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Occupational contamination with PCDD/Fs during recycling of non-gamma HCH in a chinese chemical factory.

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Abstract

Workers in a factory in which the non-gamma isomers of HCH was recycled are contaminated with high amounts of PCDD/Fs.

Blood analyses showed concentrations up to 25 ng/g fatt TEQ. The concentrations found are often much higher than the values found for workers in a herbicide plant in Germany. One of the samples (the one with the highest concentration) did not only show the 2378 substituted isomers but also a large number of the other isomers; indicating that the body was not able to metabolize the "not toxic" isomers fast enough.

The relative abundances of the isomers found in the blood is different from that of the normal population in Germany and also from a pooled sample of blood from inhabitants of the town not working in that factory.

Introduction

The authors are involved in an ongoing study among workers in a Chinese factory that produces PCP from non-gamma isomers of Hexachlorocyclohexane ¹

The process involves the heating of the nongamma Hexachlorocyclohexane during which trichlorobenzene is formed. From our previous study it was known that workers in the factory have high concentrations in their blood. In the previous study only pooled samples were analysed. Because we wanted to follow the concentrations in the blood and we also wanted to correlate the concentrations with chloracne, samples from individuals (ca 3ml) were taken now. In order to differentiate between background levels and occupational levels, samples from not exposed individuals were taken.

Experimental Methods

Small samples of blood were taken and kept frozen until analysis. Because of the small size of the samples which could be taken, samples from not exposed individuals were pooled. Standard extraction methods were used after addition of 17 internal ¹³C standards. The dioxin analyses were performed by a World Health Organization "certified" laboratory. One of the cleanup steps was the use of a carbon column. A sample from the outside of the reactor was

Tab 1. PCDD/F in whole blood. Relative (top) and absolute (bottom) concentration (TEQ). Values in pg/g (ppt) lipid based

sample	a	b	c	d	e	f	g	h	pool1	1989a	1994a	1991b	1995b
2,3,7,8-TCDD	1.4	0.0	1.3	2.9	0.0	1.1	4.4	3.2	14.3	8.5	15.2	14.5	13.0
