

HISTORICAL DEVELOPMENT OF SEDIMENT CONTAMINATION IN  
AN INDUSTRIALIZED AREA  
I. PCDDs AND PCDFs IN RIVER SEDIMENTS

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Abstract: The history of contamination of an old industrialized area in Germany has been investigated by the analysis of a sediment core from the river Lippe. The year of deposition was determined by radionuclide dating. Two more sediment samples were taken in the vicinity of a plant producing halogenated hydrocarbons (HHCs). The results indicate that the dioxins found in the sediments come mainly from that plant, the contamination starting in the early 50ies.

Introduction:

According to the investigation of a sediment core from the Great Lakes (1) relevant concentrations of PCDD/PCDF could be detected only in young sediment layers. The authors suggested that chlorine chemistry would be a main source for PCDD/PCDF in those sediments. In the Netherlands, some waste water effluents from the production of vinylchloride and some other HHCs turned out to be contaminated by PCDDs and PCDFs (2). The analysis of sediments as a marker of effluents contaminated with dioxins has been proven to be useful (2,3), because their concentrations in effluent water are very low, also varying in time. To get more information about the sources of PCDDs/PCDFs, we studied a sediment core from a small surface water system. The area of the river Lippe, a tributary to the river Rhine, has been chosen for this investigation, because it is influenced by three important types of effluents at different locations:

- Municipal waste water.
- Waste water from a chemical plant producing chlorine (capacity 310.000 t/yr), vinylchloride (410.000 t/yr), and other chlorinated aliphatics.
- Effluents from mining activities covering PCBs and PCDMs used as hydraulic fluids (4).

To assess the influence of these different source, sediment samples were taken upstream and downstream of the chemical plant. At the of mouth the river a sediment core was taken. The data of PCDD/PCDF are presented in the following. Data concerning heavy metals and other organic compounds will be published elsewhere.

#### Dating of sediment depth-profiles:

Sediment samples of about 2 m depth were collected in autumn of the year 1989 from a flood plain located near the mouth of the river Lippe in NRW. This area is flooded several times per year leading to a high sedimentation of suspended matter. The cores were obtained by simple sampling techniques in digging and partitioning in depth-profiles with steel spades.

The sediments were dried at 105°C and measured in a Marinelli beaker (a reentrant beaker) using a coaxial N-type-germanium detector for gamma assay. Corrections of selfabsorption were made for lower energies to obtain the radioactivity of Pb-210 together with Ra, Th and Cs. The well structured activity-depth profile of Cs-137 and Cs-134 could be attributed to fallout i.e. activity-time profile from nuclear bomb tests and Chernobyl reactor accidental release as described by M. Schönburg. (5)

An excellent additional prove of dating is given by the ratio that Ra-226 or Ra-228-activity bears to each other or to their daughter nuclides Pb-210 or Th-228, which are not in radioactive equilibrium with Ra and are going to do this in time. The radioactivity of Ra is delivered by one large hydrothermal source of a coal mine to the river Lippe. The best fit of calculated sedimentation rate is 1.85 cm/year. There is a good correlation between the time scales taken from Cs and Ra. (6)

#### Analysis:

100 g of sediment sample were dried and extracted with toluene after adding <sup>13</sup>C-labeled TCDD/F in definite amounts (10 ng) as internal standards.

The eluate was submitted to a clean-up on different columns:

1. multi component column with H<sub>2</sub>SO<sub>4</sub> conc./Celite  
- Na<sub>2</sub>SO<sub>4</sub>/NaHCO<sub>3</sub> - SiO<sub>2</sub>/Na<sub>2</sub>SO<sub>4</sub> elution with hexane
2. Al<sub>2</sub>O<sub>3</sub>, elution with a) benzene; b) hexane/CH<sub>2</sub>Cl<sub>2</sub>(98:2); c) hexane/CH<sub>2</sub>Cl<sub>2</sub>(1:1)
3. AgNO<sub>3</sub>/silica gel, elution with hexane

After concentration of the eluent, 10 ng of <sup>13</sup>C-1,2,3,4-TCDD were added as an internal standard for the control of recovery rates and of the sensitivity of the analytical system prior to GC/MS analysis.

