Time Trends in Levels, Patterns and Profiles for PCDD/PCDF in Sediment Cores of Lake Constance

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1. Introduction

Several attempts have been made to estimate current input of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from emission data of known emission sources. Since PCDD/PCDF emissions vary greatly for any one source, these estimates carry a considerable uncertainty and can hardly be used for the reliable deduction of recent time trends. Another approach to obtain data on recent time trends of PCDD/PCDF input in the environment is to analyse dated sediment cores. The latest available data on PCDD/PCDF levels in sediment cores were published in 1995 by Kjeller and Rappe[1] on a sediment core from the Baltic Proper sampled in January 1988. These data as well as analyses of a sediment core collected 1985 from Lake Constance[2] indicate, that the peak input of PCDD/PCDF in the environment occurred around 1975. Data on human milk and blood samples from Germany show a decrease in PCDD/PCDF levels of 30 to 50 % between 1986 and 1993. Considering the half live of 2,3,7,8-substituted PCDD/PCDF in men, the onset of the decrease in PCDD/PCDF input in the environment must be expected before this time period. To obtain data on the more recent time trends of PCDD/PCDF input in the environment, sediment cores of Lake Constance, located in the south west of Germany, bordering on Swizerland and Austria, were sampled recently and analysed for PCDD/PCDF.

2. Materials and Methods

Sampling. Sediment cores were sampled at Lake Constance in the middle of the lake at the deepest point (100 m) in December 1995 (core A) and April 1996 (core B). The cores were immediately sliced into 0.7 to 4 cm discs (core A) and 1.5 to 2 cm discs (core B) respectively and transferred to unused glassjars. Each sample analysed consists of a composite from five cores.

Experimental. The procedure for the analysis of PCDD/PCDF is described elsewhere in detail and is summarised as follows[3]. Sediments are freeze dried and crushed. After addition of all 17 2,3,7,8-substituted PCDD/PCDF as ^{13}C-labeled internal standards the samples are Soxhlet-extracted with toluene for 20 h. Sample clean-up includes heat treatment with silica/sulphuric acid and chromatography on Alumina B Super I for dioxin analysis (ICN Biomedicals) and on BioBeads S-X3. Analysis for PCDD/PCDF was carried out by high-resolution gas chromatography on a 60 m DB-DIOXIN capillary column (J&W Scientific) directly coupled to a high-resolution mass spectrometer (VG Optima).

Dating of core discs. The core discs are dated visually on a preliminary basis and are in the process of being dated by isotope analysis.

3. Results and Discussion

The results are summarised in Table 1 for sediment core A and in Table 2 for sediment core B. When sediment core A was sampled special care was taken to collect the uppermost layer representing the sediment of the last two years. For sediment core B smaller sediment discs, representing shorter time periods of about equal length for the more recent sediments, were sampled. Since the samples analysed are a composite of 5 cores, overlaps between time periods can not be excluded.

PCDD/PCDF concentrations: In all sediment discs all PCDD/PCDF homologues and all 2,3,7,8-substituted PCDD/PCDF could be detected. The detection limit for 2,3,7,8-TCDD was below 0.05 ng/kg. In the early sediments the total PCDF concentration is higher than total PCDD concentration (Figure 1). This and the concentrations measured are in agreement with the results reported by Kjeller and Rappe for the Baltic Proper core. With the onset of increasing PCDD/PCDF concentrations around 1940 the PCCD concentrations are higher than the PCDF concentrations, in contrast to findings of Kjeller and Rappe. In the core from the Baltic Proper PCDF concentrations are always higher than the PCDD concentrations, becoming about equal in concentration in the most recent sediment disc (1982-1988).

I-TEQ values: The I-TEQ values for the sediment discs of the two cores increase around 1940, have their maximum around 1970-1975, and have decreased since and are in the most recent sediments down to levels of about 1940. In Figure 2 the I-TEQ values for the two cores are plotted against the average age of the sediment cores for better comparison. The two curves are almost superimposable and are only slightly against each other on the time scale. The final dating of the core discs may correct this.

