DESORPTION BEHAVIOUR OF POLYCYCLIC AROMATIC HYDROCARBONS IN HARBOUR SLUDGE FROM THE PORT OF ROTTERDAM, THE NETHERLANDS

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Abstract. Desorption of eight polycyclic aromatic hydrocarbons (PAH) from two harbour sludges from the Port of Rotterdam, the Netherlands, was studied by column elution experiments. When water moves in a sludge layer desorbing contaminants like PAH can be dispersed in the environment. Separation of liquid and solid phase in batches of sludge, stored for more than three years, by ultra-centrifugation at 4 °C yielded equilibrium partition coefficients. Temperature effects could not account for the observed differences with reported literature values. The differences are attributed to the contact time of PAH in the sediment. Laboratory data reported in the literature were often obtained after short contact times and therefore may not represent equilibrium partitioning. Our values represent contact times in excess of three years and are therefore more representative for the field conditions. Partition coefficients obtained from column elution experiments were slightly above those obtained from the batch experiments. During column elution of the sludge from the *Beneden Merwede* sorption equilibrium was absent for the lighter compounds. This is attributed to the presence of a large portion of immobile water in the columns. Elution in the *Beerkanaal* columns occurred at near sorption equilibrium although pore water velocities were higher. Assuming that desorption is diffusion controlled, observed desorption in both materials could be explained. The non-equilibrium desorption in the *Beneden Merwede* sludge for phenanthrene, and to a lesser extent for anthracene and fluoranthene, could be described by a diffusion limited model assuming spherical particles.

Keywords: contaminants, desorption, diffusion, PAH, partition coefficients, sediments, transport

1. Introduction

In the lower Rhine delta in the Netherlands, large quantities of sediments are deposited in the major waterways and harbours. A large part of these sediments is contaminated with organic pollutants, like polycyclic aromatic hydrocarbons (PAH), and inorganic pollutants, like heavy metals (Stigliani *et al.*, 1993; Van Zoest and Van Eck, 1993). Consequently, depending on the level of these contaminants dredged sediments can not be disposed of on land or at sea and are therefore permanently stored in sludge depositories. A major depot, *De Slufter*, near the Port of
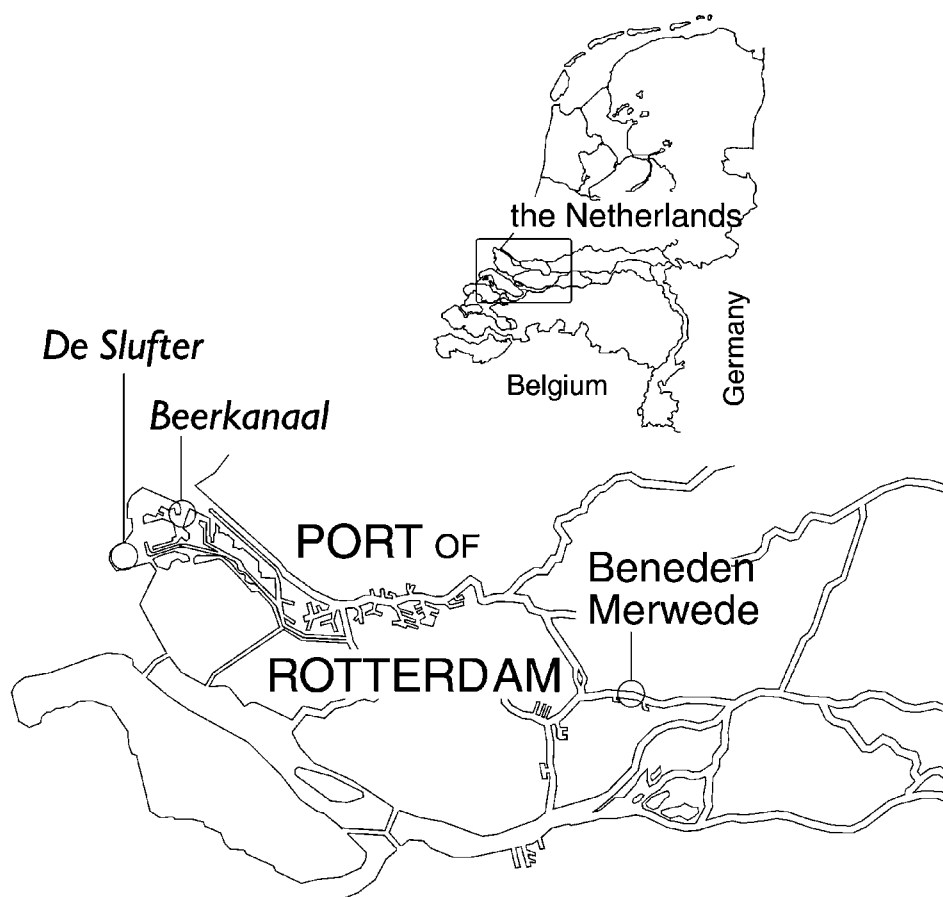
Figure 1. Locations of the Beerkanaal (BK) and Beneden Merwede-river (BMR) sampling sites in the Port of Rotterdam, The Netherlands.

