ESTIMATION OF DIETARY DAILY INTAKE OF PCDDS, PCDFS, AND DL-PCBS: TOTAL DIET STUDY IN TOKYO SINCE 1999

Hayashi M[1], Tamura Y[1], Otani H[1], Baba I[1], Morioka M[1], Sasamoto T[1], Hashimoto T[1]

[1]Tokyo Metropolitan Institute of Public Health, Shinjuku-ku, Tokyo, Japan, 169-0073, Masaki_1_Hayashi@member.metro.tokyo.jp

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) are a group of chemically related environmental pollutants, collectively referred to as dioxins. It is estimated that over 90% of the dioxins to which humans are exposed are via diet[1]. Estimating the dietary intake of dioxins is important for risk assessments. Therefore, the Tokyo Metropolitan Government has continuously surveyed the dietary intake of dioxins using the total diet method. Here we summarize the results of the survey conducted since 1999, and explain the dietary exposure to dioxins.

Materials and methods

Samples

Each year, the samples were prepared based on the official food classification of the previous year's data on food consumption in the Tokyo region. The data was obtained from the Japanese National Health and Nutrition Survey from the Ministry of Health, Labour and Welfare. Table 1 shows the food classification (14 groups) and the contents of the samples in 2016. Over 300 individual foodstuffs were bought from supermarkets and department and retail stores in Tokyo every year. In particular, over 50 food samples were prepared for group 10 (fish and shellfish). These foodstuffs were cooked or prepared in typical ways for consumption, homogenized thoroughly by food group, and then stored at −40 ºC until analysis.

Table 1: Classification of 14 food groups and the contents of foodstuff samples (2016)

No.	Food group	Number of foodstuffs	Examples
1	Rice and rice products	9	Rice, Glutinous rice cake
2	Cereals, seeds and potatoes	31	Wheat flour, Bread, Potato
3	Sugars and confectioneries	23	Sugar, Honey, Cookie, Cake
4	Fats and oils	9	Butter, Canola oil
5	Pulses	13	Tofu (Soybean curd), Red bean
6	Fruits	19	Orange, Apple, Grape, Banana
7	Green vegetables	16	Tomato, Spinach, Carrot, Pumpkin
8	Other vegetables, mushrooms and seaweeds	34	Cabbage, Onion, Japanese radish
9	Beverages	22	Beer, Coffee, Green tea
10	Fish and shellfish	55	Sardine, Tuna, Eel, Mackerel, Shrimp
11	Meat and eggs	31	Beef, Pork, Chicken, Hen's egg
12	Milk and dairy products	15	Cow milk, Yogurt, Cheese
13	Seasoning	24	Curry powder, Soy source, Solt, Pepper
14	Drinking water	1	Tap water
	Total	302	

Materials

All solvents and reagents were of dioxin-analysis grade and purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Native and $^{13}C_{12}$-PCDDs, PCDFs and dl-PCBs authentic standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). The multi-layer silica gel column (SUPELCO Multi-layer Silicagel Dioxin Column) was obtained from Sigma-Aldrich (St. Louis, Missouri, USA). Reverse column with active carbon dispersed-silica gel was acquired from Kanto Chemical Company (Tokyo, Japan).

Extraction and Cleanup

The samples were spiked with 17 types of $^{13}C_{12}$-PCDDs and PCDFs, four types of $^{13}C_{12}$-non-*ortho*-PCBs, and eight types of $^{13}C_{12}$-mono-*ortho*-PCBs before the initial extraction. The methods of extraction and cleanup have been previously described in detail[2].

High Resolution Gas Chromatography-High Resolution Mass Spectrometry (HRGC-HRMS)

