

The Impact of Lignite on the Transport of Contaminants in the Groundwater Aquifer System of the Bitterfeld Region

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ABSTRACT

Until 1990 the Bitterfeld region was heavily polluted by mining, an obsolete chemical industry and the uncontrolled deposition of chemical wastes. The cessation of lignite-mining and open-pit drainage resulted in a rise of the groundwater followed by mobilization of contaminants, especially halogenated hydrocarbons.

At the research area in Bitterfeld only highly mobile chlorinated aliphatics and aromatics have been detected both in groundwater and sediments, especially in a lignite seam.

The modern analytical method of solid-phase micro extraction (SPME) was successfully applied to analysis of the pollution level of groundwater and sediments.

It was shown that the lignite seam has accumulated large quantities of halogenated hydrocarbons and acts like a giant adsorption filter. The vertical pollution profiles of sediments and the distribution coefficients between lignite and groundwater at equilibrium conditions were determined for the key components.

The results indicate that in addition to the adsorption processes, the microbiological degradation of aliphatic halocarbons occurs in the groundwater and at the seam.

INTRODUCTION

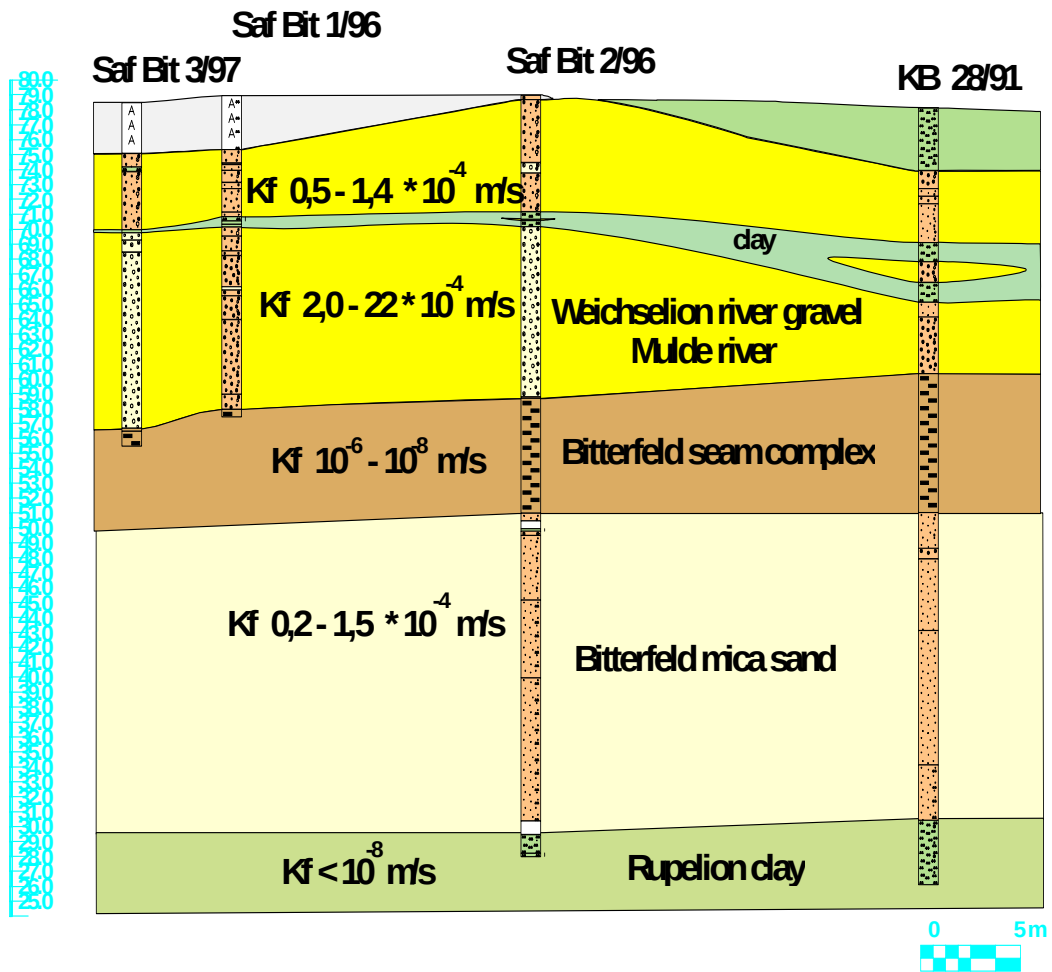
The town of Bitterfeld in eastern Germany has a remarkable industrial history. 150 years of coal mining and 100 years of chemical industry have left deep scars on the region. By 1990 the name of Bitterfeld had become a synonym for environmental destruction, large-scale air, water and soil pollution, and public health put at risk. Nowadays, although the situation regarding air and surface water has improved, the soil and groundwater are still severely contaminated by uncontrolled deposited chemical waste.

The cessation of lignite mining and open-pit drainage has result in the rise of the groundwater table followed by the mobilisation of pollutants, especially chlorinated hydrocarbons. A cautious estimate is that there are about 200 million cubic meters of contaminated groundwater in the Bitterfeld region.