#### Results:

Upstream of the plant (U., km 46.9), the sum of PCDDs and PCDFs is about 1.2 ug/kg, whereas downstream (D., km 37.1), the concentration increases to 6-8 ug/kg. The ratio between PCDDs and PCDFs shifts from 5:1 to about 1:1 (Fig.1). The increase of TCDD equivalents from '88 to '89 (D., Table 1), is due to a

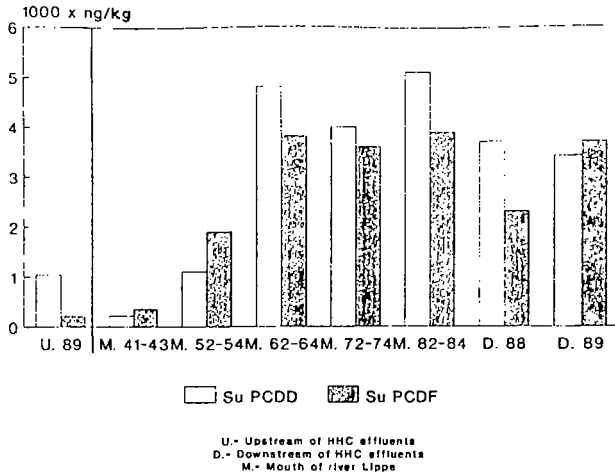


Fig. 1: Sum of PCDDs and PCDFs in sediment samples from the river Lippe

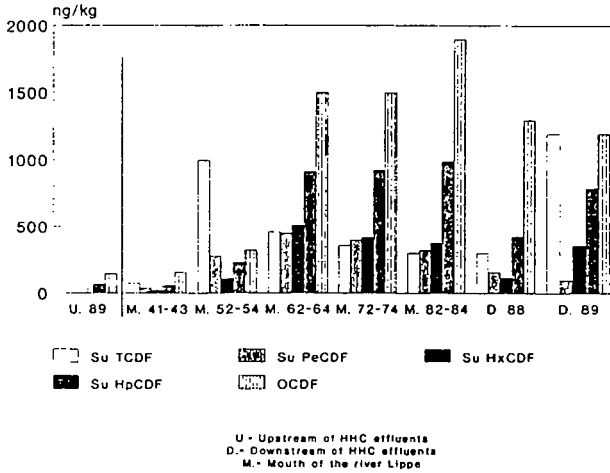


Fig. 2: Pattern of PCDF congeners in sediment samples from the river Lippe

remarkably higher amount of 2,3,7,8-TCDF on one hand, and to lower detection limits on the other hand. From the analysis of sections from the sediment core, one may take a tremendous increase of PCDDs and PCDFs beginning in the early 50ies, the concentrations slightly decreasing since the 60ies considering TCDD equivalents (Table 1). The ratio between PCDDs and PCDFs is between 0.6 and 1.3. The pattern of dibenzofurans (Fig. 2) remains constant since the 60ies resembling the pattern found downstream of the chemical plant. Astonishingly, the pattern of PCDFs from the sample taken in '89 is similar to the pattern from the 50ies characterized by a high amount of 2,3,7,8-TCDF (Fig. 2) whereas the '88 pattern resembles more to the later samples from the sediment core. The pattern of PCDD congeners consists mainly of OCDD and HpCDDs.

Concentrations of PCDDs and PCDFs in Sediment Samples expressed in TCDD Equivalent [ng/Kg]*		
Locality [Lippe]	Dating Year	TCDD Equiv.
Upstream of the chemical plant	1989	3.3
Downstream of the chemical plant	1988	22.0
	1989	130.0
Mouth of the river Lippe	1941-1943	9.1
	1952-1954	70.0
	1962-1964	74.0
	1972-1974	66.0
	1982-1984	59.0