HRGC-HRMS was performed using a JEOL (Tokyo, Japan) JMS-800D spectrometer coupled to an Agilent Technologies 7890A gas chromatograph (Santa Clara, CA, USA), or with a Micromass (Manchester, UK) Autospec Ultima spectrometer coupled to an Agilent Technologies 6890 gas chromatograph. SGE capillary columns (Melbourne, Victoria, Australia) BPX-DXN (60 m × 0.25 mm i.d.), and HT-8 (30 m × 0.25 mm i.d., 0.25 μm film thickness) were used for the analysis of the PCDDs and PCDFs, and of the dl-PCBs, respectively. Both the interface and ion source were at 260 $^{\circ}$C, with an electron energy of 38 eV and trap current of 500 μA. The mass spectrometer was operated at a resolution of 10,000. Selected ion monitoring (SIM) mode was selected based on the two most intense ions from the molecular ion cluster for each homologue. The DIOK V4.02 software was used for automatic peak area measurement and to calculate the mass of each compound. The detection limits (LOD) for PCDDs and PCDFs were 0.01–0.02 pg/g in food groups 1–13 and 0.0001–0.0002 pg/g in food group14. The LOD of dl-PCBs were 0.01 pg/g in food groups 1–13 and 0.0001 pg/g in food group 14. The 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) of the dioxin analogs in the analyzed samples was calculated based on the toxic equivalency factor re-evaluated by the World Health Organization (WHO) in 2005[1].

Results and discussion:

The annual variation in the daily intake of dioxins is shown in Table 2 for each food group and in Figure 1 for each dioxin group. Samples below the LOD of each year have accounted 59–70% of the total since 2008. These non-detected results were treated as zero to prevent overestimation of daily intake. Analysis of dioxins was carried out every year from 1999 to 2008, and then biyearly after 2008. The current total daily intake per kg calculated considering a 50 kg adult body was 0.50 pg-TEQ/kg/day and this value was lower than the TDI of 4 pg-TEQ/kg/day set by the Ministry of Health, Labour and Welfare of Japan in the entire survey period. The total daily intake of dioxins decreased from 1999 to 2001, then remained almost constant from 2001 to 2008, and further decreased from 2010. Particularly, since 2010, the total daily intake values have achieved the WHO's ultimate target value of 1pg-TEQ/kg/day and is approaching 0.5 pg-TEQ/kg/day. Although there are differences in estimation methods, the latest daily intake value obtained in this study was within the range reported in other countries[3-5].

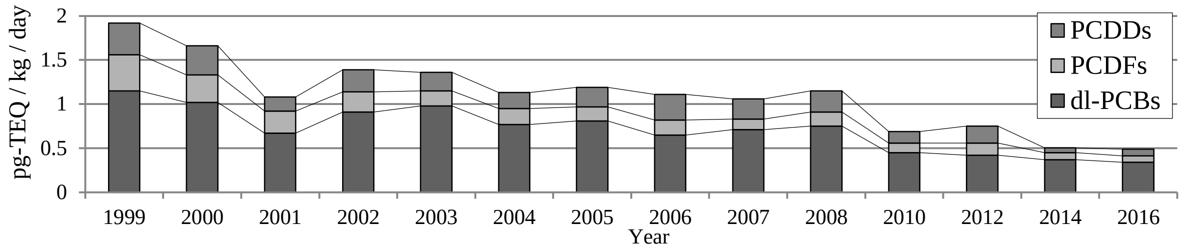
Table 2: Dietary daily intake of dioxins as TEQ(WHO 2005) in Tokyo (pg-TEQ / kg / day)[a,b]

	Year													
No. of Food group	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2010	2012	2014	2016
1	0.0079	0.00090	0.015	0.000040	0.000013	0.000038	0.000019	0.000031	0.0000080	0.000034	0.0000052	0.000066	0.000010	0
2	0.017	0.013	0.0053	0.016	0.0063	0.0064	0.0051	0.0099	0.0058	0.00062	0.00036	0.00025	0.0015	0.0014
3	0.0098	0.021	0.015	0.0088	0.012	0.0093	0.0045	0.012	0.0077	0.0043	0.0040	0.0021	0.0036	0.0017
4	0.010	0.0052	0.0094	0.014	0.017	0.0040	0.011	0.011	0.0077	0.0064	0.0042	0.0060	0.0014	0.0032
5	0.00025	0.000089	0.0015	0.0015	0.00019	0.00025	0.00022	0.000082	0.00061	0.00010	0.000055	0.00047	0.000029	0.00078
6	0.0012	0.00031	0.000037	0.0000015	0.0000015	0.0000014	0.0000048	0.000047	0.0000083	0.000012	0.0000021	0.0000064	0.000066	0.0000025
7	0.051	0.027	0.029	0.0053	0.0043	0.0052	0.0025	0.000061	0.000072	0.00052	0.00012	0.00022	0.00037	0.00030
8	0.013	0.021	0.0050	0.0014	0.0064	0.010	0.0091	0.0052	0.0053	0.0036	0.0020	0.0017	0.0012	0.0010
9	0.00011	0.00065	0.00012	0.000035	0.00062	0.00029	0.00014	0.00032	0.00017	0.00019	0.000029	0	0.000014	0
10	1.5	1.2	0.58	1.1	1.1	0.88	0.98	0.79	0.82	0.92	0.55	0.53	0.45	0.43
11	0.15	0.22	0.34	0.17	0.12	0.15	0.15	0.24	0.20	0.19	0.091	0.18	0.043	0.048
12	0.14	0.13	0.073	0.12	0.050	0.042	0.027	0.033	0.021	0.015	0.025	0.024	0.0063	0.0033
13	0.0055	0.0092	0.0043	0.0045	0.0083	0.012	0.0022	0.0028	0.0026	0.024	0.0053	0.0016	0.0021	0.0021
14	0.00000088	0.0000079	0.0000021	0.0000017	0.0000015	0.00000014	0.00036	0.00000011	0.00036	0.00036	0.00000055	0.00025	0.0000053	0.00000014
Total	1.92	1.65	1.08	1.39	1.36	1.12	1.19	1.11	1.06	1.15	0.69	0.75	0.51	0.50

