Occupational contamination with PCDD/Fs during recycling of non-gamma HCH in a Chinese chemical factory. Part II. Workers without chloracne

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Introduction

The authors are involved in an ongoing study among workers in the Dagu Chemical Factory in Tianjin, in which PCP from non-gamma isomers of Hexachlorocyclohexane is produced [1].

In 1997 we reported on the contamination of workers in a factory in which the non-gamma isomers of HCH are recycled [2]. The process involves the heating of the non-gamma Hexachlorocyclohexane during which trichlorobenzene is formed. From our previous study it was known that several workers in the factory have high concentrations of PCDD/F's in their blood. In this paper we report on workers who don't have chloracne.

Experimental Methods

Small samples of bloods were taken and kept frozen until analysis. Because of the small amount of blood available from each individual, samples were pooled. Standard extraction methods were used after adding 17 internal ^{13}C standards. The dioxin analyses were performed by a World Health Organisation "certified" laboratorium. One of the cleanup steps was the use of a carbon column. Samples from the outside of the reactor were extracted with hexane and cleaned by HPLC after the addition of 17 internal ^{13}C standards. HRMS/HRGLC was used for the blood samples and LRMS/HRGLC was used for the reactor sample.

Description of the samples

Sample A is a pool of two samples of workers who worked three years in the TCB factory. Sample B is a pool from three workers who worked only one year in the TCB factory. Sample C is from four workers occupied mainly in the part of the factory where Pentachlorophenol is produced. Sample D is a pool of blood from six workers who did not work in that part of the plant where the non-gamma isomers of HCH were regenerated. They were mainly construction workers and not operators in chemical processes.

Samples taken from the outside of the reactor are samples E, F and G.

Results and Discussion

Non of the workers we studied now had chloracne and from table 1, one can see that the highest concentrations found are round 650 pg/g. The lowest concentration in the workers who have chloracne was 1168 pg/g [2].

Tab 1. PCDD/F in whole blood. Relative (top) and absolute (bottom) concentration (TEQ). Values in pg/g (ppt) lipid based (A,B,C,D) and scrap samples (E,F,G)

Sample	A	B	C	D	E	F	G
2,3,7,8-TCDD	0.0	0.0	4.0	0.0	0.0	0.0	0.0
1,2,3,7,8-PeCDD	4.5	3.2	6.4	4.2	7.5	2.5	2.2
1,2,3,4,7,8-HxCDD	4.5	2.2	4.0	3.0	3.0	2.5	1.8
1,2,3,6,7,8-HxCDD	14.5	15.6	11.8	10.1	17.2	20.6	22.3
1,2,3,7,8,9-HxCDD	12.2	16.7	7.5	8.0	12.0	10.9	14.1
1,2,3,4,6,7,8-HpCDD	17.7	22.3	17.2	17.8	16.5	8.4	12.4
1,2,3,4,6,7,8,9-OCDD	9.8	8.3	16.0	22.6	8.2	1.8	2.7
2,3,7,8-TCDF	0.0	0.0	0.0	0.0	0.0	1.9	1.5
1,2,3,7,8-PeCDF	0.0	0.0	0.0	0.0	4.5	2.9	2.7
2,3,4,7,8-PeCDF	4.4	4.2	5.0	4.7	0.0	9.3	8.4
1,2,3,4,7,8-HxCDF	23.3	18.9	19.6	20.5	15.7	16.9	14.4
1,2,3,6,7,8-HxCDF	5.1	4.5	5.2	5.0	12.0	19.2	16.1
1,2,3,7,8,9-HxCDF	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,3,4,6,7,8-HxCDF	0.9	0.6	0.9	0.9	0.0	1.4	0.6
1,2,3,4,6,7,8-HpCDF	2.7	2.9	2.1	3.0	2.2	1.3	0.7
1,2,3,4,7,8,,9-HpCDF	0.3	0.5	0.2	0.3	0.3	0.1	0.2
1,2,3,4,6,7,8,9-OCDF	0.0	0.2	0.0	0.0	0.7	0.1	0.1
Total percent	100	100	100	100	100	100	100
2,3,7,8-TCDD	0	0	17	0	0	0	0.0
1,2,3,7,8-PeCDD	30	21	27	14	1	2.0	2.0
1,2,3,4,7,8-HxCDD	30	14	17	10	0.4	2	1.6
1,2,3,6,7,8-HxCDD	96	101	50	34	2.3	16.2	20.0
1,2,3,7,8,9-HxCDD	81	108	32	27	1.6	8.6	12.6
1,2,3,4,6,7,8-HpCDD	117	144	73	60	2.2	6.6	11.1
1,2,3,4,6,7,8,9-OCDD	65	54	68	76	1.1	1.4	2.4
2,3,7,8-TCDF	0	0	0	0	0	1.5	1.3
1,2,3,7,8-PeCDF	0	0	0	0	0.6	2.3	2.4
2,3,4,7,8-PeCDF	29	27	21	16	0	7.3	7.5
1,2,3,4,7,8-HxCDF	154	122	83	69	2.1	13.3	12.9
1,2,3,6,7,8-HxCDF	34	29	22	17	1.6	15.1	14.4
1,2,3,7,8,9-HxCDF	0	0	0	0	0	0.0	0.0
2,3,4,6,7,8-HxCDF	6	4	4	3	0	1.1	0.5
1,2,3,4,6,7,8-HpCDF	18	19	9	10	0.3	1.0	0.6
1,2,3,4,7,8,,9-HpCDF	2	3	1	1	0.04	0.1	0.2
1,2,3,4,6,7,8,9-OCDF	0	1	0	0	0.1	0.1	0.1
total	662	647	424	337	13	79	89.6

In the blood samples only 2,3,7,8-substituted PCDD/F's were found. This proves that the samples were not contaminated by sources outside the bodies of the workers. From this the conclusion can be drawn that the minimum concentration for the occurrence of chloracne is higher than 650 pg/g. The former conclusion is only valid when the TEF approach is correct for the outbreak of chloracne.

The difference in concentrations between workers from pool A and pool B is rather small. Other factors than the duration of the exposure seem to play a role.

The main difference in relative amounts of PCDD/F's between samples A and B at one hand and C and D at the other hand is the relative high concentration of the OCDD in the last two samples. For sample C this is not strange because those workers have been working mainly in the PCP plant. The concentrations found in pools C and D are somewhat lower than in pools A and B but the difference is not markedly. The contribution of the OCDD to the total TEQ value is larger in groups C and D. This is not so strange for the workers of group C, because they have been working mainly in the PCP production part of the factory.

The concentrations in the workers of pool D are remarkable because in this case we are dealing with workers who have only incidentally been in the parts of the factory where the reactors are that produce TCB and PCP. The high concentrations found in sample D give rise to concern about a more widespread contamination with PCDD/F's than round the TCB and PCP reactor area's. Workers from a PCP plant do normally only have elevated levels of mainly OCDD in their blood [3] but in this factory the TCB reactor and the PCP reactor are located close to each other, and they are in connection with the open air. This makes it possible that workers from the PCP plant and other workers are contaminated by the TCB plant.

The results of another researchgroup [4] who analysed the concentrations of PCDD/F's outside the factory confirm our conclusions about the more widespread contamination.

When we compare the relative concentrations in the blood samples A and B with the scrap samples E, F and G it is obvious that there is a very good correlation between most of the congeners. The only exception is the 1,2,3,6,7,8-HxCDF, which has a relatively low concentration in the blood samples. The explanation can be that 1,2,3,6,7,8-HxCDF has a relatively low halflive in humans.

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