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# LOW VOLATILE CHLORINATED HYDROCARBONS AND HEAVY METALS IN AQUATIC SEDIMENTS IN BERLIN AND ENVIRONS

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Chlorinated hydrocarbons of low volatility, especially DDT, HCH, and PCB, have been used as indicators of the level of pollution in aquatic sediments. These compounds are present in all the sediment samples analysed by gas chromatography. Enrichment factors between water and sediment are high ( $K_d = 85,108$  in the case of DDT), documenting the strong geoaccumulation tendency of toxic chlorinated hydrocarbons.

No linear relationship was observed between the concentration of contaminants (HCH and PCB) and the amount of organic matter in the sediments. The application of the EVOLON model to determine the kinetics of sorption showed clearly a value of saturation. The sorbed amount of these chlorinated hydrocarbons appears to be largely dependent upon that portion of organic matter which is on the surface of the sediment particles.

From the metals investigated Hg, Pb, Cu, Cd and Zn are of anthropogenic origin; Cr, Ni and Co are of geochemical origin and correspond to background values.

**KEY WORDS:** Geoaccumulation, chlorinated hydrocarbons, heavy metals, aquatic sediments, enrichment factors, modelling, sorption.

## INTRODUCTION

Sediments act as natural buffers and filtration systems in the terrestrial-limnological cycle. The sorption, enrichment, and degradation of introduced substances is not unlimited. Aquatic sediments contain an integration of the contaminants emitted over time and may be used as an indicator of local and short-term inputs.

The work reported here includes an investigation of the enrichment of DDT, HCH and PCB in aquatic sediments, modelling of the sorption of HCH and PCB as function of sediment organic matter, and the enrichment of heavy metals in surface sediments of Berlin waters and their surroundings.

## MATERIALS AND METHODS

### *Sampling locations*

Sediment samples were taken once a month, beginning in April 1987, for analysis for low volatile chlorinated hydrocarbons (LVCH) and heavy metals (HM) from the lake

Grosser Müggelsee, Strandbad Oberspree (bathing resort at the river Spree), Spree-Abzweig Britzer Zweigkanal (Britz Canal at the river Spree), Dahme-Abzweig Teltowkanal (point where the river Dahme flows into the Teltow canal), at the bridge Altglienicker Brücke, Teltow-Seehof (Zehnrutengraben), the bridge Teltow-Ramrathbrücke, the lake Machnower See near the lock, the autobahn bridge Stahnsdorf, and the lake Teltowkanal-Griebnitzsee (place where the Teltow canal flows into the lake Griebnitzsee) in the Potsdam area (end of Teltow Canal). The location of the waters investigated and of the samplings is shown in Figure 1.

Sediment samples were taken up to a maximum depth of 10 cm using a similar grab to Van-Veen whose flap and grab shells are closed by a falling weight<sup>1</sup>. The samples taken from the upper sediment layer are assumed to represent anthropogenic substance input.

### *Sample preparation and methods of analysis*

Glass bottles washed out with double distilled water were used to transport and store the sediment samples for LVCH-analysis. Where immediate analysis was impossible, the sample was stored at  $-18^{\circ}\text{C}$ . Sediment samples intended for LVCH-analysis were dried at  $30^{\circ}\text{C}$  and a relative humidity of 40% in a climatic cabinet, in porcelain basins, and subsequently homogenized.

The following preparation method for sediment samples has proven advantageous for gas chromatographic determination<sup>2</sup>: 1.5 g dried sediment was treated with 20 mL of perchloric acid and 10 mL of glacial acetic acid. The suspension was refluxed for 4 h at  $70^{\circ}\text{C}$ , cooled to room temperature, and mixed with 40 mL of *n*-hexane for ultraviolet spectrometry. The mixture was shaken for 5 min and allowed to settle for 15 min and the organic extract was washed with 40 mL of  $\text{H}_2\text{SO}_4$  for 5 min<sup>3</sup>. Depending on the quality of the sediment, the hexane extract was then further treated with 20 mL of concentrated  $\text{H}_2\text{SO}_4$ . Following this procedure (3 to 6 times) the extract was washed twice with 50 mL of double distilled water. The hexane extract was placed in a tapered graduated tube and concentrated to 0.3–0.5 mL on a rotary evaporator at  $40^{\circ}\text{C}$  and made up to 0.85 mL for gas chromatographic analysis.

Elemental sulphur, is effectively eliminated from sediment extracts by adding copper chips newly activated with  $\text{HNO}_3$ <sup>4</sup>.

Sample preparation, extraction, cleanup, and analysis has been described previously in detail by Terytze<sup>5</sup> for HM.

### *Separation and identification*

Gas chromatography: a Hewlett Packard 5890, Series II was used equipped with an HP 7673 autosampler and a 0.2 mm i.d. 50-m HP-1 capillary column (coating thickness 0.2  $\mu\text{m}$ ). Temperatures: oven  $90^{\circ}\text{C}$  (1 min),  $8^{\circ}\text{C}/\text{min}$  to  $190^{\circ}\text{C}$ ,  $1^{\circ}\text{C}/\text{min}$  to  $247^{\circ}\text{C}$ , and  $20^{\circ}\text{C}/\text{min}$  to  $260^{\circ}\text{C}$  (15 min); injector (splitless mode)  $150^{\circ}\text{C}$ ;  $^{63}\text{Ni}$  electron capture detector at  $300^{\circ}\text{C}$ . Injection volume, 2.00  $\mu\text{L}$ ; detection limit, 10  $\text{pg}/\mu\text{L}$ . Identification of the components by retention times is not reliable since a number of compounds show similar retentions. The method of standard addition was used consisting of the single components  $\alpha$ -HCH, HCB,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT at a concentration of 100  $\text{pg}/\mu\text{L}$ .

