PAPER SLUDGE DEPOSITS - HIGHLY CONTAMINATED WITH PCDD/PCDF

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ABSTRACT:

During the 1970's paper sludge residues from a paper mill had been deposited on an area. Since recent years, the area has developped into a residential area. Selected paper sludge residues from this area showed a contamination up to 5165 ng/kg I-TEq. Sixteen soil samples from different points of the area showed contamination of up to 149 ng/kg I-TEq. Indoor dust samples from houses built on the area showed no significantly elevated contamination values to be attributed to the area contamination.

KEYWORDS:

Paper sludge deposits, contaminated soil, indoor dust, chlorine bleached kraft pulp, PCP, PCDD/PCDF, GC-MS.

Introduction

Until the late 70's, pentachlorophenol (PCP) was widely used in the F.R.G. as a biocide in pulp and paper production [1]. As PCP contained, due to the production process, considerable amounts of PCDD/PCDF [2], accordingly high amounts can be expected in pulp and paper sludges.
Another important contamination source is, up till today, the production of chlorine-bleached kraft pulp [3]. Such pulp and paper waste sludges have not only been deposited, according to present criteria, in an inadequate manner, but they were also used in agriculture for soil improvement. In the example of an area contaminated in such a way and serving now as residential area, the contamination situation is described.

Materials and Methods

The area was divided into 12 sectors of about 500 to 1000 square meters each. From each sector, according to its size 20 to 35 soil samples were taken down to a depth of 0.3 m and then united and mixed thoroughly to give a representative sector sample. Some samples were taken down to a depth of 4 meters by ram core sampling.

Indoor dust samples were taken over several weeks with a normal vacuum cleaner. Rough particles like stones, glass fragments, pieces of wood or plastics etc. were removed from the sample.

45 to 80 g of soil or paper sludge sample were freeze-dried. Then the dried sample or 20 g of indoor dust sample respectively were transferred into a hot soxhlet apparatus, spiked with 1 ng of each of 10 different ^{13}C-labelled PCDD/PCDF standards, one for each of the tetra- to octa-chlorohomologues. After extraction for 24 hours with toluene, the extract

was evaporated to 2ml, then chromatographed over an alumina superactive column, a combined silica column and an alumina micro column successively, as described in **Fig. 1**. After concentration to 7 - 10µl in silylated micro vessels (CS Gewindekombi), 2 - 3µl were injected for GC-MS-measurement. GC-MS-analysis was carried out on a HP 5890A/HP 5970 resp. HP 5986 system, using direct coupling (fused silica transfer line of 0.5 x 0.25 mm), on column injection, retention gap (2 m x 0.32 mm fused silica deactivated tubing) and a 50 m SP 2331 (0.25 mm i.d., 0.2/um f.th.) fused silica capillary column with a head pressure of 0.5 bar, carrier gas helium and the following temperature programme: 130°C 1 min, 30°C/min, 200°C, 4°C/min, 240°C 52 min, 5°C/min 250°C 33 min. The GC-MS-transfer line temperature was 280°C. A selected ion monitoring (SIM) mode was used and two characteristic ions for each PCDD/PCDF congener were monitored in three groups with different dwell times, 40, 50, and 100 msec. In case of doubt the $[M\text{-}COCl]^+$-fragment ion was used for identification **[4]**.

Quantitative determination is based on ^{13}C-labelled internal standards. The EI response factors for the isomers in the same chlorohomologous group is assumed to be equal. Results were corrected due to different isotopic distribution of ^{13}C-labelled standards and natural samples. The detection limit varies, according to congener, between 0.2 ng/kg for instance for TeCDD and 2.0 ng/kg for OCDD. Recoveries of internal standards, as determined against external standards, generally varied between 60 - 110 %.

Results

A total area of 7000 m^2 is interspersed with paper sludge lumps down to a depth of 1.8 meters, the lumps on the surface sized between 0.5 to 10 cm.
Sludge lumps gathered from the soil contained between 573 to 5165 ng/kg I-TEq of PCDD/PCDF (**Tab. 1**). For location of the contaminated area 12 representative soil samples and several profile samples were analyzed yielding values between 0.3 and 149 ng/kg I-TEq (**Tab. 1**). PCP contamination of the sludge is comparatively low, lying in the µg/kg range, and does not correlate with PCDD/PCDF contamination which probably is due to the higher water solubility of PCP. The PCDD/PCDF contamination of paper sludges is predominantly caused by the use of PCP in paper production as can be derived from the associated congenere profile in the chromatograms (**Fig. 4**). In case of the lower chlorinated congeners however, a profile typical of chlorine bleaching of pulp can be recognized **[3]**.
The investigation of indoor dust gathered in two houses of that area gave values of 6.6 and 17.7 ng/kg I-TEq PCDD/PCDF which can be regarded as normal background contamination **[5]**.

A great personal engagement has been shown in performing the investigation by A. Lattner, W. Mann and S. Reiß.

