Chlorinated organic compounds in sediments of the River Danube and the River Traun (Upper Austria)

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Introduction

Sediment investigations are an effective tool for environmental monitoring /1/. The paper at hand deals with the contamination of the sediments of two rivers in Upper Austria with organochlorine substances: The River Danube flows through the provincial capital of Upper Austria, Linz, which constitutes an industrial conurbation (steel works and chemical industry) with more than 200.000 inhabitants. The waste water of Linz and the surrounding regions is collected in the waste water treatment plant Asten (around 850.000 population equivalents). The water quality of the River Traun is influenced by pulp and paper mill effluents as well as dyeworks effluents /2/. First results of this study were presented in /3/.

Investigation area

The sampling sites as well as the dates of sampling are presented in fig.1.

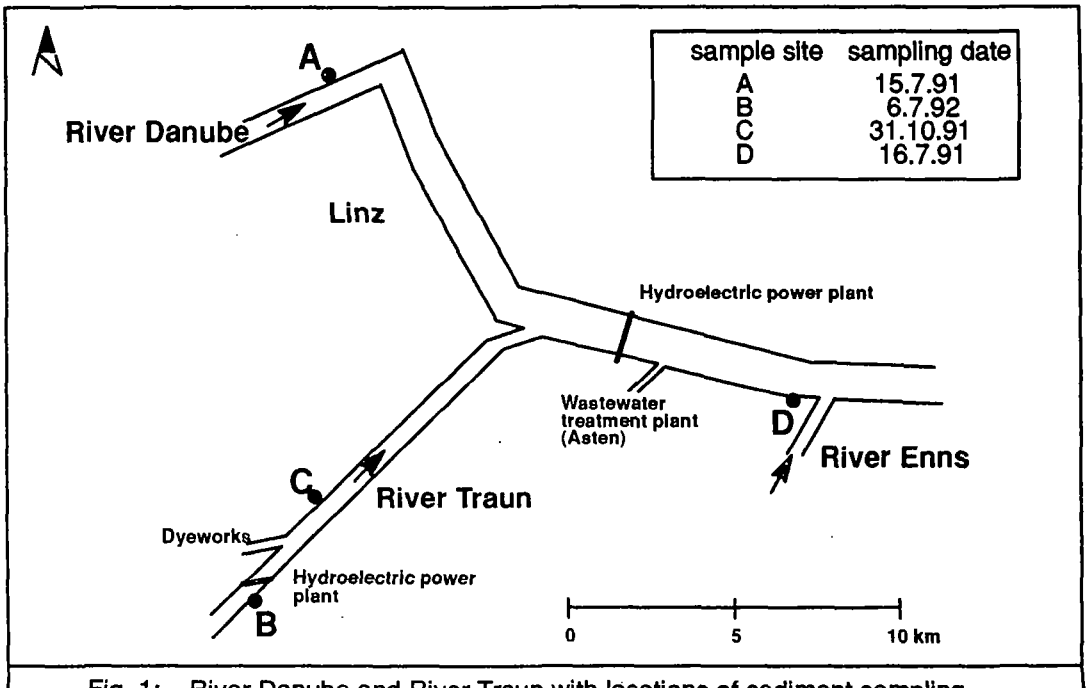

Fig. 1: River Danube and River Traun with locations of sediment sampling

Investigation programme

The sediments (fraction < 40 µm) were analyzed for: PCDDs/Fs, polychlorinated biphenyls (10 substances), chlorobenzenes (5), hexachlorocyclohexanes (5), chlorophenols (15), triazines (3).

Methods

Analysis of PCDD/PCDF

Sample preparation and dotation

30 – 50 g lyophilized sediments (fraction <40 µm) were spiked with 25 µl of a mixture of all 17 $^{13}C_{12}$–labelled 2,3,7,8–PCDD/F isomeres as surrogate standards and shaken for one hour.

Extraction

Extraction of dotated samples was carried out in a 250 ml Soxhlet–extractor with 300 ml toluene for 8 hours.