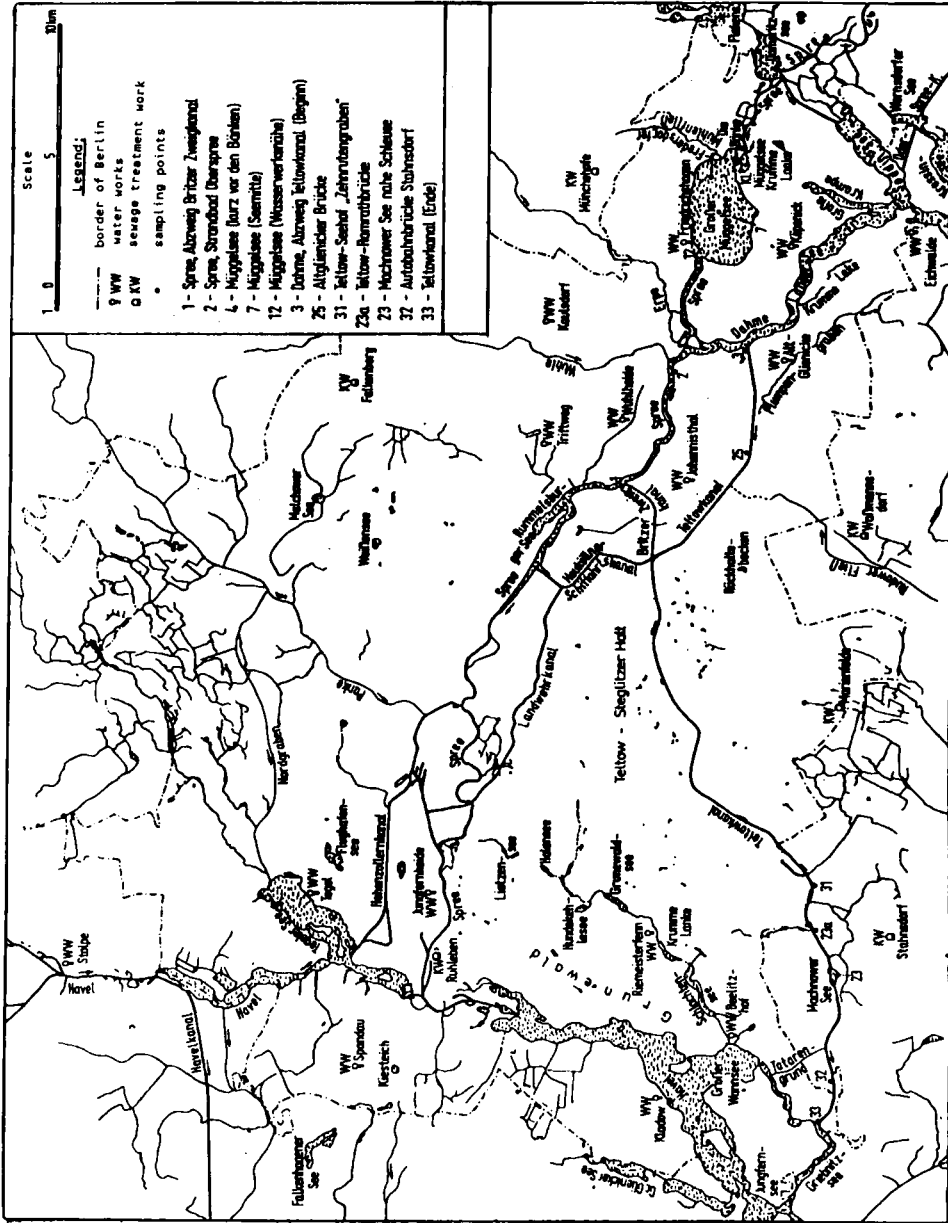


Figure 1 Survey of the field of investigation and position of the sampling points.

*Concentrations and enrichment factors of LVCH in the Berlin area*

DDT, HCH, and PCB contamination for the Teltow Canal, Lake Müggelsee, and the Spree River are illustrated in Figures 2–5. Differential-diagnostic analysis of individual metabolites of DDT and isomers of HCH not only shows their bearing patterns due to direct input but also reveals information about their current environment-induced states of metabolism. The distribution coefficient ( $K_d$ ) for the Teltow Canal, Lake Müggelsee, and Spree River are given in Tables 1 and 2.

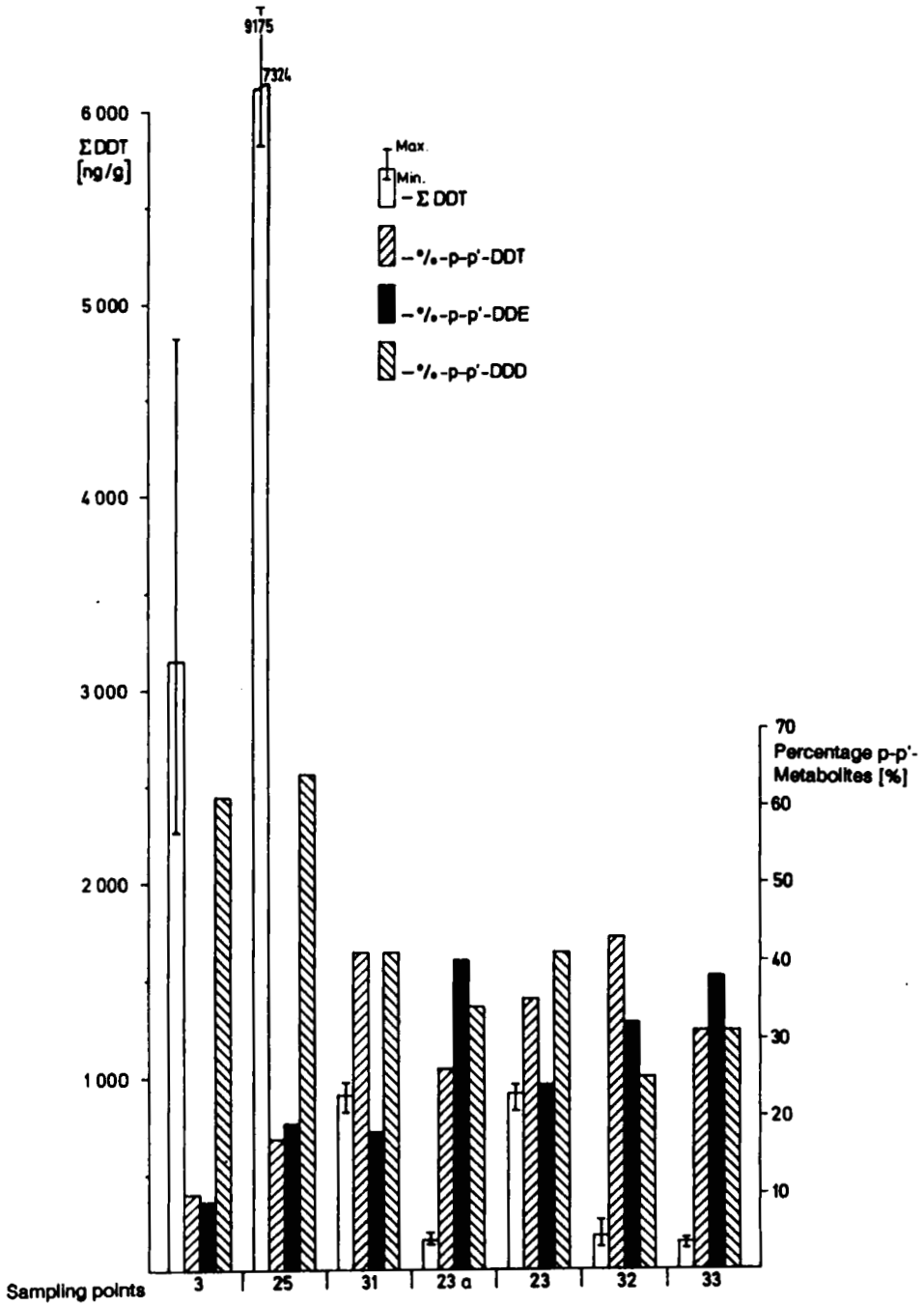
The size of the distribution coefficient  $K_d$ , which reflects the interaction of the concentration of a substance in solution  $C_1$  with that fixed in the sediment  $C_s$  ( $K_d = C_s/C_1$ ), is an indicator of the magnitude of transfer between the compartments.  $K_d$  can be regarded as an enrichment factor and provides important information about geoaccumulation. The high enrichment factors of DDT and HCH at the beginning of the Teltow Canal indicate the direct input of contaminated waters by the chemical industry in the past.