[a] Values calculated at ND = 0.

[b] Daily intake of dioxins per kg of body weight for 50 kg.

Figure 1: Dietary daily intakes of PCDDs,PCDFs and dl-PCBs as TEQ(WHO 2005) in Tokyo



The ratios to the total intake of dioxins for each food group were calculated from Table 2. Except in 2001, the groups with a high contribution to the total daily intake were group 10 (fish and shellfish) 71–88%, group 11 (meat and eggs) 8–24%, and group 12 (dairy products) 1–7%. Although the contribution of different food groups to the daily intakes varies in other countries[3-5], in this study, these three groups account for more than 90%. In contrast, group 7 (green vegetables) contributed around 2% during the first three years, then it declined to under 0.5% after 2002 and remained under 0.1% since 2006.

As shown in Figure 1, the ratio of PCDDs, PCDFs, and dl-PCBs to the total intake of dioxins gradually changed during the survey period. The total proportion of PCDDs and PCDFs was 40% in 1999 but decreased to 31% in 2016.

Intakes of each food group in the Tokyo area did not change significantly during the entire survey period. In order to know the reason for the decreasing tendency of daily intake of dioxins, the annual variation in the concentration of dioxins is shown in Figures 2–5 for groups 10–12, which have the largest contribution rate, and for the other groups.

