DETAIL SUEVEY OF PCDDS, PCDFS AND NON-ORTHO COPLANAR PCBS IN AMBIENT AIR AT THE NORTHERN AREA IN OSAKA, JAPAN

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Introduction

Recently, there is a much concern to contamination level in vegetable by dioxin analogues containing of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and non-ortho coplanar PCBs (Co-PCBs) in Japan, because of the active combustion activity by numerous solid waste incinerators. Especially, in a case of green vegetables, the major pollution route is surmised to be atmospheric transport due to their big volume aspiration of ambient air through their stomata of leaf in order to create their body. It is well known that dioxin analogues are present in two types of vapor phase and particulate phase in the atmosphere environment. In Japan, however, there have been few reports concerning to thus analytical data. Therefore, in this paper, we tried to reveal their real situation of existence condition in ambient air in Osaka, the second big prefecture of Japan.

Experiments

Sampling was performed during September of 1998 to April of 1999 on the campus of Faculty of Pharmaceutical Sciences, Setsunan University, northern Hirakata, Osaka, Japan. The location is considered to most closely to represent urban region of Japan. The high volume air sampler was equipped with a glass fiber filter (GFF) to collect particulate phase compounds and two polyurethane form plugs (PUF) to collect the gas phase compounds. The sampler was weekly run for 24 hours period at a sampling rate of 700 L/min. for total volume of 1000 m^3. Prior to sampling, 400 pg of $^{37}Cl_4$-labeled 2,3,7,8-TCDD was added on the upper polyurethane form plug in order to check the breakthrough of dioxin analogues. We obtained 48 vapor and particular samples during this experimental priod.

After sampling, each GFF specimen was crushed into fine powder and extracted with 200 ml of toluene for 4 hrs. under reflux. While the PUF specimen was cut into a small piece and extracted with 1400 ml of acetone for 4 hrs. under reflux. After spiking of internal standards (five $^{13}C_{12}$-PCDDs, five $^{13}C_{12}$-PCDFs and three $^{13}C_{12}$-Co-PCBs, each 200 pg), a half aliquot of extracts from GFF and PUF samples were respectively concentrated and the solvent was completely replaced with 10 ml of n-hexane. The extract was cleaned up according to our new simple method[1)] using a combined column with a multi-silica gel layer column (upper side) and alumina column (below side), with successive eluents of n-hexane (180 ml), 3% methylene chloride/ n-hexane (50 ml) and 50% methylene chloride/n-hexane (80 ml). The first column includes Na_2SO_4 (1.0 g), 10%(w/w) $AgNO_3$-silica (1.0 g), silica (0.8 g), 22%(w/w) H_2SO_4-silica (6.0 g), 44%(w/w) H_2SO_4-silica (6.0 g), silica (0.8 g), 2%(w/w) KOH-silica (2.0 g) and silica (0.8 g), and the second column does 10 g of neutral alumina (Merck, Activate I).

The third eluate was concentrated and finally dissolved with 20 μ l of n-decane. The solution was analyzed in EI-SIM mode at a resolution of 10,000 using a Hewlett Packard 5890J GC-JEOL M700 MS. The concentrations of PCDDs, PCDFs and Co-PCBs were corrected with the recoveries of their respective internal standards. Finally, the 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) of dioxin analogues in analyzed samples were calculated for PCDDs/DFs using I-TEFs [2)] and for Co-PCBs using TEFs by WHO[3)].

Results and discussion

Table 1 shows average monthly actual concentrations (pg/m^3) and TEQ concentrations (fg/m^3) of dioxin analogues in the vapor and particulate phases. As shown in this table, there was a great difference in each dioxin analogue in the two phases during the sampling period, showing the vapor phase level (pg/m^3) to be 0.84 to 6.83 for PCDDs, 0.72 to 25.6 for PCDFs and 0.33 to 5.05 for Co-PCBs, and the particulate phase level (pg/m^3) to be 2.58 to 15.0 for PCDDs, 2.79 to 26.6 for PCDFs and 0.07 to 5.05 for Co-PCBs, respectively. The total levels (pg/m^3) of both phases altered greatly , showing to range 6.36 to 21.9 for PCDDs, 9.64 to 43.3 for PCDFs and and 0.54 to 5.14 for Co-PCBs, respectively (Fig. 1). On the other hand, as well as the actual level, there was also observed a remarkable variation in the TEQ level. The vapor phase level (fgTEQ/m^3) was in a range of 10 to 577 for PCDDs, 9 to 160 for PCDFs and 5 to 56 for Co-PCBs, and the particulate phase level (fgTEQ/m^3) was in a range of 46 to 382 for PCDDs, 101 to 881 for PCDFs and 2.00 to 17.0 for Co-PCBs, respectively.