**Table 1** Concentration profiles and enrichment factors ( $K_d$ ) of DDT and HCH in the Teltow Canal (concentrations based on dry sediment weight).

Sampling points	Water $\Sigma$ DDT	(ng/ml) $\Sigma$ HCH	Sediment $\Sigma$ DDT	(ng/g) $\Sigma$ HCH	$\Sigma$ DDT	$K_d$ $\Sigma$ HCH
Dahme, Abzweig Teltowkanal	0.037	0.090	3,149	1,180	85,108	13,111
Altglienicker Brücke	0.230	0.292	7,324	1,305	31,844	4,469
Teltow-Seehof "Zehnruhengraben"	0.094	0.163	906	481	9,638	2,951
Teltow Ramrathbrücke	0.042	0.091	151	89	3,595	978
Machnowensee nahe Schleuse	0.054	0.108	913	484	16,907	4,481
Autobahnbrücke Stahnsdorf	0.071	0.093	168	131	2,366	1,408
Teltowkanal-Ende	0.022	0.067	139	95	6,318	1,418

**Table 2** Concentration profiles and enrichment factors ( $K_d$ ) of DDT and HCH in Lake Müggelsee and Spree River (concentrations based on dry sediment weight).

Sampling points	Water pp-DDE	(ng/ml) Y-HCH	Sediment pp-DDE	(ng/g) Y-HCH	pp-DDE	$K_d$ Y-HCH
Spree, Abzweig Britzer Zweigkanal	0.016	0.068	38	34	2,375	500
Strandbad Oberspree	0.012	0.062	12	35	1,000	500
Mueggelsee kurz vor den Bänken	0.011	0.024	203	212	18,455	8,833



3 - Dahme, Abzeig Teltowkanal (Beginn); 25 - Altglienicker Brücke; 31 - Teltow-Seehof „Zehrutengraben“; 23 a - Teltow Ramrathbrücke; 23 - Machnowsee nahe Schleuse; 32 - Autobahnbrücke Stahnsdorf; 33 - Teltowkanal (Ende)

Figure 2 Concentrations of total DDT and percentage of p-p'-DDT, -DDE and -DDD in sediment of Teltowkanal.

