

The historical record of PCB and PCDD/F deposition at Greifensee, a lake of the Swiss plateau, between 1848 and 1999

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Abstract

Dated sediment cores provide an excellent way to investigate the historical input of persistent organic pollutants into the environment and to identify possible sources of pollution. The vertical distribution of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDD/F) and polychlorinated biphenyls (PCB) was investigated in a sediment core from Greifensee to elucidate the historical trends of PCDD/F and PCB inputs between 1848 and 1999. Concentrations of PCB and PCDD/F increased by more than one order of magnitude between 1930 and 1960. PCB and PCDD/F concentrations were 5700 ng/kg dry weight (dw) and 160 ng/kg dw, respectively, in sediments originating from the late 1930s and reached a maximum of 130 000 ng/kg dw and 2400 ng/kg dw, respectively, in the early 1960s. From 1960 on, concentrations decreased to the 1930s level by the mid 1980s. A remarkable shift in the PCDD/F pattern was observed after the early 1940s. Before 1940, the PCDD/F pattern was PCDF dominated (ratio of PCDD to PCDF = 0.41 ± 0.11), while the PCDD started to be the major species after the early 1940s (ratio of PCDD to PCDF = 1.46 ± 0.38).

The temporal trends of PCB and PCDD/F correlate surprisingly well with each other. This might be due to the coincidence of two factors. The introduction of PCB on the market in the 1930s resulted in emissions due to the widespread use of these industrial chemicals. In the same time period, waste incineration became an increasingly popular way to get rid of garbage, boosting the PCDD/F emissions significantly. The rapid decline of PCDD/F and PCB concentrations in the sediment starting in the early 1960s reflects the result of better emission control techniques in thermal processes and the improvement of waste water treatment in the catchment of Greifensee.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F) and polychlorinated biphenyls (PCB) are ubiquitous, toxic environmental contaminants. PCDD/F are formed in various combustion processes and are unwanted by-products in various chlorinated chemical formulations (e.g. pentachlorophenol, PCP), while PCBs were produced

technically and have been used in a variety of applications since 1929 (Fiedler, 1993, 1994; WHO, 1989, 1993). PCDD/F and PCB enter the aquatic environment via atmospheric deposition, run off and waste water. As both classes of these persistent organic pollutants (POPs) are barely soluble in water and have high log K_{OC} values, they do not stay in the aqueous phase but have a strong affinity to particles. Therefore, sediments of rivers, lakes and oceans represent sinks for particle bound persistent organic pollutants. Consequently, dated sediment cores provide an excellent way to investigate the historical inputs of these

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chemicals (Alcock and Jones, 1996). Congener specific analysis of PCDD/F and PCB in sediment cores provides information about sources of pollution and is an excellent tool to evaluate the effectiveness of legislative actions on pollutants (Hagenmaier et al., 1986; Rappe, 1994; Macdonald et al., 1998; Gaus et al., 2001). Only few data are available on the historical record of PCDD/F and PCB in sediments from Swiss lakes. Buser and Müller (1986) analyzed methylthio metabolites of polychlorinated biphenyls from two lakes in Switzerland and Czuzwa et al. (1985) analyzed the historical record of PCDD/F in sediments from three Swiss lakes.

The goal of our study was to obtain a historical record for PCDD/F and PCB from a dated sediment core taken from Greifensee, a small and shallow lake of the Swiss plateau east of Zürich. All PCDD/F homologues, including the seventeen 2,3,7,8-substituted PCDD/F, the six PCB congeners 28, 52, 101, 138, 153 and 180, as well as the dioxin-like non- and mono-*ortho*-substituted PCB congeners 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189 were determined in this core, representing the period between 1848 and 1999.

2. Experimental section

2.1. Samples

Greifensee is a small eutrophic lake (surface area 8.49 km²) located 10 km east of Zürich. Regular deep-mixing occurs between December and March. The depth of the lake is 32 m and the mean water residence time amounts to 408 days (Ulrich et al., 1994). Eutrophication of Greifensee started in 1936/1938. A sediment core (diameter 6.3 cm) was collected on April 25th, 2003 from Greifensee at a depth of 31 m. The sediment core was dated (¹³⁷Cs) and cut into slices (1 cm). The slices were freeze dried, weighed and stored in glass jars in the dark. The content of total organic carbon (TOC) was determined in cores taken at the same site. TOC was analyzed by using an EURO EA[®] CNS auto-analyzer. PCDD/F and PCB were analyzed in 15 selected slices, representing the time period from 1848 to 1999.

2.2. Sediment core properties

The sampled sediment core spans the time period between 1848 and 1999. Sedimentation rates were between 0.340 and 0.250 cm year⁻¹ and the water content was found to be between 54 and 75% (average 65%). The organic carbon content of the sediment varied between 1.4 and 5.3% (average 2.8%). Detailed data of the analyzed sediment core slices are given in Table 1.

