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Determination of aromatic amines in surface waters and comparison of their behavior in HPLC and on sediment columns

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Abstract An analytical method based on solid-phase extraction (SPE) with a polymeric material, HPLC separation on a modified C₁₈ material, and diode-array detection is presented for the determination of aromatic amines in the ng L⁻¹-concentration range. These potentially toxic compounds in polluted water samples can be sampled by using SPE with an amino phase to clean the eluate. Column experiments were performed to characterize the transport behavior of aromatic amines in an aquifer sediment. For nineteen aromatic amines, linear correlations were found between the adsorption coefficient, K_d, estimated from column experiments, and capacity factors, k', measured by isocratic reversed-phase HPLC (RPHPLC).

Introduction

Aromatic amines are widely used, particularly in the chemical industry, for the production of, for example, dyes, pesticides, drugs, and other synthetic products. Many of these compounds are harmful to the environment and to human health [1, 2, 3, 4]. They can reach ground and surface water in different ways – directly, as components of waste water output originating from industry, and indirectly, as metabolic products of pesticides or ammunition deposits [5, 6, 7]. Different aromatic amines have been determined at the ng L⁻¹ concentration range in a variety of surface waters, including the River Elbe which is used as a water resource for drinking water production via bank filtration and artificial groundwater recharge [8, 9, 10].

Several papers have been published on the analytical determination of aromatic amines, mainly by using gas

chromatography (GC) [6, 11, 12, 13, 14] and high-performance liquid chromatography (HPLC) [7, 15, 16, 17]. In contrast with GC methods, HPLC enables the determination of thermolabile and poorly volatile compounds, although this advantage is somewhat offset by lower peak resolution and interference from the organic background of polluted water samples (e.g. humic substances).

The aims of this work were to develop a practical analytical method based on HPLC for the sensitive determination of different aromatic amines in surface water with a complex organic background, to investigate the pollution of the River Elbe, and to evaluate the fate of aromatic amines during bank filtration.

Besides biodegradation, adsorption of dissolved organic substances on to solid aquifer materials is very important for the attenuation of organic compounds during bank filtration. It is, therefore, of interest to know the adsorption coefficients (solid–water partition coefficients), K_d, of the pollutants. The adsorption behavior of organic substances in an aquifer can be estimated from sediment-column experiments using the concept of retardation (Eq. 1):

$$R_d = \frac{v_{a,w}}{v_{a,x}} = 1 + K_d \frac{\rho_b}{n_e} \quad (1)$$

where R_d is the retardation factor, v_{a,w} the effective velocity of water, v_{a,x} the effective velocity of compound x, K_d the adsorption coefficient, ρ_b the solid bulk density, and n_e the effective porosity.

In this way, adsorption coefficients K_d, and the adsorption coefficients normalized to the organic content of the solid, K_{OC}, can be calculated from the retardation factors obtained from medium scale experiments.

Sediment-column experiments are costly, however, and the coefficients determined can be erroneous because of biodegradation, evaporation, and loss of analyte during sample preparation and analysis. These disadvantages can be avoided by means of simple correlation with properties, which are readily available (e.g. water solubilities, *n*-octanol–water partition coefficients, or capacity coefficients originating from HPLC) [18, 19, 20]. Sediment-column experiments were performed to predict the mobil-

Dedicated to Professor Dr. F.H. Frimmel on the occasion of his 60th birthday

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ity of some aromatic amines in the sand and gravel aquifer adjacent to the River Elbe near Torgau in Saxony. The adsorption coefficients determined have been correlated with HPLC capacity factors to find a relationship between these properties, which can be used to predict adsorption coefficients.

