The historical record of PCB and PCDD/F deposition at Greifensee between 1848 and 1999

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Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F) and polychlorinated biphenyls (PCB) are ubiquitous, toxic environmental contaminants formed during combustion or by industrial manufacturing processes. PCDD/F and PCB enter the aquatic environment via atmospheric deposition, run off and waste water. Both classes of these persistent organic pollutants (POP) have a strong affinity to sediments. Therefore, dated sediment cores provide an excellent way to investigate the historical inputs of these chemicals. Congener specific analysis of PCDD/F and PCB in sediment cores can provide information about sources of contamination and is an excellent tool to evaluate the effectiveness of legislative actions on contaminants.
The goal of this 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, as well as the six PCB congeners 28, 52, 101, 138, 153 and 180 and 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, representing the period between 1848 and 1999.

Methods and Materials

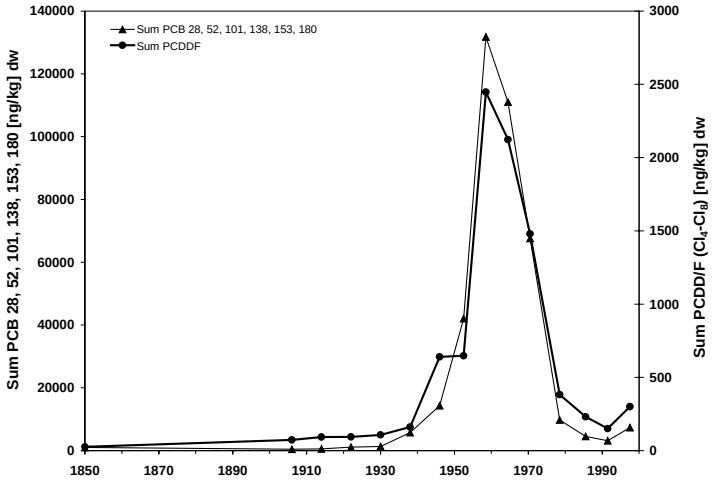
Samples: Greifensee is a small eutrophic lake (surface area 8.49 km^2) located 10 km east of Zürich. Regular deep-mixing occurs between December and March. The depth of the lake is 32 m and the mean water residence time amounts to 408 days[1]. Eutrophication in Greifensee started in 1936/38. A sediment core (diameter 6.3 cm) was collected on April 25th, 2003 from Greifensee at a depth of 31 m. The sediment core was dated (^{137}Cs) and cut into slices (1 cm). The slices were freeze dried, weighted 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 an EURO EA® CNS auto-analyzer. PCDD/F and PCB were analyzed in 15 selected slices representing the time period from 1848 to 1999.

Analytical method: About 10 g of the freeze dried material was extracted for 16 hours with toluene (soxhlet). The extracts were filtered (Na_2SO_4) and adjusted to a volume of 20 ml. An aliquot was spiked with the seventeen $^{13}C_{12}$-labeled 2,3,7,8-substituted PCDD/F, the $^{13}C_{12}$-labeld PCB indicator congeners 28, 52, 101, 138, 153 and 180, and the $^{13}C_{12}$-labeled mono- and non-*ortho*-substituted PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189. After evaporation of the solvents to about 0.5 ml (N_2 at 40 °C) the volume was adjusted to 5 ml with cyclohexane/ethylacetate (1:1). This solution was purified in a first step by gel permeation chromatography (Biobeads S-X3). The obtained fraction was concentrated to 1 ml, treated with concentrated sulphuric acid and subsequently cleaned by chromatography on multilayer silica, Alumina B Super 1 and carbon AX-21, as described previously[2]. Analysis of PCDD/F, PCB and dioxin-like PCB were carried out by HRGC/HRMS on a 60 m × 0.25 mm J&W DB-Dioxin capillary column (film 0.15 µm). Concentrations of PCB and PCDD/F are reported in ng/kg dry weight (dw). Method blank samples for PCDD/F showed no signals, except for trace amounts of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran, while blank samples for PCB were in the same range as the levels determined in sediment before the 1930's.

Results and Discussion

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 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 %).

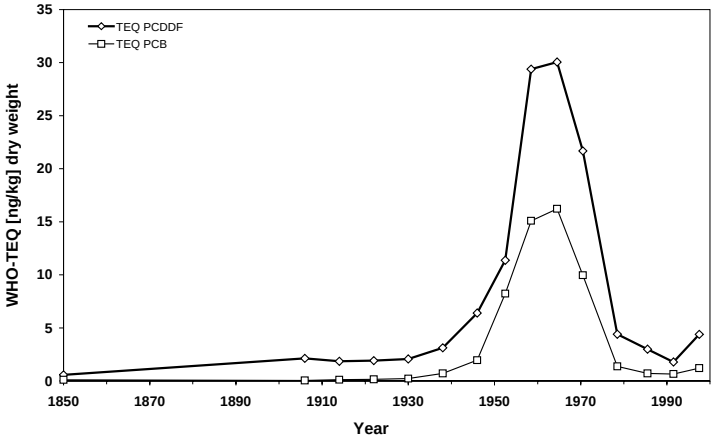
Figure 1: Historical record of PCB and PCDD/F concentrations in Greifensee sediment.



