

Geochronology and specific anthropogenic markers in a sediment core from the Teltow Canal in Berlin, Germany

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1. Introduction

The Teltow Canal situated in the urban area of Berlin (Germany) is a very slow flowing canal with a high sedimentation rates as the result of a barrier near the former GDR-border. As formerly reported numerous halogenated and non-halogenated compounds were detected in Teltow Canal sediments nearby a former industrial point source^{1,2}. Further investigations on Teltow Canal sediments considering the solvent extractable as well as the non-extractable organic fraction revealed concentrations of extractable DDT related compounds up to 300,000 ng/g (d.w.). More than 125,000 ng/g (d.w.) of these contaminants were determined in the non-extractable fraction (bound residues) as recently published³. In addition, the bound residues fraction, as analysed by flash pyrolysis and chemical degradation, indicated either transformation or degradation processes affecting the DDT pesticides, that differed significantly relative to the well known processes affecting the extractable compounds.

To prolong the previously published analysis results and to study the geochronology of anthropogenic markers in the past decades, two additional sediment cores were taken in 1999. The sediment cores were obtained in very low flow areas near the former GDR-border. Gamma-spectrometric dating applied to a comparable sediment core at the location TK-BC (see Figure 1) indicated an age of ≥ 100 years at a depth of 95-100 cm and a sediment accumulation rate of up to 3-4 cm/year at the sediment top. These data will be applied for a rough estimation of the sedimentation time periods associated to the core samples investigated in the present study.

Briefly, this study focuses on the vertical distribution of DDT and its metabolites in undisturbed sediment layers located in the same sampling area (location TKS, Figure 1). The correlation of the detected concentrations with the stratigraphical sediment profile reflects not only a geochronological increase or decrease of these compounds, but also the possibility to reflect the ban as well as the resulting restriction and termination of the DDT-production at this industrial area.

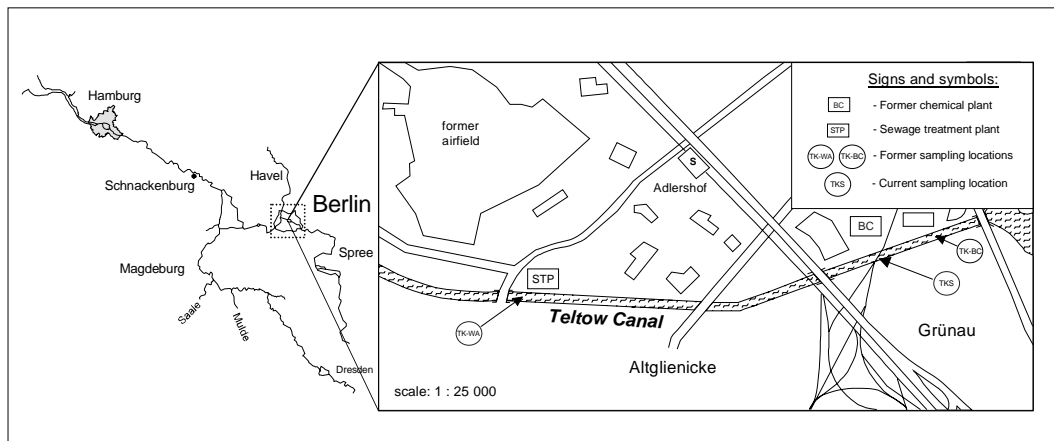


Figure 1. Map of a part of the Teltow Canal, Berlin, Germany showing former and current sampling locations³

2. Methods and Materials

Two 40 cm cores were taken by means of a tube coring system in May 1999 from a zodiac at location TKS (see Figure 1). The fresh sediment material was characterised as a black fine mud, without sand, with high water content and an anoxic sediment-water interface. Considering former results of nearby located cores, the 40 cm of these cores represent a sedimentation period of approx. 40 to 50 years.

After sampling the sediment cores were frozen immediately and stored at -20°C before subdividing. As no substructures in the sediment material were indicated, the two cores were sliced into 2 cm layers and combined in one homogeneous sediment sample and freeze-dried under mild conditions⁵. For inorganic and organic geochemical analysis the material was sub-divided into two aliquots, one small part used for trace metal analysis and a major part used for the analysis of organic contaminants. Until the extraction the samples were stored in the dark at 4°C in glass flasks.

