PCDDS AND PCDFS WITH CHLORALKALI PATTERN IN SOIL AND SLUDGE SAMPLES

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INTRODUCTION

Rheinfelden is a small city in southwest Germany, where Hüls AG is located. From 1972 to 1986, the company produced PCP/PCP-Na. The levels of PCDDs and PCDFs in surface soil samples were found to decrease with the distance from the production plant. However, the samples from 0 to 100 cm underground showed a unique isomer pattern similar to the "chlorakali pattern" reported in literature[1)], suggesting that the area was used for dumping chemical waste in the past. We analysed 17 samples from different layers of soil in four sites. The total PCDFs was found to be 62000 ng/g. Among these, the level of HexaCDFs was the highest, followed by tetra- and pentaCDFs. Tetra-, penta- and hexaCDDs were below the detection limit. The major isomers of PCDF were identified. The dominating isomers in each homologue group of PCDFs were 1,2,7,8- and 2,3,7,8-substituted. The isomer pattern was compared with that of municipal incineration exhaust. This paper presents the analytical results, isomer patterns and homologue profiles of PCDDs and PCDFs in the samples.

EXPERIMENTAL

After the sample was freeze-dried and homogenized, 1 to 20 g was spiked with $^{13}C_{12}$-labelled PCDDs and PCDFs standard and Soxhlet extracted with toluene for 18 hours. The toluene extract was loaded onto a macro alumina column packed with 25g alumina (Woelm B Super I) and prewashed with 100 mL hexane. The column was eluted with 100 mL benzene to remove sulfur. Then 200 mL of 98:2 hexane/dichloromethane were used to elute the column and remove the bulk PCBs. The PCDDs and PCDFs were eluted with

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150 mL 1:1 hexane/dichloromethane. The PCDD and PCDF fraction was further cleaned up on a "mixed" column of silica and silica/H_2SO_4 and on a small column of basic alumina. Recovery of ^{13}C-2,3,7,8-TCDD was determined by addition of $^{13}C_6$-1,2,3,4-TCDD immediately prior to the GC/MS analysis. Isomer-specific PCDD and PCDF analysis was carried out by a HP low resolution GC/MS in multiple ion selection mode. For tetra- to hexa- CDD/F, a 30 meter SP-2330 GC column was used and for hepta- and octa- CDD/F, a 30 meter DB-5 GC column was used.

Table 1: PCDD/F concentrations in soil samples from Rheinfelden, in ng/g

Sample No.	T1/78	T1/79	T1/80	T1/81	T2/82	T2/83	T2/84	T2/85	T2/86
Depth (cm)	0-10	10-35	35-50	50-100	0-15	15-30	35-45	45-60	60-75
TCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
HxCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
HpCDD	1.1	0.7	0.7	0.1	0.7	0.7	0.7	3.4	0.2
OCDD	14.2	12.4	1.6	0.3	13.0	3.9	1.3	2.9	1.2
Total PCDDs	15.3	13.1	2.3	0.4	13.7	4.6	1.9	6.3	1.4
TCDF	17.3	17.2	194.0	0.3	16.0	23.6	108.1	514.7	501.7
PeCDF	34.2	47.3	227.1	1.1	32.5	36.8	116.7	474.2	1182
HxCDF	37.1	59.6	169.2	1.9	37.7	40.7	168.9	625.7	2477
HpCDF	11.0	16.5	36.9	0.8	9.9	11.2	42.8	77.4	207.6
OCDF	6.6	7.7	17.6	0.4	7.5	7.6	17.2	40.1	84.8
Total PCDFs	106.2	148.3	644.8	4.5	103.6	119.9	453.7	1732	4454
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8-HxCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDD	0.53	0.40	0.10	0.03	0.37	0.42	0.28	2.23	0.17
2,3,7,8-TCDF	6.17	7.63	81.68	0.13	6.27	9.67	36.24	145.38	163.0
1,2,3,7,8-PeCDF	13.63	24.47	96.36	0.51	16.41	18.28	55.34	182.66	555.0
2,3,4,7,8-PeCDF	4.52	5.59	39.82	0.10	3.67	4.20	14.44	39.58	92.9
1,2,3,4,7,8-HxCDF	24.18	44.42	110.02	1.37	28.47	30.34	122.77	458.90	1884
1,2,3,6,7,8-HxCDF	3.56	8.58	23.46	0.20	4.32	5.11	19.64	94.23	348.0
1,2,3,7,8,9-HxCDF	0.27	0.42	1.72	0.03	0.28	0.28	2.57	3.64	9.78
2,3,4,6,7,8-HxCDF	0.28	0.78	3.60	0.04	0.40	0.46	1.81	4.53	19.92
1,2,3,4,6,7,8-HpCDF	6.99	9.29	21.81	0.50	5.86	6.77	24.50	49.34	125.68
1,2,3,4,7,8,9-HpCDF	2.44	4.22	10.83	0.14	2.67	3.24	10.70	20.34	60.59
TE-BGA	5.74	9.67	38.53	0.25	6.36	7.28	27.07	100.52	320.12
I-TE	6.51	10.36	47.12	0.26	6.74	7.72	28.66	100.35	318.62