2.3. Chemicals

PCB and PCDD/F reference materials were from the following sources: AccuStandard Inc. (New Haven, CT,

USA) and Cambridge Isotope Laboratories (Andover, MA, USA). The following isotope labelled standards were purchased from Cambridge Isotope Laboratories: ¹³C₁₂-PCB 28, 52, 101, 138, 153 und 180 (EC-4058 mixture), ¹³C₁₂-PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189 (EC-4937 mixture), ¹³C₁₂-1,2,7,8-TetraCDF (EF-1438), and ¹³C₁₂-2,3,7,8-chlorosubstituted PCDD and PCDF (EDF-4067 mixture).

2.4. Analytical method

About 10 g of the freeze dried material was extracted for 16 h with toluene (soxhlet). The extracts were filtered (Na₂SO₄) and adjusted to a volume of 20 ml. An aliquot of 10 ml was taken for analysis and spiked with the PCB and PCDD/F isotope labelled standards. After evaporation of the solvents to 0.5 ml using a gentle stream of N₂ at 40 °C, the volume was adjusted to 5 ml with cyclohexane/ethylacetate (1:1). This solution was purified by gel permeation chromatography (Biobeads S-X3) to eliminate sulfur and high molecular weight compounds. The purified fraction containing PCDD/F and PCB was concentrated to 1 ml, treated with concentrated sulfuric acid and subsequently cleaned by chromatography on a multilayer silica, Alumina B Super I, and carbon AX-21 columns, as described previously (Zennegg et al., 2002).

2.5. Quantitative analysis

Quantitative determination of PCDD/F and PCB was achieved by gas chromatography/high resolution mass spectrometry (GC/MS). Analyses were carried out on a MAT 95 mass spectrometer (Thermo Finnigan MAT, Bremen, Germany) coupled to a Varian 3400 gas chromatograph (Walnut Creek, CA, USA), equipped with an A200S autosampler (CTC Analytics, Zwingen, Switzerland). Samples were injected in splitless mode (splitless time 60 s) at an injector temperature of 260 °C. For separation of PCDD/F and dioxin-like PCB, a J&W DB-Dioxin column (60 m × 0.25 mm, film thickness 0.15 µm) was used with helium as carrier gas at a pressure of 200 kPa. The initial temperature was 180 °C. After 1.5 min, the temperature was ramped at 20 °C/min to 220 °C and at 2 °C/min up to 260 °C. The ion source was operated at 220 °C, the electron energy was 70 eV, and the mass spectrometer was tuned to a mass resolution of 8000. The two most abundant signals of the molecular ion clusters were recorded in single ion monitoring (SIM) mode. Detection limits are based on a signal-to-noise ratio of 3:1. Calculation of toxic equivalents (WHO-TEQ) was based on the Toxicity Equivalency Factors defined by the World Health Organization (WHO-TEF) (van den Berg et al., 1998).

2.6. Analytical quality control

Blank samples were prepared by submitting pure solvents with internal standards to the complete clean-up

Table 1

PCDD/F concentrations of single congeners, and sum of WHO-TEQ in a sediment core from Greifensee (ng/kg dw) and content of total organic carbon (TOC) in %