Figure 2: The concentration of PCDDs and PCDFs in food group 10, 11 and 12

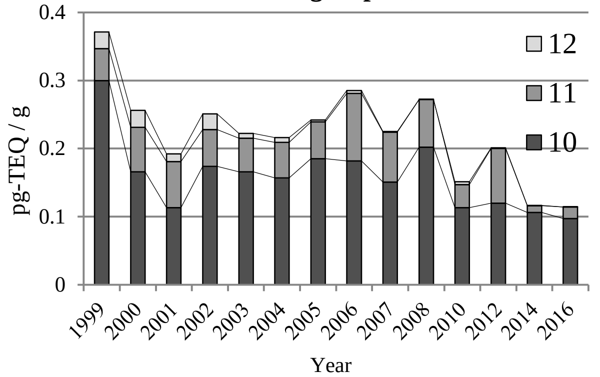


Figure 3: The concentration of PCDDs and PCDFs in food group 1-9, 13 and 14

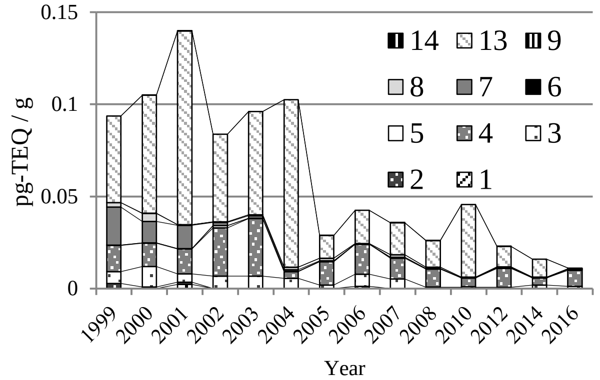


Figure 4: The concentration of dl-PCBs in food group 10, 11 and 12

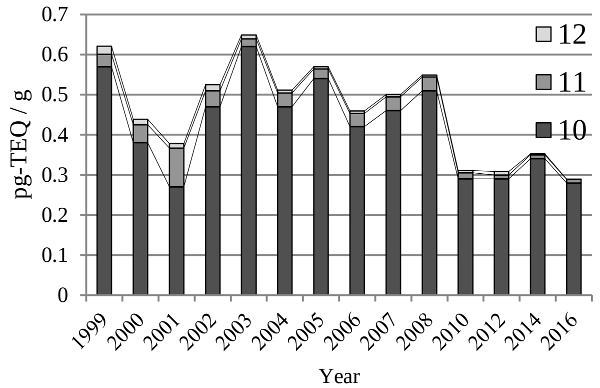


Figure 5: The concentration of dl-PCBs in food group 1-9, 13 and 14

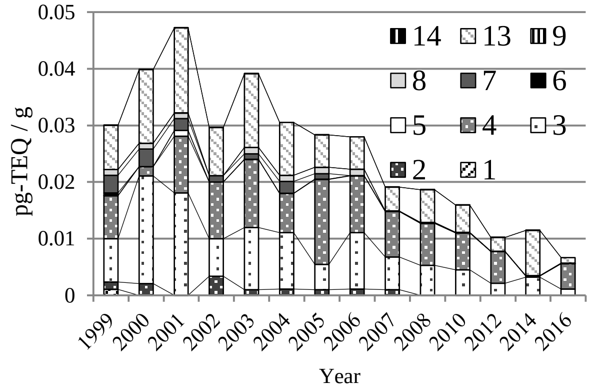


Figure 2 shows the concentration of PCDDs and PCDFs in groups 10–12. Overall, these concentrations tended to decrease. In group 10, it decreased between 1999 and 2003, and remained of at least 0.15 pg-TEQ/g until 2008, and then it was this value since 2010. The changes in group 11 were not remarkable until 2012, then the detected amount decreased from 2014. Concentrations in group 12 declined since 2003.

Figure 3 shows the concentration of PCDDs and PCDFs in groups 1–9, 13, and 14. Overall, the concentrations in these 11 groups tended to decrease from 2005. In group 7 the decrease was remarkable between 1999 and 2003, leading to a reduced contribution to daily intake. Concentrations in group 3 decreased since 2008, and in group 13 since 2005.

Figure 4 shows the concentration of dl-PCBs in groups 10–12. The concentration during this period slightly decreased in groups 11 and 12.

Figure 5 shows the concentration of dl-PCBs in groups 1–9, 13, and 14. Overall, the concentrations in these 11 groups tended to decrease after 2007. Compared to 1999, the concentrations in group 1, 2, 7, and 8 clearly declined since 2007 and in groups 3, 4, and 13, the decrease was slight.

In Japan, the law “Act on Special Measures against Dioxins” enacted in 1999 regulates the gas emissions or effluents with dioxin levels that fail to comply with the standards. As a result, the emission of dioxins from incinerators has decreased, and the concentration of PCDDs and PCDFs in the domestic atmosphere has also decreased. It is presumed that this environmental improvement contributed to the reduction of the concentration of PCDDs and PCDFs in food.

Additionally, dl-PCBs in the food distributed in Japan are considered to originate from electrical insulating oil and heat exchange fluids rather than from incineration sources[2]. Triggered by the Kanemi Yusho incident (1968), the production and use of PCBs have been banned since 1972 in Japan. Based on the PCB Waste Measures Special Measures Act enacted in 2001, disposal of PCB waste is in progress, but it takes time to complete. Also, due to past improper disposal or accidental leaks, the PCBs released in the environment are difficult to recover. Therefore the decrease on the daily intake of dl-PCBs will be slower than that of PCDDs and PCDFs.

Our results show that the total intake of dioxins in Tokyo in recent years is at a safe level based on the WHO ultimate goal of 1 pg-TEQ/kg/day. The contribution of the ratio of fish and shellfish to the total intake of dioxins exceeded 70%, but it does not suggest not eating fish. Having a balanced diet is important and it helps avoid the intake of other harmful chemicals. It is necessary to continuously monitor dioxins intake, and to promote the appropriate processing of PCB-containing materials.

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