Common pump and treat degradation methods are too expensive for problems of this order of magnitude. Therefore in-situ remediation methods seem to be more promising to prevent the danger caused by the spread of these organics.

Fig. 1

Geological profile of the SAFIRA project research area in Bitterfeld



To deal with this problem the UFZ has progressed an interdisciplinary research programm called SAFIRA in order to develop and test suitable and innovative in-situ remediation procedures. The site of the planned demonstration project is located in an area of Bitterfeld without previous mining activities, where a quaternary and a tertiary aquifer are separated by a lignite seam 4 to 8 m thick (Fig.1). Groundwater analysis has shown that aliphatic and aromatic halocarbons are present at elevated concentrations in the aquifers but distributed differently above and below the coal horizon. Additional studies of bore hole material indicate that lignite acts as an adsorbent for organic contaminants when it comes into contact with groundwater. The role of lignite as retardend for pollution transport must be clarified.

This paper tackles the following questions:

- In what concentrations and in what vertical profile are the halocarbons distributed along the seam?
- What are the concentrations in coal at equilibrium conditions?
- Are the adsorption/desorption processes reversible or not?
- Is the seam currently a sink or a source of pollutants?
- Do degradation processes occur inside the seam?

METHODS

Analysis was focused on the following key components in the groundwater, all of which (apart from benzene) are volatile halocarbons:

• trans-1.2 - Dichloroethene	(t-dce)	$C_2H_2Cl_2$
• cis-1.2 - Dichloroethene	(c-dce)	$C_2H_2Cl_2$
• Trichloroethene	(tce)	C_2HCl_3
• Benzene	(benz)	C_6H_6
• Chlorobenzene	(Clbenz)	C_6H_5Cl
• 1.4-Dichlorobenzene	(1.4-Cl ₂ benz)	$C_6H_4Cl_2$
• 1.2-Dichlorobenzene	(1.2-Cl ₂ benz)	$C_6H_4Cl_2$

The analytical method used was gas chromatography with a flame ionisation detector after the enrichment of the compounds using the so-called SPME-method. SPME stands for solid-phase micro extraction and is an elegant procedure for the extraction of volatile compounds in the headspace above a liquid or solid sample (1,2). Water samples of 10 ml or solids of 4 to 10 g were placed in glass vials closed with crimp seals. In the case of solids water was added so that the material was completely covered with water and the total volume always was constant. Equilibrium conditions between solids and water were reached by shaking the samples for at least one day at room temperature. Equilibration between liquids and gas phase took place on the of the gas chromatographs autosampler within a few minutes.

The measurements were calibrated using the external standard technique. Small volumes of methanolic calibration standard solutions at different concentration levels were added to samples of water or water/sediment mixtures which were not or only negligible contaminated. After equilibration calibration curves of quite good linearity were obtained.

This is illustrated by Figures 2 to 4. The linear equations ($y=mx+b$) and the regression coefficients (R^2) are given for all curves. The linear coefficient m is the calibration factor for the calculation of concentrations in $\mu\text{g/ml}$ or $\mu\text{g/g}$ from the detector response in area units (a.u.).

