LEVELS OF PCDDS, PCDFS AND NON-ORTHO COPLANAR PCBS IN DRINKING WATER IN JAPAN

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ABSTRACT

Drinking water samples including home tap water and well water collected in Shiga and Osaka Prefectures, Japan, were analyzed for PCDDs, PCDFs and non-ortho coplanar PCBs. The levels of three chemicals were low ppq levels in all samples analyzed. In addition, the total daily intake of them via water was only 0.0038 to 0.0054% of that via food.

INTRODUCTION

We had already reported Japanese adipose tissues to be averagely polluted with 1486 ppt (on the fat basis) of 2,3,7,8-chorine substituted PCDDs, 70 ppt of 2,3,7,8-chlorine substituted PCDFs and 1529 ppt of non-ortho coplanar PCBs (Co-PCBs)[1]. The contamination routs, however, have yet not been completely cleared in Japan.

In Canada, Birmingham et al. (1989)[2] estimated the daily intakes of PCDDs and PCDFs through various routs. In the report, 96% of the total daily intake was attributable to food. Therefore, we investigated the intakes of PCDDs, PCDFs and Co-PCBs through food in Osaka, Japan[3]. The amounts of PCDDs, PCDFs and Co-PCBs were 40, 135 and 660 TEQ pg/adult/day, respectively. The intakes through other routs, however, have not yet been revealed in Japan.

Therefore, in this study, the contamination levels of PCDDs, PCDFs and Co-PCBs in the drinking water were determined in order to estimate the daily intakes of them via water.

EXPERIMENTAL

Sampling

Drinking waters including home tap water and well water were collected in Nagahama, Shiga Prefecture, and in Hirakata and Osaka, Osaka Prefecture, in October and November, 1991. They were kept at 4°C in a cooling room until analysis.

Analytical procedure

An amount of 50 L of home tap water or well water was filtered through two 1 um and two 0.6 μm glass filters (15 cm diameter). The filters were dried, spiked with $^{13}C_{12}$ labeled PCDD, PCDF and Co-PCB internal standards and extracted with 350 ml of benzene for 8 hrs. under reflux. The extract was con-