Rotterdam (Figure 1) is currently receiving about 3 Mm^3 of contaminated harbour sludge each year.

It is often assumed that in consolidated fine-grained sediments the mobility of pollutants is negligible. The mobility of a compound is controlled by its water solubility which can be described in terms of the distribution coefficient, K_d, defined as the ratio of the concentrations in the solid and liquid phase at equilibrium. For most of the hydrophobic organic compounds, like PAH, the distribution coefficient is high and positively correlated with the organic matter content in soils and sediments (e.g., Loch, 1996). For the assessment of transport of PAH from contaminated sediments K_d-values are commonly obtained from sorption batch experiments. However, during the consolidating stage in a harbour sludge depot convective solute transport occurs in the sludge layer. After consolidation is complete water transport in the depot can still occur as the result of hydraulic and/or

osmotic gradients present (Keijzer, 2000; Keijzer and Loch, 2001). Under these convective transport conditions sorption equilibrium may be absent. For contaminated aquifer material Grathwohl *et al.* (1994) showed that distribution coefficients derived from column experiments were higher than those obtained from short term laboratory experiments. Liu and Amy (1993) showed that deviation from sorption equilibrium depended on the flow rate of the water and that it typically resulted in asymmetrical breakthrough curves and extended tailing (Brusseau *et al.*, 1991a, b; Grathwohl *et al.*, 1993; Liu and Amy, 1993).

In column experiments on sorption and transport, PAH are often introduced with the percolating solution (Brusseau *et al.*, 1991a; Liu and Amy, 1993) or with a separate, contaminated solid phase (Grathwohl *et al.*, 1993). In order to assess the long term fate of PAH in a harbour sludge depot it is necessary to measure partitioning under conditions of low advection. In this paper results are presented of the desorption of PAH using elution experiments on saturated samples of two harbour sludges under low convective regimes resulting in apparent partitioning coefficients. These results are compared to equilibrium partitioning coefficients obtained from batch experiments on the same sludges. The contact time of the PAH in these sludges is in excess of three years. The following PAH were considered: phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[ghi]perylene (BgP) and indeno[1,2,3cd]pyrene (InP).

2. Materials and Methods

2.1. CHEMICALS

Chemicals used in this study were either obtained from J. T. Baker (Deventer, NL) or Merck (Darmstadt, GE), and were of HPLC or Supra Pure grade. PAH stock solutions were prepared from J. T. Baker custom PAH mixture JTB0005a lot J-1025. Water, used for dilution and preparation of stock solutions, was prepared with a Milli-Q filtration unit.