Fig. 2
Calibration of water samples

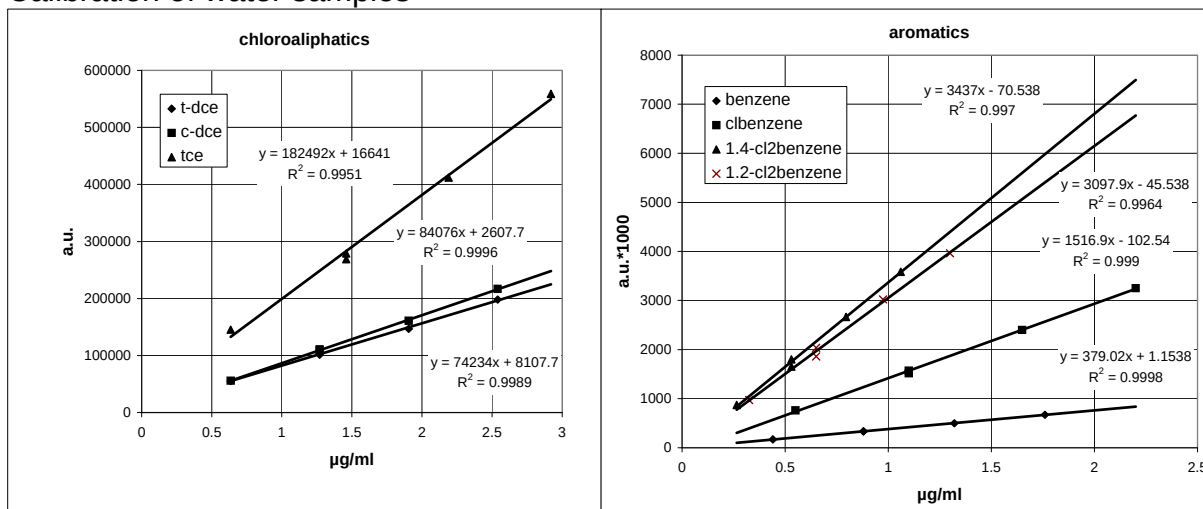
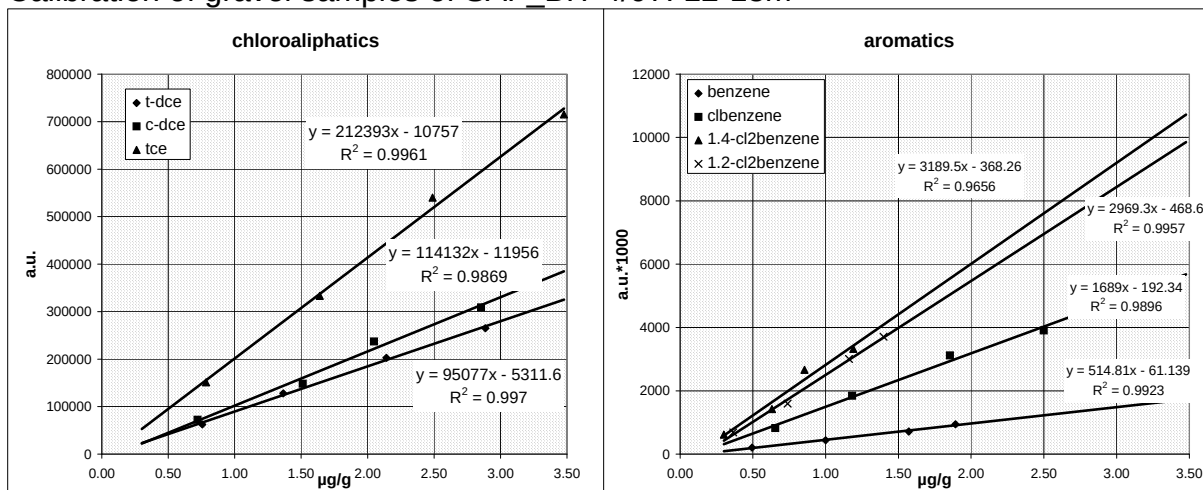


Fig. 3
Calibration of gravel samples of SAF_BIT 4/97: 12-13m



The plots show that the calibration factors of water and gravel samples are quite similar. This means that interaction between the pollutants and the solids is limited.

As may be expected, different results were obtained with coal samples (Fig. 4). Because brown coal strongly adsorbs all the organics, the calibration coefficients are more than an order of magnitude lower than those in the case of water. On the other hand, although the linearity is good, the curves do not hit the zero point. The positive deviation from the zero point in the case of c-dce is caused by the low dce content of the coal sample of about 3 µg/g. For all the other compounds the absolute term is negative. This suggests that a small amount of the contaminants (about 1-2 µg/g) is irreversibly bound to the coal and can not be detected.

In order to verify the results obtained by external standardisation, an attempt was made to extract the pollutants from the coal. Extraction methods using organic solvents are unsuitable for this problem because the high loss of the highly volatile components during sample preparation can not be avoided. Consequently, only water at room temperature was used as a solvent. A constant mass of coal (5g) was

shaken with different volumes of water in completely filled bottles for at least two days, after which equilibration was reached because the concentration of the liquid phase became constant.

As a result of such extraction sequences it was found that with the largest water volumes (> 1,000 ml) between 64% (chlorobenzene) and more than 90% (dce) of the organics was transferred from the solid to the liquid phase. Higher polar compounds with poor solubility in water such as higher chlorinated benzenes can hardly be extracted in this way.

A comparison of the calculated values by means of external standardisation with those of water extraction experiments is shown in table 1.

Table 1
Analysis of lignite by water extraction and by external standardisation

		SAF_BIT 16/97: 21.7m		SAF_BIT 6/97: 22.5m	
		water extract.	ext. standard	water extract.	ext. Standard
t-dce	(µg/g)	47.9	25.7	7.7	4.2
c-dce	(µg/g)	80.5	49.1	25.2	17.8
benzene	(µg/g)	4.5	1.9	7.6	3.6
tce	(µg/g)	36.8	18.6	140.2	111.1
clbenz	(µg/g)	147.2	131.9	128.2	74.4
1.4-cl2benz	(µg/g)				0.4