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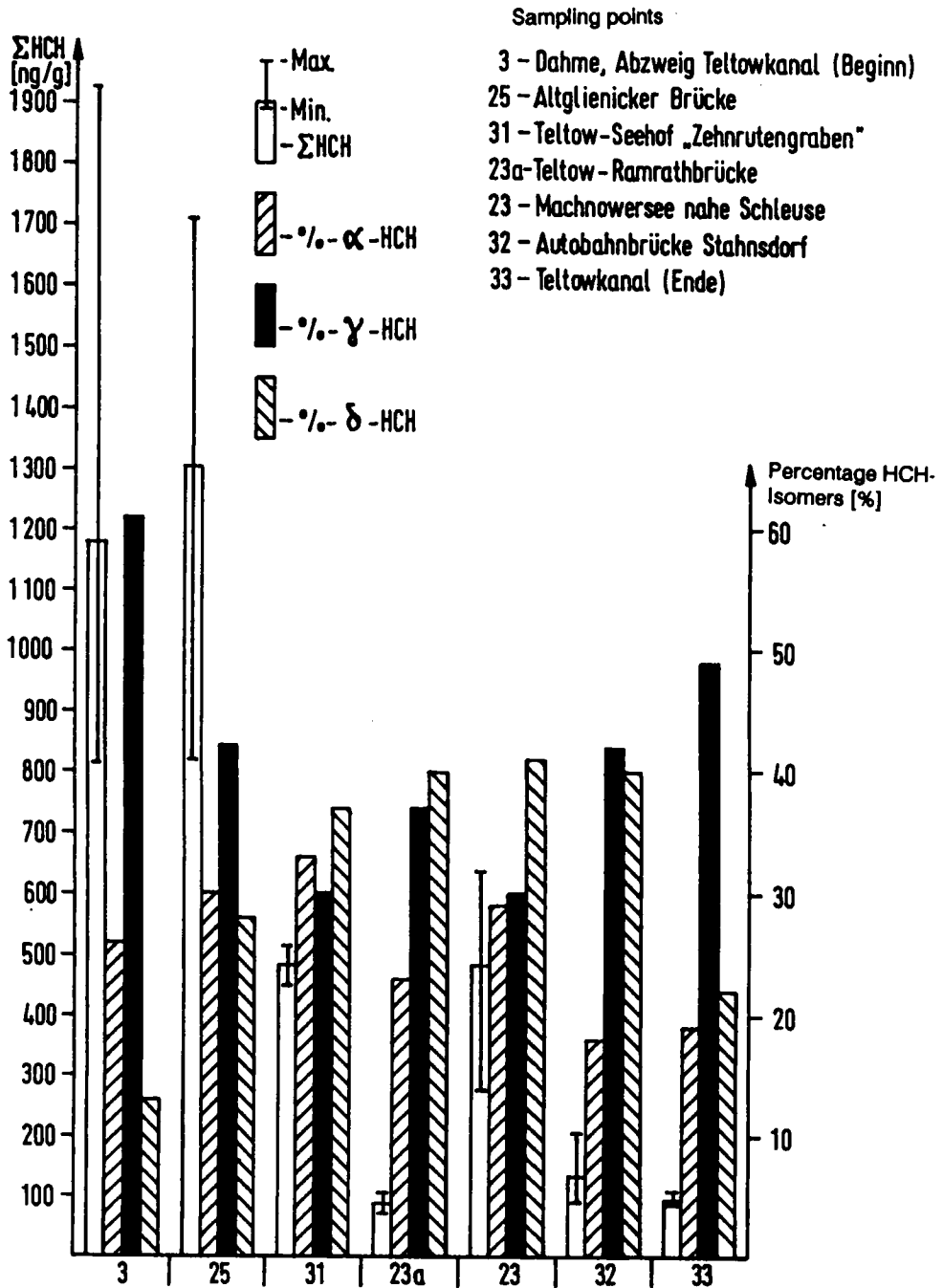


Figure 3 Concentrations of total HCH and percentage of alpha-, gamma- and delta-HCH in sediment of Teltowkanal.

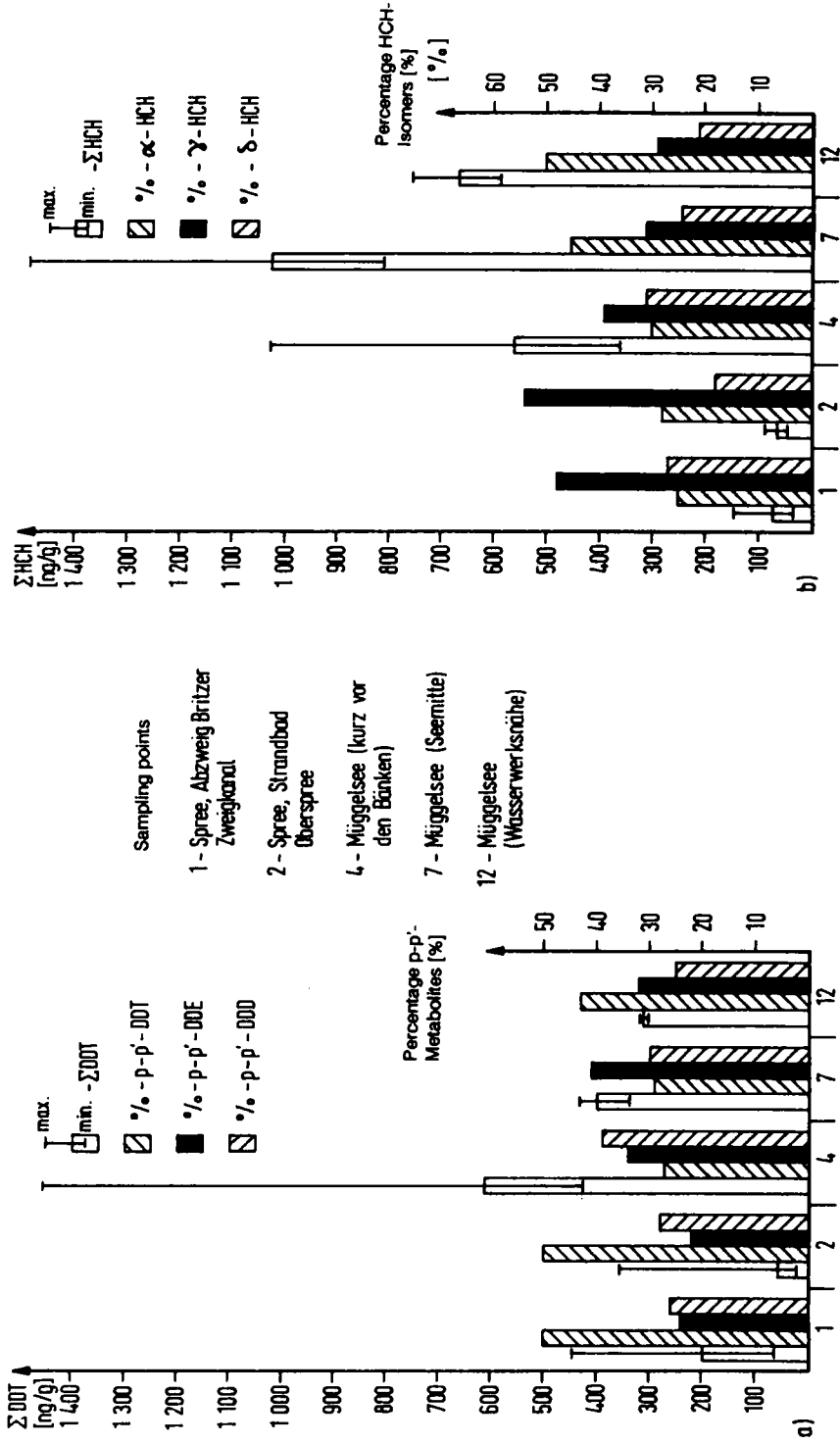
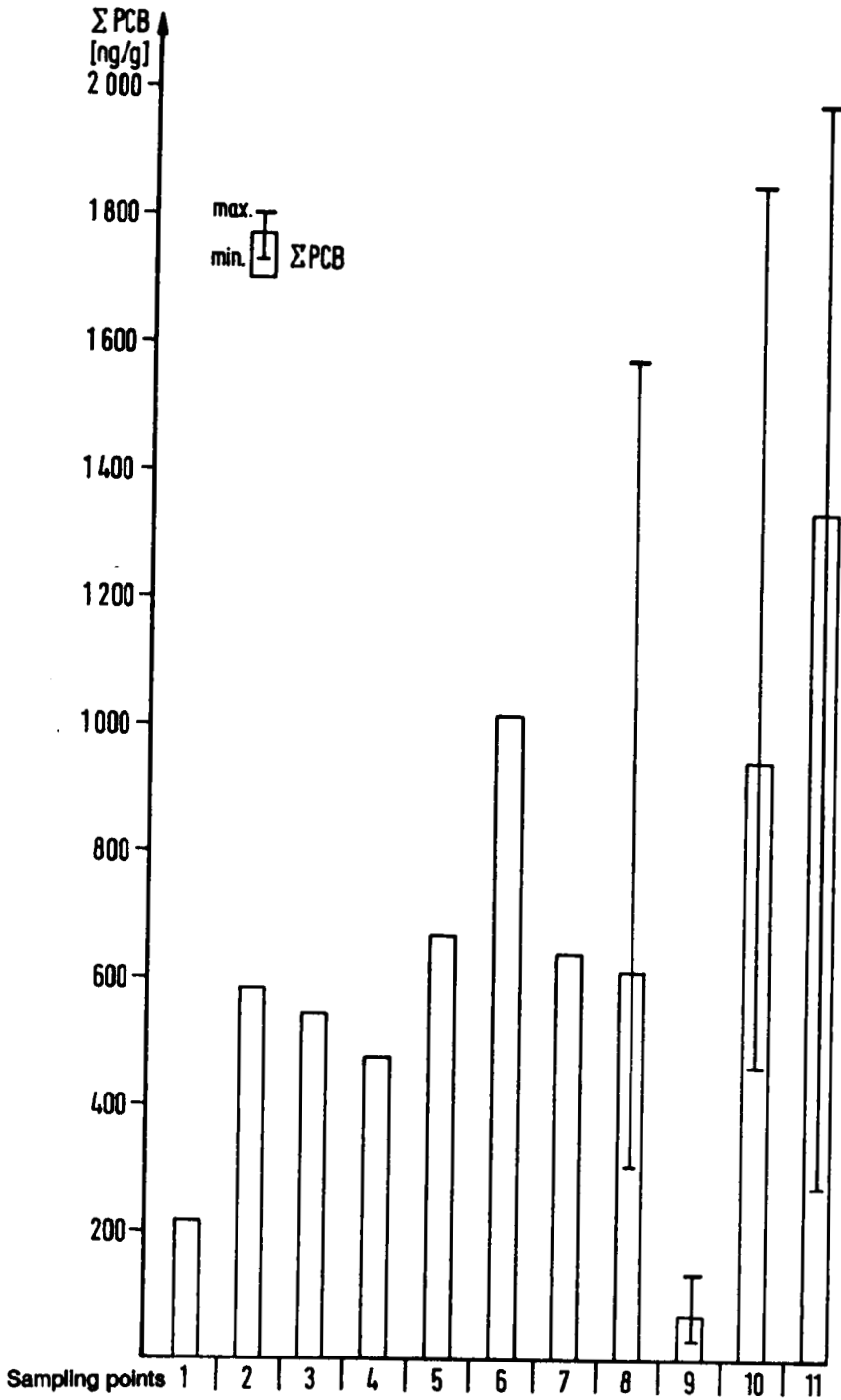