Depth (cm)		41–42	27–28	25–26	23–24	21–22	19–20	17–18	15–16	13–14	11–12	9–10	7–8	5–6	3–4	1–2
From (year)		1852	1908	1916	1924	1932	1940	1948	1954	1960	1966	1972	1980	1987	1993	1999
To (year)		1848	1904	1912	1920	1928	1936	1944	1951	1957	1963	1969	1976	1984	1990	1996
TOC (%)		1.67	1.82	2.12	2.38	2.23	3.20	3.13	3.19	3.94	3.76	3.88	3.68	2.80	3.06	3.17
	Blank															
2,3,7,8-TCDD	≤0.11	0.095	0.28	0.089	0.23	0.22	0.15	0.20	0.38	0.48	0.31	0.28	0.13	0.23	0.17	0.31
1,2,3,7,8-PeCDD	≤0.15	0.13	0.59	0.30	0.41	0.36	0.54	0.97	1.5	5.2	6.4	5.6	0.98	0.75	0.34	0.93
1,2,3,4,7,8-HxCDD	≤0.20	0.093	0.32	0.31	0.14	0.22	0.37	0.62	1.1	7.3	4.7	4.4	0.77	0.63	0.33	0.87
1,2,3,6,7,8-HxCDD	≤0.22	0.12	0.36	0.29	0.27	0.34	0.49	2.1	3.2	12	11	8.7	1.9	1.4	0.87	1.78
1,2,3,7,8,9-HxCDD	≤0.22	0.090	0.35	0.23	0.26	0.28	0.44	1.3	1.5	6.2	7.3	6.5	1.5	1.4	0.64	1.40
1,2,3,4,6,7,8-HpCDD	≤0.51	1.2	1.6	1.8	1.6	1.9	3.2	29	37	196	149	112	29	17	10	22
OCDD	2.5	4.1	6.6	6.2	7.8	11	12	288	172	729	685	518	163	91	51	106
2,3,7,8-TCDF	≤0.15	0.42	1.7	1.5	1.2	1.3	3.5	10	31	35	45	22	4.9	2.7	2.0	4.7
1,2,3,7,8-PeCDF	≤0.12	0.25	0.98	1.3	1.0	0.93	2.6	3.6	5.1	11	14	8.6	1.9	0.87	0.56	1.5
2,3,4,7,8-PeCDF	≤0.12	0.25	1.1	1.2	1.1	1.4	2.1	3.7	6.5	18	19	13	2.2	1.3	0.86	2.3
1,2,3,4,7,8-HxCDF	≤0.092	0.40	1.4	2.1	1.6	1.7	2.9	6.7	10	30	19	12	2.5	1.6	0.80	2.5
1,2,3,6,7,8-HxCDF	≤0.088	0.34	1.0	1.5	1.3	1.3	1.7	2.5	3.2	10	11	8.9	2.1	1.4	0.85	1.9
1,2,3,7,8,9-HxCDF	≤0.15	0.16	0.14	0.16	0.11	0.15	0.20	0.30	0.35	0.51	0.74	0.51	0.32	0.24	0.20	0.18
2,3,4,6,7,8-HxCDF	≤0.12	0.28	0.83	1.3	1.2	1.2	1.7	2.3	3.4	11	11	11	2.4	1.6	0.84	2.3
1,2,3,4,6,7,8-HpCDF	0.15	1.1	4.7	5.8	5.3	7.1	8.7	22	24	99	55	46	12	6.6	4.3	9.6
1,2,3,4,7,8,9-HpCDF	≤0.32	0.19	0.70	0.64	0.69	1.0	1.3	1.8	2.8	7.3	5.1	4.3	1.2	0.90	0.60	1.1
OCDF	≤0.95	1.2	6.2	10	13	13	23	46	33	129	59	38	10	7.6	4.3	11
WHO-TEQ	≤0.46	0.58	2.1	1.9	1.9	2.1	3.1	6.4	11	29	30	22	4.4	3.0	1.8	4.4

≤ = limit of detection, the limit of detection is defined as three times the signal-to-noise ratio.

procedures. Method blank samples for PCDD/F showed no signals, except for trace amounts of octachlorodibenzo-*p*-dioxin and heptachlorodibenzofuran, while blank samples for PCB were in the same range as the PCB concentrations determined in sediment before the 1930s.

3. Results and discussion

3.1. Temporal trends of PCB concentrations

Detailed results on PCDD/F and PCB concentration in the analyzed sediment core slices representing the time period between 1848 and 1999 are given in Tables 1–3. The historical trends of the measured concentrations of PCB (sum of PCB congeners 28, 52, 101, 138, 153 and 180) and PCDD/F (sum of all tetra- to octachlorinated dibenzo-*p*-dioxins and dibenzofurans) in Greifensee sediment are presented in Fig. 1. Concentrations of both, PCB and PCDD/F increased by more than one order of magnitude starting in the late 1930s (PCB: 5700 ng/kg, PCDD/F: 160 ng/kg), reaching peak levels in the early 1960s (PCB: 130000 ng/kg, PCDD/F: 2400 ng/kg). From 1960 on, concentrations decreased to the 1930s levels by the mid 1980s. The most recent sediment slice, representing the years 1996–1999, showed a slight increase of PCB and PCDD/F, probably due to sampling artefacts at the top-most layer.

If PCB and PCDD/F were to originate from different sources, the temporal trends of PCB and PCDD/F do correlate surprisingly well. The increasing concentrations of PCB after 1940 reflect the beginning of the industrial production and the use of PCB in the 1930s. Similar concentrations and trends for PCB in two sediment samples from nearby lake Zürich for the time period between 1960 and 1980 were reported by Buser and Müller (1986). They found 210000 ng/kg for the time period 1960–1965 and 70000 ng/kg for the time period 1975–1980 calculated with reference to Aroclor 1254 and Aroclor 1260. The sum of the indicator PCB concentrations in the sediment core from Greifensee are in the same range with 110000 ng/kg for the years 1963–1966 and 10000 ng/kg for the time segment 1976–1980. The steeply declining concentrations between the 1960s and the mid 1970s are quite remarkable. PCB concentrations in Greifensee sediments dropped by more than an order of magnitude within one decade. We believe that this decrease reflects the introduction of new and the modernization of existing waste water treatment plants in the catchment area of Greifensee and the generally restricted use of PCB starting in the early 1970s. The use of PCB in open systems such as printing inks, sealants, lubricating and cutting oils, plastics, paints and varnishes was banned in Switzerland in 1972.