RESULTS AND DISCUSSION

The PCDD and PCDF concentrations are shown in Tables 1 and 2. Tetra-, penta- and hexaCDDs could not be detected. Hepta- and octaCDD concentrations were lower than their correspondent PCDFs. PCDFs dominate over PCDDs. Among the PCDFs, hexaCDFs are the highest, followed by tetra- and pentaCDFs. The dominating isomers in each homologue group of PCDFs are 1,2,3,7- and 2,3,7,8- substituted. All the samples

Table 2: PCDD/F concentrations in soil and sludge samples from Rheinfelden, in ng/g

Sample No.	T2/87	T2/Sludge	T3/88	T3/89	T3/90	T3/200	T4/201	T4/202
Depth (cm)	75-90	unknown	0-15	15-30	30-45	45-60	0-15	15-30
TCDD	ND	ND	ND	ND	ND	ND	ND	ND
PeCDD	ND	ND	ND	ND	ND	ND	ND	ND
HxCDD	ND	ND	ND	ND	ND	ND	ND	ND
HpCDD	0.1	1.5	1.1	0.4	0.1	0.0	1.1	0.4
OCDD	0.4	12.8	17.6	7.6	2.2	0.6	23.7	11.7
Total PCDDs	0.5	14.3	18.7	8.0	2.4	0.6	24.8	12.1
TCDF	27.4	6172	1.8	0.9	0.7	0.2	62.9	68.2
PeCDF	78.5	16677	4.3	1.6	1.2	0.5	89.1	105.2
HxCDF	185.9	29497	8.0	3.6	2.6	1.1	116.9	114.4
HpCDF	46.3	6547	3.3	1.7	1.1	0.6	21.6	25.1
OCDF	15.6	3400	3.3	1.4	0.8	0.3	16.0	15.6
Total PCDFs	353.7	62293	20.7	9.1	6.4	2.8	306.5	328.5
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8-HxCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDD	0.08	1.22	0.55	0.25	0.07	0.02	0.84	0.28
2,3,7,8-TCDF	10.68	1999	0.72	0.33	0.24	0.09	24.20	22.42
1,2,3,7,8-PeCDF	28.30	7188	2.15	0.88	0.56	0.25	31.50	31.03
2,3,4,7,8-PeCDF	9.66	1369	0.46	0.18	0.13	0.06	13.40	16.33
1,2,3,4,7,8-HxCDF	114.6	21667	6.08	2.75	1.94	0.80	71.40	64.16
1,2,3,6,7,8-HxCDF	36.2	4143	1.04	0.43	0.26	0.12	18.02	19.49
1,2,3,7,8,9-HxCDF	1.13	75	0.03	0.01	0.02	0.01	0.79	1.08
2,3,4,6,7,8-HxCDF	1.74	267	0.07	0.04	0.03	0.01	1.91	2.19
1,2,3,4,6,7,8-HpCDF	24.51	3428	1.93	0.98	0.69	0.37	12.39	14.39
1,2,3,4,7,8,9-HpCDF	15.73	2084	0.73	0.35	0.24	0.12	6.40	7.41
TE-BGA	21.56	3887	1.14	0.50	0.34	0.14	17.44	17.23
I-TE	23.10	3985	1.18	0.51	0.35	0.15	20.14	20.90

show similar isomer patterns. The PCDDs and PCDFs concentrations from the sludge sample are the highest. The similar isomer pattern between soil samples and sludge samples and the higher concentration of PCDDs and PCDFs in sludge suggest that the PCDD/F contamination in the area comes from the sludge. Based on the similarity of the isomer patterns, we assume that the sludge is from a chloralkali process.