Figure 4 a/b Concentrations of DDT and HCH in sediments of river Spree in the Berlin area and lake Müggelsee.





**Figure 5** Concentrations of total PCB (Arochlor 1254) in sediments 1–Neuendorfer See; 2–Alt-Schadow; 3–Beeskow; 4–Ögelsee; 5–Altarm Oder-Spree-Kanal; 6–Fürstenwalde; 7–Mönchwinkel; 8–Müggelsee (kurz vor den Bänken); 9–Stranbad Oberspree; 10–Britzer Zweigkanal; 11–Dahme, Abzweig Teltowkanal.

*HCH and PCB sorption as function of sediment organic matter*

The sorption process for HCH and PCBs were modelled by a phenomenological approach, the EVOLON model<sup>6</sup>, which can be used to model complex interactions of two factors without a knowledge of the physiochemical relationship between them. The model describes a monotonous transition process between two stationary levels and can be interpreted as a dose-effect relationship. It depends on only five parameters, three of which are simple scale parameters, which adapt the model to the measured data and the chosen units. These parameters can be removed by simple linear scale transformation. The other two parameters represent exponents which reflect characteristic units and scale independent system qualities.

They are measures of the deviation from a linear growth or linear saturation (logistic model), respectively.

The EVOLON model consists of two terms, one representing no linear growth and one no linear saturation. The exponents represent the deviation from an exponential base process ( $k, l = 1$ ) and they build a highly aggregated measure for stimulating or hampering co-operative processes in the system. The model can be described by the following differential equation:

$$\frac{dy}{dx} = C_y^{k(B-y)^l} \quad (1)$$

where  $C$  is a velocity parameter;  $B$  represents the upper stationary level, and  $k$  and  $l$  are real exponents.