Extraction of the water samples was realised after centrifugation and filtration through $1.2\ \mu\text{m}$ GF/F filters (Whatman) by enrichment on Lichrolut ENTM (200 mg) at pH 2 with HCl acidification (suprapur). The conditioning was performed with methanol, aqua demin with a subsequent enrichment within 2 hours under gravity and a subsequent elution with ethylacetate/methanol (v:v 1:1) with an incubation time of 5 minutes and a sequential elution with $2 \times 3\ \text{ml}$ of the solvents at a rate of $<1\ \text{ml/min}$. The samples were first screened after volume reduction with $50\ \mu\text{l}$ final volume (acetone) and then derivatised with a 3:1 ratio (TMSH:sample) and DDA 1:1 via ultrasonic treatment for 10 minutes and a final volume of $200\ \mu\text{l}$.

The fluffy-layer sample was sequentially extracted with toluene/methanol (20 ml, 1:1) and then with acetone/hexane (20 ml, 1:1) ultrasonically (15 min) and the solvent was evaporated under a gentle nitrogen stream to $300\ \mu\text{l}$ for the screening and $200\ \mu\text{l}$ for the DDX-analysis.

To investigate the content of low molecular lipophilic organic compounds the analysis of the sediment samples was realised according to previous published investigations (6).

GC/MS analyses were performed on a Finnigan Trace MS mass spectrometer (Thermoquest, Egelsbach, FRG) linked to a Mega Series HRGC 5160 gas chromatograph (Carlo Erba, Milano, I) which was equipped with a 45 m x 0,25 mm x 0,25 μ m i.d. film SE 54-CB fused silica capillary column (CS Chromatographie Service, Langerwehe, FRG). Chromatographic conditions were as follows: 270 °C injector temperature, 1 μ L split/splitless injection at 60 °C, splitless time 60 s, 3 min isotherm, then programmed at 3 °C/min to 300 °C, hydrogen carrier gas velocity 40 mL/s. The mass spectrometer was operated in electron impact ionisation mode (EI⁺, 70 eV) with a source temperature of 200 °C scanning from 35 to 700 amu at a rate of 0.5 s/decade with an interscan of 0.1 s. Acidic compounds in the polar fraction were methylated prior to analysis by adding a diazomethane solution and subsequent re-concentration. Identification of the individual compounds was based on comparison of EI⁺-mass spectra with reference compounds of mass spectra data base libraries (NIST98, Wile/NBS, 7th Ed., electronic version), reference compounds and gas chromatographic retention times.

Quantitative data were obtained by integration of specific ion chromatograms extracted from the TIC. The ions used for quantification, structural information of the compounds as well as the recoveries for the extraction and evaporating procedures are presented in Table 2. An external four-point-calibration with authentic reference compounds was used for quantification.

All used reference compounds (purity > 96 – 99 %) were purchased from Promochem (Wesel, FRG), with the exception of 4, 4'-DDCN, which was synthesised. Recoveries were determined by spiking pre-extracted sediment samples with a mixture of reference compounds and subsequent execution of the extraction after incubation and fractionation procedures described.

3. Results and Discussion

Two combined sediment cores (TKS) of the Teltow Canal, Berlin, Germany (see Figure 1) were investigated by inorganic and organic geochemical analysis, especially focused on the pesticides. According to former investigations³ elevated amounts of DDT and its metabolites were determined. Assuming undisturbed sediment layers the depth correlated identification and quantification of these compounds allowed a temporal integration of the historical input of DDT and its metabolites.

In the water samples the more hydrophilic compounds of the DDT-metabolites were detected. In addition, traces of DDOH, DDM and no HCH were analysed and 4 pesticides (Chlorobenzilat, Etoxinol, Chloropropylat or Rospan, Kelthane) with an analogous structure to DDT.

The fluffy-layer sample revealed the same compounds as in the sediment samples, the screening illustrated additionally all 4 HCHs (α - δ) and HCB, not detected in the water samples.

