

PCDDs, PCDFs AND SOME UNKNOWN CHLORINATED PLANAR AROMATIC COMPOUNDS
IN PULP MILL PRODUCTS, EFFLUENTS, SEDIMENTS AND EXPOSED BIOTA

Jaana Koistinen¹, Rainer Herzs Schuh² and Joachim Stach²

¹University of Jyväskylä, Department of Chemistry
Tellervonkatu 8, SF-40100 Jyväskylä, Finland

²Karl-Marx University, Department of Chemistry
Talstrasse 35, Leipzig 7010, GDR

ABSTRACT

Pulp and paper mill products, effluents, sediments, fishes and mussels were analysed for PCDDs and PCDFs by HRGC/LRMS to study compounds associated with chlorine bleaching. In these analyses unknown chlorinated planar aromatic compounds were observed as TCDD and PnCDD interferences at concentration levels orders of magnitudes higher than PCDDs and PCDFs.

INTRODUCTION

The determination of PCDDs and PCDFs in a coffee filter and a pulp mill effluent showed interfering compounds at the m/z values used to monitor TCDDs (1,2). These unknown planar aromatic compounds (UPACs) were suggested to be alkylated PCDFs, but model synthesis of C_{12} -PCDFs did not support this theory (3). Because these chlorinated compounds, which obviously originate from bleaching procedure, are found in the "dioxin fraction", they might have toxicological significance.

This report provides some information about semiquantitative concentrations of C_{12} -UPACs with respect to PCDD/Fs in pulp and paper products, pulp mill effluent as well as in sediment and biota exposed to the effluents of pulp and paper mills.

EXPERIMENTAL

Samples

A pulp sample was obtained from a mill producing bleached kraft pulp. Paper products analyzed were commercially available products. A pulp mill effluent was taken after biological purification from the active sludge treatment plant of a kraft pulp mill in 1988 (2). Sediment samples were surface sediments, which were collected in 1988 for the study of persistent organochlorine compounds in the Lake Päijänne watercourses (4). Mussels were incubated for

four weeks near to a paper mill and the effluent pipe of the active sludge treatment plant of a kraft pulp mill in Lake Kuhnamo in 1987 for monitoring organochlorine pollutants in water (5). Fish samples were caught in Lake Vatia in 1990. The sampling sites are shown in Figure 1.

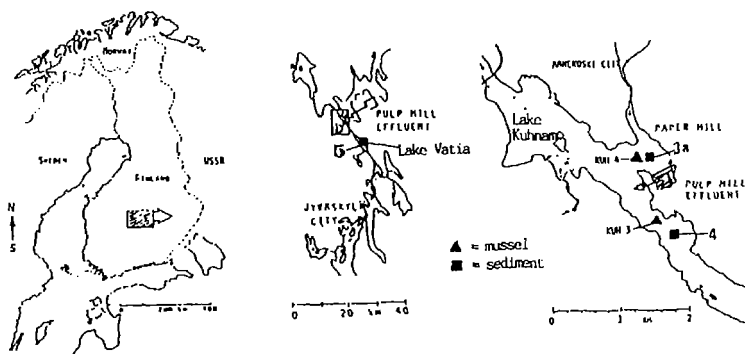


Fig 1. The sampling sites.

Extraction and clean-up

For the extraction, sediments and the soft parts of the mussels were freeze-dried, fish samples were homogenized with sodium sulphate and air dried. Pulp and paper products were cut into small pieces. Internal standard (1,2,3,4-TCDD or ^{13}C -2,3,7,8-TCDD) was added prior to soxhlet extraction. Biological samples were extracted (6 h) with a solvent mixture (6), sediments, pulp and paper products with toluene (48 h) and pulp mill effluent (48 h) with diethyl ether (2). The solvents were evaporated and residues were dissolved in hexane. Fat and non persistent compounds were removed by shaking with conc. sulfuric acid, then the extracts were cleaned and fractionated using activated charcoal and basic alumina chromatography as described previously (6). The final extracts were analyzed for PCDDs and PCDFs by low resolution mass spectrometer using HP 5970 mass selective detector in selected ion monitoring mode.