References

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Fig. 1: Flow chart of the analytical procedure

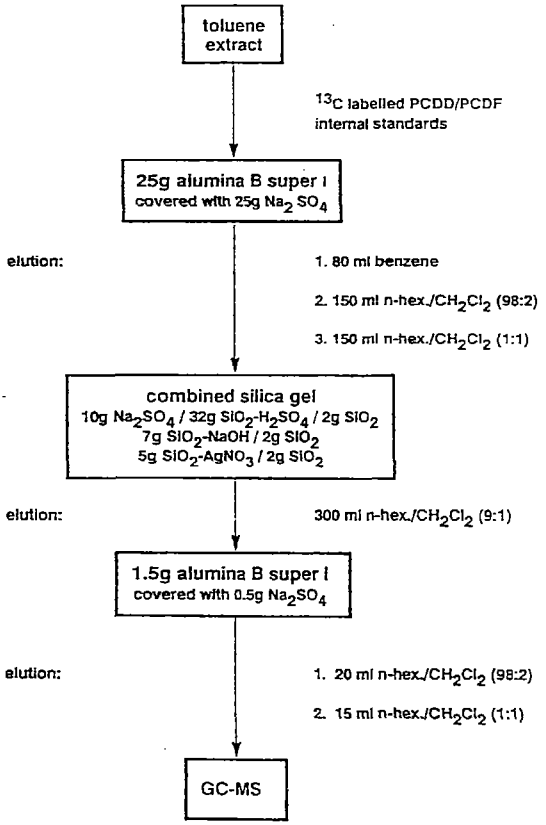


Fig. 2: PCDD/PCDF PROFILES IN HOME DUST SAMPLES

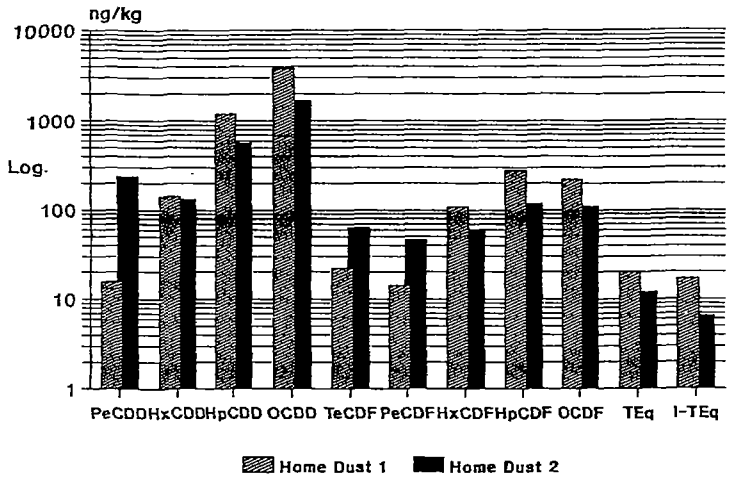


Fig. 3: CONGENERE PROFILE IN HOME DUST SAMPLES

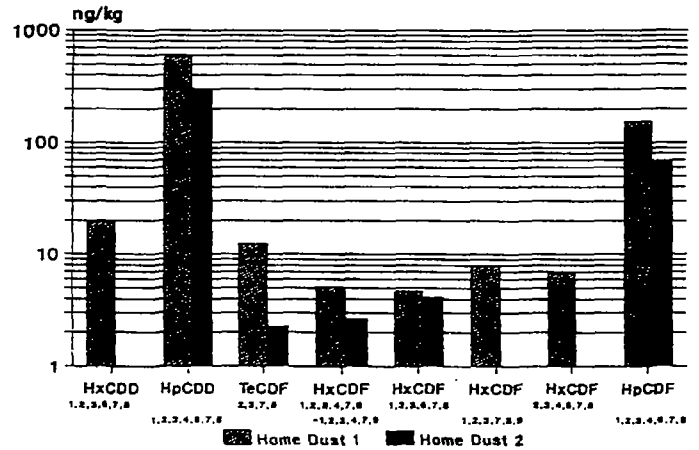
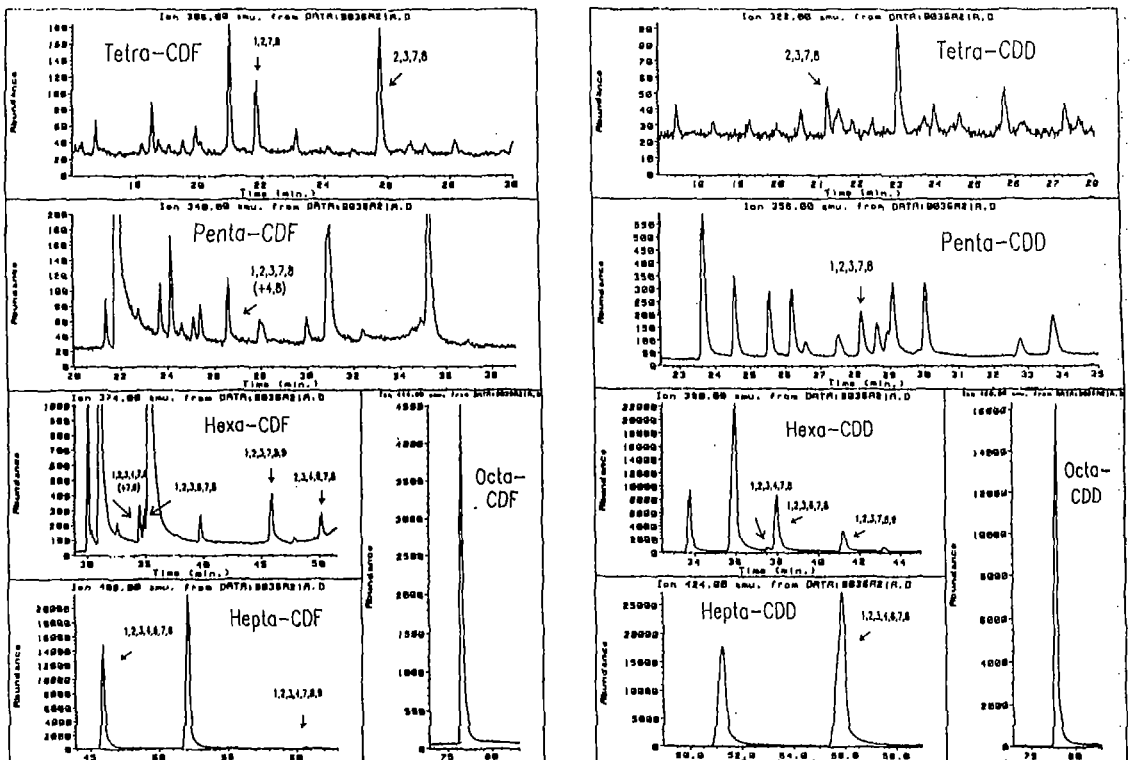