There was also observed that a wide variation in the ratio of each dioxin analogue in the vapor phase to their respective total concentrations. The average ratio (%) was arranged in a order of Co-PCBs (75.2), PCDFs (45.9) and PCDDs (35.5). This result is considered to be attributable to a discrepancy of their average vapor pressures. Figure 2 shows the ratio (%) of each dioxin analogue congeners in the vapor phase to their respective total. As shown in this figure, there was a decrease tendency according to the chlorine number substituted in their molecules. For example, in a case of PCDDs, the average ratios (%) were 79.1 for TCDDs, 38.9 for PeCDDs, 19.0 for HxCDDs, 20.8 for HpCDDs and 28.6 for OCDD, respectively. Similar observation was seen in the cases of PCDFs and Co-PCBs. The average vapor pressures (mmHg) were reported to be 3.5 x 10^{-4} for TCDDs, 1.2 x 10^{-4} for PeCDDs, 4.4 x 10^{-6} for HxCDDs, 2.4 x 10^{-6} for HpCDDs and 4.0 x 10^{-7} for OCDD[4)]. Taking this report into consideration, the vapor phase ratios of dioxin analogues are able to refer to correlate closely their respective vapor pressures. However, their ratios changed greatly during the experimental period. The maximum level was observed in September 1998 with the highest atmospheric temperature of 26.3℃ and the minimum was December 1998 with the second lowest temperature of 8.0℃, indicating the ratio of vapor phase to correlate also to the air temperature. This brought a remarkable discrepancy in the contribution of dioxin analogues in the vapor phase to the respective total TEQ throughout the survey period, showing the contribution percentages to range 18.0 to 78.9 (average: 43.0) for PCDDs, 7.1 to 61.2 (average: 21.0) for PCDFs and 46.9 to 96.2 (average: 71.9) for Co-PCBs, respectively (Fig. 3). From this result, it was revealed that all dioxin analogues are mostly present in the vapor phase in the high air temperature. This finding is very important because chemicals in the vapor phase have a great impact for their pollution to green vegetables.

Literature cited

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Table 1. Concentration of PCDD, PCDF and Co-PCB congeners in ambient air at Hirakata, Osaka, Japan

