PCDD/PCDF Levels in the Blood of Workers in a Pulp and Paper Mill

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1. Introduction

Concern has been voiced about environmental and occupational exposure to polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) that are formed as by-products when pulp is bleached with chlorine-based chemicals[1]. We recently reported the airborne levels of PCDDs/PCDFs at a pulp and paper mill[2]. In the present study, we measured the levels of 2,3,7,8-substituted PCDDs and PCDFs in the blood of workers at the same mill. The primary aim was to compare the levels between potentially exposed workers and non-exposed controls working at other sites in the mill.

2. Materials and methods

2.1. Participants

The mill employees participating in the study comprised 14 workers from the bleaching plant, 20 workers from the paper mill and 14 controls from sites not involving contact with the PCDD/PCDF compounds found in bleached pulp and paper. The sites in the paper mill that involved contact with bleached pulp or paper were the wire sections, the dry ends and the rewind areas of the paper machines as well as the stock department. All participants had worked for more than five years at the mill, the longest period of employment being 37 years. The age of the workers ranged from 26 to 60 years. The participants were interviewed about nutritional and smoking habits known to affect the concentrations of PCDDs/PCDFs in blood lipids.

2.2. Sample treatment and quantification

Blood specimens were collected in pre-cleaned heparinised[3] glass bottles, and the plasma was frozen immediately after separation and kept frozen until analysis. The blood plasma lipid content was determined by an enzymatic "summation" method[4]. The enrichment procedure was operated manually and was a modification of the methods described by Patterson et al.[5,6] and Nygren [3]. Briefly, the extraction of blood plasma was based on partitioning among hexane, ethyl alcohol and water. The recovered hexane extract was washed with sulphuric acid, followed by washes with deionised water. The extract was passed through a series of five columns with acid-impregnated

silica gel in the first column, potassium silicate in the, activated carbon (18 % Carbopack C on Celite) in the third, cesium silicate in the fourth and acid alumina (Bio-Rad, AG-4) in the fifth.

The 2,3,7,8-substituted PCDDs/PCDFs were separated using high-resolution gas chromatography / high-resolution mass spectrometry and quantified by the isotope dilution technique with $^{13}C_{12}$-labelled congeners as internal standards[7]. We report the results as lipid-adjusted (pg/g) blood plasma concentrations and as toxic equivalents (I-TEQ values) based on the international toxic equivalence factors (I-TEF).

3. Results and discussion

Table 1 presents the lipid-adjusted concentrations of each compound in workers exposed to bleached pulp or paper, and in non-exposed controls. The detection limit for the tetra-, penta-, hexa- and hepta-chlorinated congeners was 0.2 pg/g and that of the octa-chlorinated congener 1 pg/g lipid. The recoveries of the congeners in the plasma samples ranged from 30 % to 76 % and those of the procedure blanks from 54 % to 99%.

The lipid-adjusted levels of the controls were comparable to those reported in other countries[7,8] with the exception of congeners 1,2,3,6,7,8-HxCDD and 1,2,3,4,6,7,8-HpCDF, the levels of which were slightly higher.

According to total PCDD/PCDF I-TEQ values the highest levels were found in bleaching plant workers (61 pg/g-TEQ), the figures being 24 % higher than among the controls (49.3 pg/g-TEQ). The total PCDD/PCDF I-TEQ levels in paper mill workers (59.9 pg/g-TEQ) were 21 % higher than among the controls.

We performed a multivariate analysis of covariance to determine whether there was an association between work involving contact with bleached pulp and paper and PCDD/PCDF concentrations calculated on the lipid basis. We used both absolute and ranked values in the analysis. We examined the effect of work site, simultaneously controlling for the effects of duration of employment, age, body mass index, cigarette smoking and consumption of locally caught fish.

The results were first examined according to work site in the bleaching plant versus the paper mill. We found no statistically significant differences in the results, and therefore the data for all workers in the bleaching plant and the paper mill were subsequently analysed together. Furthermore, when the total PCDD/PCDF levels were examined as pg/g lipid or pg/g-TEQ, separately or together, we found no statistically significant differences between the bleaching plant and paper mill workers and the controls. When examining individual isomers, we noted that the 2,3,7,8-TCDF levels were higher ($p < 0.05$) among bleaching plant workers compared with paper mill workers and controls. Similarly, the 2,3,7,8-TCDD levels were higher ($p < 0.05$) in bleaching plant workers than in paper mill workers. However, the 2,3,7,8-TCDF and 2,3,7,8-TCDD levels detected in the present study were similar to those found in Swedish men without occupational exposure but having a relatively high fish consumption[8].

