

PCDD/F in Recent and Historical Sediment Layers of Two German Lakes

Schramm, K.-W.¹, Jüttner, I.¹, Winkler, R.², Steinberg, C.¹, Kettrup, A.¹

GSF-Forschungszentrum für Umwelt und Gesundheit

¹Institut für Ökologische Chemie

²Institut für Strahlenschutz

Ingolstädter Landstr. 1, D - 85764 Oberschleißheim

Introduction

Hites et al.¹ reported for sediments from Lake Siskiwit, Isle Royale an increase of PCDD/F after 1935 and the highest values in 1982. Similar increases are published by Kjeller et al.² for soils and grass herbage. The Rothamsted soil PCDD/F-content for instance seems to rise after 1914 and the grass herbage after 1944 to recent values by a factor of 3 and 6, respectively. The Rothamsted soil has levels not below 31 ng/kg Σ PCDD/F in the time range between 1846 and 1914, and the Siskiwit sediments about 64 ng/kg in 1935 mainly contributed by OCDD. In this case the recent values are higher by a factor of 10. Both locations represent localities which are mainly influenced by atmospheric deposition. For soil in Germany from 40-70 p. Chr. Hartmann et al.³ measured values of 13.8 and 45 ng/kg Σ PCDD/F which is 0.6 and 2 ng I-TE/kg, respectively. These levels are similar to recent topsoils in rural regions. PCDD/F are distributed due to local and long-term atmospheric transport. Thus, it is astonishing that rural areas are not measurably influenced by long-term atmospheric transport of the past and recent industrial activities. Before this background we analysed two sediments from lakes in the Black Forest in Germany to evaluate the historical situation in southwest Germany.

Experimental

Sampling

The sediment cores were taken by a gravity corer and immediately divided into layers of 2 cm. These layers were freeze dried and analysed as a whole.

PCDD/F Analysis

The PCDD/F analysis includes the following steps:

1. Addition of labeled standards to the sample (isotope dilution method).

Prior to extraction the sample is spiked in minimum with 17 ¹³C₁₂ labeled internal standards (Cambridge Isotope Laboratories, Woburn, Massachusetts, USA):

2. Quantitative extraction of 2 to 5 g of lyophilised sample is done by the Soxhlet extraction method for 24 hours with toluene.

3. Clean-up

In order to remove interferences, a clean-up based on several liquid chromatography steps is applied to the concentrated raw extract. The solvents must be of residue quality.

The clean-up combines a set of established chromatographic steps in series:

3.1. 25 g alumina, basic, super active, 50-200 mm, filled wet with benzene and eluted with 80 ml benzene, 200 ml n-hexane/dichloromethane (98/2 v/v). The third fraction of 200 ml n-hexane/dichloromethane (50/50 v/v) contains the PCDD/F congeners. This fraction is evaporated (1000-550 mbar, 343 K) to a volume of 2 - 3 ml.

3.2. Mixed column filled wet with n-hexane from bottom to top with 4 g silica, 10 g silica (44 % conc. sulfuric acid w/w), 2 g silica. The silica type is active and 63 - 200 mm. The elution is done with 250 ml n-hexane and the eluat is evaporated (550 mbar, 343 K) to a final volume of 2 - 3 ml.

3.3 Florisil (for pesticide analysis) column filled wet and prewashed with 200 ml n-hexane. Elution is performed with 180 ml n-hexane followed by 300 ml dichloromethane. The dichloromethane fraction containing the PCDD/F is evaporated (1000 mbar, 343 K) to 2 -3 ml.

All columns are covered with Na₂SO₄.

This clean extract is stepwise transfered into a micro-vial and evaporated to dryness with a stream of nitrogen. To the micro-vial a defined volume (20 µl) of tetradecane is added containing the recovery standard (1,2,3,4 ¹³C₁₂ Cl₄DD, 100 pg/ml).

4. Quantification

The identification and quantification are done with capillary GC/MS systems where a high resolution gaschromatography (HRGC) is obligate. For isomer specific detection the RTx2330 (Restek) polar capillary column of 60 m in length (0.25 mm ID, 0.1 mm df) are applied. The temperature program is

$$\frac{50^{\circ}\text{C}}{1.5\text{min}} \quad 25^{\circ}\text{C}/\text{min} \quad \frac{180^{\circ}\text{C}}{0\text{min}} \quad 2^{\circ}\text{C}/\text{min} \quad \frac{260^{\circ}\text{C}}{30\text{min}}$$

The injection is done with a Gerstel system where the sample is injected as liquid. The injector is programmed as follows

$$\frac{120^{\circ}\text{C}}{2\text{min}} \quad 12^{\circ}\text{C}/\text{s} \quad \frac{280^{\circ}\text{C}}{10\text{min}} \quad 12^{\circ}\text{C}/\text{s} \quad \frac{300^{\circ}\text{C}}{10\text{min}}$$

The column head pressure is 24 psi. The interface is heated at 260°C. The stationary phase of these capillary columns contain nitril groups. Especially the octachlorinated dibenzofuran is easily discriminated on these columns of limited temperature stability . Thus, the measurement of this compound has to be done on a non-polar 60 m column (0.25 mm ID, 0.1 mm df) DB-5 (J+W). The temperature program is

$$\frac{130^{\circ}\text{C}}{2\text{min}} \frac{15^{\circ}\text{C}}{\text{min}} / \frac{180^{\circ}\text{C}}{0\text{min}} \frac{5^{\circ}\text{C}}{\text{min}} / \frac{280^{\circ}\text{C}}{15\text{min}}$$

The injection is done in a split/splitless injector at 280°C. The column head pressure is 23 psi. The interface is heated at 280°C.