1,2,3,7,8-PeCDD	6.4	5.2	4.7	4.8	4.6	5.3	12.3	2.7	0.0	16.3	16.5	17.1	17.7
1,2,3,4,7,8-HxCDD	4.1	3.4	4.7	3.8	3.4	4.4	6.8	3.0	4.8	2.6	3.6	3.3	3.0
1,2,3,6,7,8-HxCDD	19.8	19.1	19.0	14.8	20.4	23.1	16.3	14.3	7.2	12.9	14.0	12.5	13.5
1,2,3,7,8,9-HxCDD	17.4	8.0	12.4	13.7	22.7	14.2	13.3	11.3	8.1	2.6	2.6	2.0	1.8
1,2,3,4,6,7,8-HpCDD	4.6	5.2	9.3	14.9	10.3	9.2	8.6	11.0	5.3	2.2	2.4	1.5	1.4
1,2,3,4,6,7,8,9-OCDD	2.8	10.5	3.7	6.7	3.5	4.5	1.8	3.4	2.9	1.4	1.9	0.7	0.7
2,3,7,8-TCDF	0.0	0.0	0.0	0.2	0.1	0.2	0.9	0.6	3.3	0.5	1.0	0.3	0.4
1,2,3,7,8-PeCDF	0.1	0.0	0.0	0.2	0.2	0.1	0.4	0.3	1.4	0.2	0.1	0.1	0.1
2,3,4,7,8-PeCDF	5.9	4.8	6.3	7.0	5.2	6.5	9.4	8.5	33.0	43.8	33.5	41.0	41.9
1,2,3,4,7,8-HxCDF	28.7	35.1	30.7	21.5	21.7	22.7	11.4	31.5	7.6	3.6	4.1	3.2	3.0
1,2,3,6,7,8-HxCDF	5.4	7.1	5.2	5.3	4.4	5.1	5.4	6.1	4.3	3.1	3.0	2.3	2.3
1,2,3,7,8,9-HxCDF	0.0	0.0	0.0	0.4	0.3	0.4	1.1	0.5	2.4	0.4	0.0	0.0	0.0
2,3,4,6,7,8-HxCDF	0.4	0.0	0.0	0.8	0.6	0.6	3.8	0.7	3.3	1.0	1.4	1.1	1.1
1,2,3,4,6,7,8-HpCDF	2.8	1.5	2.4	2.7	2.3	2.4	3.6	2.5	1.4	0.6	0.6	0.2	0.2
1,2,3,4,7,8,9-HpCDF	0.2	0.0	0.2	0.3	0.2	0.2	0.3	0.4	0.5	0.0	0.0	0.0	0.0
1,2,3,4,6,7,8,9-OCDF	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0
Total percent	100	100	100	100	100	100	100	100	100	100.0	100.0	100.0	100.0
2,3,7,8-TCDD	106	0	36	49	0	53	988	240	3	3.6	2.9	3.4	2.1
1,2,3,7,8-PeCDD	479	61	136	81	159	253	2740	200	0	6.9	3.15	4	2.85
1,2,3,4,7,8-HxCDD	309	40	134	64	117	212	1513	219	1	1.1	0.69	0.78	0.48
1,2,3,6,7,8-HxCDD	1478	223	546	249	700	1108	3641	1061	1.5	5.46	2.67	2.93	2.18
1,2,3,7,8,9-HxCDD	1302	94	355	230	780	683	2974	833	1.7	1.1	0.49	0.46	0.29
1,2,3,4,6,7,8-HpCDD	344	61	267	250	354	443	1910	813	1.1	0.92	0.45	0.36	0.22
1,2,3,4,6,7,8,9-OCDD	211	123	107	113	120	215	408	249	0.6	0.61	0.37	0.17	0.12
2,3,7,8-TCDF	0	0	0	3	2	9	197	43	0.7	0.23	0.19	0.08	0.06
1,2,3,7,8-PeCDF	5	0	0	3	6	4	97	25	0.3	0.1	0.025	0.02	0.015
2,3,4,7,8-PeCDF	440	56	180	118	177	314	2092	628	6.9	18.5	6.4	9.6	6.75
1,2,3,4,7,8-HxCDF	2146	410	880	361	745	1090	2545	2328	1.6	1.54	0.79	0.75	0.49
1,2,3,6,7,8-HxCDF	402	83	150	89	151	244	1198	454	0.9	1.33	0.58	0.54	0.37
1,2,3,7,8,9-HxCDF	0	0	0	7	10	17	248	40	0.5	0.17	0	0	0
2,3,4,6,7,8-HxCDF	30	0	0	14	22	29	857	50	0.7	0.43	0.26	0.26	0.17
1,2,3,4,6,7,8-HpCDF	211	17	70	46	79	113	806	183	0.3	0.234	0.114	0.044	0.028
1,2,3,4,7,8,9-HpCDF	15	0	5	5	8	9	63	30	0.1	0.015	0.006	0	0
1,2,3,4,6,7,8,9-OCDF	2	0	1	0.5	1	1	31	2	0.0	0.004	0.003	0.001	0.001
total	7480	1168	2867	1682.5	3431	4796	22308	7398	20.9	42.243	19.088	23.395	16.124