Experimental

Materials

The chemicals used were: aniline (Laborchemie Apolda, Germany), 2-methylaniline, 2-nitroaniline, 2,5-dichloroaniline, 3-chloro-4-methylaniline, 2,4,6-trichloroaniline, *N,N*-dimethylaniline, 4-bromoaniline, 3-chloroaniline, 4-fluoro-2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-isopropylaniline, *N*-ethylaniline, 4-methyl-2-nitroaniline, and 2-chloro-5-nitroaniline (all from Aldrich, Steinheim, Germany); 2-chloroaniline, 2,4,5-trichloroaniline and 4-chloroaniline (Fluka, Neu-Ulm, Germany); 3, 4-dichloroaniline (Riedel-de Haën, Seelze, Germany). The purity of each chemical was >97%. Initially *o*-toluidine was used as internal standard; for later investigations 4-fluoro-2-nitroaniline was used. All solvents (methanol, acetonitrile, dichloromethane, and water) were of HPLC-grade and all buffer salts and reagents of p.a. grade. The Supelcosil ABZ+Plus C-18 (5 μm , 250 mm \times 4.6 mm) HPLC column was obtained from Supelco (Bellefonte, PA, USA). The SDB-1, Amino, and Polar Plus SPE cartridges were purchased from Baker (Groß Gerau, Germany).

Apparatus

HPLC was performed with an L-450 diode array detector (DAD), L6200 A pump, D6000 IF interface, L-5025 column oven, and D-6500 DAD-manager software (all from Merck-Hitachi, Darmstadt, Germany). The Baker SPE-12 G system was used for enrichment of the amines. The Bandelin (Berlin, Germany) RK 100 instrument was used for ultrasonic treatment of the extract.

Enrichment procedures

SDB-1-cartridges (200 mg, self-filled glass cartridge; Baker) were conditioned with methanol and water. Standard solutions or filtered water samples containing the internal standard were passed through the solid phase. After washing with water and drying by application of a vacuum and nitrogen gas (approximately 10 min) the amines on the cartridges were eluted with acetonitrile. The extract was concentrated under nitrogen gas, and the resulting extract (0.5 mL) was diluted to 1 mL with ammonium acetate buffer (0.04 mol L⁻¹).

Clean-up procedure

To remove interfering compounds (e.g. humic acids) from the samples, four different methods were tested:

- derivatization of primary aromatic amines with *N*-(1-naphthyl)ethylenediamine (diazotization and coupling), HPLC separation of the originated azo dyes, and UV-detection in the visible range (460 nm);
- flocculation of the water sample with Al³⁺ ions before SPE to remove humic compounds selectively;
- SPE in two steps: firstly at pH 2 with C₁₈ material to adsorb the humic compounds, secondly at pH 10 to extract the amine on SDB-1; and
- clean-up of the acetonitrile extract on amino-modified silica gel (pretreated with 3 mL dichloromethane and 3 mL acetonitrile).

HPLC conditions

The extract was analysed by HPLC-DAD on an ABZ+Plus column with a mobile phase gradient prepared from acetonitrile and ammonium acetate buffer solution. Eluent A was 80% (v/v) ammonium acetate buffer solution (0.025 mol L⁻¹) and 20% acetonitrile, eluent B was 85% acetonitrile and 15% ammonium acetate buffer solution (0.065 mol L⁻¹). From 0–10 min the proportion of eluent B in the mobile phase was increased from 0 to 40%; this composition was maintained isocratic from 10–13 min and then, from 13–25 min, the proportion of B was increased to 100%. This composition was then maintained isocratic for a further 6 min. A sample loop with a volume of 50 μL was used and the mobile phase flow rate was 1 mL min⁻¹.

The wavelength for measurement of aniline, *o*-toluidine, and 2-nitroaniline was 231 nm; that for the other aromatic amines was 241 nm. Peaks were identified by comparison of retention times with those from standard solutions and by comparison of spectra (wavelength from 220 to 290 nm). Isocratic conditions (58% eluent A and 42% B) were chosen for determination of relative retention times, to enable correlation of these with adsorption coefficients; no guard column was used.

Sediment-column experiments

Columns (length 2 m, i.d. 74 mm) were filled with cored material from the aquifer near Torgau (Germany) and sieved to a size fraction <1 mm. The organic carbon content of the sediment material was 0.01 to 0.02% and the iron and manganese content were approximately 3 and 0.02 g kg⁻¹, respectively. The main component of the material was quartz, including some feldspar. An effective porosity of 0.37 and an average solid bulk density of dry solids of 1.7 g cm⁻³ were determined as basic properties for calculation of partition coefficients.

For the experiments, River Elbe water (pH 7.5 to 7.8) spiked with 6 to 30 $\mu\text{g L}^{-1}$ of each amine was pumped through the column at a rate of 1.5 to 2.5 mL min⁻¹. After passing through the column the water was sampled in fractions, enriched by a factor of 100, and analyzed by HPLC-DAD.