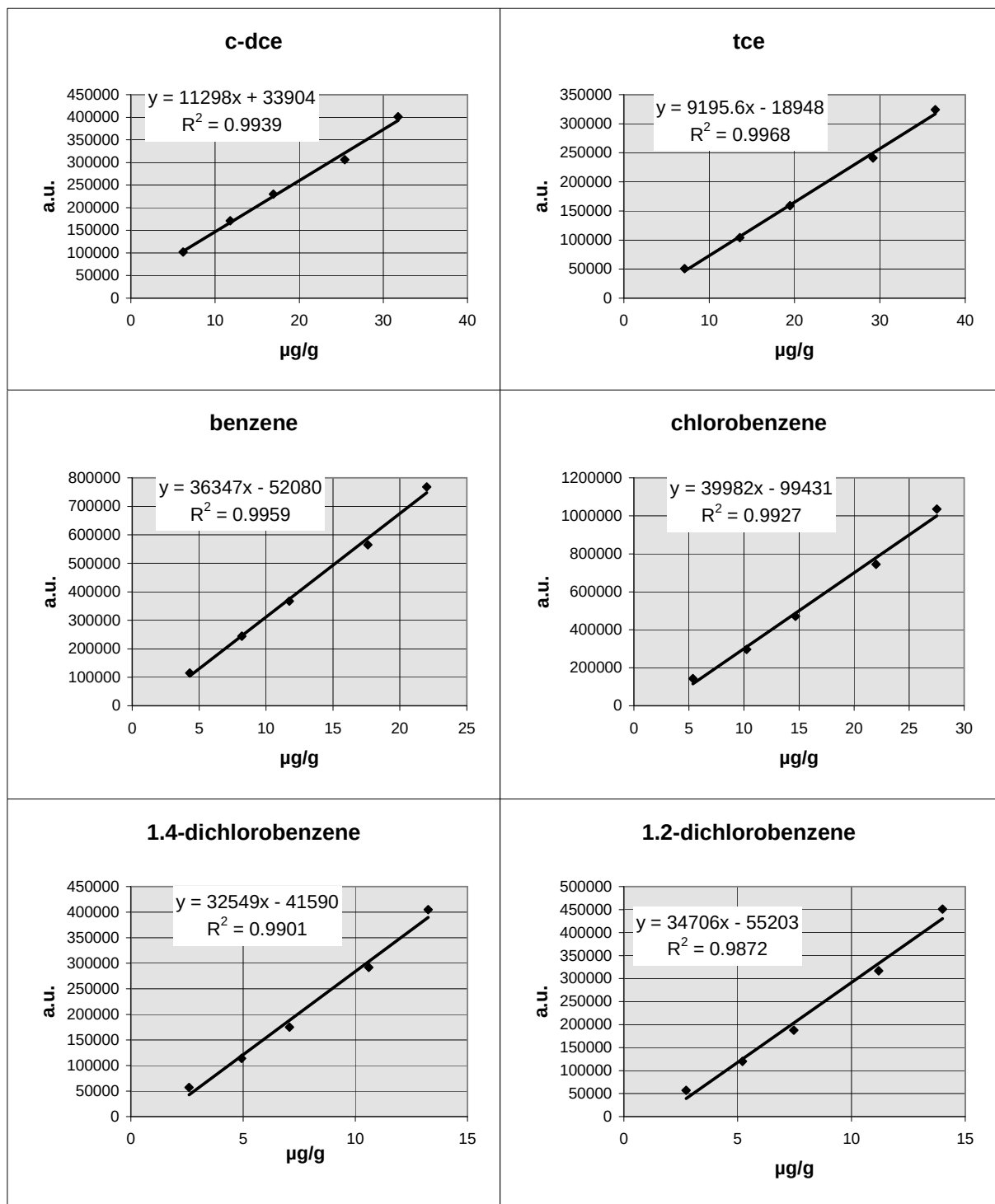
The heterogeneity of the coal and the strong concentration gradients inside the seam are responsible for poor reproducibility and precision in comparison to homogeneous liquid samples. It may be observed that the routine method with external standardisation yields lower values because loss of volatile substances from the small vials during equilibration and analysis can not be ruled out. Nevertheless the method is suitable for large sample series to give a good approximation of sediment's pollutant profiles.

RESULTS

Groundwater analysis

Some characteristic data of groundwater from the quarternary and from the tertiary aquifer are presented in table 2. Great differences exist concerning conductivity, age (tritium content) and the concentration of the organics. In the upper aquifer chlorobenzene is the most important contaminant, whereas the chloroaliphatics dominate in the aquifer below the lignite seam.

Fig.4
Calibration with not contaminated lignite samples of SAF_BIT 13/97: 27m



The low tritium content of the quarternary groundwater suggests that more than 50% of the water is at least 40 years old.