Fig. 4: MASS FRAGMENTOGRAMS OF PCDD/PCDF FOR A PAPER SLUDGE



Tab. 1: CONTENTS OF PCDD/PCDF IN CONTAMINATED SOIL AND PAPER SLUDGE DEPOSITS [ng/kg]

PCDD/PCDF	Soil Samples (n = 16)				Paper Sludge Deposits		
	Min	Max	Mean	50 %	17	18	19
TeCDD (2,3,7,8)	n.d.	6.3	3.7	1.1	20.3	2.4	67.0
Su TeCDD	n.d.	14.0	3.5	1.5	34.8	44.1	93.1
PeCDD (1,2,3,7,8)	n.d.	4.8	3.3		260.9	8.6	7.0
Su PeCDD	n.d.	40.4	10.6		3984.2	255.8	139.0
HxCDD(1,2,3,4,7,8)	n.d.	4.1	4.1		771.0	n.d.	55.2
HxCDD(1,2,3,6,7,8)	n.d.	179.8	61.0	11.9	19273.8	1139.9	1172.7
HxCDD(1,2,3,7,8,9)	n.d.	24.8	15.6	13.8	7951.1	143.5	177.7
SuHxCDD	n.d.	596.9	95.0	13.3	114121.5	5521.1	4387.3
HpCDD(1,2,3,4,6,7,8)	9.5	2309.7	380.7	40.6	153212.4	16774.0	11708.4
SuHpCDD	20.2	2871.3	524.5	51.8	246114.3	26074.1	18306.1
OCDD	32.8	2427.3	440.8	107.2	81475.5	25370.8	15369.7
TeCDF(2,3,7,8)	n.d.	17.0	5.4	2.7	122.8	77.0	90.8
SuTeCDF	n.d.	87.4	19.0	13.6	441.0	272.8	436.6
PeCDF(1,2,3,7,8)+(4,8)	n.d.	27.0	11.3	4.1	73.4	40.4	51.5
PeCDF(2,3,4,7,8)	n.d.	1.3	1.0	0.7	n.d.	n.d.	42.0
SuPeCDF	n.d.	459.6	82.3	13.6	3109.5	1404.7	1619.3
HxCDF(1,2,3,4,7,8)+(7,9)	n.d.	52.2	9.3	2.5	248.1	76.5	345.1
HxCDF(1,2,3,6,7,8)	n.d.	28.9	7.1	1.9	193.2	62.5	206.9
HxCDF(1,2,3,7,8,9)	n.d.	114.9	29.8	5.1	700.2	275.2	791.5
HxCDF(2,3,4,6,7,8)	n.d.	50.5	13.8	1.8	270.1	82.4	208.0
SuHxDCF	n.d.	5678.9	640.4	19.0	31211.5	14630.9	46141.6
HpCDF(1,2,3,4,6,7,8)	5.9	6114.9	710.7	48.0	40271.7	16541.2	35129.3
HpCDF(1,2,3,4,7,8,9)	n.d.	130.8	39.2	5.3	711.7	249.0	501.4
SuHpCDF	5.9	17206.1	2095.6	135.7	108058.0	46908.3	112789.5
OCDF	16.1	5513.2	670.0	58.6	33976.0	17320.5	29293.5
TEq (BGA/UBA)	0.5	224.3	27.7	2.6	6456.9	813.0	1479.7
I-Teq	0.3	149.2	19.5	1.8	5164.9	527.7	916.9

n.d. = not detectable