The retardation coefficients of *N*-ethylaniline, 4-methyl-2-nitroaniline, and 2-chloro-5-nitroaniline were determined by Epinger [21] in column experiments under the same conditions.

Results and discussion

Optimization of enrichment and sample preparation

The properties varied to achieve a high level of recovery were:

- the pH of the water sample;
- the amount of NaCl in the water;
- the variety and amount of SPE-materials; and
- the type and amounts of solvents used for elution.

Figure 1 shows the optimized conditions for enrichment of the compounds. The best recoveries were obtained by use of polymeric materials such as SDB-1.

The material Polar Plus (not endcapped, a little more polar than standard C₁₈) is also suitable for enrichment of aromatic amines, although breakthrough is rapid for polar amines (e.g. aniline). Thus larger amounts of SPE material and salt additives are needed to obtain better results using Polar Plus.

The eluate was concentrated to 0.5 mL only because concentration to dryness caused significant loss of analytes.

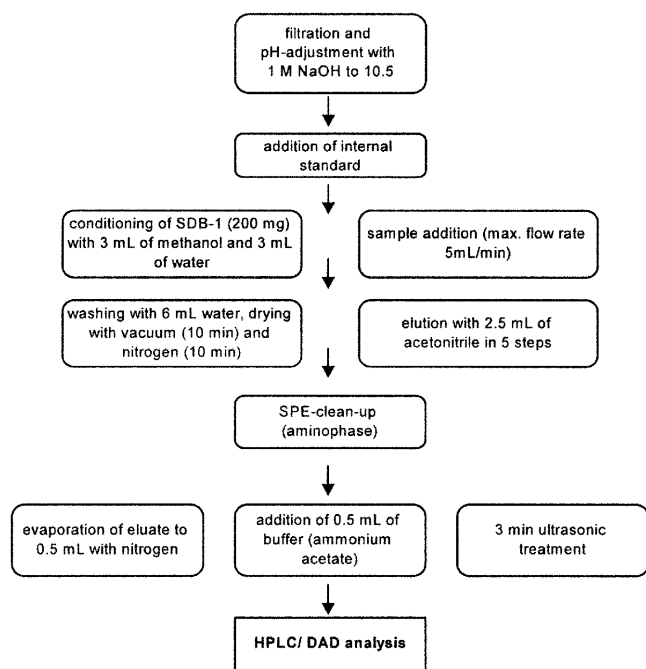


Fig. 1 Schematic diagram of the optimized analytical method for determination of aromatic amines, including enrichment and clean-up

Separation of a mixture of aromatic amines; optimization of HPLC; calibration

To optimize separation efficiency and the peak shape different types of column material were tested. The modified C-18 ABZ⁺Plus gave the best results with regard to column efficiency and long-term stability. Polar groups in the C₁₈ chain inhibit secondary interactions of basic analytes with residual OH-groups on the silica gel surface. The chromatogram obtained from a mixture of 13 amines after optimizing the chromatographic conditions is presented in Fig. 2.

Statistical data were established for calibration of 11 amines in drinking water (Table 1) and for their recoveries from River Elbe water (400 ng L⁻¹, n=10; Table 2). The concentration range used for the calibration was from 40 to 600 ng L⁻¹ (eight stages), the enrichment factor was 1000 and 4-fluoro-2-nitroaniline was used as internal standard.

Analysis of real water samples

Humic acids and other organic compounds occurring in surface waters can disturb the HPLC analysis of aromatic amines. Figure 3 shows an example of such a chromatogram (water sample from the River Elbe spiked with a mixture of 13 amines; enrichment factor 500).