It is noteworthy that the congener 1,2,3,4,6,7,8-HpCDF, exhibiting somewhat higher levels in all the present participants compared with levels in other countries[7,8], was also found in highest concentration in workplace air samples[2]. The second congener found in elevated amounts, 1,2,3,6,7,8-HxCDD, might reflect high fish consumption[8]. About half the bleaching plant and

paper mill workers, including controls, reported a similar consumption of locally caught fish (1-2 meals of fish/week).

4. Conclusions

There were no statistically significant differences in total lipid-adjusted PCDD/PCDF concentrations in blood plasma between the potentially exposed bleaching plant or paper mill workers and the controls. Therefore, it can be assumed that the bleaching plant and paper mill workers have not been exposed to essentially higher concentrations of these compounds than the controls at their respective workplaces. However, the results on individual isomers suggest that the blood plasma concentrations might be affected by the consumption of locally caught fish.

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5. References

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Table 1. PCDD/PCDF levels in the blood samples of workers in a pulp and paper mill, calculated on lipid basis (pg/g)

Congener	Bleaching plant (n = 14)				Paper mill (n = 20)				Controls (n = 14)			
	Range	Mean	Median	m	Range	Mean	Median	m	Range	Mean	Median	m
2,3,7,8-TCDD	0.6 - 22	5.7	4.9	14	0.2 - 9.3	3.1	2.4	20	1.3 - 10	4.1	3.3	14
1,2,3,7,8-PnCDD	3.4 - 68	24	20	14	6.3 - 39	20	20	20	7.0 - 45	17	15	14
1,2,3,4,7,8-HxCDD	1.7 - 11	3.9	3.2	13	1.5 - 6	3.3	3.0	18	1.8 - 6.1	4	3.9	
1,2,3,6,7,8-HxCDD	75 - 389	160	136	14	70 - 307	168	159	20	87 - 216	150	160	14
1,2,3,7,8,9-HxCDD	2.3 - 27	12	10	12	3.8 - 33	15	16	20	5.8 - 26	12	10	14
1,2,3,4,6,7,8-HpCDD	33 - 202	107	89	14	39 - 294	112	113	20	36 - 317	132	126	14
OCDD	285 - 1471	689	591	14	288 - 1198	625	555	19	369 - 1745	804	772	14
2,3,7,8-TCDF	1.1 - 9.7	3.8	2.9	14	0.2 - 9.3	2.4	1.5	20	0.4 - 5.3	1.9	1.6	13
1,2,3,7,8,-PnCDF	0.7 - 5.2	2.1	1.6	13	0.4 - 6.3	1.8	1.5	20	0.3 - 2.7	1.2	1.1	12
2,3,4,7,8-PnCDF	13 - 76	39	36	14	15 - 85	43	38	20	7.8 - 60	29	27	14
1,2,3,4,7,8-HxCDF	5.9 - 26	14	10	14	7.5 - 32	17	14	20	3.8 - 17	10	11	14
1,2,3,6,7,8-HxCDF	6.3 - 26	13	9.8	14	4.8 - 41	13	11	20	4.4 - 18	9.5	9.1	14
1,2,3,7,8,9-HxCDF	0.6 - 0.6	0.6	0.6	2	0.6 - 2.2	1.2	1.0	5	1.4 - 1.8	1.6	1.7	3
2,3,4,6,7,8-HxCDF	1.6 - 9.4	4.4	4.1	13	1.1 - 10	4.9	4.0	17	2.6 - 10	4.8	4.3	11
1,2,3,4,6,7,8-HpCDF	37 - 262	75	57	14	17 - 103	61	58	20	14 - 136	64	52	14
1,2,3,4,7,8,9-HpCDF	1.5	1.5	1.5	1	0.7	0.7	0.7	1	nd (0.2)	-	-	-
OCDF	nr	-	-	-	nr	-	-	-	nr	-	-	-
PCDD Total	401 - 2190	1002	854		409 - 1886	946	868		508 - 2365	1123	1090	
PCDF Total	68 - 416	153	124		47 - 286	145	67		34.7 - 251	122	108	
PCDD/F Total	469 - 2606	1155	574		456 - 2176	1091	998		543 - 2616	1245	1198	
PCDD I-TEQ	10.8 - 102.2	37.0	31.3		11.6 - 67.5	33.5	31.9		15.0 - 62.2	31.3	30.2	
PCDF I-TEQ	8.5 - 48.1	24.0	21.4		9.1 - 53.3	26.1	22.8		5.3 - 36.7	18.0	16.8	
PCDD/F Total I-TEQ	19.3 - 150.3	61.0	52.7		20.7 - 120.8	59.6	54.7		20.3 - 98.9	49.3	47.0	

n = number of participants
m = number of samples above detection limit
nr = not reported