\*TCDD equiv. following HCB

#### Discussion:

The concentration of PCDDs/PCDFs in the sample taken upstream of the chemical plant is in accordance with findings from other sediment investigations of low polluted rivers (2,3,7). The concentrations found downstream as well as in the sediment from the mouth of the river are higher than those in the river Rhine, though they do not reach the level found in the Rotterdam harbour (>1000 ng/kg T.E. (2)). The PCDD/PCDF ratio in the sediment core and in the samples taken downstream of the chemical plant is unusual. The influence from municipal waste water characterized normally by a high PCDD/PCDF ratio (7,8) seems to be low. Though the river is remarkably contaminated by PCBs from sources upstream, the concentration of PCDFs in sample, U. is only slightly increased. Obviously, the contamination is mainly caused by the chemical plant. The pattern of PCDFs in the core shifts from the 50ies to the 80ies, the TCDFs becoming less important. On the other hand, the sample from '89 taken downstream of the plant shows higher concentrations of TCDFs as compared to the upper sections of the sediment core. We cannot exclude that lower chlorinated congeners migrate slowly into deeper sections thus leading to the pattern shown in Fig. 2.

Considering the findings in the sediment core, the concentration of PCDDs/PCDFs increased dramatically in the 50ies, when the production of HHCs, especially vinylchloride, chlorinated solvents etc. started. Up to then, the main product was artificial rubber (9). This is in agreement with some results from the Great Lakes (1) indicating a relationship between dioxin contamination and chlorine chemistry. In analogy to the results from combustion of HHCs (10), the high amount of furans as compared to other sediments may be due to the production of chloroaliphatics. This holds also true for the isomer pattern of HpCDFs dominated by 1234678-HpCDF.

#### Conclusion:

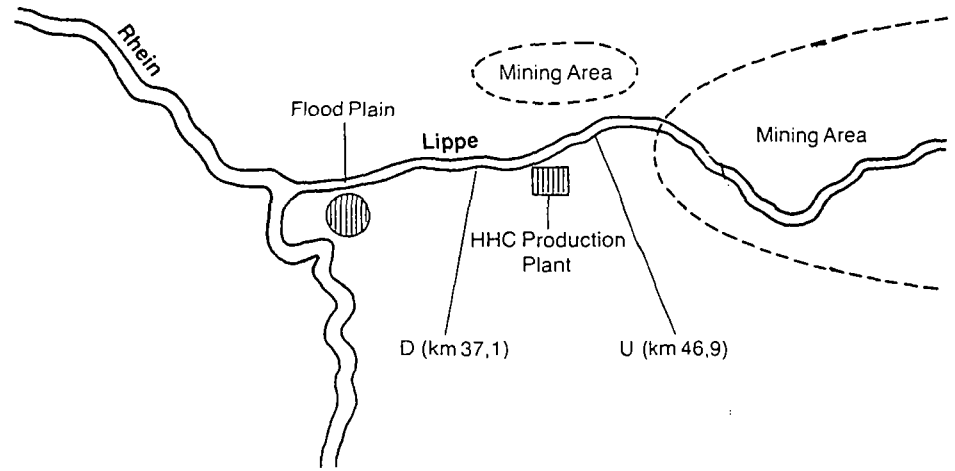
Our results show the close relationship between PCDD/PCDF contamination of surface water and chlorine chemistry. Primary sources of dioxins and furans like the production and use of aliphatic HHCs should be checked carefully for the generation of such toxic by-products. Having the of the environmental precaution principle in mind, the production and use of chlorinated organic compounds should be decreased to avoid dioxin contamination.

We thankfully acknowledge the careful work of our colleagues Paul Bachhausen, Dr. Jorg Alberti, Ingo Klinke, Dr. Ernst Plöger, Claus Schoch.

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Sampling points of the Dioxin monitoring program: River sediments were sampled upstream (U) and downstream (D) of the HHC production facility and on the flood plain. Most of the effluents from the mining area are situated upstream of U.



