Analysis of Polychlorinated Diphenyl Ethers (PCDE) in Environmental Samples

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1. Introduction

Polychlorinated diphenyl ethers $C_{12}H_{10-x}Cl_{x(x=1-10)}$ (PCDE, Cl_xDE) are a group of halogenated aromatic compounds which are structurally located between polychlorinated biphenyls (PCB) and polychlorinated dibenzo-p-dioxins/-furans (PCDD/F). The systematic numbering of the PCB congeners by Ballschmiter and Zell[1] as corrected in [2], is also applied for the PCDEs.

The main possible sources for the PCDEs are the technical production of chlorinated phenols, where they have been identified as by-products at a level of 100-1000 mg/kg [3] and all processes of incomplete combustion [4]. PCDEs are persistent enough to be found in a broad range of environmental and biological samples [5]. They have been determined in sediments and fish samples from Lake Ontario [6], in bird tissue and eggs [7], in white-tailed eagle muscles [4, 8], in salmon [9], and in human adipose tissue [10, 11] PCDEs are transformed by irradition or pyrolysis with a dehydrogenation or dehydrochlorination step into PCDFs [12, 13].

We have synthesised 106 PCDE congeners for an isomer-specific analysis of PCDEs in order to start a detailed study of their environmental fate. The availability of such a large number of PCDE congeners facilitated also the determination of physico-chemical parameters as vapour pressure, water solubility, K_{OW}, K_{GW} and K_{GO} [14].
Levels of PCDEs were determined in two cod liver oils from the years 1985 and 1993, respectively, and compared with two wood preserving formulations, which contain approximately 10% pentachlorophenol, with technical sodium 2,4,5-trichlorophenolate and 2,3,4,6-tetrachlorophenol, respectively, and with fly ash from a municipal waste incinerator. The two cod liver oil samples reflect the contamination of the marine environment with PCDEs, while the technical samples can be considered as sources of PCDEs.

2. Materials and Methods

Materials. SRM 1588 (Organics in Cod Liver Oil) was obtained from the Standard Reference Program, National Institute of Standards and Technology (Gaithersburg, MD, USA) produced in 1985. The second cod liver oil is a commercial product obtained in July 1993 in a pharmacy in Ulm, Germany. This fish oil origins from cods caught in the North Sea in 1993 The wood preserving formulations were Xyladesor (1983, Desowag-Bayer Holzschutz GmbH, Germany) and Sadolins PX 65 (1984, Sadolin GmbH, Germany). The technical chlorophenols sodium-2,4,6-trichlorophenolate and 2,3,4,6-tetrachlorophenol were purchased by Fluka AG, Germany. The fly ash originated from a municipal waste incinerator located in northern Germany from 1987.

Extraction and cleanup. The extraction and cleanup procedure has to be modified for the different matrices and is described in detail in [15]. Samples were spiked with PCDEs 1, 10, 25, 166, and 187 as internal standards before the extraction step. These PCDE congeners are not present in the samples. During sample preparation a 2-(1-pyrenyl)ethyldimethylsilylated silica column (Cosmosil 5 PYE, Promochem GmbH; Germany) has been used in normal phase mode to separate the PCDEs from possible PCDF interferences.

Analysis. The samples have been analysed by GC/MS in SIM-Mode using EI ionisation. The GC/MS-system used was a gas chromatograph HP 5890 A with on-column injector and low resolution mass selective detector HP 5970 B. For gas chromatographic separation a fused silica capillary column with 5% phenyl-substituted methylpolysiloxane (SE 54) was used. The retention behaviour of the PCDEs on this capillary column was investigated with 106 PCDE single congeners synthesised in our department [16].

3. Results and Discussion

The results of some PCDE congeners are presented in Table 1. Overall 79 PCDE congeners could be identified in the different samples. The total amounts of PCDEs in the different samples are: SRM 1588 = 659 µg/kg, Cod liver oil 1993 = 49 µg/kg, Na-2,4,5-trichlorophenolate = 4360 µg/kg, 2,3,4,6-tetrachlorophenol = 212620 µg/kg, Xyladecor = 20765 µg/kg, Sadolins = 33375 µg/kg, and the fly ash = 93 µg/kg.