The fifth parameter is the initial value  $y_0 = y(t_0)$  of the process of parameter fitting. This initial parameter should be in the center of the interval. In the Figures,  $y_0$  always corresponds to the abscissa value  $x_0$ . In our case  $B = Y$  and  $y > 0$ . The EVOLON approach in equation (1) is used with the lower limit  $Y = 0$ . Such an approach is justified if a simple monotone correlation is expected. The mode used here is sufficiently universal and may be simplified later if a linear relationship between  $B$  and  $l$  is found in various fits with similar regression coefficients. Thus it is possible to conclude for the logarithmic limit

$$\frac{dy}{dx} = C_y^{k \cdot \exp(B-y)} \quad (2)$$

In some instances, only a simple concave or convex process occurs, which can be described by a growth and saturation term. Thus  $k$  or  $l$  become very small when using the complete EVOLON model. In this instance no differential equation is given, but the explicit solution can be given in terms of parabolic or a hyperbolic equation to describe the growth or saturation process. If the process must be described as combined growth and saturation process, then the model cannot be explicitly solved, and a differential equation must be integrated numerically:

$$y(x_0) + \int_{x_0}^x \frac{dv}{C_y^{k(B-y)^l}} = F_x(C, B, k, l, y(x_0)) \quad (3)$$

For the identification of the parameters, the following equation must be integrated to find the minimum solution:

$$\sum_{i=1}^n (F_{xi} - Y_{dat})^2 = \text{Min!}$$

This cannot be solved by a linear equation. A combined process for the identification of the parameters was developed, which uses the following steps. In the initial step, the initial combination of the initial values is calculated from the logistic equation  $k = 1 = 1$  using a linear regression model. These initial parameters are improved by using the Simplex Method by Nelder and Mead<sup>6</sup>. A cluster procedure is used to identify the agglomeration of values. These are fitted by the Marquardt gradient procedure, thereby dissolving the clusters. As a convergence for the end of this process, Marquardt's gradient is  $< 10^{-4}$ . Thus at least four successful iteration steps must follow, without subiteration, and the square sum of the relative changes of the parameters is lower than  $10^{-3}$ . This formal stipulation criterion could not be achieved due to the large scatter of the data. As an indication of the quality of the data fitting, with each fitting the mean relative deviation (MRD) is

$$\text{MRD: } \sum_i \left| \frac{F_{xi} - Y_{dat}}{F_{xi}} \right| \quad n. \quad (4)$$

Figures 6–9 illustrate the sorption of HCH and its isomers as a function of the organic matter content in the sediments. The isomers show a clear saturation value. The figures show the raw data for sediment organic matter and concentration of contaminants and the modelled fits.

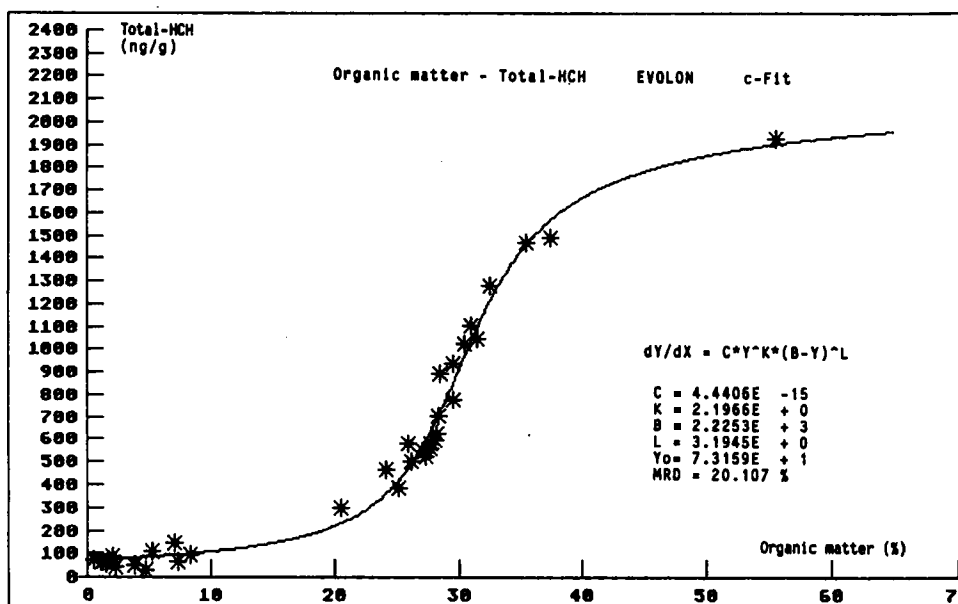


Figure 6 Sorption of Total-HCH as a function of organic matter in the sediments.

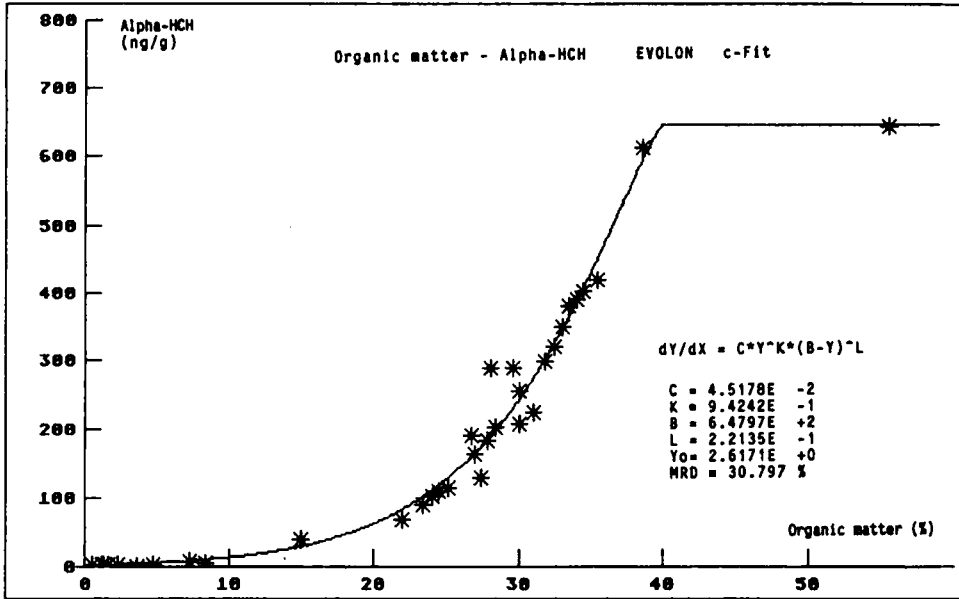


Figure 7 Sorption of Alpha-HCH as a function of organic matter in the sediments.