The methods described above were tested for the separation of humic acids from basic amines. The conclusions reached were that reaction products of azo coupling were

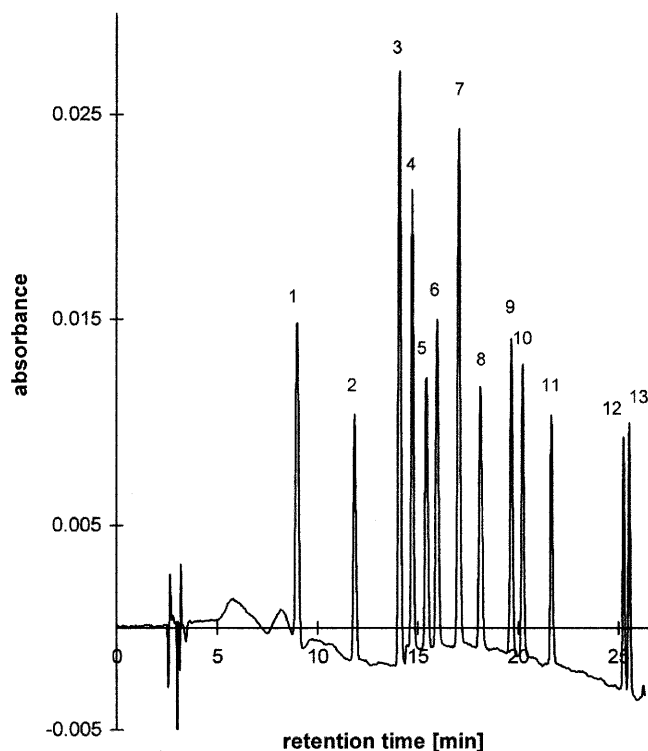


Fig. 2 Chromatogram obtained from a standard mixture of thirteen aromatic amines (30 ng absolute amount per compound): 1, aniline; 2, 2-methylaniline; 3, 2-nitroaniline; 4, 4-chloroaniline; 5, 2-chloroaniline; 6, 4-bromoaniline; 7, 1-naphthylamine; 8, 3-chloro-4-methylaniline; 9, *N,N*-dimethylaniline; 10, 3,4-dichloroaniline; 11, 2,5-dichloroaniline; 12, 2,4,5-trichloroaniline; 13, 2,4,6-trichloroaniline

Table 1 Statistical data for the calibration of 11 aromatic amines. (Enrichment factor, 1000; working range, 40–600 ng L⁻¹; n=4 replicates; matrix, drinking water; internal standard, 4-fluoro-2-nitroaniline; data were calculated on the basis of a linear regression $y=a_0+a_1x$, in accordance with a method described elsewhere [32]. The correlation factors for all compounds were >0.99)

Compound	Slope a_1	Intercept a_0	Determination limit (ng L ⁻¹)	Standard deviation of method
Aniline	1.138	-0.005	52	0.029
2-Methylaniline	1.383	-0.046	28	0.016
2-Nitroaniline	2.526	-0.016	32	0.018
4-Chloroaniline	1.553	-0.043	36	0.020
1-Naphthylamine	2.631	-0.035	45	0.025
3-Chloro-4-methylaniline	1.054	-0.020	44	0.024
<i>N,N</i> -Dimethylaniline	1.163	-0.060	41	0.023
3,4-Dichloroaniline	1.200	-0.018	33	0.018
2,5-Dichloroaniline	0.972	0.005	44	0.025
2,4,5-Trichloroaniline	0.699	0.025	54	0.030
2,4,6-Trichloroaniline	0.713	-0.001	62	0.035

well separated by chromatography on C₁₈ but that sensitivity was lower than for direct HPLC analysis of amines, i.e. substantial loss of analyte occurred during the pre-treatment steps flocculation and C₁₈ SPE.

Table 2 Average recovery of 11 aromatic amines. (Enrichment factor, 1000; concentration, 400 ng L⁻¹; n=10 replicates; matrix, River Elbe water)

Compound	Average recovery (%)	Relative standard deviation (%)
Aniline	84	17.2
2-Methylaniline	91	6.3
2-Nitroaniline	85	3.3
4-Chloroaniline	73	4.5
2-Chloroaniline	92	5.5
3-Chloro-4-methylaniline	102	5.7
<i>N,N</i> -Dimethylaniline	79	7.6
3,4-Dichloroaniline	89	4.1
2,5-Dichloroaniline	98	4.2
2,4,5-Trichloroaniline	78	4.7
2,4,6-Trichloroaniline	82	5.4