Tab.2

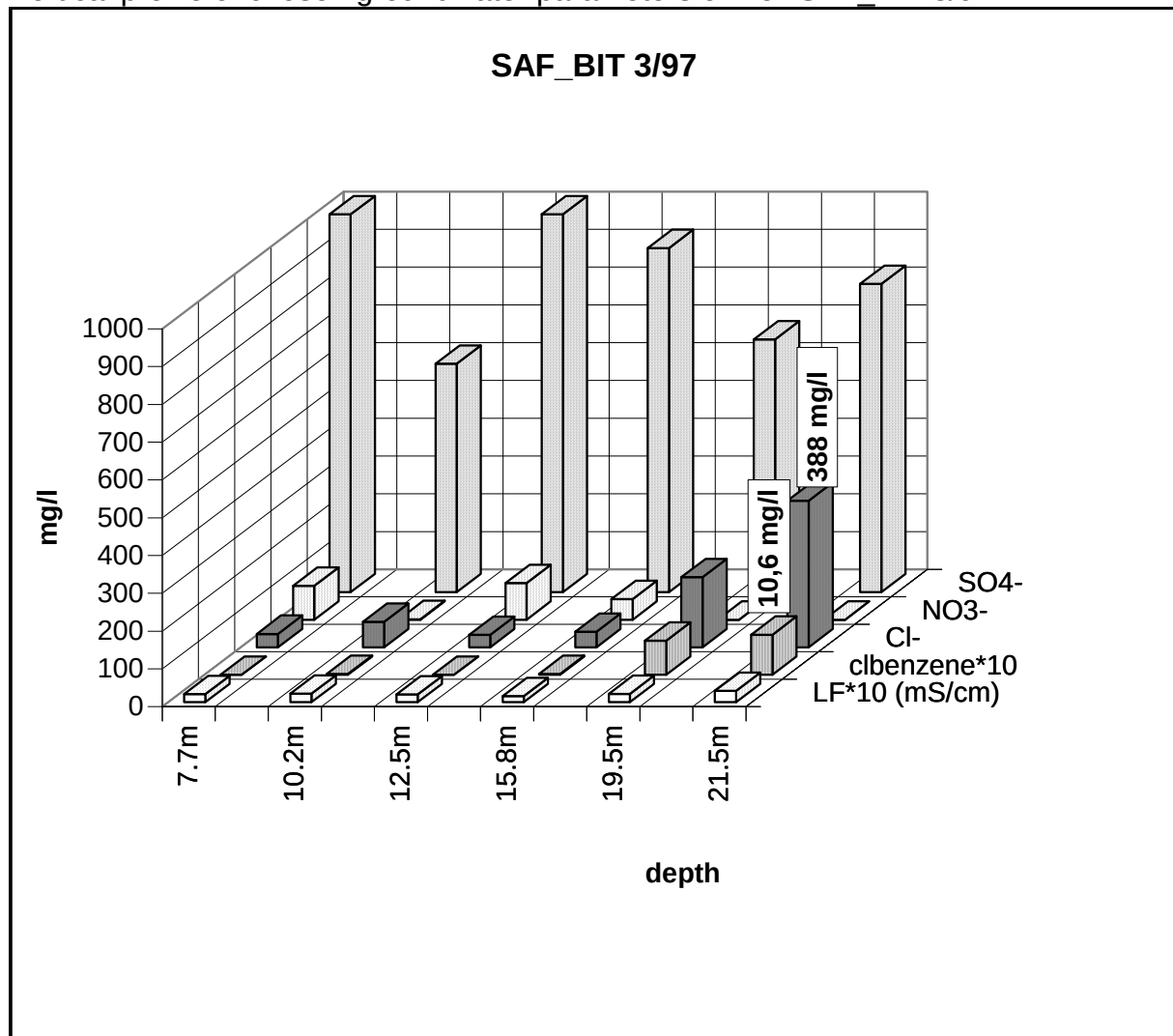
Groundwater data of the quarternary (6/97) and the tertiary (16/97) aquifer

well	depth	date	conduct.	Cl ⁻	H-3	t-dce	c-dce	benz	tce	clbenz	1,4-Cl2benz	1,2-Cl2benz
	m		mS/cm	mg/l	TU	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
SaBi 6/97	4-22m	26.03.97	2.05	230	14.4	0.05	0.18	0.07	0.04	11.9	0.15	0.04
SaBi 16/97	35-38	19.06.97	4.33	815	6.1	3.85	9.98	0.74	9.53	0.27	0.01	0.01

Detailed information about the vertical concentration profile of the aquifer was obtained by groundwater sampling at specific depths of well SAF_BIT13/97 (fig.5). The picture shows unambiguously that the upper part of the aquifer is nearly clean and that organic pollution is concentrated in the last few meters above the seam surface. Chlorobenzene, conductivity, and chloride concentration simultaneously increase, whereas nitrate nearly disappears. In contrast to this the high sulfate content seems to be independent of depth.

Fig. 5

Vertical profile of chosen groundwater parameters of well SAF_BIT 3/97



Analysis of sediments

The high contamination of the groundwater layer above the seam surface results in pollution exchange reactions between the liquid and the solid phase. Figures 6 and 7 show a vertical profile of pollutant distribution for the material from bore hole 16. It is situated at the inflow area where the seam is only 4m thick.

Fig. 6

Vertical distribution of chloroaliphatics in the bore hole material of SAF_BIT 16/97

