

Assessment of human exposure to PCDDs, PCDFs and non-ortho coplanar PCBs by human hair as an indicator sample

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1. Introduction

It was revealed that the hair levels of PCBs and polychlorinated quaterphenyls (PCQs) reflected their body burden of Yusho patients¹⁾. Regarding toxic polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), the human hair was also found to be a good indicator sample of their atmospheric burden to human being²⁾. In addition, the hair sample was reported an excellent material for detection of human exposure to PCDDs and PCDFs by cigarette smoking³⁾. These results indicate that hair analysis seems to be one of useful means for monitoring human exposure to PCDDs, PCDFs and non-ortho chlorine substituted coplanar PCBs (Co-PCBs), because the hair can be easily collected from people in wide ranges of age, resident area, eating habits and work. Therefore, in 1995, we developed a new analytical method at ppt level for dioxin analogues (PCDDs, PCDFs and Co-PCBs) in human hair samples⁴⁾.

In this study, we investigated on a difference in the exposure levels of dioxin analogues between normal persons (controls) and municipal solid waste (MSW) incineration workers.

2. Material

Hair samples were collected from 82 male controls and 60 MSW incineration male workers from July, 1994 to July, 1995. After washing with a commercial shampoo, each sample was cut into a length of ca. 5 mm by hair clippers, stirred well up and then lyophilized.

3. Method

Hair analysis was carried out according to our previous method⁴⁾.

After spiking of internal standards (five ¹³C₁₂-PCDDs and five ¹³C₁₂-PCDFs, each 500 pg; three ¹³C₁₂-Co-PCBs, 1000 pg), the hair sample (ca. 7 g) was decomposed in 100 ml of 2N KOH aqueous solution for 4 hrs at room temperature by mechanical shaking. The alkaline solution was extracted twice with 100 ml of n-hexane. The extract was washed with water, dried over anhydrous Na₂SO₄ and then concentrated. The concentrated

with water, dried over anhydrous Na_2SO_4 and then concentrated. The concentrated extract was cleaned up on a multi-layer column containing Na_2SO_4 (2 g), 10%(W/W) AgNO_3 -silica (4 g), silica (0.6 g), 22%(W/W) H_2SO_4 -silica (4 g), 44%(W/W) H_2SO_4 -silica (3 g), silica (0.6 g) and 2%(W/W) KOH -silica (2 g) with an eluent of n-hexane (170 ml). After concentrated to 5 ml, the eluate was chromatographed into four fractions by HPLC with a porous graphitic carbon column. The 3rd. and 4th. fractions were respectively analyzed for Co-PCBs and PCDDs/PCDFs using HRGC-HRMS ($R=7000\sim 10000$).

The concentrations of Co-PCBs, PCDDs and PCDFs were corrected with the recoveries of their respective internal standards.

4. Results and discussion

Table 1 shows the actual concentrations and TEQ (2,3,7,8-TCDD toxic equivalency) concentrations of PCDDs, PCDFs and Co-PCBs in hair samples from controls and MSW incineration workers, and the TEQ ratios of the three chemical congeners in workers versus controls.

Total actual levels of PCDDs, PCDFs and Co-PCBs in controls were 189, 16.6 and 63.3 ppt, respectively. The main components were 1,2,3,4,6,7,8-HpCDD and OCDD for PCDDs, OCDF for PCDFs, and 3,3',4,4'-TCB and 3,3',4,4',5-PeCB for Co-PCBs, respectively.

In workers, the total actual levels of PCDDs, PCDFs and Co-PCBs were 214, 33.3 and 327 ppt, respectively. The main components were almost the same to a case of controls. However, 1,2,3,4,6,7,8-HpCDF was confirmed as one of majors for PCDFs. The total actual PCDD level was almost equal to that of controls. However, the concentrations of toxic lower chlorinated congeners such as TCDD to HxCDDs were remarkably lifted at the levels of 2.8 to 4.8 times greater. For the total actual levels of PCDFs and Co-PCBs, workers were noticeably polluted at 2.3 and 5.2 times higher than did controls. As well as in a case of PCDDs, an elevated of contamination was also confirmed in lower chlorinated congeners of PCDFs and Co-PCBs.

In order to evaluate the toxic effect by dioxin analogues, their 2,3,7,8-TCDD toxicity equivalency quantities (TEQ) were calculated on the basis of I-TEF⁵⁾ and Safe's report⁶⁾. The total TEQ levels of PCDDs, PCDFs and Co-PCBs in controls were 0.744, 0.148 and 1.18 pg/g, respectively. On the other hand, the values of workers were 2.08, 0.720 and 4.36 pgTEQ/g, respectively. These results revealed that the workers were toxicologically exposed to 2.8 times greater of PCDDs, 4.9 times of PCDFs and 3.7 times of Co-PCBs than did controls.