Sampling period	98. 9		98. 10		98 .11		98 .12		99. 2		99. 3		99. 4	
Ave. temp (℃)	26.3		21.5		10.9		8.00		7.20		8.95		14.0	
Phase	V	P	V	P	V	P	V	P	V	P	V	P	V	P
TCDDs (pg/m^3)	2.16	0.16	0.83	0.13	4.60	0.94	1.31	1.25	1.49	0.45	1.64	0.18	0.52	0.20
PeCDDs (pg/m^3)	3.09	1.37	0.41	0.40	1.28	3.51	0.28	2.65	0.52	1.31	1.19	0.65	0.14	0.48
HxCDDs (pg/m^3)	1.77	1.16	0.27	1.26	0.40	5.13	0.49	3.95	0.81	4.97	0.23	1.55	0.07	0.64
HpCDDs (pg/m^3)	1.31	0.95	0.13	1.28	0.15	2.54	0.55	2.66	0.28	0.28	0.03	1.21	0.03	0.69
OCDD (pg/m^3)	2.28	1.08	0.24	1.40	0.40	2.92	1.03	2.88	0.44	0.44	0.28	1.40	0.08	0.57
Sum (pg/m^3)	10.6	4.73	1.89	4.47	6.83	15.0	3.65	13.4	3.54	7.44	3.36	4.98	0.84	2.58
TEQ (fg/m^3)	577	155	54.0	43.0	101	207	178	160	138	382	38.0	64.0	10.0	46.0
TCDFs (pg/m^3)	6.58	0.50	1.96	0.41	10.7	2.51	24.9	3.45	3.86	1.45	3.95	0.22	0.23	0.28
PeCDFs (pg/m^3)	2.26	0.77	1.22	1.01	4.50	7.57	0.98	5.16	0.73	3.02	2.40	1.06	0.36	0.54
HxCDFs (pg/m^3)	1.22	1.39	0.26	2.01	0.68	9.90	0.12	2.73	0.18	3.12	0.44	2.21	0.07	0.65
HpCDFs (pg/m^3)	0.39	1.55	0.07	3.20	0.12	4.77	0.03	3.63	0.18	0.15	10.7	1.81	0.03	0.94
OCDF (pg/m^3)	0.03	0.43	0.03	1.40	0.03	1.88	0.02	1.34	0.03	0.11	0.05	0.70	0.03	0.39
Sum(pg/m^3)	10.5	4.65	3.54	8.02	16.0	26.6	26.0	16.3	4.97	7.84	17.5	5.99	0.72	2.79
TEQ (fg/m^3)	160	101	25.0	145	104	881	19.0	554	28.0	371	130	177	9.00	109
TCB-1 (pg/m^3)	0.35	0.00	0.08	0.00	0.18	0.01	0.14	0.02	0.19	0.19	0.20	0.01	0.06	0.01
TCB-2 (pg/m^3)	4.15	0.06	0.29	0.03	0.44	0.06	0.44	0.13	0.67	0.67	0.42	0.05	0.21	0.03
PeCB (pg/m^3)	0.50	0.02	0.03	0.02	0.20	0.08	0.10	0.19	0.17	0.17	0.14	0.03	0.05	0.03
HxCB (pg/m^3)	0.06	0.01	0.01	0.02	0.03	0.06	0.02	0.09	0.03	0.03	0.10	0.10	0.01	0.02
Sum (pg/m^3)	5.05	0.09	0.40	0.07	0.84	0.21	0.70	0.43	1.06	1.06	0.86	0.18	0.33	0.08
TEQ (fg/m^3)	56.0	2.00	10.0	2.00	23.0	8.00	12.0	13.0	20.0	17.0	25.0	4.00	5.00	3.00
Total (pg/m^3)	26.1	9.46	5.82	12.6	23.7	41.9	30.4	30.1	9.58	16.4	21.8	11.2	1.89	5.46
Total TEQ (fg/m^3)	793	258	90.0	190	228	1096	208	727	187	771	193	245	24.0	158

V : Vapor phase P : Particle phase TCB-1 : 3,4,4',5-TCB TCB-2 : 3,3',4,4'-TCB
PeCB: 3,3',4,4',5-PeCB HxCB: 3,3',4,4',5,5'-HxCB

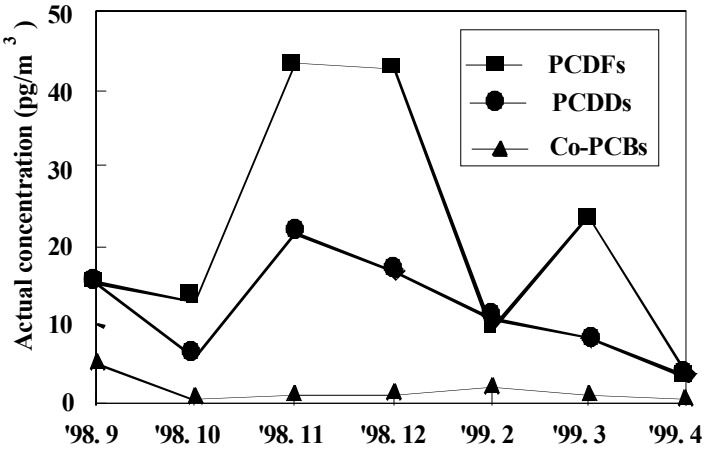

Fig. 1. Monthly alteration on actual levels of PCDDs, PCDFs and Co-PCBs in ambient air at Hirakata, Osaka, Japan

