GEOCHRONOLOGY AND SPECIFIC ANTHROPOGENIC MARKERS IN A SEDIMENT CORE FROM THE TELTOW CANAL IN BERLIN

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ABSTRACT: To study the geochronology of biogenic and anthropogenic markers in the past decades, two 40 cm sediment cores were collected from the Teltow Canal in Berlin (Germany). Preliminary analysis on a pre-sample from the Berlin area indicated high concentrations of halogenated organic compounds. Different DDT-related metabolites, identified in this samples, are quantified and the results are published elsewhere (Schwarzbauer et al. 2001). The cores will are dated and the geochronology of the organic compounds during the past ~40 years is analysed by means of a non-target approach with subsequent quantification of compounds classes of different physico-chemical features. The analytical method includes a sequential fluid extraction and liquid chromatographic fractionation of the sediment layers. Qualitative and quantitative analyses are performed with simultaneous GC/FID-ECD and GC/MS combinations. Screening analyses reveal a complex mixture of organic substances including a wide range of anthropogenic contaminants like pharmaceuticals, plasticizers, organotin compounds, additives, halogenated aromatics and pesticides.

RÉSUMÉ: Afin de connaître l'histoire géologique des marqueurs biogéniques et anthropogéniques des dernières décennies, deux carottes de sédiments ont été extraites du Canal Teltow à Berlin. Les premières analyses faites sur un échantillon ont mis en évidence une contamination par des polluants organiques persistants (POPs), dont notamment des hydrocarbures aromatiques halogénés du groupe DDT. Ces analyses ont été réalisées à partir d'une extraction liquide-liquide et d'une séparation chromatographique sur colonne de silice. L'approche à la fois qualitative et quantitative s'est faite grâce à une chromatographie en phase gazeuse couplée avec une spectrométrie de masse. Par ailleurs, une analyse globale a révélé la présence d'un mélange complexe de substances organiques comprenant un grand nombre de contaminants anthrogéniques tels que des produits pharmaceutiques, des plastifiants, des composants organostanniques ainsi que des additifs, des hydrocarbures aromatiques halogénés et des pesticides

1. INTRODUCTION

The Teltow Canal situated in the urban area of Berlin (Germany) is a very slow flowing canal with a high sedimentation rate 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 an former industrial point source (Schwarzbauer et al. 2001, Ricking et al. 2003). 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 300000 ng/g (d.w.). More than 125000 ng/g (d.w.) of these contaminants were determined in the non-extractable fraction (bound residues) as recently published (Schwarzbauer et al. 2003). 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 as compared 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 presented 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 geochronolgical 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.

2. INVESTIGATION METHODS

2.1 Samples

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

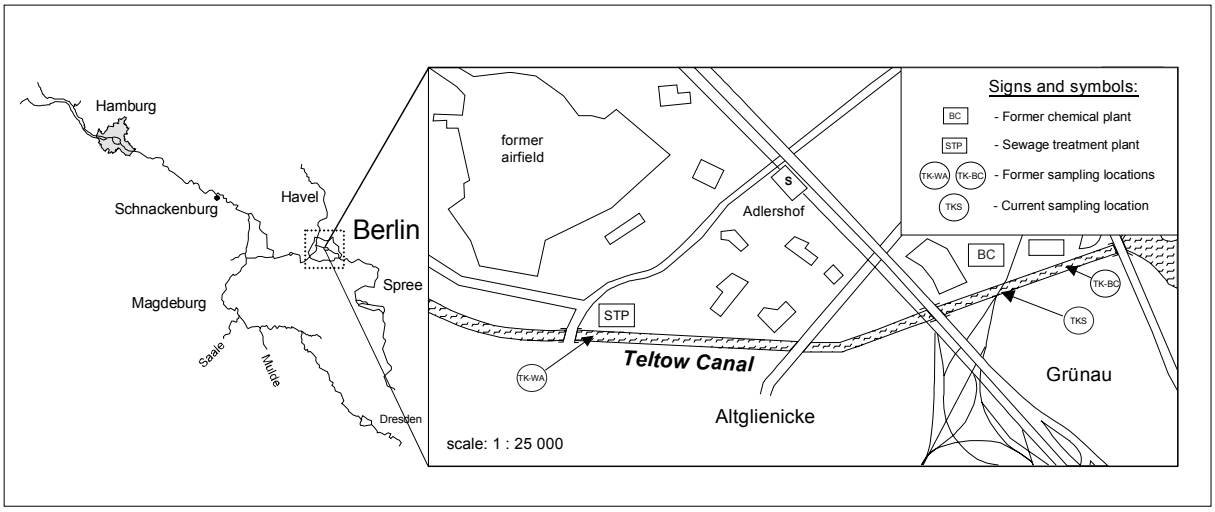


Figure 1. Map of a part of the Teltow Canal, Berlin, Germany showing former and current sampling locations (from Schwarzbauer *et al*. 2003)