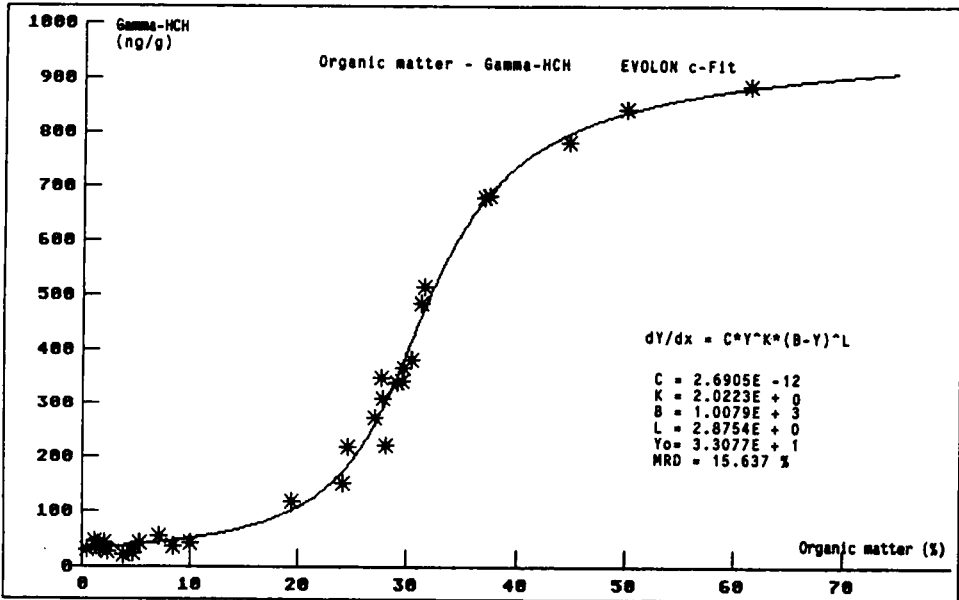


Figure 8 Sorption of Gamma-HCH as a function of organic matter in the sediments.

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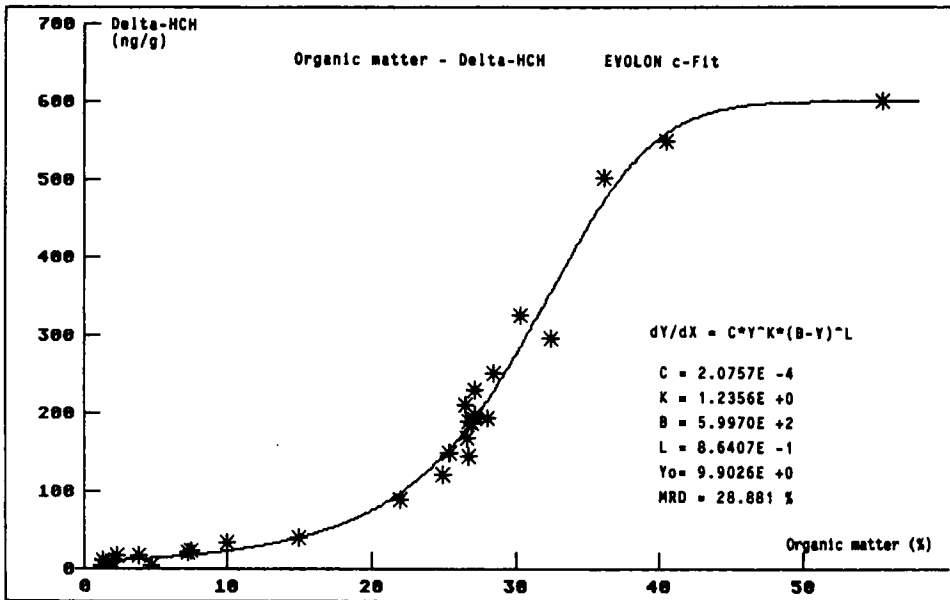


Figure 9 Sorption of Delta-HCH as a function of organic matter in the sediments.

The description of the sorption of PCB (Figure 10) as a function of the organic matter content represented by the loss on ignition, was realised by application of a hyperbolic saturation function. It expresses the solution of the EVOLON differential equation for a disappearing growth exponent  $k(\text{Evolon}) = 0$ . The corresponding saturation exponent is  $1(\text{Evolon}) = 1/C + 1; 1 = 1.3455$ . This weak hyperbolic saturation indicates a complex process rather than a single molecular reaction. The saturation value is  $2,378.9 \text{ ng g}^{-1}$ . The limit of  $y$  for  $x = 0$  is zero in an adequate approximation (4%) 0. The sorption is totally based on the organic matter content. MRD value of the model (27%) reflects the precision of the analysis of the contaminants.

The existence of this saturation value leads to the following interpretation: The organic matter is predominantly fixed to the sediment matrix and the content depends linearly on the thickness of the sediment layer. Thick sediment layers overlap each other and the sorption positions are partly blocked.

Following this hypothesis, sorption of LVCHs is dominantly controlled by the organic matter at the sediment surface. This hypothesis agrees with Müller-Wegener and Ziechmann<sup>7</sup> who observed similar sorption behaviour of some herbicides in terrestrial soils.

The destruction of the surface sediment by the navigation traffic and excavation activities may have serious consequences for the underlying groundwater aquifers. The analysed sediments of the investigation area may be subdivided into three groups based on loss on ignition: < 1%, 1–20%, and > 20%.

#### *Enrichment of HM in surface sediments*

The contamination of surface sediments with HM are listed in Table 3.