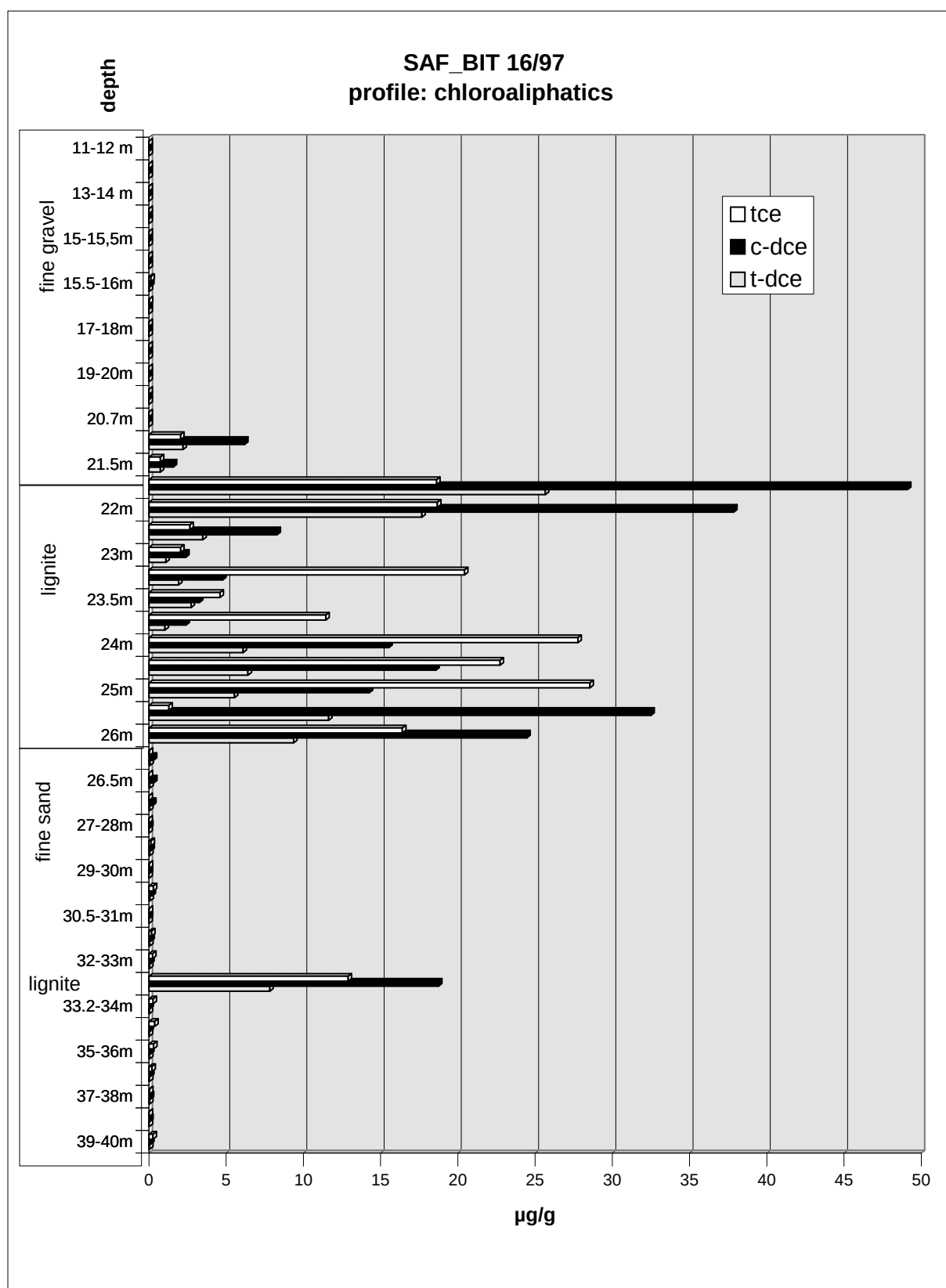
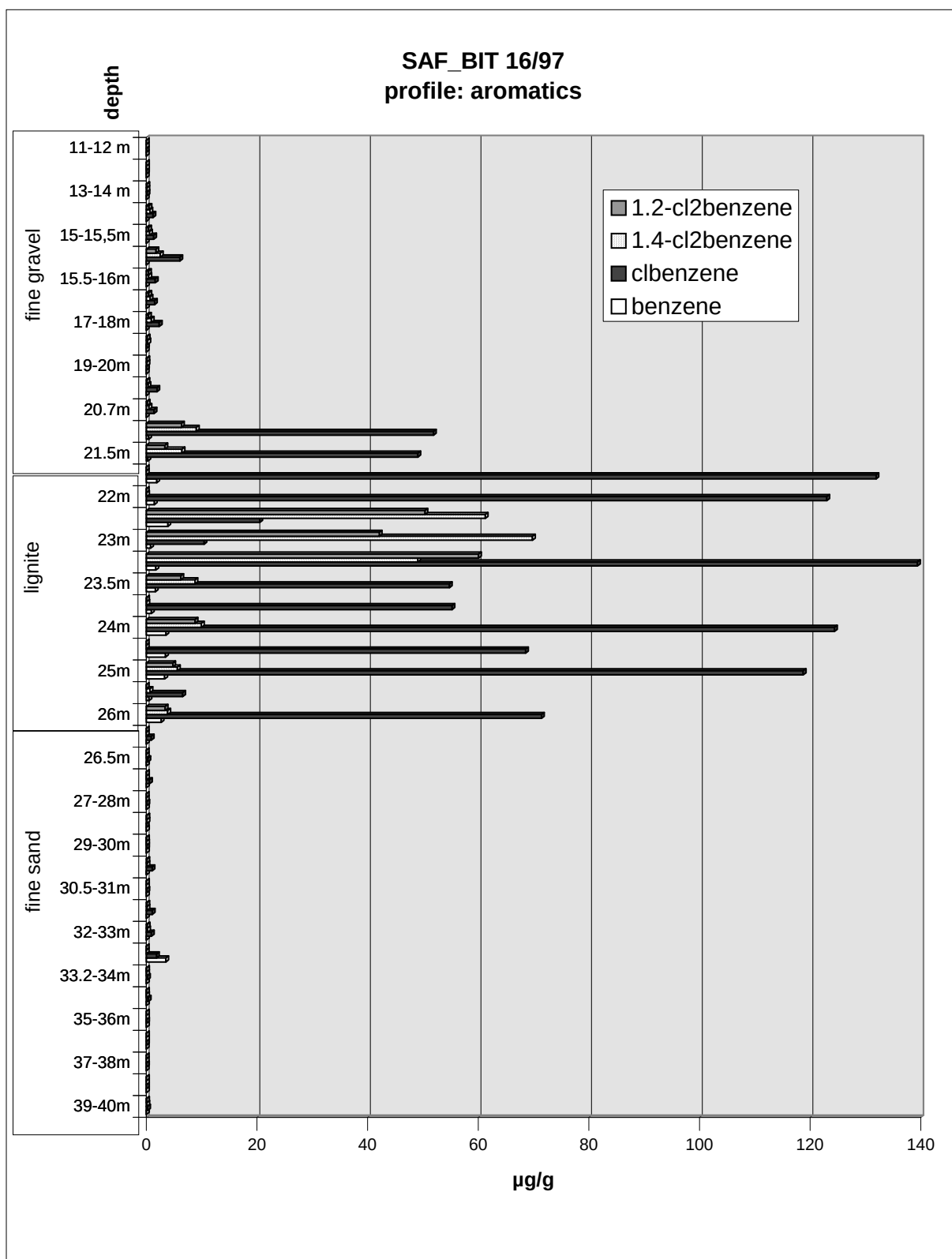