a-h workers

pool1 background chinese blood

1989a,1994a, 1991b,and1995b values from ref 2

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extracted with hexane and cleaned by HPLC after the addition of 17 internal ¹³C standards. HRMS/HRGLC was used for the blood samples and LRMS/HRGLC was used for the reactor sample.

Tab 2. TCDD/F in whole blood (values in pg/g whole blood basis) worker g from table 1

1,3,6,8-TCDD	2,0	1,2,4,6,7,9/1,2,4,6,8,9/1,2,3,4,6,8-HxCDD	105.6
1,3,7,9-TCDD	1,5	1,2,3,6,7,9/1,2,3,6,8,9-HxCDD	77.7
1,3,7,9-TCDD	1,0	1,2,3,4,7,8-HxCDD	27.6
1,3,6,9/1,2,4,7/1,2,4,8-TCDD	0,9	1,2,3,6,7,8-HxCDD	66,4
2,3,7,8-TCDD	1,8	1,2,3,7,8,9-HxCDD	54,3
1,2,3,4/1,2,3,7/1,2,3,8-TCDD	2,6	1,2,3,4,6,7-HxCDD	14,4
1,2,4,6/1,2,4,9-TCDD	2,7	<i>total</i>	<i>346,1</i>
1,2,3,6/1,2,7,9-TCDD	0,9		
<i>total</i>	<i>13,5</i>	1,2,3,4,6,8-HxCDF	13.3
		1,3,4,6,7,8/1,3,4,6,7,9-HxCDF	21,8
1,2,3,7/1,4,7,8/1,3,6,9-TCDF	0,2	1,2,4,6,7,8-HxCDF	15,9
1,4,6,7/2,4,6,8/1,2,3,6-TCDF	0,2	1,2,4,6,7,9-HxCDF	4,5
2,4,6,7-TCDF	0,3	1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	46,5
1,2,3,9-TCDF	0,9	1,2,3,6,7,8-HxCDF	21,9
2,3,7,8-TCDF	3,6	1,2,3,4,6,7-HxCDF	16,8
2,3,4,6-TCDF	0,2	1,2,3,6,7,9-HxCDF	5,1
2,3,6,7-TCDF	0,4	1,2,3,4,6,9/1,2,3,6,8,9-HxCDF	4,1
3,4,6,7-TCDF	0,3	1,2,3,7,8,9HxCDF	4,5
<i>total</i>	<i>6,1</i>	2,3,4,6,7,8-HxCDF	15,6
		<i>total</i>	<i>169,9</i>
1,2,4,7,9/1,2,4,6,8-PnCDD	25,8		
1,2,3,6,8-PnCDD	28,1	1,2,3,4,6,7,9-HpCDD	176.5
1,2,4,7,8-PnCDD	7,6	1,2,3,4,6,7,8-HpCDD	348,7
1,2,3,7,9-PnCDD	22,9	<i>total</i>	<i>525.2</i>
1,2,4,6,9/1,2,3,4,7-PnCDD	6,5		
1,2,3,7,8-PnCDD	15,0	1,2,3,4,6,7,8-HpCDF	147,1
1,2,3,4,6/1,2,3,6,7-PnCDD	7,8	1,2,3,4,6,7,9-HpCDF	23,4
1,2,3,8,9-PnCDD	8,4	1,2,3,4,6,8,9-HpCDF	12,6
<i>total</i>	<i>121,9</i>	1,2,3,4,7,8,9-HpCDF	11,5
		<i>total</i>	<i>194,7</i>
1,3,4,6,8-PnCDF	3,7		
1,2,4,6,8-PnCDF	3,0	1,2,3,4,6,7,8,9-OCDD	743.8
2,3,4,7,9-PnCDF	3,2		
1,3,4,7,8/1,2,3,6,8-PnCDF	7,1	1,2,3,4,6,7,8,9-OCDF	57.1
1,2,4,7,8-PnCDF	5,4		
1,3,4,6,7/1,2,4,7,9-PnCDF	21,0		
1,2,4,6,7-PnCDF	3,3		
1,2,3,4,7/2,3,4,6,9-PnCDF	3,9		
1,2,3,4,8/1,2,3,7,8-PnCDF	3,6		
1,2,3,4,6-PnCDF	2,9		
1,2,3,6,7-PnCDF	3,1		
1,2,4,6,9/2,3,4,8,9-PnCDF	5,1		
2,3,4,6,8-PnCDF	3,5		
2,3,4,7,8-PnCDF	7,6		
2,3,4,6,7-PnCDF	8,7		
<i>total</i>	<i>85,0</i>		

HUMAN EXPOSURE

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.

Results and Discussion

In table 1 the results are given for the PCDD/F's found in the blood of the workers together with the results of the control group and the data published for the background in Germany ². It is obvious that the levels controlgroup is rather good comparable with the background levels in Germany. The concentrations in the blood of the workers are much higher than background levels and often even much higher as found in workers from a herbicide plant ³ in Germany. In that plant the same process on non-gamma Hexachlorocyclohexane was used. The worker with the highest concentration in that study did have 1634.8 pg/g lipid. In the group we analysed only one was lower than that. The highest one was even more than ten times higher.

Most of the concentrations found are higher than we found in the pooled samples three years ago.

In table 1 we have also given the relative concentrations and from this table it is clear that the relative concentrations of the different congeners is nearly the same in the blood of all the workers and different from the pattern which is found for the background pool and the background levels in Germany. The highest contribution to the total TEQ is from the 1,2,3,4,7,8-HxCDF. And not from the 2,3,4,7,8-PnCDF.

The contribution of 2,3,7,8-TCDD to the total amount in TEQ is also rather low. It is always lower than 5%.

In one of the samples we found high amounts of non-2,3,7,8-substituted PCDD/Fs. The results are given in table 2. It is also the sample with the highest concentration of 2,3,7,8-substituted PCDD/Fs. It is likely that the amount of PCDD/Fs in the body of this worker is so high that his metabolic system is not able to metabolise the non-2,3,7,8 substituted PCDD/Fs fast enough.

A sample which was taken from the outside of the reactor did contain large amounts of PCDD/Fs. The relative amounts of the congeners found, did differ significantly from the relative amounts in a normal municipal waste incinerator flyash sample. The relative concentrations also differs quite a lot from those found in a laboratory experiment, in which the non-gamma HCH from the same factory was treated with Fe^{3+} as a catalyser ⁴.

More samples have to be analysed before relations can be found between occupational contamination and the source.

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