Clean Up

Macro–Alumina B Super I – Column
Column: 25 g aluminum oxide and 20 g Na_2SO_4
Eluant: benzene, hexane:dichloromethane (98:2) and hexane:dichloromethane (1:1).
Mixed Column
Column (from the bottom to the top): 2 g silica gel, 5 g silica gel/33% 1 N NaOH, 2 g silica gel, 10 g silica gel/44% conc. H_2SO_4 2 g silica gel, 10g Na_2SO_4
Eluant: hexane.
Mini–Alumina B Super I – Column
Column: 2.5 g aluminum oxide and 2 g Na_2SO_4
Eluant: hexane:dichloromethane (98:2) and hexane:dichloromethane (1:1). To this eluate 2.5 ng 1,2,3,4–$^{13}C_{12}$–TCDF as an injection standard solved in 25 µl of toluene was added. The mixture was then concentrated to 100 µl and filled in an amber autosampler vial.

GC/MS–Analysis

The analysis was carried out on two different GC–columns (DB5 and DBDIOXIN) on a gaschromatograph (HP 5890) with an Cold Injection System (CIS 2) and an autosampler (HP 7643) coupled with a high resolution masspectrometer (MAT 90) working in multi ion detection mode. The quantification of the isotope dilution analysis was carried out according to EPA 1613.

The detection limits of the method were between 0.2 and 1pg/g sample per isomere.

Analysis of PCBs, HCHs and Chlorobenzenes

Extraction

20 – 30 g lyophilized sediments (fraction <40 µm) were extracted with acetone/water (2+1). The filtrate was extracted by dichloromethane.

Clean–up

Gelpermeationchromatography on Bio–Beads S–X3 with cyclohexane:ethyl acetate (1:1)
removal of sulfur by heating the extract in toluene with powdered copper
chromatography on silica gel with hexane:toluene (65:35)

GC–ECD Analysis

The analysis was carried out on two different capillary columns (DB5, DB 1301).

GC–MS Analysis

The GC–MS analysis was carried out with a benchtop GC–MS (HRGC FI 8060/Trio 1000) on a PTE5, splitless injection, EI–ionisation at 70eV and SIM–mode.

It should be mentioned that corresponding positive GC–ECD results from two columns for some coplanar PCBs (PCB 77, PCB81, PCB 126) could not be verified by GC–MS, whereas the other positive PCB–results could be verified.

Recovery and detection limit

The entire method was tested by the analysis of sediment samples which were spiked with the above mentioned substances at concentration levels of 1.7 µg/kg and 3.3 µg/kg. Recovery rates of 60 – 79 % for chlorobenzenes, 75 – 90 % for HCHs and 75 – 95 % for PCBs were achieved.
The detection limit of the method varies according to parameter and sample between 0.1 – 0.2 µg/kg.

Results and discussion

PCDD/F (fig.2, tab.1): In all samples PCDDs and PCDFs were detected; 2,3,7,8–TCDD could not be found in any sample. In general the concentrations are not very high, they are lower than most of the literature data on polluted rivers, e.g. /4/,/5/,/6/,/7/. The profiles of the total PCDF at all sampling sites are similar, with a predominant TCDF group. On the contrary, OCCD dominates the total PCDD profiles of A, B, and C. The peak values of the total TCDD, TCDF and PeCDF at sampling site D are remarkable and seem to be influenced by the waste water treatment plant Asten charged with the effluents of the chemical industry in Linz.

Other organochlorine compounds (concentrations in **ng/g** d.w.):

PCB: Only PCB 138 (minimum: 0.48 at A, maximum: 1.18 at B), PCB 153 (min.: 0.42 at A; max.: 0.89 at B), and PCB 180 (min.: 0.38 at A; max.: 0.76 at B) were found in all samples. Coplanar congeners were not detected.

Chlorobenzenes: Hexachlorobenzene was the only substance found (0.6 at A; 0.14 at B).

Hexachlorocyclohexanes: Only gamma HCH was found in all samples, it ranges from 0.20 to 0.31.

Chlorophenols: All samples were below the detection limit (5–25 ng/g).

Triazines: Atrazine (0.44 at B and 0.64 at D) and Desethylatrazine (1.04 at B) were observed.

Like the PCDD/F, the samples show lower concentrations than other sediment samples influenced by industrial waste water effluents (e.g. /8/). These results do not indicate a remarkable impact of the waste water effluents on the sections of the rivers the samples are taken from.