Table 1. Levels (ppq) of PCDDs, PCDFs and Co-PCBs in drinking water samples

Compound	Sample component	Location and Collection Date						
		Laboratory blank	Well water			Home tap water		
			Nagahama Nov. 2	Nagahama Nov. 2	Hirakata Oct. 29	Hirakata Oct. 31	Osaka Oct. 23	Osaka Oct. 24
2,3,7,8-T4CDD	Soluble	ND(0.04)	ND(0.04)	ND(0.05)	ND(0.03)	ND(0.03)	ND(0.05)	ND(0.03)
	Particle-bound	ND(0.04)	ND(0.04)	ND(0.04)	ND(0.03)	ND(0.06)	ND(0.03)	ND(0.04)
1,2,3,7,8-P5CDD	Soluble	ND(0.05)	ND(0.04)	ND(0.04)	ND(0.04)	ND(0.03)	ND(0.04)	ND(0.03)
	Particle-bound	ND(0.07)	ND(0.04)	ND(0.04)	ND(0.07)	ND(0.03)	ND(0.03)	ND(0.03)
1,2,3,4,7,8-H6CDD	Soluble	ND(0.10)	ND(0.07)	ND(0.06)	ND(0.07)	ND(0.07)	ND(0.05)	ND(0.05)
	Particle-bound	ND(0.07)	ND(0.08)	ND(0.03)	ND(0.07)	ND(0.05)	ND(0.04)	ND(0.03)
1,2,3,6,7,8-H6CDD	Soluble	ND(0.10)	ND(0.07)	ND(0.08)	ND(0.06)	ND(0.06)	ND(0.05)	ND(0.05)
	Particle-bound	ND(0.07)	ND(0.06)	ND(0.03)	ND(0.07)	ND(0.05)	ND(0.04)	ND(0.03)
1,2,3,7,8,9-H6CDD	Soluble	ND(0.10)	ND(0.06)	ND(0.06)	ND(0.08)	ND(0.06)	ND(0.05)	ND(0.05)
	Particle-bound	ND(0.07)	ND(0.05)	ND(0.02)	ND(0.07)	ND(0.05)	ND(0.04)	ND(0.02)
1,2,3,4,6,7,8-H7CDD	Soluble	ND(0.05)	ND(0.13)	ND(0.07)	ND(0.05)	ND(0.07)	0.14	0.09
	Particle-bound	ND(0.06)	0.62	ND(0.06)	ND(0.07)	ND(0.08)	ND(0.10)	ND(0.10)
OBCDD	Soluble	ND(0.11)	0.19	0.29	0.72	0.88	0.85	1.33
	Particle-bound	0.40	11.73	0.24	0.74	0.51	0.86	0.58
2,3,7,8-T4CDF	Soluble	ND(0.04)	ND(0.02)	ND(0.02)	ND(0.05)	ND(0.03)	ND(0.03)	ND(0.05)
	Particle-bound	ND(0.03)	ND(0.03)	ND(0.02)	ND(0.02)	ND(0.02)	ND(0.02)	ND(0.02)
1,2,3,7,8-P5CDF	Soluble	ND(0.03)	ND(0.03)	ND(0.01)	ND(0.03)	ND(0.03)	ND(0.03)	ND(0.03)
	Particle-bound	ND(0.03)	ND(0.02)	ND(0.01)	ND(0.03)	ND(0.03)	ND(0.01)	ND(0.01)
2,3,4,7,8-P5CDF	Soluble	ND(0.03)	ND(0.03)	ND(0.01)	ND(0.03)	ND(0.03)	ND(0.03)	ND(0.03)
	Particle-bound	ND(0.03)	ND(0.02)	ND(0.01)	ND(0.03)	ND(0.03)	ND(0.01)	ND(0.01)
1,2,3,4,7,8-H6CDF	Soluble	ND(0.06)	ND(0.04)	ND(0.03)	ND(0.04)	ND(0.06)	ND(0.07)	ND(0.04)
	Particle-bound	ND(0.09)	ND(0.05)	ND(0.04)	ND(0.07)	ND(0.05)	ND(0.05)	ND(0.03)
1,2,3,6,7,8-H6CDF	Soluble	ND(0.06)	ND(0.04)	ND(0.03)	ND(0.04)	ND(0.06)	ND(0.07)	ND(0.04)
	Particle-bound	ND(0.08)	ND(0.05)	ND(0.04)	ND(0.07)	ND(0.04)	ND(0.04)	ND(0.03)
1,2,3,7,8,9-H6CDF	Soluble	ND(0.08)	ND(0.05)	ND(0.04)	ND(0.05)	ND(0.08)	ND(0.08)	ND(0.05)
	Particle-bound	ND(0.11)	ND(0.06)	ND(0.05)	ND(0.08)	ND(0.06)	ND(0.06)	ND(0.04)
2,3,4,6,7,8-H6CDF	Soluble	ND(0.07)	ND(0.05)	ND(0.04)	ND(0.04)	ND(0.07)	ND(0.07)	ND(0.04)
	Particle-bound	ND(0.09)	ND(0.05)	ND(0.04)	ND(0.07)	ND(0.05)	ND(0.05)	ND(0.04)
1,2,3,4,6,7,8-H7CDF	Soluble	ND(0.04)	ND(0.04)	ND(0.02)	ND(0.06)	ND(0.06)	ND(0.05)	ND(0.02)
	Particle-bound	ND(0.06)	ND(0.05)	ND(0.02)	ND(0.04)	ND(0.04)	ND(0.06)	ND(0.02)
1,2,3,4,7,8,9-H7CDF	Soluble	ND(0.04)	ND(0.06)	ND(0.04)	ND(0.05)	ND(0.03)	ND(0.04)	ND(0.02)
	Particle-bound	ND(0.08)	ND(0.05)	ND(0.05)	ND(0.02)	ND(0.04)	ND(0.12)	ND(0.07)
OBCDF	Soluble	ND(0.08)	ND(0.17)	ND(0.14)	ND(0.07)	ND(0.18)	ND(0.10)	ND(0.11)
	Particle-bound	ND(0.12)	ND(0.15)	ND(0.12)	ND(0.12)	ND(0.16)	ND(0.23)	ND(0.13)
3,3',4,4'-T4CB	Soluble	0.52	0.75	1.23	2.29	2.85	1.82	1.35
	Particle-bound	0.13	0.13	0.04	0.23	0.22	0.48	0.45
3,3',4,4',5-P5CB	Soluble	0.02	0.02	0.13	0.10	0.10	0.12	0.07
	Particle-bound	ND(0.04)	0.03	ND(0.02)	ND(0.04)	ND(0.02)	ND(0.01)	0.10
3,3',4,4',5,5'-H6CB	Soluble	0.01	ND(0.04)	ND(0.03)	ND(0.05)	ND(0.04)	0.09	ND(0.03)
	Particle-bound	0.04	ND(0.03)	ND(0.02)	ND(0.05)	ND(0.02)	ND(0.02)	ND(0.02)

Soluble = Compounds from filtrate Particle-bound = Compounds collected from filter
Each figure of parenthesis shows the detection limit.

centrated, replaced completely with n-hexane, and then purified on a multi-layer column containing 10% (w/w) $AgNO_3$-silica (2.0 g), silica (0.6 g), 22% (w/w) H_2SO_4-silica (4.0 g), 44% (w/w) H_2SO_4-silica (2.0 g), silica (0.6 g) and 2% (w/w) KOH-silica with an eluent of n-hexane (80 ml). The eluate was concentrated to 3 ml and chromatographed into two fractions with successive eluents of 33 ml of 1.5% methylene chloride in n-hexane and 67 ml of 50% methylene chloride in n-hexane on an alumina column (5 g, Merck neutral, activate I). The second eluate contaning PCDDs, PCDFs and Co-PCBs was left for dryness in a room temperature and then dissolved with 20 ul of n-decane.