3.2. Temporal trends of PCDD/F concentrations

The steep increase of PCDD/F concentrations in Greifensee sediment starting in the early 1950s (see Fig. 1)

Table 2
Sum PCDD/F concentrations of the homologues (tetra- to octachloro-DD/F) in a sediment core from Greifensee (ng/kg dw)

Depth (cm)	41–42	27–28	25–26	23–24	21–22	19–20	17–18	15–16	13–14	11–12	9–10	7–8	5–6	3–4	1–2
From (year)	1852	1908	1916	1924	1932	1940	1948	1954	1960	1966	1972	1980	1987	1993	1999
To (year)	1848	1904	1912	1920	1928	1936	1944	1951	1957	1963	1969	1976	1984	1990	1996
Blank															
Σ TCDD	n.d.	2.0	3.1	3.1	4.9	4.9	5.6	11	19	26	17	5.0	2.0	5.6	5.7
Σ PeCDD	n.d.	3.5	4.1	4.2	5.1	8.1	8.2	10	37	69	45	9.1	6.1	2.5	7.5
Σ HxCDD	n.d.	5.1	8.2	4.5	5.2	7.0	26	34	196	151	123	25	19	15	24
Σ HpCDD	n.d.	3.3	3.8	3.7	4.0	7.2	57	77	396	299	214	59	30	22	40
OCDD	2.6	6.6	6.2	7.8	11	12	288	172	729	685	518	163	91	51	106
Σ TCDF	n.d.	13	20	20	22	38	75	133	297	316	183	36	23	19	37
Σ PeCDF	n.d.	16	18	16	17	32	53	89	279	281	171	33	24	15	30
Σ HxCDF	n.d.	11	12	13	14	16	33	41	157	149	95	24	17	9.45	20
Σ HpCDF	0.15	6.5	8.0	8.2	10	13	49	46	206	87	76	18	11	6.61	18
OCDF	n.d.	6.2	10	13	13	23	46	33	129	59	38	10	7.58	4.30	11
Σ PCDD	2.6	20	25	23	30	39	385	305	1378	1230	917	261	149	96	184
Σ PCDF	0.15	52	67	70	77	121	255	342	1069	893	563	121	82	54	116
Σ PCDD/F	2.8	73	92	93	107	161	640	647	2447	2123	1480	382	231	150	300
Ratio PCDD:PCDF	–	0.39	0.38	0.33	0.40	0.32	1.5	0.89	1.3	1.4	1.6	2.1	1.8	1.8	1.6

n.d. = not detectable.

Table 3
Concentration of non- and mono-*ortho*-substituted PCB in a sediment core from Greifensee (ng/kg dw)

Depth (cm)		41–42	27–28	25–26	23–24	21–22	19–20	17–18	15–16	13–14	11–12	9–10	7–8	5–6	3–4	1–2
From (year)		1852	1904	1916	1924	1932	1940	1948	1954	1960	1966	1972	1980	1987	1993	1999
To (year)		1848	1904	1912	1920	1928	1936	1944	1951	1957	1963	1969	1976	1984	1990	1996
	Blank															
PCB-77	0.60	4.2	1.5	3.4	5.8	5.9	19	82	323	510	661.4	353	48	23	24	46
PCB-81	0.15	0.13	0.11	0.20	0.43	0.36	0.56	1.0	3.1	8.6	14	6.7	1.1	0.47	0.57	1.3
PCB-105	8.1	46	19	36	60	59	136	641	3215	6612	4365	2214	292	198	168	363
PCB-114	0.50	2.0	1.1	1.7	3.5	3.2	5.6	28	147	275	191	70	12	8.3	7.5	15
PCB-118	30	184	62	118	229	226	656	2736	11715	20055	12979	6524	1083	612	562	1055
PCB-123	1.5	13	4.7	8.8	16	18	63	212	1203	1902	1322	608	98	60	50	89
PCB-126	0.16	0.64	0.39	0.88	1.1	1.5	5.0	13	54	95	123	78	11	5.3	5.0	9.1
PCB-156	7.0	20	8.4	17	23	42	185	401	1759	4076	2949	1850	206	132	94	196
PCB-157	0.67	4.3	1.8	2.7	3.7	6.1	23	79	336	684	484	263	38	20	19	41
PCB-167	3.4	9.1	4.1	6.6	11	21	77	199	722	1851	1410	903	108	54	48	107
PCB-169	0.15	0.22	0.35	0.32	0.51	0.82	1.1	1.6	4.1	10	14	11	1.3	0.9	0.67	1.5
PCB-189	1.1	2.6	1.3	2.0	4.3	5.8	26	48	174	518	445	320	36	16	14	28
Σ WHO-TEQ	0.026	0.10	0.057	0.12	0.16	0.22	0.71	2.0	8.2	15	16	10	1.4	0.71	0.65	1.2
PCB-28	30	54	21	31	68	67	180	470	622	2671	5990	3567	432	157	115	252
PCB-52	63	146	60	85	219	172	390	1358	3903	9958	7608	3599	628	319	263	464
PCB-101	71	235	100	115	263	260	898	2267	7197	19271	14995	7955	1352	685	473	1006
PCB-138	77	229	86	128	220	320	1628	4032	12137	38275	30660	18519	2714	1271	882	2129
PCB-153	82	258	88	130	235	336	1747	4023	11676	38498	30710	19035	2868	1289	910	2148
PCB-180	38	116	54	63	97	175	901	2139	6502	23105	21031	14872	1762	782	503	1318
Σ indicator PCB	361	1038	409	552	1102	1329	5744	14288	42037	131777	110994	67547	9756	4503	3145	7318