Table 1. Results of the organic geochemical analysis applied to fluffy-layer sample, the first two sediment layers (TKS 0-2 and 2-4) of the current sediment cores and to a sample of the corresponding water column (TKS 4-0). (n.d.= below detection limit)

ng/L	TK 4-0	TK 0-2	TK 2-4	ng/g	TK FL
o-p'-DDA	207	330	834	o-p'-DDA	513
p-p'-DDA	548	1480	3146	p-p'-DDA	1958
p-p'-DDE	n.d.	n.d.	n.d.	p-p'-DDE	1118
o-p'-DDD	n.d.	n.d.	n.d.	o-p'-DDMS	traces
p-p'-DDD	n.d.	n.d.	n.d.	p-p'-DDMS	58
p-p'-DDMU	n.d.	n.d.	n.d.	o-p'-DDD	4060
o-p'-DBP	265	208	59	p-p'-DDD	8789
p-p'-DBP	622	1637	345	p-p'-DDNU	177
p-p'-DBPH	n.d.	249	n.d.	p-p'-DDMU	5618
				o-p'-DBP	450
				p-p'-DBP	3734

The organic geochemical analyses applied to all sediment samples of the core TKS reveal very high concentrations of DDT and its metabolites. These expected amounts were formerly attributed to a closed chemical plant⁵. The quantitative analysis included the 4,4'-isomers of DDT, DDD, DDE, DDCN, DBP, DDMS, DDMU, DDEt and DDM. All corresponding 2,4'-isomers were also detected, but the recovery and calibration data were kept from the 4,4'-isomers. For quantification of DDMS and DDEt the calibration data and recovery of 4,4'-DDD were used due to commercially non available reference material. Quantitative data are presented in Table 2 and Figure 2.

Following, the occurrence of DDT and its metabolites will be discussed with respect to their vertical distribution in the sediment core investigated. Main contaminants were DDD, DDMS and DDMU. DDD is the main metabolite of the anaerobic degradation pathway, with maximum values of approx. 30,000 ng/g dry weight in the deeper layers. The concentrations detected in all sediment layers ranged between 2,000 to 30,000 ng/g.

A second group of metabolites including DDE, DBP and DDEt appeared with concentrations significantly lower than DDD. Very low concentrations were determined for DDCN and DDM in the range of 1 to 650 ng/g. The concentration of DDE, the metabolite predominately accumulated in the more aerobic environment, was in the range of almost 10 to 30% of DDD. Regarding the maximum concentrations of DDD up to 30,000 ng/g in comparison to the highest values of DDE (up to 9,000 ng/g), a predominantly anaerobic environment can be stated. DDT itself was determined with concentrations of an average of 2,500 ng/g, reflecting a progressive degradation of the pesticide. Figure 2 illustrates the distribution of all 4,4'-isomers as a function of sediment depth. The presented data are arranged according to their different concentration levels. For all compounds a sharp increase in concentration was observed in deeper layers relative to the top layer samples. In addition, it is remarkable that the maximum concentration of 4,4'-DDD, 4,4'-DDMU, 4,4'-DDMS and 4,4'-DDT peaked at a depth of 24 cm, whereas the maximum values of 4,4'-DBP, 4,4'-DDEt, 4,4'-DDCN and 4,4'-DDM were located in a slightly deeper layer (28 and 30 cm). In comparison to the quantitative vertical distribution of all other metabolites the concentrations of 4,4'-DDCN showed a significant higher variation within the core. Higher concentrations were observed in two sediment horizons, but noteworthy the highest concentration was also detected at a depth of 28 cm.

As expected, the quantitative data of all 2,4'-Isomers detected indicate very similar trends in the concentration gradients as compared to the 4,4'-isomers. The concentration ranges vary approximately between 10 to 30 % as compared to 4,4'-isomers. Only the 2,4'-DDMS showed higher contributions of up to 50 % (see Table 2).

According to the distribution described for the 4,4'-isomers, the concentration of 2,4'-DDD and 2,4'-DDMS reached their highest concentration at a depth of 24 cm, whereas the maximum concentration of 2,4'-DDEt, 2,4'-DDCN, 2,4'-DDT, 2,4'-DDE and 2,4'-DBP was detected at a depth of 28 cm.