RESULTS

Part of the PCDD/PCDF analyses have already been done in 1987-1989 (effluent, sediments, mussels) and their results reported earlier (2,5) or will be published later in other report (4).

2,3,7,8-substituted PCDD/PCDFs were not detected in any samples reported in this study, except the kraft pulp (for detection limits see Tables 1-3). The pulp contained 2,3,7,8-TCDF 15 pg/g and other TCDFs 25 pg/g. The highest levels of PCDD/PCDFs were found in sediments, where TCDDs dominated (900-1400 pg/g) (4), whereas in paper products and fishes no PCDD/PCDFs were detected. The approximate levels of Cl_2 -UPACs are given in Tables 1-3 (calculated

Table 1. Approximate concentrations of UPACs in pulp and paper products (pg/g).

Congener	Pulp	Coffee filter	Tissue paper	Diaper paper
Cl ₂ -UPAC 1	400	40	10	40
	2	80	80	50
	3	490	80	10
Cl ₂ -UPAC 1	30	ND	ND	ND
	2	10	ND	ND
	3	5	ND	ND
	4	30	ND	ND

ND = not detected (<5 pg/g)

Table 2. Approximate concentrations of UPACs in pulp mill effluent (pg/l) and sediments (pg/g).

Congener	Effluent	Sediment			
		3a	4	5	
Cl ₂ -UPAC 1	580	210	2700	1000	
	2	470	60	910	320
	3	630	310	4500	1300
Cl ₂ -UPAC 1	150	ND	650	350	
	2	90	ND	70	ND
	3	ND	ND	ND	ND
	4	150	ND	190	ND

ND = not detected (<50 pg/l for effluent and <50 pg/g for sediment)

Table 3. Approximate concentrations of UPACs in mussel and fish samples (pg/g).

Congener	Mussel		Fish	
	KUH 3	KUH 4	Pike	Id
Cl ₂ -UPAC 1	3200	ND	ND	ND
	2	440	160	ND
	3	3000	190	ND
Cl ₂ -UPAC 1	470	ND	ND	ND
	2	ND	ND	ND
	3	ND	ND	ND
	4	630	140	ND

ND = not detected (<50 pg/g for mussel and <5 pg/g for fish)

using the same response as for the internal standard). Trichloro compounds found with PnCDD ions were suggested to be same UPACs as dichlorinated. The mass fragmentograms of UPACs of the pulp are presented in Figure 2. The pulp was also analyzed by high resolution mass spectrometer (VG 11-250J) at which same dichloro compounds were obtained by ions 320.0735 and 322.0705. Compared to the concentrations of PCDDs and PCDFs levels of Cl_{2-3} -UPACs were orders of magnitudes higher. The effluent, mussel sample KUH 3 and sediment sample 4 had similar patterns of UPACs as the pulp indicating the same origin for these compounds. However, fishes seemed not to accumulate UPACs, although they were found in the sediment sample 5 from the same lake. The toxicological significance of these findings is uncertain due to the lack of model substances and toxicological testing. Higher chlorinated UPACs might be more toxic, but they were not detected in this screening study.

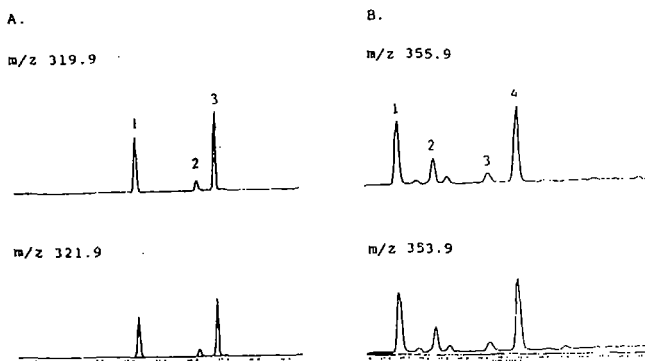


Fig.2. Mass fragmentograms of UPACs of a kraft pulp sample (HP 5970).
 A. Cl_2 -UPACs with TCDD ions.
 B. Cl_2 -UPACs with PeCDD ions.

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