Table 1. Levels of PCDEs in the examined samples in µg/kg (ppb)

PCDE-No.	SRM 1688 *µg/kg lipid weight*	Cod Liver Oil(1993) *µg/kg lipid weight*	Na-2,4,5-trichloro-phenolate *µg/kg*	2,3,4,6-tetrachloro-phenol *µg/kg*	Xyladecor *µg/kg*	Sadolins *µg/kg*	Fly ash *µg/kg*
35	35	19	39	50	6	n.d.	15
91/99/115	9	n.d.	3	642	4	n.d.	n.d.
147/153	4	n.d.	42	3065	52	55	1
154	3	2	35	5719	40	8	1
180	253	1	72	3794	59	81	n.d.
196	15	n.d.	1124	68117	8100	9306	n.d.
203	24	3	83	1818	134	216	n.d.
206	n.d.	n.d.	375	1563	1317	2572	n.d.
209	n.d.	n.d.	226	177	468	1072	n.d.

n.d.: not detected (amount < 1 µg/kg)

The levels of PCDEs in the 1993 cod liver oil were more than ten times lower than in SRM 1588. The 1993 cod liver did not only show low concentrations of the PCDEs, but also correspondingly low levels of the PCBs. The rather low organochlorine contamination of the more recent sample may be explained by a generally desreased presence of these two groups of compounds in the North Atlantic water or by an origin of the more recent cod liver oil from a less polluted area.

The wood preserving formulations are representative for the possible input of PCDEs deriving from technical pentachlorophenol. For the pentachlorophenol itself that has an

approximate content of 10 % in the two formulations an amount of 200 to 300 mg/kg PCDEs can be calculated. This in an agreement with the levels of PCDEs present in chlorophenol samples as reported by Nilsson and Renberg [3].
The level of PCDEs in 2,3,4,6-tetrachlorophenol is 50 times higher than in Na-2,4,5-trichlorophenolate. The concentration of the PCDEs in 2,3,4,6-tetrachlorophenol (213 µg/kg) is at the level similar to that described by Nilsson and Renberg [3]. The PCDEs determined in both chlorophenols and the wood preservind formulations spread over the chlorination degrees of 3 to 10 with a maximum for chlorination degree 7 to 8. The PCDEs are formed during the production of the chlorophenols by condensation followed by chlorination, dechlorination and rearrangement steps.
In the fly ash sample PCDEs of a chlorination degree 2 to 6 were observed. Higher chlorinated PCDEs were not detected. In comparison with the other samples discussed above, the number of PCDE congeners in the fly ash sample is much higher. This fact is due to the less specific formation and rearrangement of the PCDEs congeners during the combustion process.
The ubiquitous contamination of the environment with the PCDEs leads to the question of the origin of the observed PCDEs. The cod liver oil samples are an example for the averaged environmental contamination, while the chlorophenol and the fly ash sample can be seen as specific possible sources. For the clarification of the relationship between the sources and the remaining of the PCDEs an isomer-specific comparison had been done. As example the occurrence of PCDE 197 and 196 in the cod liver oils indicates, that the chlorophenol production is a likely source for PCDEs found in the environments. While the PCDE 180, 195 and 203 are dominating in the cod liver oil, these congeners have low levels in the chlorophenol samples. On the other hand PCDE 196 and 197 are very low in the cod liver oils in contrast to the chlorophenol products, where they are major components. These differences may be explained with the degradability or biopersistence of the respective congeners. The PCDEs with low levels in the technical and high levels in the marine samples (PCDE 180, 195, and 203) can be regarded as biopersistent and therefore are accumulated by the cods. The opposite occurs if PCDE congeners are biodegradable. They will have low levels in the marine samples (PCDE 196 and 1976) in spite of a major input.

4. Conclusions

Cod liver oils are representative examples for the investigation of the contamination of the marine environment with PCDEs. The PCDEs found in the cod liver oils resemble only partly with the occurrence of PCDEs found in the chlorophenol products. The major PCDE congeners found in the chlorophenol products show low levels in the cod liver oils while other PCDE congeners seem to accumulate more efficiently. As for the large group of PCBs, the PCDEs are further indicator molecules for the global pollution of the environment by oranochlorine compounds.

5. References

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