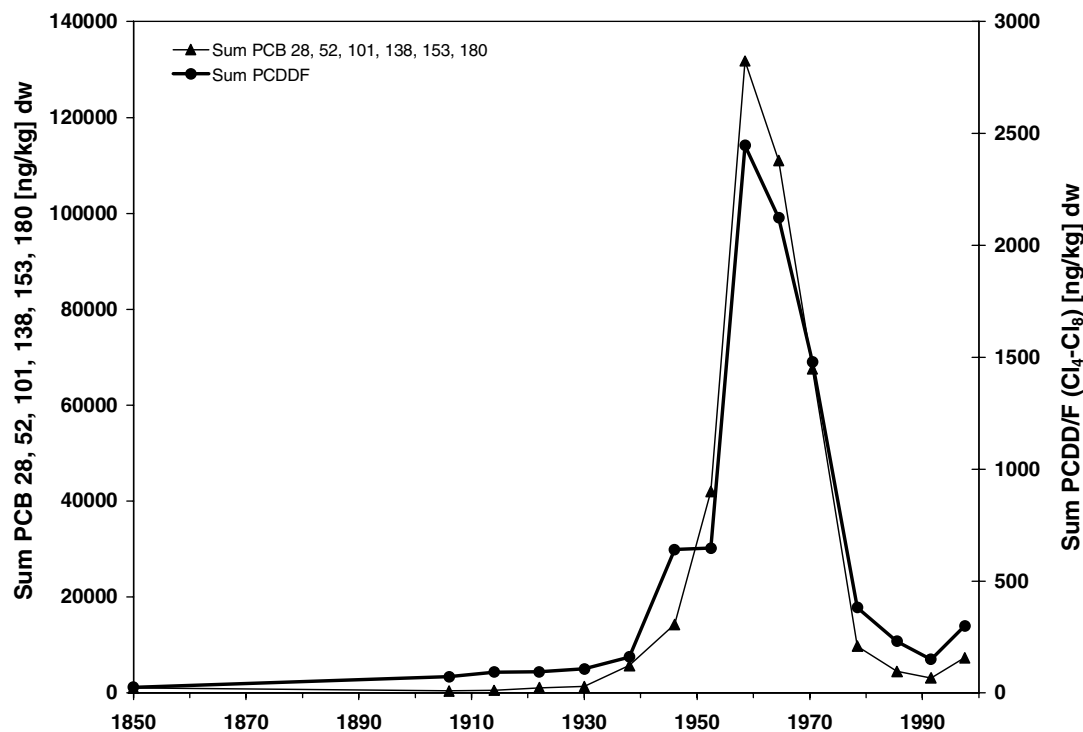


Fig. 1. Historical record of PCB and PCDD/F concentrations in Greifensee sediment.

reflects the introduction of municipal waste incineration in Switzerland in the 1950s, although other PCDD/F sources have to be considered as well (e.g. chlorinated phenols, chlorinated herbicides, and combustion engines running on fuel with chlorinated additives). The PCDD/F concentrations of 2100 ng/kg (1963–1966) and 380 ng/kg (1976–1980) are also in good agreement with the levels found by Buser and Müller for Lake Zürich and Lake Baldeg. They reported PCDD/F levels of 1000–2000 ng/kg from Lake Zürich (1960–1965 and 1975–1980) and Lake Baldeg (1975–1980). The use of organochlorine chemicals such as those mentioned above as well as the road traffic volume increased greatly since the 1950s and would therefore also explain the increase of PCDD/F inputs to Greifensee at this time. Masunaga et al. (2003) analyzed sediment cores from the Tokyo Bay basin and used principal component analysis compared with conventional dioxin information to attribute the main sources for the PCDD/F input. They found that Tokyo Bay basin sediment core contained dioxins originating from three major sources: combustion, pentachlorophenol (PCP), and chloronitrophen (CNP). PCP and CNP were used extensively as paddy field herbicides in Japan in the past. The authors calculated that the concentrations of PCP- and CNP-originating dioxins in the sediment core peaked during the mid 1960s and beginning of the 1970s, respectively. Kjeller and Rappe (1995) found similar results for a sediment core from the Baltic Proper. Increased PCDD/F levels were reported in sediment slices representing the years 1970–1980 (total PCDD/F 520–1800 ng/kg). The increased concentrations coincided with

