daily intake of dioxins per kg body weight for an average adult body of 50 kg with WHO-TEF (1998) was 2.18 pg TEQ/kg/day in 1999, 1.87 pg TEQ/kg/day in 2000, 1.25 pg TEQ/kg/day in 2001, 1.60 pg TEQ/kg/day in 2002 and 2003, 1.55 pg TEQ/kg/day in 2004, and 1.54 pg TEQ/kg/day in 2005. Meanwhile, with WHO-TEF (2005), the daily intake was 1.92 pg TEQ/kg/day in 1999, 1.65 pg TEQ/kg/day in 2000, 1.08 pg TEQ/kg/day in 2001, 1.39 pg TEQ/kg/day in 2002, 1.36 pg TEQ/kg/day in 2003, 1.12 pg TEQ/kg/day in 2004, and 1.34 pg TEQ/kg/day in 2005. The reevaluation of TEF in 2005 showed a decrease in dioxins intake of approximately 15%. The total daily intake was on a downward trend during the first 3 years, and thereafter, was broadly flat. These total intake values were below the TDI of 4 pg TEQ/kg/day set by the Environmental Agency and Ministry of Health and Welfare of Japan. The values are similar to or lower than those found in previous studies in Japan.[5, 6] We speculate that the total dietary intake of dioxins is currently about 1.3～1.5 pg TEQ/kg/day. The contribution ratio of dl-PCBs to the total intake was greater than that of PCDDs and PCDFs, and the relative contribution of dl-PCBs increased since 2002.

Tables 2 and 3 show the ratio to the total intake of dioxins for each food group. As for the 14 food groups, the highest contribution ratio to total intake was from fish and shellfish (group 10) each year, and the contribution from this group accounted for over 70%, except for 2001. Meat and eggs (group 11) and milk and dairy products (group 12) made the next-highest contributions. The sum TEQ from these three groups accounted for 91.7 – 97.7% of the total intake. On the other hand, green vegetables (group 7) accounted for 1pg TEQ/day and over during the first three years, but it was significantly reduced from 2002 to 2005.

The highly toxic isomers 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, and 3,3',4,4',5-PeCB (#126) were detected over the entire investigation period. Especially, 3,3',4,4',5-PeCB (#126) was the highest-contributing congener, and accounted for over 40% of the daily intake of dioxins from fish and shellfish. Additionally,

2,3’,4,4’,5-PeCB (#118) was the next-highest contributing congener, because the actual concentration was very high even though TEF was low.
Japan is one of the world’s leading consumers of fish and shellfish. It was reported that Japanese retail fish contain an average 1.6 pg TEQ/g dioxins and that about 60% of the dietary intake of dioxins is likely to come from the intake of fish and shellfish.[5, 8] In our study, the fish and shellfish group made an even higher contribution to the total dietary intake of dioxins than in that report.
The overall TEQ level of PCDDs and PCDFs is much lower than that of dl-PCBs. dl-PCBs are thought to originate from electrical insulating oil and heat exchange fluid, with the exception of a few congeners. After widespread environmental contamination by commercial PCB was confirmed in the late 1960s in Japan, the production and use of PCB was prohibited in 1972. However large-scale destruction of PCB had not been conducted in Japan until some firms started to chemically or physically treat their PCB waste recently. Presently, large PCB-containing materials remain and are stored in depositories. Therefore, there has been no sign of a sudden drop in their concentration in the environment such as air, seawater, sediment, and soil. Accordingly, particular importance should be attached to the levels of dl-PCBs when estimating the total dietary intake of dioxins in the future, especially in nations that are major consumers of fish and shellfish. Additionally, attention should be focused on 3,3’,4,4’,5-PeCB (#126), the dominant isomer of dl-PCBs in fish and shellfish.
Since the fish catches in the seas close to Japan have decreased remarkably in recent years, Japan has begun to import many marine products. Fish and shellfish consumption in Japan is growing increasingly diverse for this reason.
In conclusion, the results of the current study, show that recent total intakes of dioxins in Tokyo are much lower than the TDI of 4 pg TEQ/kg /day. However, we have yet to achieve the ultimate goal to reduce human intake levels below 1 pg TEQ/kg/day set by the WHO. Therefore, a more detailed survey should be carried out based on the anticipated changes of fish and shellfish consumption, and at the same time, we should promote the appropriate disposal of PCB-containing materials.

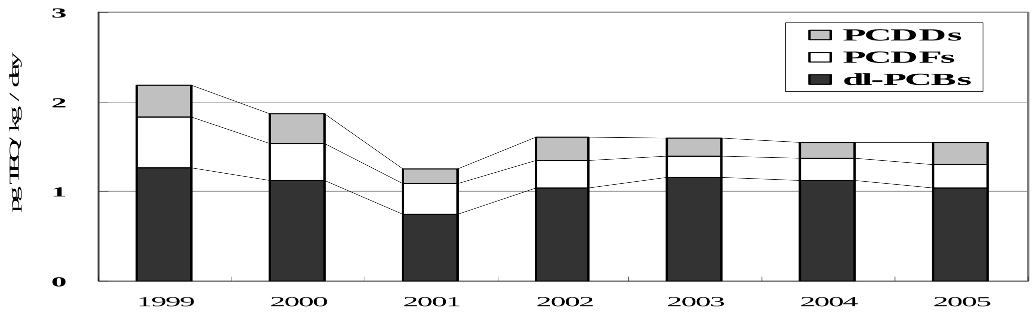

Fig.1 Daily dietary intakes of dioxins as WHO-TEQ (1998) in the Tokyo metropolitan area