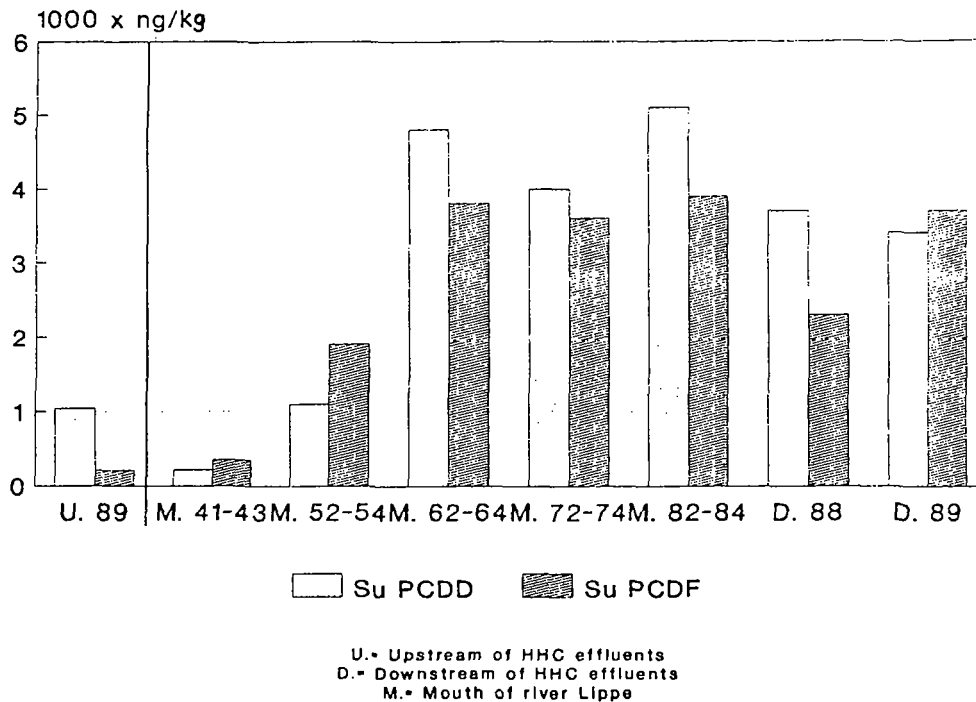
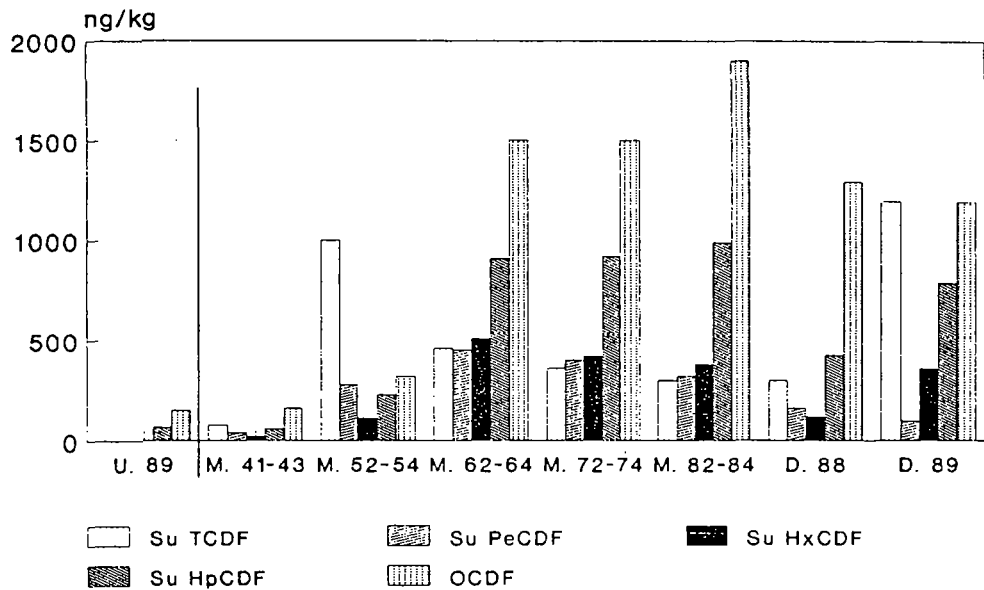


Fig. 1: Sum of PCDDs and PCDFs in sediment samples from the river Lippe



U.- Upstream of HHC effluents  
 D.- Downstream of HHC effluents  
 M.- Mouth of the river Lippe

Fig. 2: Pattern of PCDF congeners in sediment samples from the river Lippe