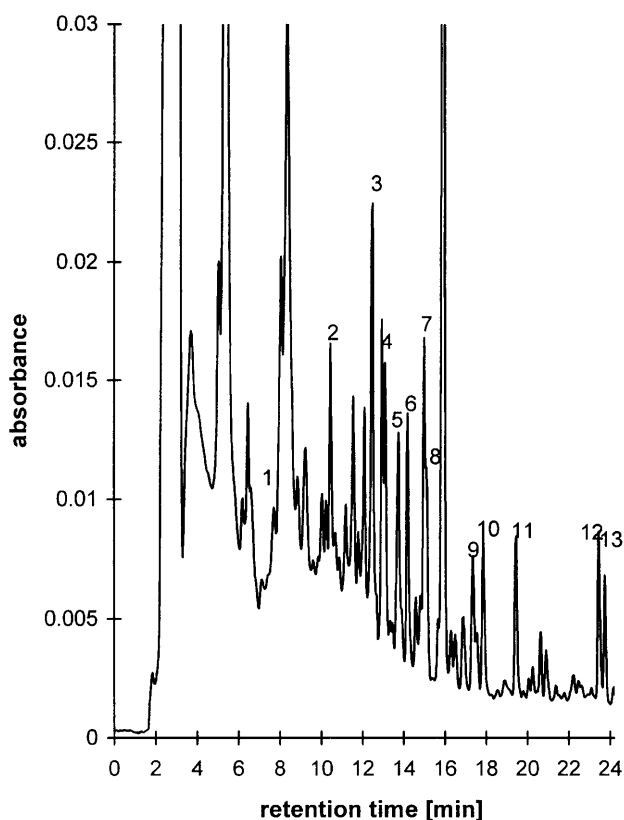


Fig. 3 Chromatogram obtained from a mixture of thirteen aromatic amines in River Elbe water (800 ng L⁻¹ of each compound; enrichment factor 500; without clean-up; compound identities as for Fig. 2)

The best efficiency was achieved by use of the NH₂ phase (Fig. 4, same sample as for Fig. 3). Recoveries of the investigated amines were reduced by up to 15% but the results were acceptable when internal calibration was used.

In River Elbe water sampled at Dresden between 1994 and 1998 aniline was the most frequently determined aromatic amine; concentrations were up to 20 µg L⁻¹. 3,4-Dichloroaniline, *o*-toluidine, 2,5-dichloroaniline, 3-chloro-

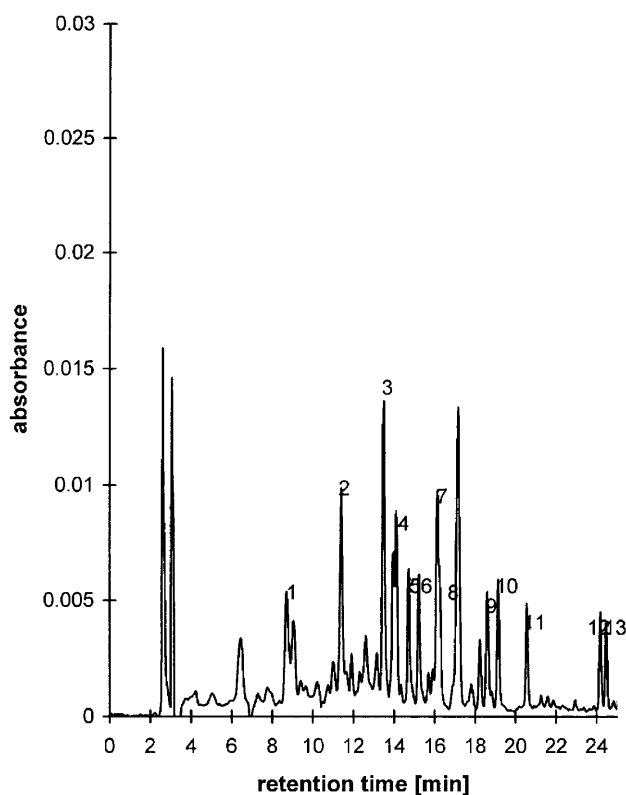


Fig. 4 Chromatogram obtained from a mixture of thirteen aromatic amines in River Elbe water (800 ng L⁻¹ per compound; enrichment factor 500; clean-up of the acetonitrile extract on amino-modified silica gel; compound identities as for Fig. 2)

4-methylaniline, *N,N*-dimethylaniline, 4-chloroaniline, 2,4,6-trichloroaniline, 2-nitroaniline, and 2,5-dichloroaniline were detected sporadically, in the ng L⁻¹ concentration range [22]. Amine concentrations determined in groundwater from wells influenced by river bank filtration were low. The maximum concentrations measured were 370 ng L⁻¹ for aniline, 70 ng L⁻¹ for *o*-toluidine, 57 ng L⁻¹ for 2-chloroaniline, and 60 ng L⁻¹ for 2,5-dichloroaniline.