On the other hand, the filtrate was fortified with $^{13}C_{12}$-labeled PCDD, PCDF and Co-PCB internal standards and extracted with metylene chloride. The extract was concentrated , replaced completely with n-hexane and then successively purified on a multi-layer column and an alumina coluumn as described above. The final second fraction from the alumina column was concentrated, left for dryness in a room temperature and then dissolved with 20 µl of n-decane.

Above finally purified samples from the filter and filtrate were separately analyzed for PCDDs, PCDFs and Co-PCBs on Supelco SPB-5 (30 m x 0.32 mm, 0.25 µm) and Supelco 2331 (60 m x 0.32 mm, 0.20 µm) capillary columns in an elecron impact-single ion monitoring mode at a resolution of 7000 using a Hewlett Packard 5890J gas chromatograph-JEOL SX-102 mass spectrometer. The results were corrected for the recovery of $^{13}C_{12}$-labeled internal standards.

RESULTS AND DISCUSSION

Table 1 shows the concentraions of 2,3,7,8 chlorine substituted PCDD and PCDF isomers, and Co-PCB isomers in samples of drinking water collected in Nagahama, Shiga Prefecture, and in Hirakata and Osaka, Osaka Prefecture.

As shown in this Table, values of PCDDs and PCDFs in laboratory blank were extremely low, showing only O8CDD to be detected at a level of 0.40 ppq in the extract from the filter. In all drinking samples analyzed, tetra- through hexachlorinated dibenzo-p-dioxins and tetra- through octachlorinated dibenzofurans were below the detection level (0.02 to 0.23 ppq) defined as two times the noise. 1,2,3,4,6,7,8-H7CDD was present only in the filtrate extracts from home tap water samples collected in Osaka.

O8CDD was found in the most of filter and filtrate extracts from drinking water samples. Compared with filter extract, the filtrate one contained higher or equal the O8CDD level in home tap water samples. This agreeds with the result from finished water samples collected in New York, USA[4]. In the well water, however, O8CDD was abundantly present in the filter extract than in the filtrate one, indicating O8CDD to be predominantly bound on filterable particulates less than 0.6 µm in the well water. Similar results were observed about 2,3,7,8-T4CDD in effluents from Midland Plant sites, The Dow Chemical Company, USA.[5], and about PCDDs and PCDFs in surface water samples near known chemical dump site in Canada[6].

The levels of O8CDD in drinking samples in Japan are similar to those in New York, USA[5] and Sweden[7].

Co-PCB isomers were also detected at low ppq levels (Table 1). Contrast in a case of O8CDD, the level was higher in the home tap waters than in the well water. 3,3',4,4'-T4CB was present as a main component in the both of filter and filtrate extracts. In addition, the filtrate extract contained much higher levels of Co-PCBs than did the filter one.

Table 2. Estimated daily intakes (TEQ pg/adult/day) of PCDDs, PCDFs and Co-PCBs in Japan and Canada

Rout	Japan		Canada	
	PCDDs/PCDFs	Co-PCBs	PCDDs/PCDFs	Co-PCBs
Food	175	660	140	-
Home tap water (Ontario)			0.1	-
Home tap water (Nagahama)	0.0044	0.041		
Home tap water (Hirakata)	0.0015	0.038		
Home tap water (Osaka)	0.0038	0.035		
Well water (Nagahama)	0.027	0.0044		

The daily intakes (TEQ pg/adult/day) of PCDDs, PCDFs and Co-PCBs via drinking water (1.5 L) were calculated on the bases shown in Table 1 and TEF values for PCDDs/PCDFs[8] and Co-PCBs[9] (Table 2).

As shown in Table 2, Co-PCBs gave one digit higher the daily intake than did PCDDs/PCDFs in the home tap water samples. In Canada[2], the estimated daily intake fo PCDDs/PCDFs via water (1.5 L) was reported to be 0.1 TEQ pg/adult/day. However, this study cleared that the intake amount of PCDDs/PCDFs through water in Japan was much smaller (0.0015 to 0.027 TEQ pg/adult/day) than that in Canada. In addition, the total daily intake of PCDDs/PCDFs and Co-PCBs through water was revealed to be only 0.0038 to 0.0054% of that[3] through food in Japan.

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