a black fine mud, without sand, with a high water content and an anoxic sediment-water interface. Considering former results of nearby located cores, the 40 cm of these cores represent an sedimentation period of approx. 40 to 50 years.

After sampling the sediment cores were frozen immediately and stored at –20°C before sub-dividing. 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 conditions (Ricking et al. 2002). 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.

2.2 Extraction

To investigate the low molecular lipophilic organic compounds approximately 5g of each sample were extracted by a sequential solid-liquid extraction procedure with a high speed dispersion device (Ultra Turrax, T25, IKA, Stauffen, FRG). The extraction parameters were as followed: dispersion time of 3 minutes with 16000 rpm for 5 times with 30 mL solvent; (1.) acetone, (2.,3.) acetone/hexane (1:1, vol:vol), (4., 5.) hexane. Each extraction step was followed by centrifugation at 4000 rpm, separation and combining of the organic layers. After separating the aqueous phase the solvent extract was contracted down to a volume of 1mL and dried over anhydrous granulated sodium sulphate. To remove sulphur 50 mg of activated copper powder was added. After ultrasonic agitation and a reaction time of 16 h the extract was prepared for chromatographic fractionation by concentration down to a volume of 0,5 mL by rotary evaporation at room temperature.

2.3 Fractionation

Fractionation of the raw extracts was performed by column chromatography (Baker, 2 g silica gel 40 µm). Six fractions were obtained by using solvent-mixtures of n-pentane and dichloromethane as eluent according to Schwarzbauer et al (2000). The extraction conditions were as follows: 1. fraction: 5 mL n-pentane, 2. faction: 8,5 mL n-pentane/dichloromethane (95:5; vol:vol), 3. fraction: 5 mL n-pentane/dichloromethane (90:10; vol:vol), 4. fraction: 5 mL n-pentane/dichloromethane (40:60; vol:vol), 5. fraction: 5 mL dichloromethane, 6.fraction: 5 mL methanol.

For quantification 50 µL of an internal standard solution containing 5,8 ng/µL fluoroacetophenone, 6,0 ng/µL d_{36}-hexadecane and 5,1 ng/µL d_{10}-anthracene were added to each fraction. The volume was reduced to 50-100 µL in a gentle stream of purified nitrogen at room temperature. All extracts were analysed by gas chromatography and gas chromatography-mass spectrometry.

2.4 Gas Chromatographic Analysis

The gas chromatographic analyses were carried out using a GC 8000 series gas chromatograph (Fisons instruments, Wiesbaden, FRG), equipped with a 25 m x 0,25 mm i.d. x 0,25 µm film SE-54 fused silica capillary column (CS Chromatographie Service, Langerwehe, FRG). The end of the capillary column was connected to an eluate-splitter for simultaneous detection of the analytes with a flame ionisation detector (FID) and an electron capture detector (ECD with nitrogen make up gas). Chromatographic conditions were as followed: 270 °C injector temperature; 300 °C detector temperature; 1 µL 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.

2.5 GC/MS Analysis

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 µm 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 µL 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, 4th 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 content. According to former investigations (Schwarzbauer et al. 2003) 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.

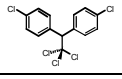
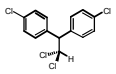
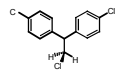
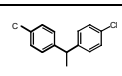
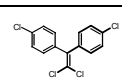
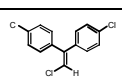
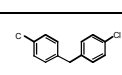
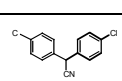
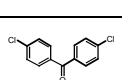
Prior to the organic analyses the samples were characterised by inorganic geochemical analyses of pore water of the first two upper sediment layers (see Table 1). In comparison to these data the values of a former investigated sample (TKWA) close to the location were also presented (Ricking, unpublished).