a change in the PCDD/F congener profile and isomeric pattern, and the main contributors to this profile change were identified as chloroorganics, including pentachlorophenol (PCP). In contrast to our data, the sediment core from the Baltic Proper was always dominated by higher PCDF concentrations compared to PCDD. For now, it cannot be concluded to what extent PCP could have contributed to the PCDD/F deposition at Greifensee, but a very similar change in the PCDD/F congener profile and isomeric pattern as mentioned by Kjeller and Rappe was observed in the present study (see Fig. 3). Bruckmeier et al. (1997) analyzed the historical trend in lake sediments of the Grosser Arbersee in the Bavarian forest in south east Germany. They reported an increase of PCB concentrations (indicator PCB congeners 28, 52, 101, 138, 153 and 180) between the years 1946 and 1972 from 4200 ng/kg to 32000 ng/kg, followed by a decrease to 25000 ng/kg in the years 1991–1993. PCDD/F concentrations increased in the sediment from Grosser Arbersee between 1950 from 600 ng/kg to 2300 ng/kg in 1977 and decreased to 1700 ng/kg in 1993. PCDF concentrations exceeded those of PCDD until 1968, but afterwards, a shift to a PCDD dominated profile was observed with noticeable high levels of OCDD. The authors suggested that domestic heating and waste combustion were the most likely sources. These shifts in PCDD/F and PCB concentrations took place more than ten years later than the trends observed in our study, although PCDD/F and PCB concentrations were in the same order of magnitude.

As shown in Fig. 2, the temporal trend remains similar, when PCB and PCDD/F data are plotted as toxicity

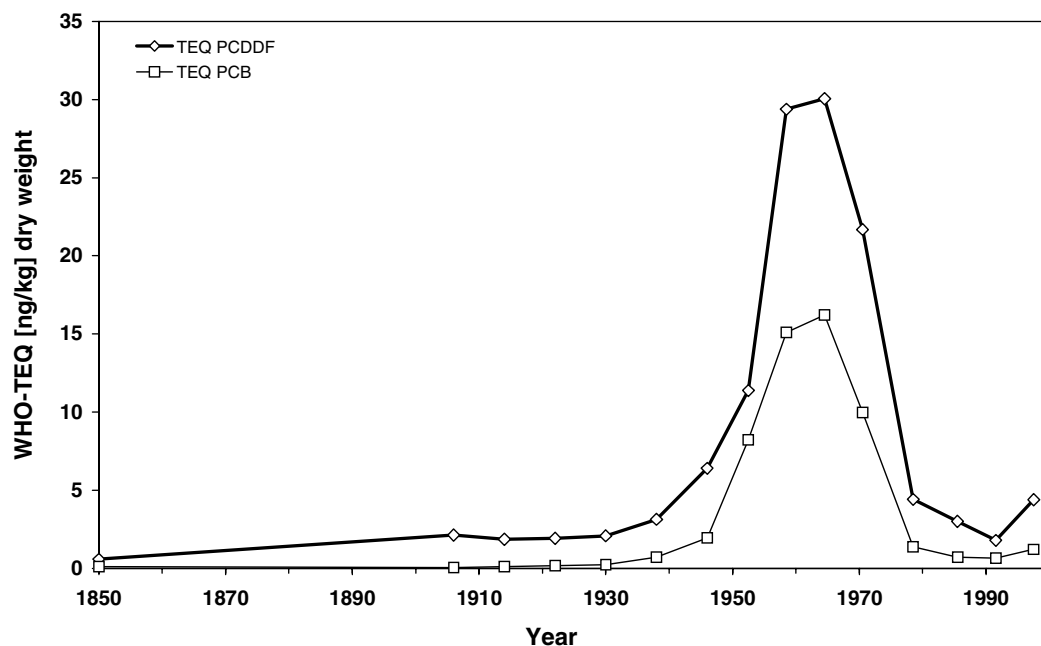


Fig. 2. Historical record of PCB and PCDD/F concentrations in Greifensee sediment, calculated as WHO-TEQ.

equivalents (WHO-TEQ), WHO-TEQ of PCB and PCDD/F both peaking in the early to mid 1960s at 16 ng/kg and 30 ng/kg, respectively. Hagenmaier and Walczok (1996) detected similar peak PCDD/F concentrations of 34.1 ng/kg I-TEQ in sediments from nearby Bodensee (Lake Constance) for the time period between 1963 and 1967.