The average TEQ levels of flue gas from 17 continuous combustion type incinerators with big capacity in Japan were arranged in order of PCDFs (20.9 ng/Nm³) > PCDDs (7.90 ng/Nm³) > Co-PCBs (1.46 ng/Nm³)⁷⁾. The greatest emission of PCDFs might be related to the elevated TEQ level in workers (see Table 1). However, although the emitted TEQ amount of Co-PCBs was the smallest among dioxin analogues, the TEQ ratio in hair samples of workers versus controls was more lifted in comparison with that of PCDDs. This result might closely relate to a fact that Co-PCBs gave the greatest bioaccumulation factor among dioxin analogues⁸⁾.

In the workers, a difference in the exposure level was examined on the occupational category (Fig. 1). Groups of Worker A and Worker B engaged mainly in the job concerning to the maintenance and checking for incinerator inside, and to the

Table 1 Concentrations (ppt) and total TEQ levels (pg TEQ/g) of PCDDs, PCDFs and Co-PCBs in hair samples from control persons and MSW incineration workers

Compound	Controls Mean (n=82)	MSW incineration workers Mean (n=60)	Ratio (Worker/ Control)
2,3,7,8-TCDD	0.284	1.35	4.8
1,2,3,7,8-PeCDD	0.111	0.314	2.8
1,2,3,4,7,8-HxCDD	0.271	1.07	4.0
1,2,3,6,7,8-HxCDD	1.42	0.757	0.53
1,2,3,7,8,9-HxCDD	0.326	0.340	1.0
1,2,3,4,6,7,8-HpCDD	9.27	15.3	1.7
1,2,3,4,6,7,8,9-OCDD	177	195	1.1
Total	189	214	1.1
Total TEQ	0.744	2.08	2.8
2,3,7,8-TCDF	0.296	1.11	3.8
1,2,3,7,8-PeCDF	0.149	0.571	3.8
2,3,4,7,8-PeCDF	0.082	0.532	6.5
1,2,3,4,7,8-HxCDF	0.088	0.635	7.2
1,2,3,6,7,8-HxCDF	0.126	0.635	5.0
1,2,3,7,8,9-HxCDF	0.060	0.091	1.5
2,3,4,6,7,8-HxCDF	0.165	0.822	5.0
1,2,3,4,6,7,8-HpCDF	0.971	7.76	8.0
1,2,3,4,7,8,9-HpCDF	0.034	0.114	3.4
1,2,3,4,6,7,8,9-OCDF	14.6	21.9	1.5
Total	16.6	33.3	2.3
Total TEQ	0.148	0.720	4.9
3,3',4,4'-TCB	55.7	314	5.6
3,3',4,4',5-PeCB	6.96	11.5	1.7
3,3',4,4',5,5'-HxCB	0.602	1.30	2.2
Total	63.3	327	5.2
Total TEQ	1.18	4.36	3.7

conveyance of incinerated materials, respectively. As shown in Fig. 1, the TEQ levels of PCDDs (2.29 pg/g) and PCDFs (0.93 pg/g) in the worker A were almost the same to those in the Worker B. However, the Co-PCBs level (14.9 pg/g) was remarkably higher, indicating the hair of Worker A to be polluted 5.4 times greater by Co-PCBs than did the Worker B. This suggests that Co-PCBs are more dangerous compound than PCDDs or PCDFs for the MSW incineration workers. The strategy for the inhalation decrease of dioxin analogues including Co-PCBs is important for the MSW incineration workers. From above result, our study first revealed that MSW incineration workers were remarkably exposed to all dioxin analogues. Hereafter, it is necessary to investigate the indoor environment for dioxin analogues at MSW incineration facilities.

5. Acknowledgement

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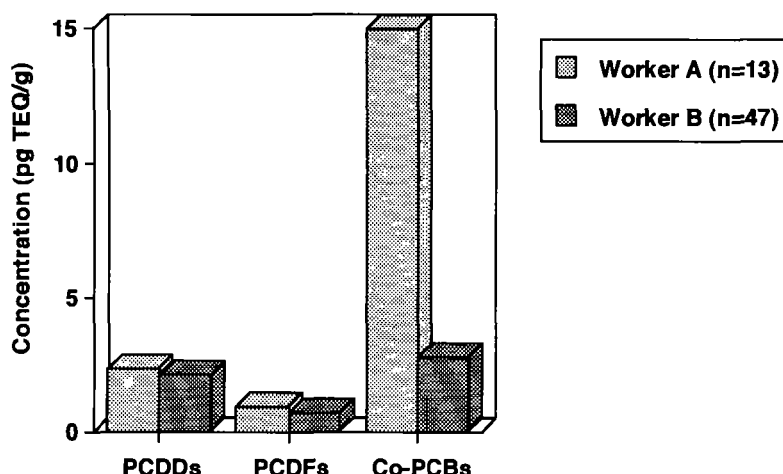


Fig. 1 TEQ level (pg TEQ/g) of PCDDs, PCDFs and Co-PCBs in hair samples from MSW incineration workers

Worker A : engaged in maintenance and inspection of incinerator

Worker B : engaged in occupation except for maintenance and inspection of incinerator

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