Homologue profiles: The homologue profiles for core B are shown in Figure 3. There is a distinct difference between the homologue profiles of the sediments before 1940 and the more recent sediments. With the increase in PCDD/PCDF concentration around 1940 the homologue profiles are more or less identical with those which we find in recent deposition samples[3]. It is obvious that the PCDD/PCDF found in the more recent sediments are of atmospheric origin and are mainly due to thermal formation of PCDD/PCDF.

Isomer pattern: What is seen in the homologue profiles is also evident in the isomer distribution pattern. All the isomer pattern in the sediments after 1945 show „thermal" isomer distribution pattern, which are practically identical for all these sediment discs. In the early sediments a isomer distribution pattern is found which at least for the PCDF resembles a „chlorine" pattern.

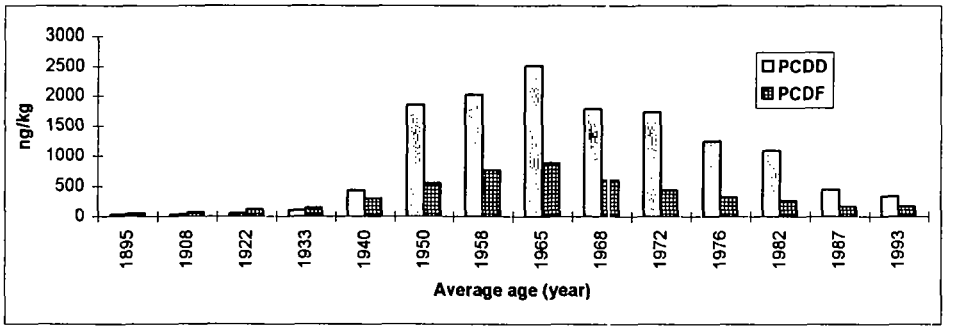


Figure 1: Levels of total tetra- to octaCDD/CDF for each disc of sediment core B

Table 1: Sediment core A: Sum of tetra- to octaCDD, sum of tetra- to octaCDF and I-TEQ values

core depth cm time period*	0-0.7 1993/95	0.7-4.8 1985/93	4.9-9 1974/85	9-13 1963/74	13-16 1951/63	16-18 1938/51	18-20 1926/38	20-22 1915/26
PCDD	292**	657	1809	3291	1576	293	33	36
PCDF	129	254	688	1226	821	339	95	69
I-TEQ	4.9	14.7	21.3	34.1	16.4	8.8	1.8	2.0

*dating is preliminary **concentrations in ng/kg dry weight

Table 2: Sediment core B: Sum of tetra- to octaCDD, sum of tetra- to octaCDF and I-TEQ values

core depth cm time period*	0-2 1990/95	2-4 1985/90	4-6 1979/85	6-8 1974/79	8-9.5 1970/74	9.5-11 1967/70	11-13.5 1963/67	13.5-15 1955/63
PCDD	342**	454	1091	1249	1730	1795	2519	2018
PCDF	177	168	270	323	438	595	881	760
I-TEQ	7.6	7.0	12.5	13.4	18.8	24.1	34.1	25.1

Table 2 continued

core depth cm Period*	15-17 1945/55	17-19 1935/45	19-21 1928/35	21-22.5 1915/28	22.5-24 1900/15	24 26 1890/00
PCDD	1854	437	96	57	35	34
PCDF	544	300	144	120	74	52
I-TEQ	20.0	8.4	3.8	2.8	1.8	2.0