Fig. 7
Vertical distribution of aromatics in the bore hole material of SAF_BIT 16/97



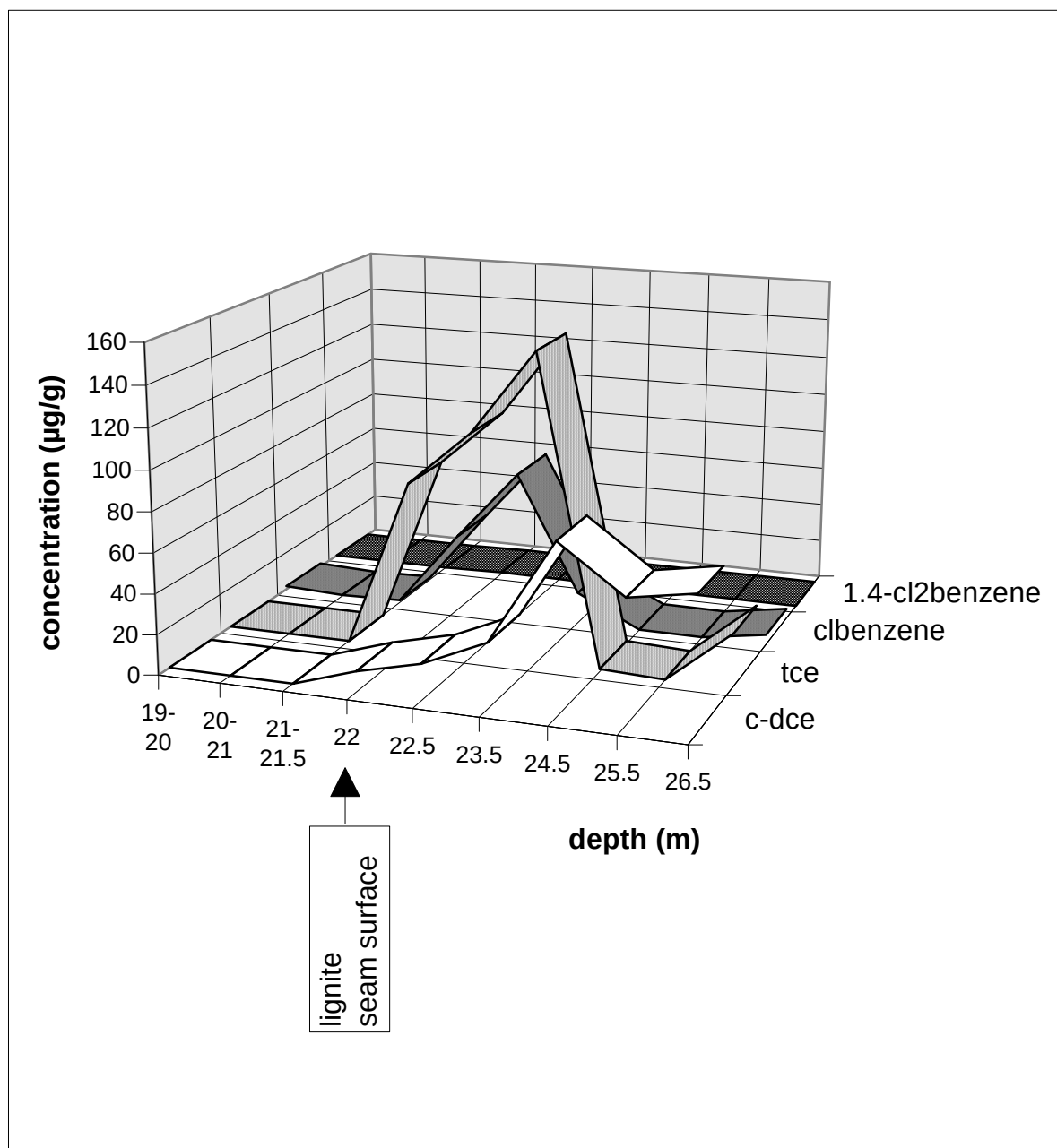
At first glance it is apparent that adsorption on sand and gravel above and below the seam is negligible. Only the lignite seam itself acts as a giant adsorption filter. Upon further study, the vertical pattern of distribution is very informative. Near the seam borders we find higher concentrations of chlorinated aliphatics and more dce's than tce. It is well known that dce's and especially cis-dce are degradation products of higher chlorinated precursors such as tce and perchloroethylen (pce) under anaerobic conditions (3). Hence the results suggest that microbiological degradation

