OCCURRENCE OF PCDD/PCDF IN NEWSPAPERS, MAGAZINES, BOOKS AND OTHER CONSUMER PAPER PRODUCTS

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ABSTRACT:

Thirty-five different paper products and pulps have been investigated for their content of PCDD/PCDF. In the extraction step, highest yields were obtained with toluene as solvent. Highest PCDD/PCDF concentrations, ranging up to 32 ng/kg I-TEq, were found in colour print magazines, printed with the rotogravure printing technique. In paper products based on oxygen-bleached pulp only very low amounts of PCDD/PCDF could be detected.

KEYWORDS:

PCDD/PCDF, extraction yields, chlorine/oxygen-bleached pulps, recycled paper, GC-MS.

Introduction

In the last three years, several authors **[1, 2, 3, 4]** have reported on the formation of PCDD/PCDF in connection with the use of chlorine in the bleaching process, as well as the occurence of PCDD/PCDF in paper products based on such pulps. Also, through the use of pentachlorophenol (PCP) as a biocide in the pulp and paper production process in the F.R.G. until the late 70's, additional amounts of PCDD/PCDF were introduced into pulp and paper products **[5]**. In paper production, different amounts and different types of bleached pulp or recycled paper pulp are used. High quality papers may consist of up to 35 % of chlorine bleached kraft pulp.

As there have been, up to now, no comprehensive investigations on the contents of PCDD/PCDF in various types of paper, we have analyzed 35 different types of paper or paper products like newsprint, magazines, books, hygienic papers based on original pulp (either chlorine or oxygen bleached) or on recycled paper pulp.

Materials and Methods

The analyzed products all were commercially available. The pulp samples were supplied by a paper mill. 30 - 140 g of sample were cut to pieces and transferred into a hot soxhlet

extraction apparatus. Then the sample was spiked with 1 ng of each of 10 different ^{13}C-labelled PCDD/PCDF standards, one for each of the tetra- to octa-chloro-homologues. After extraction for 24 hours with toluene, the extract was evaporated to 2 ml, then chromatographed over an alumina superactive column, a combined silica column and an alumina micro column successively. After concentration to 7 - 10 µl in silylated micro vessels, 2 - 3 µl were injected for GC-MS-measurement [4]. Clean up procedure and GC-MS quantification are described in detail in another report in this volume [5]. The detection limit varies, according to congener, between 0.09 ng/kg for instance for TeCDD and 1.0 ng/kg for OCDD. Recoveries of internal standards, as determined against external standards, generally varied between 60 - 110 %.

Results

For choice of the most effective extraction solvent, two different types of paper were extracted each with ethanol (96 %), toluene/ethanol (32/68), and toluene. With toluene the overall extraction yields are significantly better, as **Fig. 1** shows. It has to be noted, however, that ethanol proved better in extracting higher chlorinated furans.

Surprisingly high levels of PCDD/PCDF ranging up to 32 ng/kg I-TEq were found in colour print magazines, printed with the rotogravure printing technique (**Tab. 1**). Newsprint and hygienic papers based on recycled paper shows values up to 17 ng/kg I-TEq (**Tab. 2**). A pocket book, printed in 1961 also shows comparably high contamination. Newspapers printed on normal newsprint with no use of recycled paper show a considerably lower contamination (**Tab. 1**). Papers based on oxygen-bleached or unbleached pulp also show in general a rather low contamination by PCDD/PCDF (**Tab. 2**). Here, the normally high values of 2,3,7,8- and 1,2,7,8-TCDF as typical for chlorine-bleached pulp, are reduced to a very low level (**Fig. 2**). Also, accordingly to results given in **Tab. 3** it seems possible to produce high-quality kraft pulp which is equally low contaminated like sulfite pulp.

From the data obtained in our investigations it can be estimated that the PCDD/PCDF contamination of sewage sludges which normally contain up to 7 % of paper, is only to a rather low degree (approximately 1 ng/kg I-TEq) caused by toilet paper.
A possibly occurring contamination of indoor air for instance in libraries through evaporation of PCDD/PCDF from paper was investigated. Analysis of the indoor air of the library of our institute showed no elevation in PCDD/PCDF values in comparision to outdoor levels.