Figs. 1 and 2 show the isomer pattern from soil and sludge samples from Rheinfelden in comparison with that of municipal incineration exhaust. Fewer TCDF, PeCDF and HxCDF peaks can be detected from the Rheinfelden samples than from municipal incineration exhaust. Also, the homologue profile of the Rheinfelden samples is different from that of municipal incineration exhaust. The homologue profile and isomer patterns of the Rheinfelden samples are different from those of PCP and PCB contaminated with PCDDs and PCDFs [2,3]. The isomer pattern of tetraCDF has some characteristics which are similar to those from pulp bleaching[4].

According to our present knowledge, major sources of PCDDs and PCDFs are thermal processes in the presence of a chlorine source, such as combustion and metallurgic processes, industrial processes based on chlorine chemistry and application of PCDD/PCDF-containing chemicals[5]. Emmissions from thermal sources are considered to be mostly responsible for the atmospheric dioxin background. Industrial sources, as pointed out by Fiedler and Hutzinger[6], may generate high amounts of PCDDs and PCDFs and may or may not enter the environment and contribute to human exposure. The "chloralkali pattern" found in the soil samples suggests that PCDDs and PCDFs formed in the chloralkali process could possibly contribute to human exposure. The "chloralkali pattern" can also be found in sediment and water samples taken downstream from a chloralkali plant near the Gottenburg harbor[7].

The isomer pattern in Figs 1 and 2 can be used as a marker for tracing PCDDs and PCDFs in the environment. The ppm levels of PCDFs, particularly the highly toxic-2,3,7,8-substituted congeners, suggest the importance of intustrial sources of PCDDs and PCDFs.

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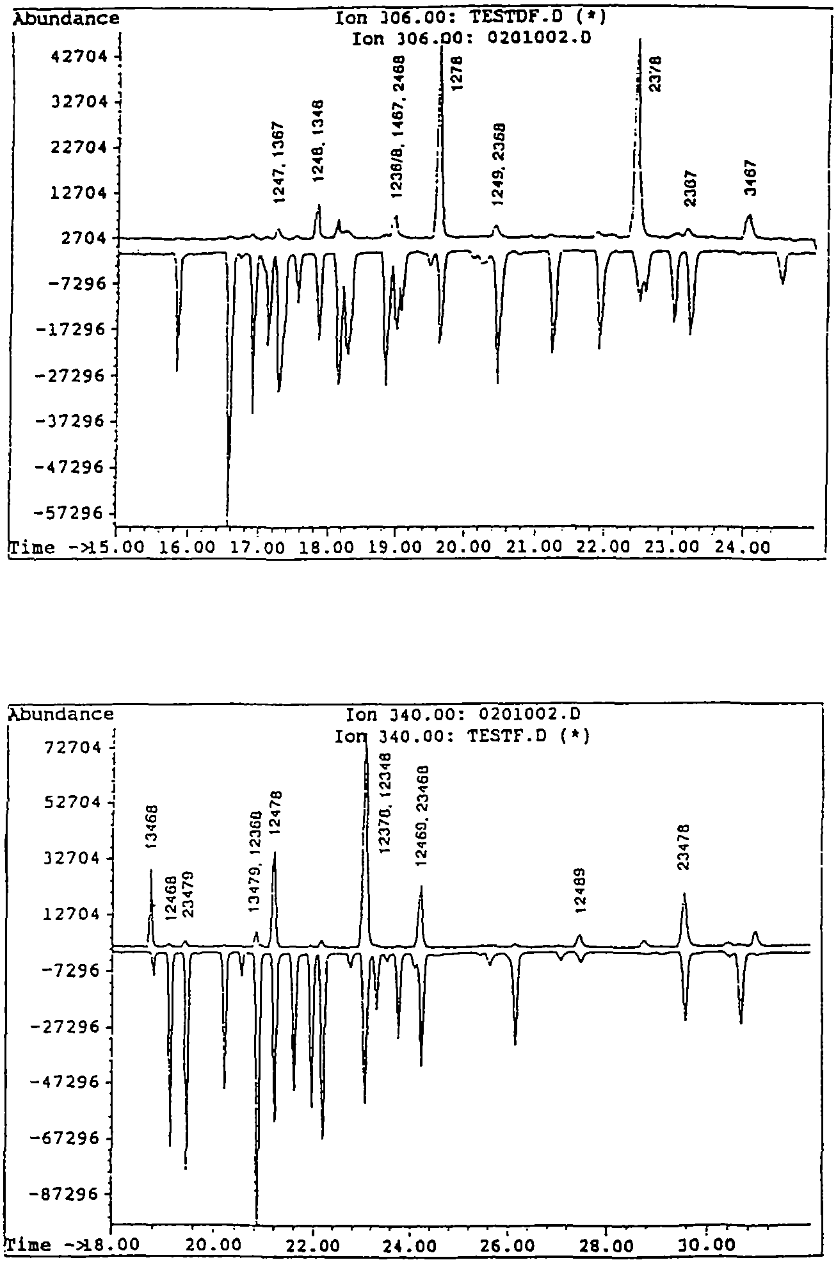