processes take place in the seam whose intensity decreases with increasing distance from the borders. By contrast, chlorobenzene seems to be statistically distributed throughout the whole seam, whereas dichlorobenzenes exhibit maximum concentration two meters below the upper border. This picture resembles a chromatographic peak with a tailing in the direction of the flux.

About 200 m downstream, the distribution pattern changed. Fig.8 only shows the coal horizon and the picture suggest that the main direction of pollution transport inside the seam is from the upper to the lower aquifer.

Evidently the adsorption processes started later than at the position of well 16. Hence we see a "chromatographic process" in action: The dce's pass the coal layer followed by tce and chlorobenzene. The dichlorobenzenes were only detected near the seam surface in small concentrations. The most striking fact is that in the quarternary groundwater only traces of haloaliphatics are found (see table 2) but many of them have been adsorbed by the lignite seam. Thus, the present state of the lignite seam stores information about the state of groundwater in the past.

Fig.8
Pollution profile of the lignite seam of bore hole SAF_BIT 6/97



Distribution coefficients lignite/water

Assuming that equilibrium is achieved by shaking contaminated lignite with water, the distribution coefficients of the soluble components can be evaluated. The results are given in Tab. 3 for two different lignite samples.

Despite the scattered values, some differences between the compounds are visible. It is obvious that the rather well soluble cis-dichloroethene is adsorbed to a lesser extent on lignite than chlorobenzene. The values given are valid for the original fresh raw coal with a water content of about 60% and a coal content of the dried residue of about 40%. Related to pure carbon (K_{oc}), the values have to be corrected by a factor of about 4. The corrected results are in the order of magnitude for K_{oc} values given in the literature (4).

Table 3:

Lignite/water distribution coefficients of different pollutants obtained by desorption of two contaminated lignite samples with water

compound	SAF_BIT 6/97	SAF_BIT 16/97
	22,5 m	21,7 m
trans-1.2-dichloroethene	32 +/- 14	27 +/- 12
cis-1.2-dichloroethene	13 +/- 3	23 +/- 14
trichloroethene	43 +/- 13	51 +/- 12
benzene	35 +/- 12	
chlorobenzene	80 +/- 15	53 +/- 1

CONCLUSIONS

The modern analytical technique of solid-phase micro extraction (SPME) can be successfully applied to the analysis of the pollution potential of groundwater and sediments.

In the research area of Bitterfeld only rather well soluble halocarbons were detected in groundwater and sediment, especially in the lignite seam. Exchange experiments in the water/lignite system by both adsorption from the liquid phase on coal and desorption from the coal into the water showed that the majority of contaminants are reversibly adsorbed on coal. Coal/water distribution coefficients at equilibrium conditions were evaluated and showed an increasing trend from dce's to chlorobenzene and dichlorobenzenes. According to this, dce's were transported through the seam, whereas the majority of the more polar and less soluble dichlorobenzenes are adsorbed near the seam border.

The present pollution potential of the lignite seam is a result of the groundwater pollution in the past. Thus, the lignite is heavily polluted with trichloroethene, whereas the quarternary groundwater is nearly free of it at present.

This means that the long-term interaction between groundwater and coal has resulted in a different situation concerning aliphatic and aromatic halocarbons.

The adsorption capacity of lignite for chlorobenzenes is not yet been exhausted and at the present level of groundwater contamination further adsorption will take place.

On the other hand the tce content of the coal is up to three orders of magnitude greater than the groundwater concentration. This means that the desorption of tce from the lignite into the water has to be expected at equilibrium conditions.

Adsorption/desorption processes under actual conditions are not so much thermodynamically controlled as subject to kinetic and hydrodynamic parameters.

Furthermore, the high concentrations of dce's indicate that the microbiological degradation of tce may be faster than the desorption rate of tce from lignite.

Thus, the actual impact of the lignite seam on the retardation and degradation of pollutants needs to be evaluated by additional kinetic simulation experiments - which are already underway.

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