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: COMPARISION OF THE EXTRACTION EFFICIENCY FOR 2,3,7,8 - SUBSTITUTED PCDD/PCDF WITH THREE DIFFERENT SOLVENTS

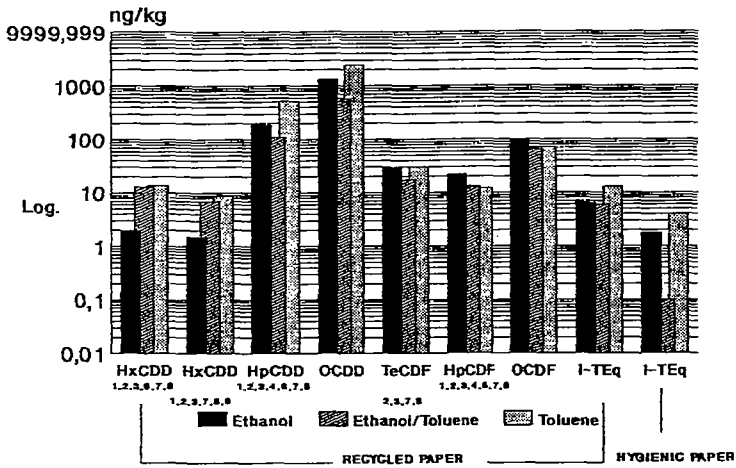
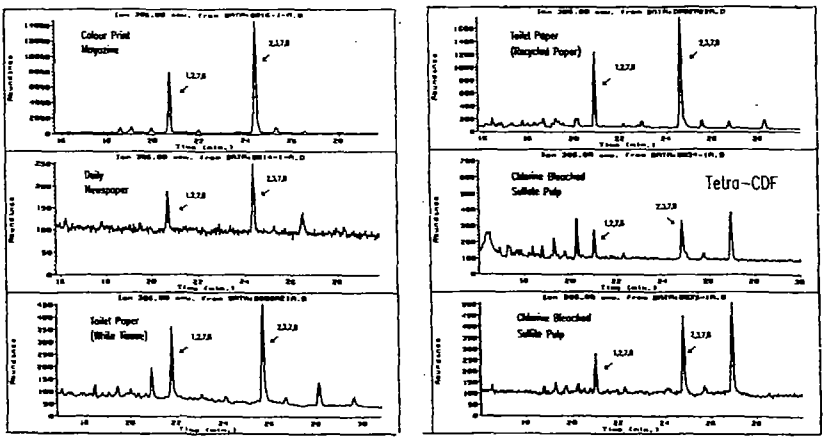


Fig. 2: MASS FRAGMENTOGRAMS OF TeCDF FOR SELECTED SAMPLES



Tab. 1: CONTENTS OF PCDD/PCDF IN MAGAZINES, NEWSPAPERS AND BOOKS [ng/kg]