Sediment-column experiments

The aromatic amines selected are highly mobile in the aquifer material investigated. The most polar amines have low affinity to sediments with a low organic carbon content. Stronger ionic interactions are theoretically possible at pH < 5, because the pK_a of the aromatic amines in the protonated form ranged from -0.28 to 5.2. Such effects, however, also depend on the isoelectric properties of the surface of the sediment particles.

Figure 5 shows the breakthrough curves for two amines as an example. There is little difference between the increases in the concentrations of the NaCl tracer (monitored using on-line measurements of electrical conductivity) and the concentrations of the amines. The same behavior was observed for the process of desorption when the spiked water was replaced by non-spiked river water.

Fig. 5 Breakthrough curves for chloride and for two amines, $6 \mu\text{g L}^{-1}$ per compound (matrix, River Elbe water; V =water volume running through the column, V_p =pore space volume)

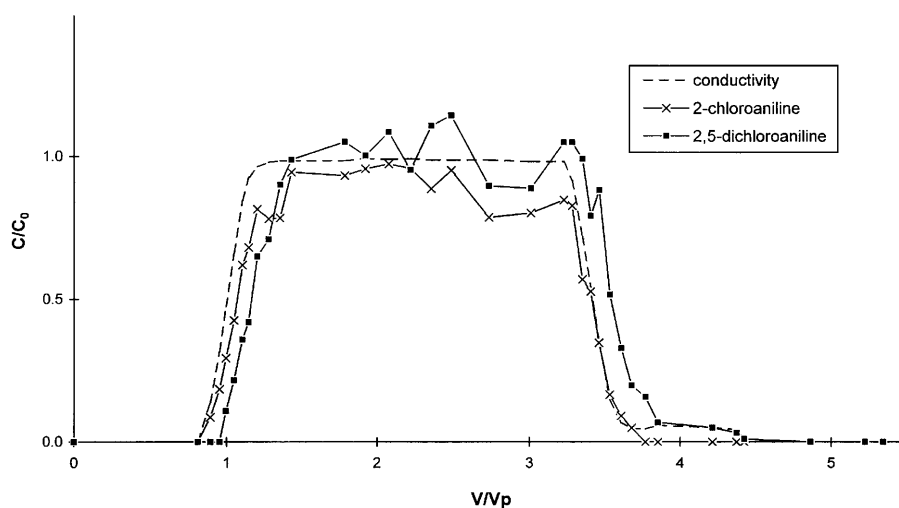


Table 3 CAS numbers, *n*-octanol–water partition coefficients^a ($\log P_{OW}$), retardation factors determined experimentally (R_d), adsorption coefficients (K_d), and average capacity factors (k' ; $n=5$ replicates) determined by HPLC for 19 aromatic amines

Compound	CAS no.	$\log P_{OW}$	R_d	K_d	k'
Aniline	62–53–3	0.9	1.04	0.009	–0.35
4-Chloroaniline	106–47–8	1.83	1.12	0.026	0.07
2-Chloroaniline	95–51–2	1.9	1.1	0.022	0.00
<i>N,N</i> -Dimethylaniline	121–69–7	2.31	1.13	0.029	0.46
3,4-Dichloroaniline	95–76–1	2.69	1.38	0.083	0.51
2,5-Dichloroaniline	95–82–9	2.75	1.32	0.070	0.76
2-Methylaniline	95–53–4	1.32	1.06	0.013	–0.23
2-Nitroaniline	88–74–4	1.85	1.17	0.037	–0.12
2,4,6-Trichloroaniline	634–93–5	3.52	1.78	0.171	2.26
4-Bromoaniline	106–40–1	2.26	1.14	0.031	0.06
2,4,5-Trichloroaniline	636–30–6	3.45	1.72	0.158	2.04
2-Chloro-5-nitroaniline	6283–25–6	2.12	1.18	0.037	0.23
<i>N</i> -Ethylaniline	103–69–5	2.16	1.06	0.028	0.26
4-Methyl-2-nitroaniline	89–62–3	2.57	1.2	0.044	0.14
3-Nitroaniline	99–09–2	1.37	1.06	0.013	–0.20
4-Nitroaniline	100–01–6	1.39	1.1	0.022	–0.25
3-Chloroaniline	108–42–9	1.88	1.2	0.044	0.00
4-Isopropylaniline	99–88–7	2.49	1.15	0.033	0.23
3-Chloro-4-methylaniline	95–74–9	2.27	1.25	0.055	0.25