Table 1. Results of the inorganic geochemical analysis applied to pore water of a preliminary sample (TKWA), 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)

sample	DOC (mg/L)	Cd (mg/L)	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)
TKWA	17.00	n.d.	14.00	n.d.	0.10
TKS 4-0	17.00	n.d.	1.00	n.d.	0.02
TKS 0-2	60.00	n.d.	14.00	n.d.	0.03
TKS 2-4	16.00	n.d.	9.00	n.d.	0.03

The pore-water samples of the sediment layers close to the surface of both samples, TKWA and TKS, were characterised by DOC values between 16 and 60 mg/L. The maximum values were obtained in the top layer of the TKS sample. The results of the inorganic analyses revealed concentrations of copper and zinc within a range between 1 to 14 mg/L and 0,02 to 0,1 mg/L, respectively. For the TKS samples the highest values were determined in the top layer. The concentrations of lead and cadmium were below the detection limit in all samples investigated.

Table 2. Compound information for identification and quantification

Compounds	Chemical structure	
4,4´-DDT 2,2-Bis(4-chlorophenyl)-1,1,1-trichloroethane		characteristic ion (m/z): 235, 237 recovery: 64%
4,4´-DDD 2,2-Bis(4-chlorophenyl)-1,1-dichloroethane		characteristic ion (m/z): 235, 237 recovery: 70%
4,4´-DDMS 2,2-Bis(4-chlorophenyl)-1-chloroethane		characteristic ion (m/z): 235, 237 recovery: 70%
4,4´-DDEt 1,1-Bis(4-chlorophenyl)-ethane		characteristic ion (m/z): 235, 237 recovery: 70%
4,4´-DDE 2,2-Bis(4-chlorophenyl)-1,1-dichloroethene		characteristic ion (m/z): 246, 248 recovery: 89%
4,4´-DDMU 2,2-Bis(4-chlorophenyl)-1-chloroethene		characteristic ion (m/z): 212, 282 recovery: 75%
4,4´-DDM Bis(4-chlorophenyl)-methane		characteristic ion (m/z): 236, 238 recovery: 68%
4,4´-DDCN Bis(4-chlorophenyl)-acetonitrile		characteristic ion (m/z): 226, 228 recovery: 90%
4,4´-DBP 4,4-Dichlorobenzo-phenone		characteristic ion (m/z): 139, 141 recovery: 77%

The organic geochemical analyses applied to all sediment samples of the core TKS reveals very high concentrations of DDT and its metabolites. These expected amounts were

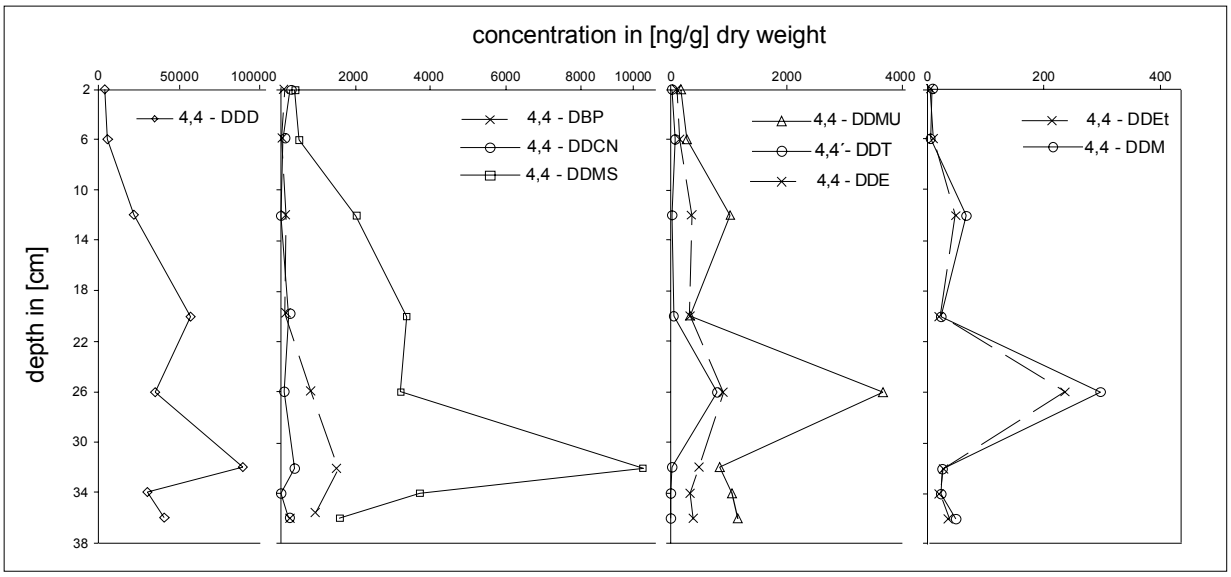


Figure 2. Concentration range of DDT and some metabolites as a function of depth in the sediment core. The subdivision was done by decrease main concentration levels.