PCDD/PCDF	Magazines					Daily Newspapers			Books		Detection Limit
	Colour Print			Oecolog.*	Scientific				1947	1961	
	1	2	3	4	5	6	7	8	9	10	
TeCDD (2,3,7,8)	n.d.	3.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09
Su TeCDD	n.d.	3.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14.8	
PeCDD (1,2,3,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.26
Su PeCDD	13.1	1.2	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	51.9	
HxCDD(1,2,3,4,7,8)	5.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
HxCDD(1,2,3,6,7,8)	51.2	10.1	11.0	7.1	n.d.	n.d.	n.d.	2.9	n.d.	12.8	
HxCDD(1,2,3,7,8,9)	47.2	6.0	8.3	n.d.	n.d.	n.d.	n.d.	1.5	n.d.	n.d.	0.33
SuHxCDD	393.0	74.0	92.5	47.7	n.d.	n.d.	9.5	15.3	n.d.	88.9	
HpCDD(1,2,3,4,6,7,8)	1040.1	103.0	123.5	27.6	2.5	8.2	15.7	12.6	2.6	58.0	0.78
SuHpCDD	1907.7	192.3	232.8	61.7	4.5	13.4	28.0	23.1	2.6	108.7	
OCDD	912.9	159.4	125.4	95.9	26.3	11.4	66.8	63.1	10.3	196.3	1.0
TeCDF(2,3,7,8)	40.4	198.3	278.4	23.5	1.3	n.d.	7.3	10.2	1.5	20.8	0.07
SuTeCDF	70.4	371.1	465.4	39.0	11.2	n.d.	11.6	20.4	24.0	84.3	
PeCDF(1,2,3,7,8)+(4,8)	n.d.	6.6	1.6	n.d.	n.d.	n.d.	n.d.	0.6	n.d.	5.5	0.11
PeCDF(2,3,4,7,8)	n.d.	6.5	n.d.	n.d.	n.d.	n.d.	n.d.	0.5	n.d.	n.d.	
SuPeCDF	n.d.	20.6	1.6	1.8	7.4	n.d.	n.d.	3.3	7.6	5.5	
HxCDF(1,2,3,4,7,8)+(7,9)	n.d.	0.6	n.d.	n.d.	0.6	n.d.	n.d.	n.d.	4.6	4.0	0.19
HxCDF(1,2,3,6,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d	n.d.	1.9	1.7	
HxCDF(1,2,3,7,8,9)	n.d.	1.5	2.4	4.8	n.d.	n.d.	n.d.	0.7	n.d.	n.d.	
HxCDF(2,3,4,6,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
SuHxDCF	n.d.	5.0	5.5	13.1	9.4	2.0	n.d.	3.6	16.7	36.2	
HpCDF(1,2,3,4,6,7,8)	n.d.	27.1	57.7	121.9	1.7	9.8	18.8	9.7	5.7	31.2	0.47
HpCDF(1,2,3,4,7,8,9)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	n.d.	
SuHpCDF	n.d.	42.4	90.6	184.1	2.4	15.7	33.1	14.9	11.3	49.1	
OCDF	n.d.	65.5	215.6	467.8	12.8	30.4	75.4	30.7	15.2	32.0	0.98
TEq (BGA/UBA)	29.9	30.0	35.1	6.4	0.5	0.3	1.4	2.2	1.3	8.1	
I-TEq	25.7	29.5	32.2	5.6	0.3	0.2	1.2	2.1	0.9	5.3	

n.d. = not detectable, * Recycled Paper

Tab. 2: CONTENTS OF PCDD/PCDF IN DIFFERENT KIND OF HYGIENIC PAPERS [ng/kg]

PCDD/PCDF	Pulp							Recycled Papers (n = 7)		
	Chlorine Bleached (n = 6)			Oxygen Bleached		Unbleached				
	Min	Max	Mean	17	18	19	20	Min	Max	Mean
TeCDD (2,3,7,8)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	0.7
Su TeCDD	n.d.	2.4	2.4	n.d.	n.d.	0.5	0.4	n.d.	75.6	18.3
PeCDD (1,2,3,7,8)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	1.8	1.8
Su PeCDD	n.d.	9.9	8.9	n.d.	n.d.	n.d.	n.d.	7.3	65.2	22.8
HxCDD(1,2,3,4,7,8)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
HxCDD(1,2,3,6,7,8)	n.d.	4.2	3.5	n.d.	n.d.	n.d.	n.d.	6.3	32.6	17.3
HxCDD(1,2,3,7,8,9)	n.d.	3.0	3.0	n.d.	n.d.	n.d.	n.d.	3.6	12.4	7.7
SuHxCDD	n.d.	26.4	14.8	n.d.	n.d.	0.9	n.d.	41.2	215.5	115.8
HpCDD(1,2,3,4,6,7,8)	3.1	19.9	7.9	9.8	3.7	8.8	4.0	30.0	515.2	137.5
SuHpCDD	4.7	39.9	14.0	15.7	6.1	15.1	6.9	51.6	822.7	233.0
OCDD	8.4	155.5	44.4	70.4	26.7	49.5	11.9	123.6	2414.8	1020.9
TeCDF(2,3,7,8)	2.6	38.1	12.3	n.d.	1.1	n.d.	n.d.	4.7	69.3	28.1
SuTeCDF	2.6	68.7	20.4	n.d.	1.8	n.d.	n.d.	8.1	122.4	49.7
PeCDF(1,2,3,7,8)+(4,8)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	1.4
PeCDF(2,3,4,7,8)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	1.1
SuPeCDF	n.d.	1.0	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	11.8	4.6
HxCDF(1,2,3,4,7,8)+(7,9)	n.d.	n.d.	/	0.3	n.d.	n.d.	n.d.	n.d.	0.9	0.6
HxCDF(1,2,3,6,7,8)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	0.9	0.3
HxCDF(1,2,3,7,8,9)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	1.1
HxCDF(2,3,4,6,7,8)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	0.2
SuHxDCF	n.d.	2.5	1.0	1.9	n.d.	0.4	n.d.	2.0	9.4	5.9
HpCDF(1,2,3,4,6,7,8)	0.5	3.1	1.6	3.3	0.7	1.0	n.d.	3.9	42.3	27.7
HpCDF(1,2,3,4,7,8,9)	n.d.	n.d.	/	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	0.9
SuHpCDF	0.5	7.0	3.6	8.3	1.4	2.5	n.d.	9.4	126.6	52.5
OCDF	2.2	10.9	5.3	9.6	3.5	3.0	n.d.	15.3	266.8	133.3
TEq (BGA/UBA)	0.7	4.3	1.9	0.3	0.2	0.2	<0.1	2.4	17.1	9.8
I-TEq	0.5	4.0	1.7	0.2	0.2	0.2	<0.1	1.9	15.3	8.4