^aAll values were taken from Interactive LogKow (KowWin), Syracuse Research Corporation (developed and maintained by webmaster@syrres.com)

All retardation factors determined in the experiments and the calculated water sediment partition coefficients are given in Table 3.

Poorly biodegradable aromatic amines, e.g. nitroanilines or higher chlorinated anilines [23], are transported at nearly the same velocity as the water during bank filtration and could reach boreholes and thus contaminate the raw water.

Correlation between results from sediment columns and chromatography

As expected, the retardation of aromatic amines in the sediment material decreased with increasing hydrophilicity. This corresponds to the separation behavior of anilines during reversed-phase chromatography. The aim of further investigations was to find a relationship between chromatographic properties and the adsorption coefficients determined in sediment-column experiments.

To obtain reproducible retardation data from reversed-phase chromatography, the aromatic amines listed in Table 1, and six other compounds, were separately determined by isocratic HPLC after addition of 4-fluoro-2-nitroaniline as internal standard. The capacity factors were calculated by use of Eq. (2):

$$k' = \frac{t_x - t_{IS}}{t_{IS}} \quad (2)$$

where k' is the capacity factor (isocratic HPLC method), t_x the retardation time of compound x , and t_{IS} the retardation time of the internal standard.

The mean values from five replicate determinations are listed in Table 3.

The correlation between the adsorption coefficients, K_d , and the capacity factors, k' , determined by HPLC for 19 amines is highly linear (Fig. 6) and can be expressed as:

$$K_d = a^*k' + b^* \quad (3)$$

where the constants a^* and b^* are $0.061 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ and $0.0287 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$, respectively.

It should be noted, that k' is a modified capacity factor, defined on the basis of the retention time of an internal standard, t_{IS} , instead of the commonly used dead time, t_0 . This modification was necessary because the determination of t_{IS} was more accurate than the determination of t_0 . Because of the existing linear relationship between the differently defined capacity factors, the type of the factor is without significance in respect of the linearity of the

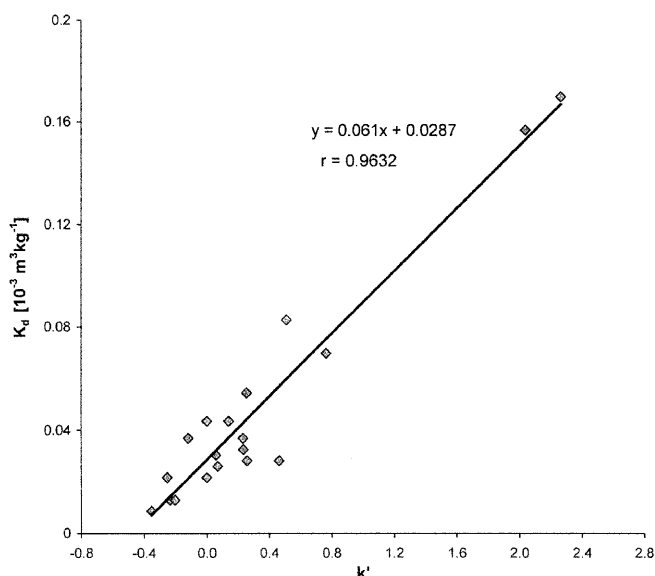


Fig. 6 Correlation between the capacity factors (HPLC) and sediment adsorption coefficients of 19 aromatic amines

correlation between the adsorption coefficient and the capacity factor.

