OCCUPATIONAL CONTAMINATION WITH PCDD/Fs DURING RECYCLING OF NON- GAMMA HCH IN A CHINESE CHEMICAL FACTORY. PART III FORMATION OF PCDD/Fs

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Introduction
In the past we have reported on the high levels of PCDD/Fs in workers from a chemical factory in China .[1] (Dagu Chemical Factory in Tianjin) In one part of the factory nearly all the workers have chloracne and extremely high levels of PCDD/Fs in their body. In that part of the factory the non-gamma isomers of HCH are dehydrochlorinated to trichlorobenzene. To get a better idea about the problem we have investigated the process where most of the workers who are highly contaminated. We did microscale experiments where the non-gamma isomers of HCH were heated while in contact with salts. Also soil samples from the plant area and samples of the HCH were analysed.

Experimental Methods
Mixtures of SiO_2 , non-gamma HCH(5%) and $CuCl_2$(5%) or $FeCl_3$(5%) were placed in an oven as described before[4]. Reaction temperatures of 150, 200 and 250^0 C were used. After the heating of the samples a standard procedure for the analysis of the formed PCDD/F's was used. An experiment without the addition of a copper or iron salt was also was also performed as well as the analysis of the material. Soil samples from the soil in the factory were taken and analysed.

Experimental Results
The material that was used did contain PCDD/Fs in rather high amounts but only the hepta and octa dibenzodioxins and dibenzofurans are present in measurable amounts. The results are given in table1.
The total amount of the PCDD/F's formed during the experiments is the highest at the experimental temperature of 250^0 C with the exception of the copperchloride experiment where the optimum formation temperature is 200^0 C.
The results for those compounds, which are formed in the highest amounts, are given in table 1.

Discussion
From the results as given in table 1 it is clear that PCDD/F's are formed during the labscale experiments and that the scrap samples from the reactor is a mixture of the Cu and Fe experiments. Also the experiment where the heating took place without the addition of metal salts did generate large amounts of PCDD/F's. From the results it is not possible to conclude whether the formation is due to dechlorination of the PCDD/F's in the starting material or formation from the non-gamma HCH or intermediates. The fact that at higher temperatures of the experiments the amount of higher chlorinated PCDD/F's rises conflicts with this. Even the total amount of PCDD/F's found after the experiments is higher with higher temperatures. The relative amounts of the hepta dioxins and dibenzofurans in the starting material and the scrap sample as well as the lab experiments are nearly the same. The relative high concentration of the 1,2,3,4,6,8,9H7CDF

is rather characteristic for the all the samples. Also the rather low amount of the 1,2,3,4,6,7,8H7CDD compared to the 1,2,3,4,6,7,8H7CDD is characteristic.
From the experiments it is clear that the PCDD/F's to which the workers in the plant are exposed are formed at the hot outside of the chemical reactor.
The 2,3,7,8TCDD is a compound that is found in relative low amounts in all the samples. Also the workers have not much elevated quantities of this compound in their bodies.
The relative amounts of PCDD/F's in the soil samples do differ rather much from the scrap samples from the reactor. This may indicate that other processes that do form PCDD/F's are going on in the factory.

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References
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Table 1: Absolute and relative amounts of most abundant compounds found in experiments and scrap samples.

	start.mat. amount		250Cu amount	%	250Fe amount	%	250Bi amount	%	#5 amount	%
T4CDD										
1,2,4,7+a					234	28	22886	24		
1,2,3,8+b					0	0	18112	19		
Total			921	100	829	100	94505	100		
T4CDF										
1,3,4,7			1511	1	0	0		0	105597	53
1,4,6,8			0	0	2792	17	51021	7		0
1,3,4,8			1157	1	375	2	131133	17		0
1,3,4,6+c			5427	3	2886	17	283734	38		0
1,2,4,6+d			1424	1	1822	11	111356	15		0
1,2,3,7+e			10100	5	477	3	17339	2		0
2,3,4,9+f			0	0	124	1	42032	6		0
1,2,7,8			38591	19	234	1	2148	0		0
1,2,6,7+g			1249	1	0	0	3964	1	58036	29
1,4,6,9			0	0	0	0	14652	2		0
2,4,6,7			1239	1	480	3	11245	1	7272	4
2,3,7,8			117652	58	729	5		0		0
2,3,4,6			0	0	882	5	29677	4	13171	7
2,3,4,6			2069	1	0	0	20337	3		0
Total			203052	100	16181	100	751952	100	197914	100
P5CDD										
1,2,4,7,9+h					5251	27	5530	20	78679	29
1,2,3,6,8					4301	22	4756	18	129409	47
Total					19339	100	27065	100	275851	100
P5CDF										
1,2,4,7,8			11453	5	2929	9	1185	3	25663	5
1,2,3,4,7+i			10375	4	4097	12	2915	8	195690	38
1,2,3,4,8+j			189475	79	1455	4	2907	8	47183	9
Total			238532	100	33243	100	35646	100	519459	100
H6CDD										
1,2,4,6,8,9+k					15086	31	3243	43	309168	34
1,2,3,6,7,9+l					15418	32	1375	18	231184	26
1,2,3,4,7,8					3199	7	397	5	15762	2
1,2,3,6,7,8					9191	19	1050	14	200074	22
1,2,3,7,8,9					4384	9	639	8	125896	14
Total					48514	100	7594	100	886638	100
H6CDF										
1,2,3,4,6,8			841	0	3240	13	408	36	62364	11
1,2,4,6,7,8			2489	1	9006	36	561	50	45468	8
1,2,3,4,7,8+m			204853	72	3913	15		0	128993	24
1,2,3,6,7,8			38398	14	2417	10		0	143564	26
Total			283367	100	25254	100	1129	100	546501	100
H7CDD										
1,2,3,4,6,7,9	8754	11	1427	21	22788	34	2981	13	365098	25
1,2,3,4,6,7,8	72995	89	5491	79	44587	66	19211	87	1106450	75
Total	81749	100	6917	100	67373	100	22192	100	1471550	100
H7CDF										
1,2,3,4,6,7,8	22345	60	170016	79	6869	75	2043	50	65634	52
1,2,3,4,6,7,9	3694	10	0	0	0	0	326	8	11099	9
1,2,3,4,6,8,9	9219	25	7415	3	1375	15	752	18	32814	26
1,2,3,4,7,8,9	1814	5	38805	17	860	9	966	24	16252	13
Total	37072	100	214034	100	9103	100	4087	100	125799	100
OCDD	154584		29008		43897		134421		2428060	
OCDF	29257		1349618		29440		12297		125630	
total amount	302668		2225448		293171		1091088		8587410	

a=1,2,4,8; b=1,2,4,6+1,2,4,9; c=1,2,4,8; d=1,2,6,8; e=1,4,7,8; f=1,2,3,4+1,2,3,8; g=1,2,7,9; h=1,2,4,6,8; i=2,3,4,6,9; j=1,2,3,7,8; k=1,2,4,6,7,9+1,2,3,4,6,8; l=1,2,3,6,8,9; m=1,2,3,4,7,9.