n.d. = not detectable, Detection Limits see Tab. 1

Tab. 3: CONTENTS OF PCDD/PCDF IN PULP AND PAPER PRODUCTS [ng/kg]

	Chlorine Bleached Pulp				Coffee Filter			
PCDD/PCDF	Kraft 28	Kraft 29	Sulfite 30	Diaper 31	Bleached 32	Unbleached 33	Cardboard 34	Form 35
TeCDD (2,3,7,8)	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Su TeCDD	1.9	2.2	n.d.	n.d.	n.d.	8.3	n.d.	n.d.
PeCDD (1,2,3,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Su PeCDD	n.d.	2.6	n.d.	n.d.	n.d.	13.5	4.3	1.1
HxCDD(1,2,3,4,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HxCDD(1,2,3,6,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10.2
HxCDD(1,2,3,7,8,9)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.7
SuHxCDD	n.d.	n.d.	n.d.	n.d.	n.d.	4.1	2.5	64.4
HpCDD(1,2,3,4,6,7,8)	n.d.	n.d.	4.9	n.d.	1.6	n.d.	28.2	10.7
SuHpCDD	n.d.	n.d.	7.9	n.d.	2.6	n.d.	50.1	19.7
OCDD	1.6	2.2	30.1	2.7	4.1	1.4	312.5	18.7
TeCDF(2,3,7,8)	5.1	1.8	3.8	1.0	5.9	n.d.	4.7	9.4
SuTeCDF	14.6	12.0	6.4	1.6	11.5	n.d.	7.6	17.3
PeCDF(1,2,3,7,8)+(4,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PeCDF(2,3,4,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SuPeCDF	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	5.7
HxCDF(1,2,3,4,7,8)+(7,9)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.8	n.d.
HxCDF(1,2,3,6,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	n.d.
HxCDF(1,2,3,7,8,9)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HxCDF(2,3,4,6,7,8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SuHxDCF	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.5	0.9
HpCDF(1,2,3,4,6,7,8)	n.d.	n.d.	0.6	n.d.	n.d.	n.d.	4.9	0.6
HpCDF(1,2,3,4,7,8,9)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	n.d.
SuHpCDF	n.d.	n.d.	1.4	n.d.	n.d.	n.d.	16.1	0.6
OCDF	n.d.	n.d.	2.8	n.d.	n.d.	n.d.	30.2	n.d.
TEq (BGA/UBA)	1.5	0.3	0.5	0.1	0.7	0.3	1.4	3.3
I-TEq	1.4	0.2	0.5	0.1	0.6	<0.1	1.3	2.7

n.d. = not detectable, Detection Limits see Tab. 1