3.3. Fluxes of PCB and PCDD/F

Annual fluxes in the early 1960s for PCB and PCDD/F were $13\,000\text{ pg cm}^{-2}\text{ year}^{-1}$ and $240\text{ pg cm}^{-2}\text{ year}^{-1}$, respectively. In the 1990s, annual fluxes decreased to $350\text{ pg cm}^{-2}\text{ year}^{-1}$ for PCB and to $17\text{ pg cm}^{-2}\text{ year}^{-1}$ for

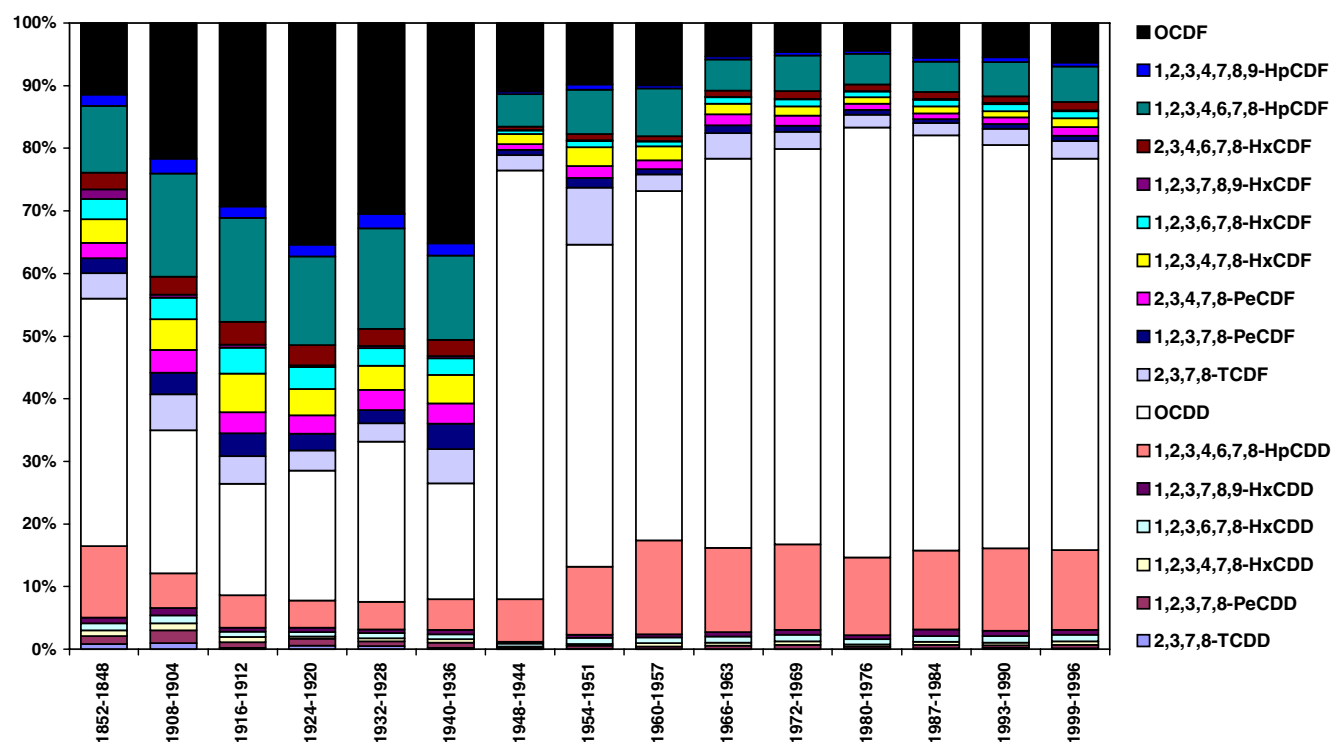


Fig. 3. Normalized ratios of 2,3,7,8-substituted PCDD/F congeners in Greifensee sediment.

PCDD/F. In comparison, Czuzwa et al. (1985) reported total fluxes of PCDD/F of $250 \text{ pg cm}^{-2} \text{ year}^{-1}$ for nearby Lake Zürich for 1960.

3.4. Congener patterns of PCB and PCDD/F

Fig. 3 shows the normalized distribution of PCDD/F in Greifensee sediment as a function of time. While the PCB patterns, including non- and mono-*ortho* substituted PCB, remained stable over time (data not shown), the patterns of the 2,3,7,8-substituted PCDD/F congeners showed a remarkable shift in the early 1940s. After 1940, the relative amounts of octa- and heptachlorodibenzofurans (OCDF and HpCDF) decreased and the relative amounts of octachlorodibenzo-*p*-dioxin (OCDD) and 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1,2,3,4,6,7,8-HpCDD) increased considerably. This was seen for the ratio of the total PCDD to the total PCDF concentrations, as well.