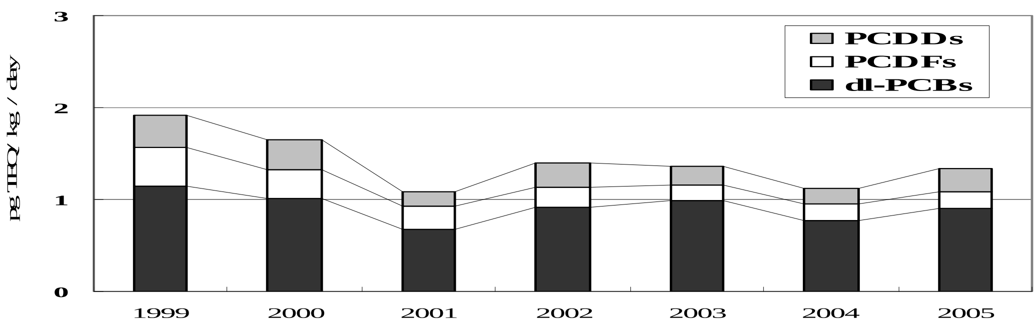

Fig.2 Daily dietary intakes of dioxins as WHO-TEQ (2005) in the Tokyo metropolitan area

Table 2 The ratio (%) to the total intake of dioxins for each food group as WHO-TEQ (1998)

No.	Food group	1999	2000	2001	2002	2003	2004	2005
1	Rice and rice products	0.51	0.054	1.23	0.011	0.0019	0.0066	0.0032
2	Cereals, seeds, and potatoes	0.83	0.73	0.42	1.1	0.43	0.46	0.28
3	Sugars and confectioneries	0.52	1.3	1.30	0.66	0.91	0.64	0.30
4	Fats and oils	0.47	0.29	0.60	0.90	1.08	0.26	0.73
5	Pulses	0.01	0.01	0.1	0.1	0.013	0.013	0.013
6	Fruits	0.14	0.02	0.006	0.0003	0.0003	0.0003	0.001
7	Green vegetables	2.8	1.7	3.4	0.36	0.25	0.35	0.19
8	Other vegetables, mushrooms, and seaweeds	0.62	1.13	0.43	0.10	0.43	0.69	0.64
9	Seasoning and beverages	0.02	0.03	0.02	0.01	0.05	0.03	0.01
10	Fish and shellfish	77.21	73.53	53.66	76.25	84.14	82.37	82.74
11	Meat and eggs	8.53	13.02	30.98	12.04	8.53	10.79	12.72
12	Milk and dairy products	8.07	7.70	7.10	8.29	3.56	3.58	2.22
13	Other foods (prepared foods)	0.29	0.53	0.37	0.30	0.56	0.80	0.14
14	Drinking water	0.000022	0.0015	0.0004	0.0004	0.0003	0.00003	0.02

Table 3 The ratio (%) to the total intake of dioxins for each food group as WHO-TEQ (2005)

No.	Food group	1999	2000	2001	2002	2003	2004	2005
1	Rice and rice products	0.41	0.055	1.42	0.003	0.0010	0.0034	0.0014
2	Cereals, seeds, and potatoes	0.91	0.77	0.49	1.2	0.47	0.56	0.30
3	Sugars and confectioneries	0.51	1.3	1.38	0.63	0.91	0.83	0.34
4	Fats and oils	0.52	0.31	0.87	1.00	1.21	0.36	0.83
5	Pulses	0.01	0.01	0.1	0.1	0.014	0.022	0.017
6	Fruits	0.07	0.02	0.003	0.0001	0.0001	0.0001	0.000
7	Green vegetables	2.6	1.6	2.7	0.38	0.29	0.46	0.21
8	Other vegetables, mushrooms, and seaweeds	0.69	1.28	0.47	0.10	0.47	0.91	0.71
9	Seasoning and beverages	0.01	0.04	0.01	0.00	0.05	0.03	0.01
10	Fish and shellfish	78.32	73.17	53.87	75.50	83.40	78.40	81.91
11	Meat and eggs	8.07	13.23	31.45	12.30	8.89	13.62	13.46
12	Milk and dairy products	7.56	7.65	6.78	8.49	3.64	3.75	2.02
13	Other foods (prepared foods)	0.29	0.56	0.40	0.32	0.66	1.06	0.17
14	Drinking water	0.000046	0.0005	0.0002	0.0001	0.0001	0.00001	0.03

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References

1. Päpke O. *Environ. Health Perspectives* 1998; 106:723.
2. Nakamura Y, Matsuura N, Kondo N, Tada Y. *Organohalogen Compounds* 2000; 48:1.
3. Ono M, Kashima Y, Wakimoto T, Tatsukawa R. *Chemosphere* 1987; 16:1823.
4. Takayama K, Miyata H, Aozasa O, Miura M, Kashimoto T. *J. Food Hyg. Soc. Jpn.* 1991; 32:525 (in Japanese).
5. Toyoda M, Iida T, Hori T, Yanagi T, Kono Y, Uchibe H. *J. Food Hyg. Soc. Jpn.* 1999a; 40:98 (in Japanese).
6. Tsutsumi T, Yanagi T, Nakamura M, Kono Y, Uchibe H, Iida T, Hori T, Nakagawa R, Tobiishi K, Matsuda R, Sasaki K, Toyoda M. *Chemosphere* 2001; 45:1129.
7. Sasamoto T, Ushio F, Kikutani N, Saitoh Y, Yamaki Y, Hashimoto T, Horii S, Nakagawa J, Ibe A. *Chemosphere* 2006; 64:634.
8. Toyoda M, Iida T, Hori T, Yanagi T, Kono Y, Uchibe H. *J. Food Hyg. Soc. Jpn.* 1999b; 40:111 (in Japanese).