*dating is preliminary **concentrations in ng/kg dry weight

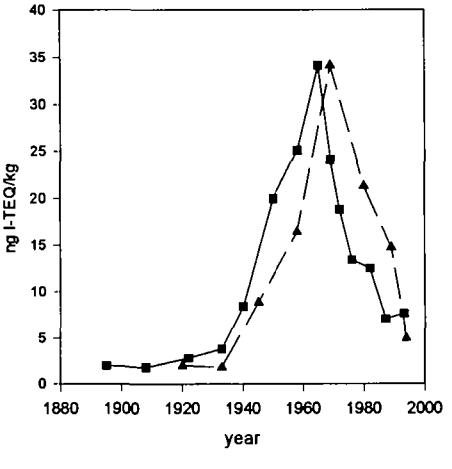
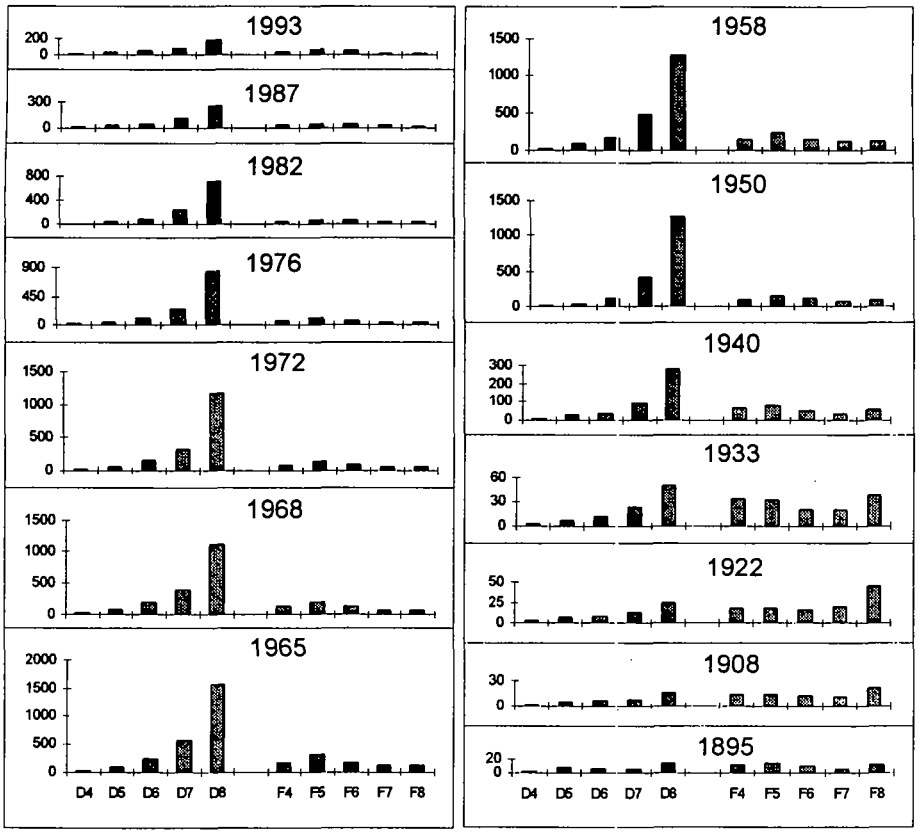


Figure 2: Comparison of I-TEQ values for the sediment discs of the two cores A and B.



(triangles = core A; squares = core B)

Figure 3: Homologue profiles for the sediment discs of Core B. Average age of discs is indicated.

4. Conclusions

The PCDD/PCDF analyses of the two sediment cores from Lake Constance show that the major input of PCDD/PCDF occurred much earlier than generally assumed. This is a rather plausible result, since in the early seventies air pollution control measures decreased the emission of dust of various facilities considerably, decreasing also PCDD/PCDF emission. If PCDD/PCDF input by the aquatic route plays a role, this route was also more or less blocked by the construction of sewage treatment plants around Lake Constance in the seventies. The recent decrease of PCDD/PCDF emission is due to various measures in the last 10 years to minimise the emission of PCDD/PCDF in Germany, e.g. the prohibition of halogenated scavengers in leaded gasoline and the prohibition of pentachlorophenol.

5. References

[1]) Kjeller L.O. and Rappe C. (1995): Time Trends in Levels, Patterns, and Profiles for polychlorinated Dibenzo-p-dioxins, Dibenzofurans and Biphenyls in a Sediment Core from the Baltic Proper. Environ. Sci. & Technology 29, 346-355.

[2]) Haag R. (1989), Ph.D. Thesis, University of Tübingen

[3]) Höckel J., Düsterhöft L., Körner W., Hagenmaier H. (1995): Modified clean-up procedure for PCDD/PCDF. Organohalogen Compounds Vol. 23, 135-139