formerly attributed to a pesticides producing chemical plant (Heberer et al 1999). The quantitative analyses 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 commercial non available reference material. All quantitative data are presented in Table. 3 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 contaminant was DDD, the main metabolite of the anaerobic degradation pathway, with maximum values of approx. 90000 ng/g dry weight at a depth of 32 cm. The concentration detected in all sediment layers ranged between 4000 to 90000 ng/g.

A second group of metabolites including DDMS, DDMU DBP and DDCN appeared with concentrations significantly lower than DDD. Very low concentrations were determined for DDEt and DDM with values between 5 to 300 ng/g. The concentration of DDE, the metabolite predominately accumulated in the more aerobic environment, was in the range of almost 10% of DDD. Regarding the maximum concentrations of DDD up to 90000 ng/g in comparison to the highest values of DDE (up to 900 ng/g) a predominantly anaerobic environment can be stated. DDT itself was determined with concentrations up to 800 ng/g, reflecting a progressive degradation of the pesticide. Figure 2 illustrates the distribution of all 4,4´-isomers in relation to the sedimentation depth. The presented data are arranged according to their different concentration levels. For all compounds a sharp increase in concentration was observed relative to the top layer samples. In addition it is remarkable that the maximum concentration of 4,4´-DDD, 4,4´-DBP, 4,4´-DDCN and 4,4´-DDMS peaked at a depth of 26 cm, whereas the maximum values of 4,4´-DDMU, 4,4´-DDT, 4,4´-DDE, 4,4´-DDEt and 4,4´-DDM, were located in a slightly deeper layer (32cm).

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. A distinct maximum was not observed, but noteworthy the highest concentration was also detected at a depth of 32 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 40 % as compared to 4,4´-isomers. Only the 2,4´-DDCN showed higher contributions of up to 60 % (see Table 3).

Nevertheless, the distribution of 2,4'-DDCN revealed no distinct quantitative maximum but a higher variation of concentrations, similar to the occurrence of the corresponding 4,4'-isomer. According to the distribution described for the 4,4'-isomers, the concentration of 2,4´-DDD and 2,4´-DBP reached their highest concentration at a depth of 32 cm, whereas the maximum concentration of 2,4´-DDEt was detected at a depth of 26 cm.

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 (unpublished results, M. Ricking) a geo-chronological description of the DDT related emissions into the sediments of Teltow Canal is enabled.

Table 3. Quantitative data of the 2,4´- and 4,4´-isomers of DDD, DDEt, DDCN and DBP in [ng/g] dry weight and the 2,4´- to 4,4´- ratios.

depth [cm]	*DDD*			DDEt			*DDCN*			*DBP*		
	2,4´-	**4,4´-**	***ratio***	**2,4´-**	**4,4´-**	***ratio***	**2,4´-**	**4,4´-**	***ratio***	**2,4´-**	**4,4´-**	***ratio***
2	1150	4000	*0.29*	1	5	*0.20*	130	250	*0.52*	20	50	*0.40*
6	1650	5700	*0.29*	3	11	*0.27*	30	50	*0.60*	3	15	*0.20*
12	4950	22000	*0.23*	14	49	*0.29*	5	10	*0.50*	20	130	*0.15*
20	11350	56900	*0.20*	4	19	*0.21*	100	200	*0.50*	100	190	*0.53*
26	28900	356000	*0.08*	56	236	*0.24*	50	80	*0.63*	180	700	*0.26*
32	29150	90000	*0.32*	5	28	*0.18*	180	370	*0.49*	250	1480	*0.17*
34	10300	37000	*0.28*	5	22	*0.23*	11	35	*0.31*	160	625	*0.26*
36	4600	41200	*0.11*	8	36	*0.22*	90	210	*0.43*	190	400	*0.48*

The decreasing concentrations from the 32 cm layer towards the top of the sediment core characterise a decline in emission in this area. This can be attributed to the reduction of the industrial DDT-production and a ban of DDT. Following, the highest concentrations in the sediment layers between 32 and 40 cm can be related to the highest production rates (Hartmann, personal communication.

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