Fig. 1 The identification of TCDF and PeCDF isomers in Rheinfelden samples and comparison with that of municipal incineration exhaust

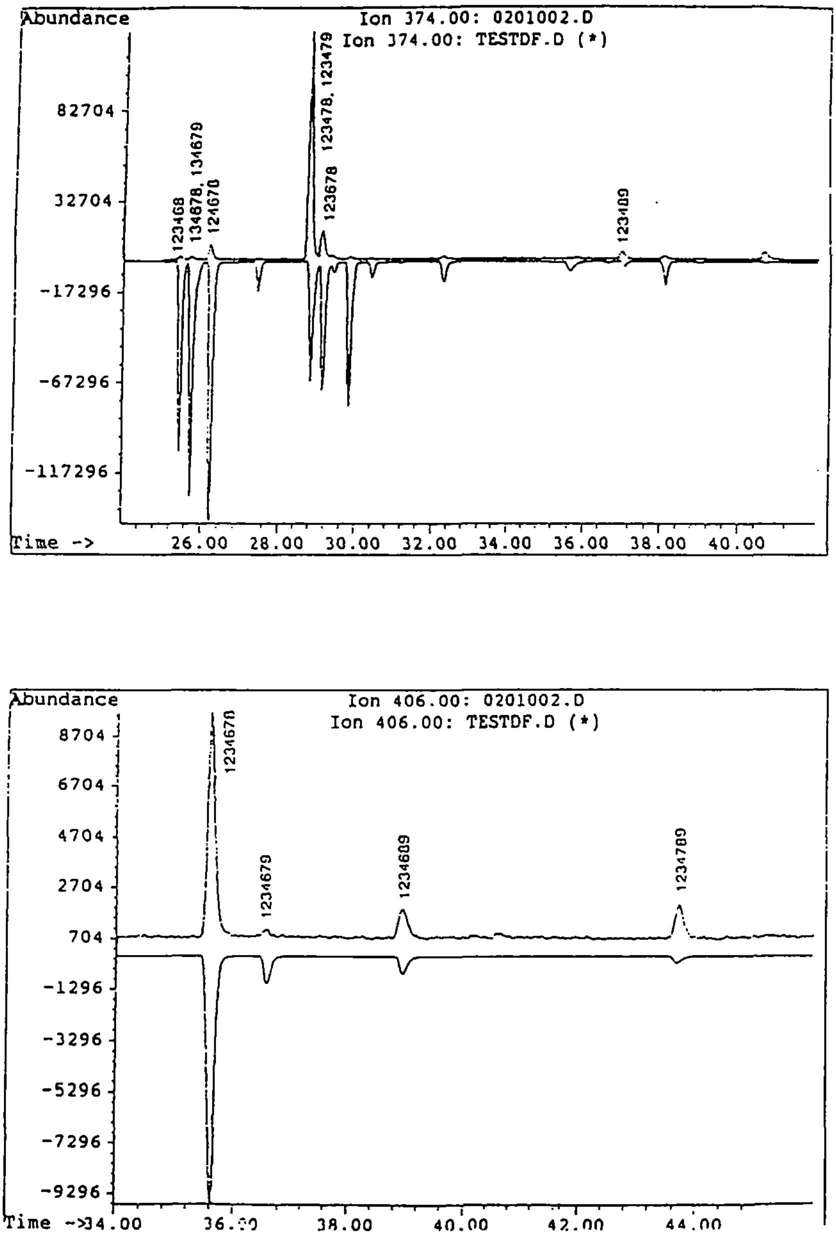

Fig. 2 The identification of HxCDF and HpCDF isomers in Rheinfelden samples and comparison with that of municipal incineration exhaust