References

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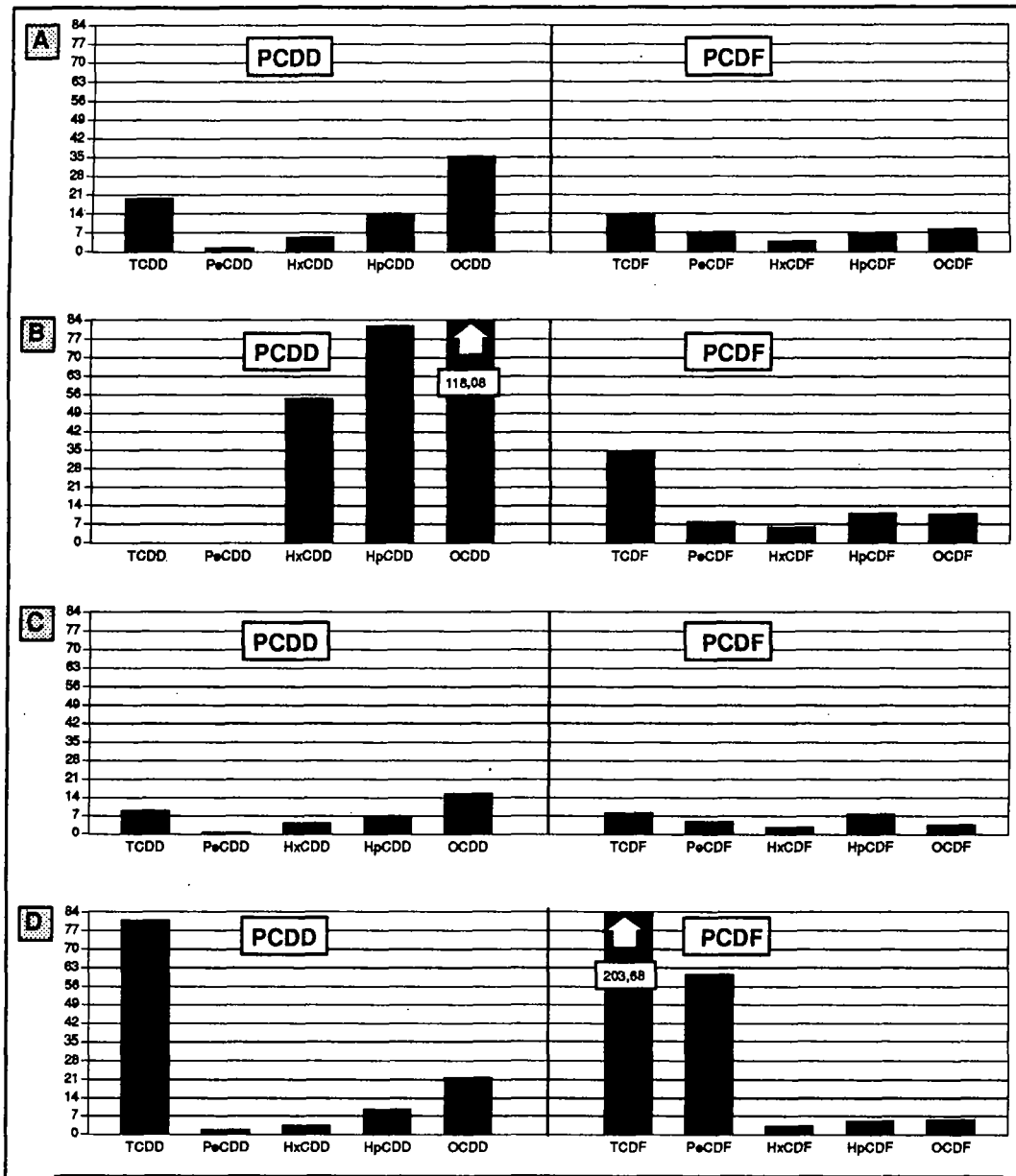

	A	B	C	D
total PCDD	76.00	255.00	36.76	118.32
total PCDF	40.50	71.00	27.80	278.68
total PCDD/F	116.50	326.00	64.56	397.00
total 2378–isomeres	63.10	216.04	30.12	39.64
TEQ (ITEF)	1.25	3.69	0.74	0.89

Fig.2, Tab1: PCDD and PCDF in sediments of the River Danube (A, D) and River Traun (B, C), pg/g d.w.