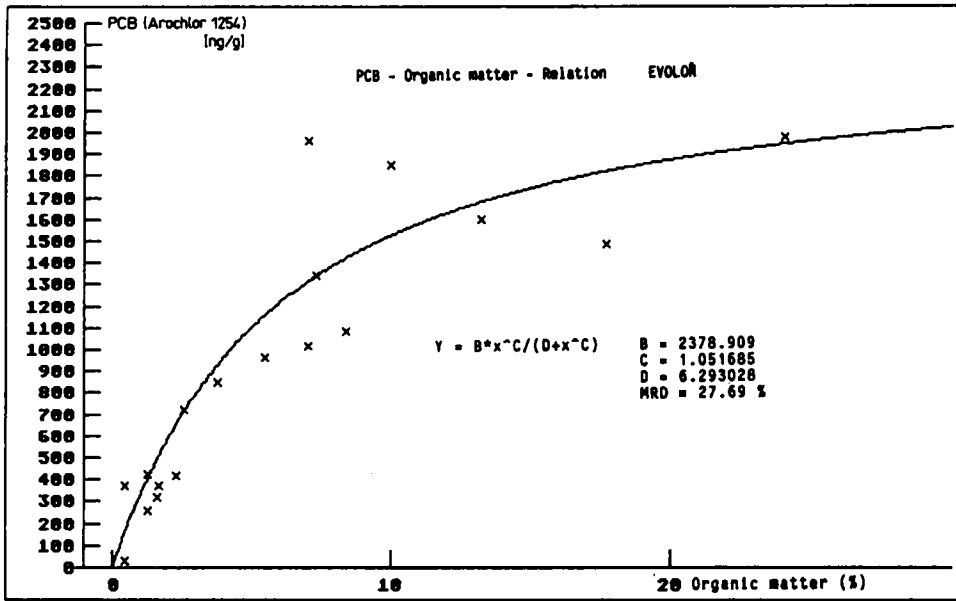


Figure 10 Sorption of PCBs (Arochlor 1254) as a function of organic matter in the sediments.

Table 3 Heavy metal contents in sediments (in mg/kg dry sediment weight).

Sampling points	Hg	Cd	Pb	Cu	Zn	Cr	Ni	Co
Neundorfer See	0,35	<0,1	<0,4	<0,1	95,1	39,8	17,5	<0,2
Alt-Schadow	0,47	<0,1	<0,4	14,0	129,4	32,6	20,0	<0,2
Beeskow	0,18	<0,1	<0,4	<0,1	72,0	22,5	16,1	<0,2
Ögelsee	0,25	<0,1	<0,4	<0,1	77,3	9,6	22,0	<0,2
Altarm Oder-Spree-Kanal	0,17	<0,1	<0,4	<0,1	30,0	14,2	12,7	<0,2
Fürstenwalde	0,09	<0,1	74,0	62,5	555,0	<0,2	12,0	<0,2
Mönchwinkel	0,14	<0,1	<0,4	<0,1	53,3	<0,2	<0,1	<0,2
Großer Müggelsee	0,52	1,3	79,4	22,2	248,0	47,1	25,5	6,3
Strandbad	0,08	<0,1	<0,4	<0,1	19,3	47,6	17,8	<0,2
Oberspree								
Spree, Abzweig	0,47	<0,1	76,3	247,2	192,3	24,6	15,6	<0,2
Britzer Zweigkanal								
Dahme, Abzweig	0,74	<0,1	51,5	72,1	175,8	60,5	14,1	<0,2
Teltowkanal (Beginning)								
Teltow-Seehof "Zehnrutengraben"	0,95	<0,1	108,7	200,7	691,0	173,8	25,7	<0,2
Teltow-Rahmratzbrücke	0,03	<0,1	<0,4	<0,1	9,8	100,1	<0,1	<0,2
Machnower See	0,07	<0,1	<0,4	11,6	72,3	83,9	<0,1	<0,2
Teltowkanal: Einmündung	0,05	<0,1	<0,4	<0,1	48,0	118,6	<0,1	<0,2
Griebnitzsee (End)								
Havel: Einmündung Jungfernsee	1,3	<0,1	129,4	157,3	1.780,0	161,1	42,4	<0,2

**Table 4** Background contents of selected metals in the fraction ( $< 2 \mu\text{m}$ ) in clay rocks according to Turekian and Wedepohl in mg/kg.

<i>Cd</i>	<i>Pb</i>	<i>Zn</i>	<i>Hg</i>	<i>Cu</i>	<i>Cr</i>	<i>Co</i>	<i>Ni</i>
0.3	20	95	0.4	45	90	19	68

**Table 5** Enrichment factors ( $K_p$ ) of selected metals based on dry weight in sediments (extraction with aqua regia; analysis by AAS-3).

Sampling points	Water, mg/l							Sediment, mg/kg							Enrichment factors, $K_p$						
	<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Ni</i>	<i>Mn</i>	<i>Fe</i>		<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Ni</i>	<i>Mn</i>	<i>Fe</i>	<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Ni</i>	<i>Mn</i>	<i>Fe</i>		
Spree, Abzweig Britzer Zweigkanal	0.019	0.043	0.008	0.008	0.117	0.428		344.3	306.3	82.8	23.7	437.1	12,406.1	18,121	7,123	10,350	2,963	3,736	28,986		
Strandbad Oberspree	0.013	0.042	0.007	0.007	0.116	0.307		9.7	89.7	14.3	2.4	145.0	6,403.5	746	2,136	2,043	343	1,250	20,858		
Dahme, Abzweig Teltowkanal	0.005	0.041	0.008	0.007	0.106	0.213		140.6	317.7	65.8	11.6	437.6	12,522.1	28,120	7,748	8,225	1,657	4,128	58,789		
Mueggelsee kurz vor den Bänken	0.007	0.037	0.006	0.013	0.107	0.256		73.3	427.4	133.3	25.1	1,480.4	57,730.0	10,471	11,551	22,216	1,931	13,835	225,509		

To determine the degree of enrichment of the HM in sediments, the clay rock standard of Turekian and Wedepohl as geogenic "background" has been taken as basis.

Here, the enrichment is described as geoaccumulation and signifies an increase in the numbered background value of HM. The comparison of results from the sampling point Dahme, Abzweig Teltowkanal, with the background values (Table 4) shows higher HM contents, particularly for Hg, Pb, Cu and Zn. Of the metals studied in the sediment of the Großer Müggelsee, only Hg, Cd, Pb, and Zn are anthropogenically affected, whereas, all the other metals are affected geochemically then corresponding with the background values.

The enrichment factors ( $K_d$ ) of selected HM at four sample points in the investigation area are shown in Table 5.

Particularly high enrichment factors ( $K_d$ ) can be shown for all given metals in the sediment of the Großer Müggelsee. These enrichment factors are much higher than comparison of HM-concentration with the background-values in case of background geochemical accumulations.

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