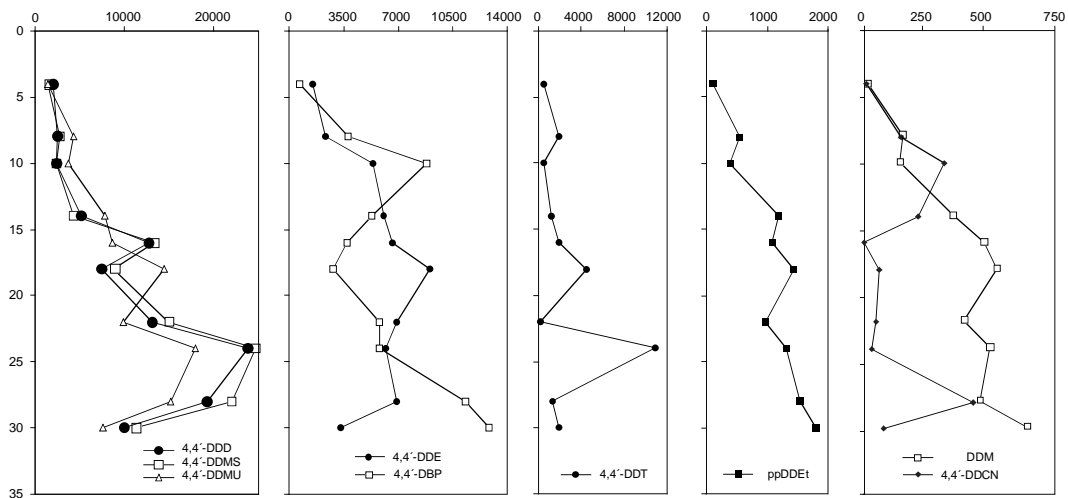


Figure 2. Concentration range of DDT and some metabolites in dependence of the depth. The subdivision was done by decrease main concentration levels.

With respect to the described results a significant contamination of sediment samples of the Teltow Canal, Berlin (Germany) with DDT and related compounds was pointed out for a longer time period. Considering the sedimentation rate and γ -spectrometric dating formerly applied to a comparable sediment core (M. Ricking, in prep.) a geo-chronological description of the DDT related emissions into the sediments of Teltow Canal is enabled.

The decreasing concentrations from the 30 cm layer towards the top of the sediment core characterise a decreasing emission in this area. This can be attributed to the reduction of the industrial DDT production since 1975. Following, the highest production rates can attribute to a time period corresponding to the lowest sediment layers between 24 and 30 cm.

Table 2: Quantitative data of the 2,4'- and 4,4'-isomers of DDEt, DDCN, DBP and DMS and the 2,4'- to 4,4'- ratios. All represented values are concentrations in [ng/g] dry weight.

depth [cm]	DDEt [ng/g] d.w.			DDCN [ng/g] d.w.			DBP [ng/g] d.w.			DDMS [ng/g] d.w.		
	2,4'-	4,4'-	ratio	2,4'-	4,4'-	ratio	2,4'-	4,4'-	ratio	2,4'-	4,4'-	ratio
4	30	110	0.27	1	20	0.05	130	720	0.18	650	1420	0.46
8	90	540	0.17	4	160	0.03	850	3800	0.22	1500	2830	0.53
10	60	400	0.15	6	340	0.02	1600	8800	0.18	1200	2360	0.51
14	230	1200	0.19	7	230	0.03	230	900	0.26	1880	4350	0.43
16	210	1100	0.19	1	14	0.07	14	780	0.02	5400	13430	0.40
18	260	1430	0.18	5	70	0.07	70	700	0.10	4330	8820	0.49
22	200	980	0.20	7	55	0.13	60	1070	0.06	7100	14930	0.48
24	260	1300	0.20	3	40	0.08	40	1010	0.04	12390	24620	0.50
28	300	1550	0.19	14	460	0.03	460	1930	0.24	10510	21580	0.49
30	280	1800	0.16	7	100	0.07	90	1870	0.05	5820	11250	0.52

Acknowledgements

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4. References

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