To discuss the correlation found here, the dependence of the adsorption coefficient of neutral organic substances on their hydrophobicity must be taken into account. In general, the adsorption coefficients of such adsorbates can be correlated with their *n*-octanol–water partition coefficients [24, 25]:

$$\log K_{OC} = a \times \log P_{OW} + b \quad (4)$$

or

$$\log K_d = a \times \log P_{OW} + b' \quad (5)$$

where

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (6)$$

and

$$b' = b + \log f_{OC} \quad (7)$$

and where K_d is the solid–water partition coefficient (adsorption coefficient), P_{OW} the *n*-octanol–water partition coefficient, K_{OC} the adsorption coefficient, normalized to the organic carbon content of the solid, f_{OC} the weight fraction of solid which is organic carbon, and a , b , and b' are constants

Equation (8) was found to be valid for the aromatic amines investigated (Fig. 7):

$$\log K_d = 0.463 \log P_{OW} - 2.44 \quad (8)$$

The capacity factor determined by RPHPLC can also be regarded as an index of hydrophobicity. In the literature, linear correlations between $\log k'$ and $\log P_{OW}$ [26, 27] or between k' and $\log P_{OW}$ [28] are reported. Following from this, it might be expected that there is also a correlation

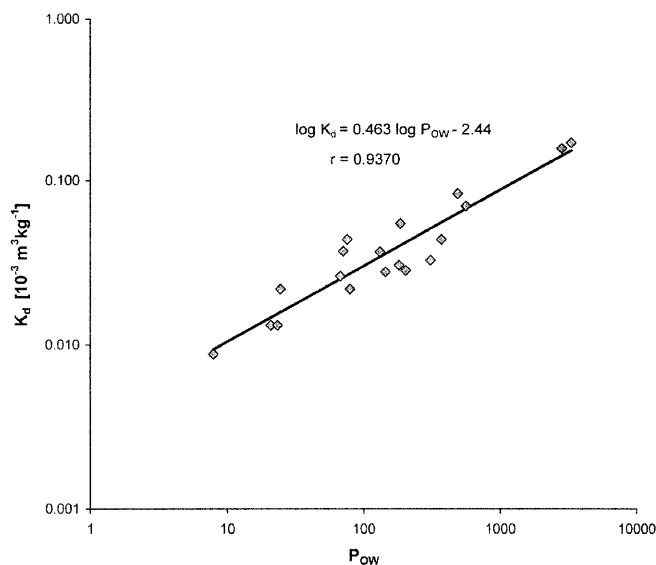


Fig. 7 Correlation between the *n*-octanol–water partition coefficient P_{OW} and the sediment adsorption coefficients of 19 aromatic amines

between K_d and k' , but it is not possible to predict the exact type of correlation. The results presented show a simple linear correlation given in Eq. (9), whereas other authors have described a linear $\log K_{OC}$ – $\log k'$ correlation [29, 30, 31].

$$K_d = 0.061 \cdot 10^{-3} \frac{\text{m}^3}{\text{kg}} k' + 0.0287 \cdot 10^{-3} \frac{\text{m}^3}{\text{kg}} \quad (9)$$

The correlation is restricted to linear isotherms, and thus to K_d values which are independent of compound concentration.

Conclusions

The method presented using SPE enrichment and reversed-phase chromatography is suitable for the measurement of aromatic amines at concentrations in the low ng L^{-1} range. The method thus meets the requirements of drinking water regulations, stipulated by different European countries, for pesticides and their degradation products. Matrix effects were reduced by means of supplementary SPE clean-up of the extract on an amino phase.

Results from sediment-column experiments were indicative of high mobility of aromatic amines in an aquifer near the river Elbe; retardation increased with increasing hydrophobicity. The adsorption coefficient, K_d , correlated strongly with the *n*-octanol–water partition coefficients (Eq. 8). A linear correlation was found between the chromatographic property k' and the adsorption parameter K_d obtained from sediment-column experiments. Such correlations are useful tools for approximate prediction of the behavior of dissolved organic substances in the environment, in particular for assessing subsurface mobility determined by adsorption processes. Expensive sediment-

column experiments can be reduced to a limited number of runs and compounds and can be partly replaced by RPHPLC, which readily yields a large amount of precise and reproducible data.

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