The PCDD/F are commonly determined by mass spectrometry in the EI mode by tracing their M⁺, (M+2)⁺ ions or the most intensive ions of the isotope cluster. The measurement is conducted with high resolution at a Finnigan MAT 95 (R = 10000) or Finnigan MAT 8230 (R = 5000) instrument for isomer specific measurements and octachlorodibenzofuran, respectively.

Dating the sediment layers

The two fallout maxima in 1986 and 1963 are clearly identified by the ¹³⁷Cs activity. The other dating has been done by the ²¹⁰Pb-technique.

Results and Discussion

Two sediments from the Herrenwiesersee and Huzenbachersee were dated and analysed for PCDD/F. Figure 1 shows the results for the Herrenwiesersee

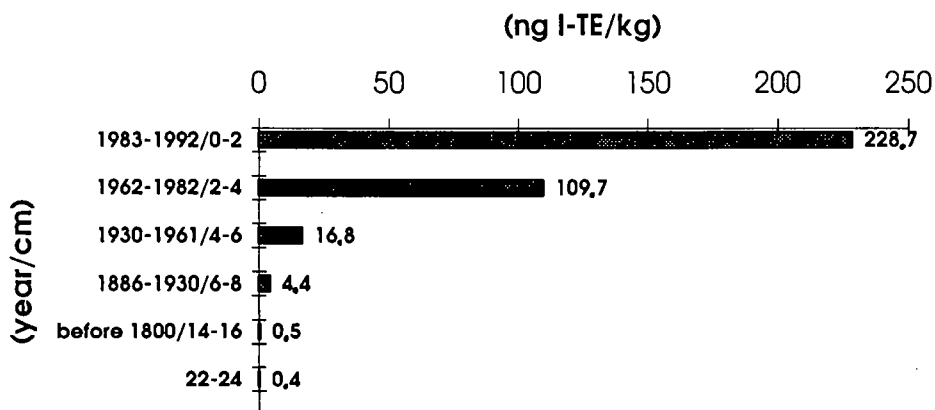


Figure 1: PCDD/F concentrations in layers of lake Herrenwiesersee sediments

There is a huge increase of PCDD/F-I-TE concentrations since 1930 by a factor of about 13. This result is similar to that of lake Siskiwit, but the difference to the layers from 1886 and before 1800 is more than a factor of 50 and 440, respectively. This is totally different to the findings of Kjeller et al.² in Rothamsted soils. These authors postulate no increase between 1840 and 1880. Assuming a half-time for PCDD/F in minimum in the range of wood destruction by the attack of unspecific peroxidases (30 years) a decrease in the upper sediment layers to 109 ng I-TE/kg might be possible. Lower sediment layers are often anaerobic and the permanent presence of peroxidases is not likely.

Thus the decay in the lower layers could not be explained by unspecific enzymatic destruction. Figure 2 shows the PCDD/F profile in the sediment layers of the lake Huzenbachersee.

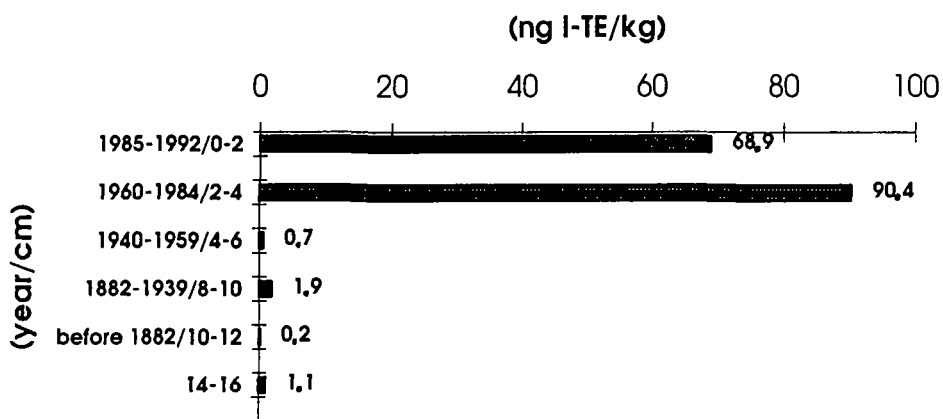


Figure 2: PCDD/F concentrations in layers of lake Huzenbach sediments

Although the two lakes are nearby there is a difference in the top layers by a factor slightly higher than 2, but in the year 1960-1984/1962-1982 the values are nearly equal. The factor between layer 4-6 cm and 2-4 cm is 140. In this lake the levels before 1940 seem to be constant. Before 1800 the values are in the range of rural soils. In summary the differences between toplayer contents of PCDD/F and lower layers are higher in the two German lakes than in the Rothamsted soils.

References

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