Temporal trends of PCB and PCDD/F concentrations: The historical trends of the measured concentrations of PCB (sum of PCB congeners 28, 52, 101, 138, 153, 180) and PCDD/F (sum of all tetra- to octachlorinated dibenzo-*p*-dioxins and dibenzofurans) in Greifensee sediment are shown in Figure 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 of in

the early 1960's (PCB: 130000 ng/kg, PCDD/F: 2400 ng/kg). From 1960 on, concentrations decrease to the 1930's levels by the mid 1980's. The last data point of the series, representing the years 1996-1999, shows a slight increase of PCB and PCDD/F. The significance of this increase needs to be verified based on more samples from this lake. Assuming that PCB and PCDD/F originate from different sources, the temporal trends of PCB and PCDD/F do correlate surprisingly well with each other.

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



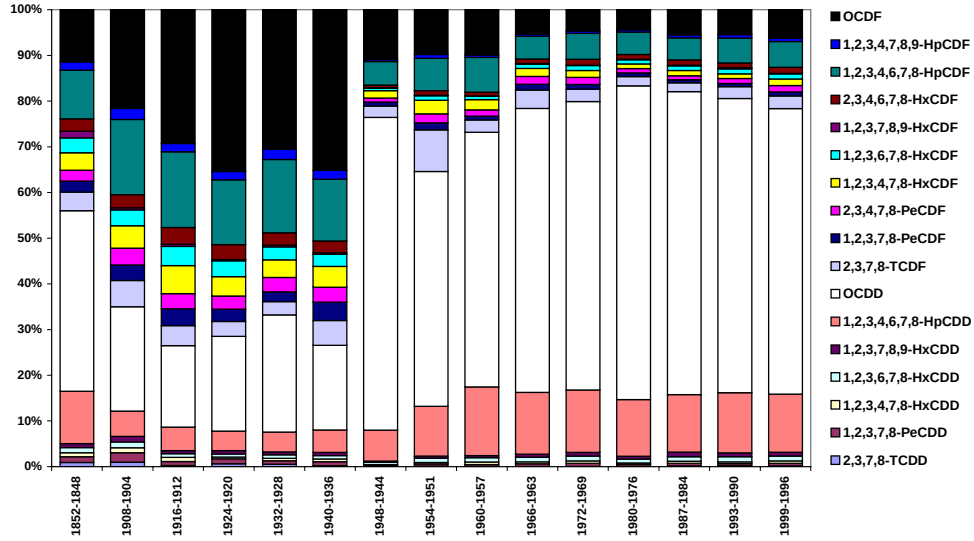
The picture remains similar (see Figure 2) when the data for PCB and PCDD/F are plotted as toxicity equivalents (TEQ), based on the WHO toxicity equivalent factors (WHO-TEF). In this case, WHO-TEQ of PCB and PCDD/F are peaking in the early to mid 1960's at 16 ng/kg and 30 ng/kg, respectively. For comparison, Hagenmaier and co-workers detected peak PCDD/F concentrations of 34.1 ng/kg I-TEQ in sediments from nearby Bodensee (Lake Constance) sediments for the time period between 1963 and 1967[3].

Fluxes of PCB and PCDD/F: Annual fluxes for PCB and PCDD/F, calculated from sediment concentrations, annual sedimentation rate and surface area were 13000 pg cm^{-2} $year^{-1}$ for the PCB and 240 pg cm^{-2} $year^{-1}$ for the PCDD/F in the early 1960's. In the 1990's, annual fluxes decreased to 350 pg cm^{-2} $year^{-1}$ for the PCB and to 17 pg cm^{-2} $year^{-1}$ for the PCDD/F. For comparison, Czuczwa and co-workers reported total fluxes of PCDD/F of 250 pg cm^{-2} $year^{-1}$ for nearby Zürichsee (Lake Zürich) for 1960[4]**.**

Congener patterns of PCB and PCDD/F: Figure 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, remain considerably stable in time (data not shown), the patterns of the 2,3,7,8-substituted PCDD/F congeners show a remarkable shift occurring in the early 1940's. After 1940, the relative amounts of octa- and heptachlorodibenzofurans (OCDF and HpCDF) decrease and the relative amount of octachlorodibenzo-*p*-dioxin (OCDD) and 1,2,3,4,6,7,8-hepta-

chlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD) increases considerably. This was seen for the ratio of the total PCDD to the total PCDF concentrations, as well.

Figure 3: Normalized ratios of 2,3,7,8-substituted PCDD/PCDF congeners in Greifensee sediment.



Before the 1940's, the average PCDD/PCDF ratio was 0.41 ± 0.11. After 1940, a sudden shift of the mean PCDD/PCDF ratio to 1.46 ± 0.38 was observed. The same shift of the PCDD/PCDF ratio was observed by Hagenmaier and co-workers previously[3] and rationalized by a shift to a PCDD/PCDF congener pattern typical for thermal PCDD/PCDF sources around the year 1940.

References

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