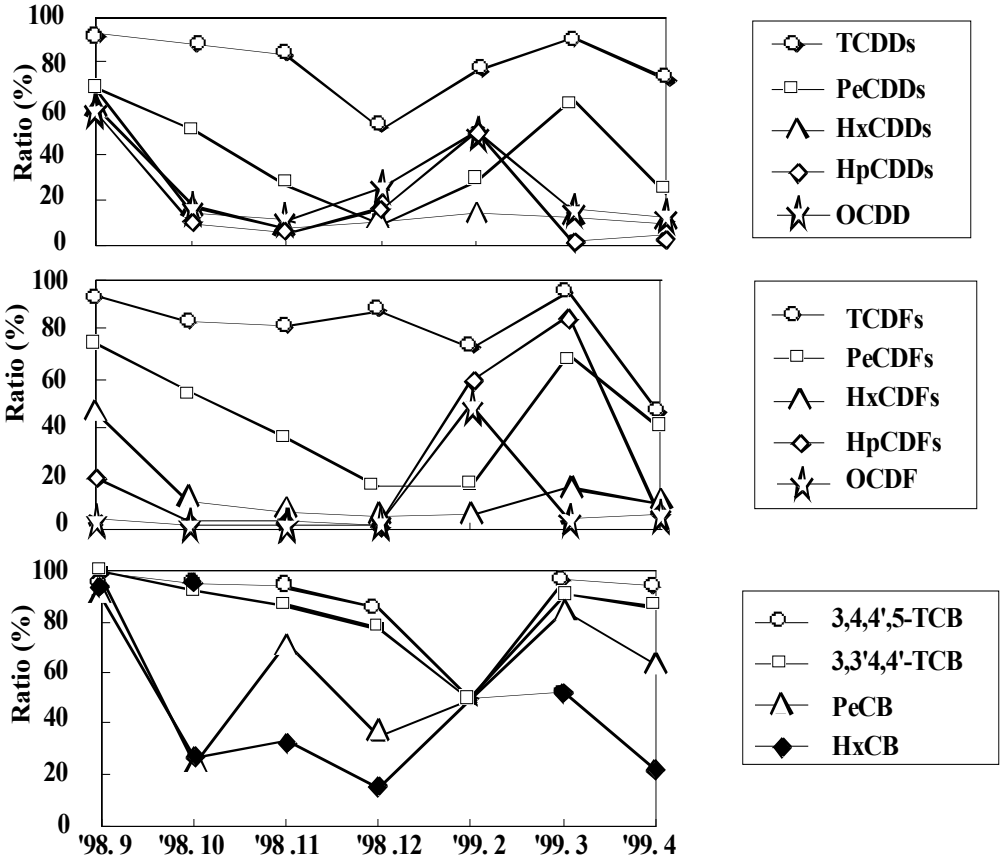

Fig. 2. Monthly alterration on the ratio of PCDD, PCDF and Co-PCB congeners in the vapor phase to their respective total concentration

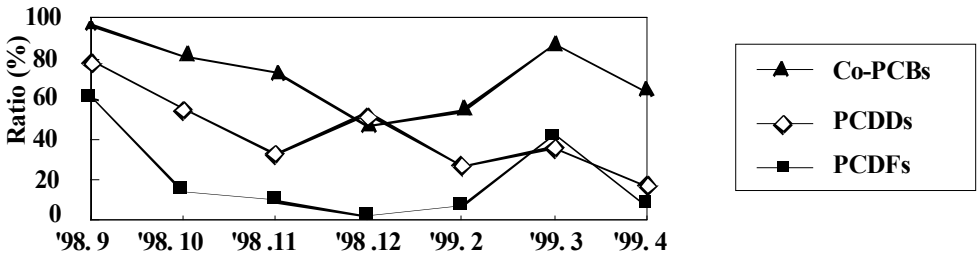

Fig. 3. Monthly alterration on the ratio of PCDDs, PCDFs and Co-PCBs in the vapor phase to their respective TEQ concentration