Before the 1940s, the average PCDD/F ratio was 0.41 ± 0.11 . After 1940, a sudden shift of the mean PCDD/F ratio to 1.46 ± 0.38 was observed. The same shift of the PCDD/F ratio was previously observed by Hagenmaier and Walczok (1996) and rationalized by a shift to a PCDD/F congener pattern typical for thermal PCDD/F sources around the year 1940. The PCDD/F analyses of the sediment core from Greifensee showed that the rapid decline from the early 1960s on led to PCDD/F and PCB levels comparable to those of the 1930s by the mid 1980s. This early decline might be a result of better emission control techniques in municipal waste incineration and thermal combustion processes, the introduction and extension of waste water treatment plants and the ban on use of organochlorine chemicals such as PCB, PCP and halogenated scavengers in leaded gasoline. An additional factor is the reduction of waste incineration in open fires on landfill sites, an important source of PCDD/F (Lemieux et al., 2000; Gullett et al., 2001).

Sediment cores provide important information on historical trends of persistent organic pollutants like PCDD/F and PCB and therefore represent an excellent instrument to evaluate the effectiveness of legislative actions on contaminants. Therefore newly emerging environmental contaminants like brominated flame retardants or fluorocarbon surfactants should be included in the analyses of sediment core samples in future projects.

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References

- Alcock, R.E., Jones, K.C., 1996. Dioxins in the environment: a review of trend data. *Environmental Science & Technology* 30, 3133–3143.
- Bruckmeier, B.F.A., Jüttner, I., Schramm, K.W., Winkler, R., Steinberg, C.E.W., Kettrup, A., 1997. PCBs and PCDD/Fs in lake sediments of Grosser Arbersee, Bavarian forest, south Germany. *Environmental Pollution* 95, 19–25.
- Buser, H.R., Müller, M.D., 1986. Methylthio metabolites of polychlorobiphenyls identified in sediment from two lakes in Switzerland. *Environmental Science & Technology* 20, 730–735.
- Czuzwa, J.M., Niessen, F., Hites, R.A., 1985. Historical record of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Swiss lake sediments. *Chemosphere* 14, 1175–1179.
- Fiedler, H., 1993. Formation and sources of PCDD/PCDF. *Organohalogen Compounds* 11, 221–228.
- Fiedler, H., 1994. Sources of PCDD/F and impact on the environment. *Organohalogen Compounds* 20, 229–236.
- Gaus, C., Brunskill, G.J., Weber, R., Pöpke, O., Müller, J.F., 2001. Historical PCDD inputs and their source implications from dated sediment cores in Queensland (Australia). *Environmental Science & Technology* 35, 4597–4603.
- Gullett, B.K., Lemieux, P.M., Lutes, C.C., Winterrowd, C.K., Winters, D.L., 2001. Emissions of PCDD/F from uncontrolled, domestic waste burning. *Chemosphere* 43, 721–725.
- Hagenmaier, H., Brunner, H., Haag, R., Berchtold, A., 1986. PCDDs and PCDFs in sewage sludge, river and lake sediments from South West Germany. *Chemosphere* 15, 1421–1428.
- Hagenmaier, H., Walczok, M., 1996. Time trends in levels, patterns and profiles for PCDD/F in sediment cores from lake Constance. *Organohalogen Compounds* 28, 101–104.
- Kjeller, L.O., 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. *Environmental Science & Technology* 29, 346–355.
- Lemieux, P.L., Lutes, C.C., Abbott, J.A., Aldous, K.M., 2000. Emissions of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from the open burning of household waste in barrels. *Environmental Science & Technology* 34, 377–384.
- Macdonald, R.W., Ikononou, M.G., Paton, D.W., 1998. Historical inputs of PCDDs and PCDFs and PCBs to a British Columbia interior lake: the effect of environmental controls on pulp mill emissions. *Environmental Science & Technology* 32, 331–337.
- Masunaga, S., Yao, Y., Ogura, I., Sakurai, T., Nakanishi, J., 2003. Source and behavior analyses of dioxins based on congener-specific information and their application to Tokyo Bay basin. *Chemosphere* 53, 315–324.
- Rappe, C., 1994. Dioxin, patterns and source identification. *Fresenius Journal of Analytical Chemistry* 348, 63–75.
- Ulrich, M.M., Müller, S.R., Singer, H.P., Imboden, D.M., Schwarzenbach, R.P., 1994. Input and dynamic behavior of the organic pollutants tetrachloroethene, atrazine, and NTA in a lake: a study combining mathematical modeling and field measurements. *Environmental Science & Technology* 28, 1674–1685.
- van den Berg, M., Birnbaum, L., Bosveld, B.T.C., Brunström, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Waern, F., Zacharewski, T., 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives* 106, 775–792.
- World Health Organization (WHO), 1989. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environmental Health Criteria* 88, 1–409.
- World Health Organization (WHO), 1993. Polychlorinated biphenyls and terphenyls. *Environmental Health Criteria* 140, 1–479.
- Zennegg, M., Schmid, P., Gujer, E., Kuchen, A., 2002. PCDD, PCDF, and dioxin-like PCB in fish from Swiss lakes. *Organohalogen Compounds* 58, 489–492.