2.2. HPLC

All PAH analyses were carried out using a high performance liquid chromatograph (HPLC – Hewlett Packard model 1050) equipped with a fluorescence detector (Hewlett Packard 1046A) on a ChromSpher 5PAH reverse-phase column (Chrompack, Bergen op Zoom NL) using a water:acetonitril gradient. Calibration curves of all PAH under investigation were determined prior to each sample run. A standard PAH solution from the National Institute of Standards and Technology (NIST, 1947c) was used to assess the reproducibility of retention times and detection signals.

TABLE I

Selected bulk sample properties of the *Beerkanaal* (BK) and the *Beneden Merwede*-river (BMR) harbour sludge samples

	BK	BMR	
Cation exchange capacity	24.2 ± 0.3	14.9 ± 0.5	$\text{cmol}_c \text{ kg}^{-1}$
Organic carbon content	1.35	1.24	wt%
Carbonate content	35.2	18.0	wt%
Particle density	2.46	2.58	g cm^{-3}
Particle size distribution, fraction:			
>60 μm	3	46	%
2–60 μm	41	28	%
<2 μm	56	26	%

2.3. SAMPLE DESCRIPTION AND TOTAL PAH DETERMINATION

The harbour sludge samples were retrieved from locations in the *Beerkanaal* (BK) and *Beneden Merwede*-river (BMR) in the port of Rotterdam, the Netherlands (Figure 1), during the autumn of 1993. Selection of the sampling locations was based on the expected contamination with PAH. The BK sample was deposited in a brackish environment influenced by the tidal regime of the North Sea, which may result in low PAH contamination. The BMR sample is from a fresh water environment, having potentially a high contamination with PAH as a result of its proximity to industrial sites and a relatively large influence of river transported material and contaminants. These sites represent two different types of harbour sludge disposed in the harbour sludge depot *De Slufter*. The samples were stored for over three years under dark, anaerobic conditions at 4 °C until used in the experiments described. Selected bulk sample properties are listed in Table I.

Before the start of the batch and column experiments the individual PAH content of the samples was determined after an eight hour soxhlet extraction with a 1:3 aceton:hexane mixture. The extract was cleaned on a Al_2O_3/Na_2SO_4-column at a flow rate of 2 mL min^{-1} using 12 mL hexane as eluent. Before their use Al_2O_3 (ICN, Eschwege GE) was dried during 18 hr at 180 °C, after which 10 wt% water was added, and Na_2SO_4 was dried for 3 hr at 500 °C. Two mL of acetonitril were added to the eluate, and subsequently concentrated to approximately 1 mL under a gentle N_2 flow and analysed by HPLC. In order to determine the efficiency of the extraction method and the recovery of the individual compounds, a PAH contaminated standard (NIST, 1941a) was also analysed.

2.4. Batch experiment

It is assumed that after the three years sample storage an equilibrium partitioning existed between the solid and aqueous phase. Consequently, the equilibrium distribution coefficient, K_d^{eq} can be determined by measuring the concentrations in both phases.

Hundred grams of wet sediment, without additional water was centrifuged at 24 000 rpm and 4 °C for 20 min using an ultra-centrifuge (MSE Europe 24M, 11.1 cm roter). According to Puchelt and Bergfeldt (1992) ultra-centrifugation yields the pore water directly subjected to convective transport. Water trapped in dead-end pores or present as a water film on grains is not retrieved by this method. The supernatant after centrifugation was aspirated over a previously conditioned Bakerbond C_{18}/NH_2 PAH solid-phase extraction (SPE) column. The PAH are adsorbed onto the SPE-column and elution of the compounds from the SPE-column was done by aspirating 3 mL hexane at a flow rate of 1 mL min^{-1} after a soaking period of 20 min. This procedure was repeated three times. Finally, two mL acetonitril was added to the SPE-eluate and the sample was concentrated under a gentle N_2 flow to approximately 1 mL and analysed by HPLC. The method to retrieve the PAH from the aqueous solution is based on the Bakerbond Application Note ENV103 and yields the water soluble PAH and the fraction bound to the dissolved organic carbon (DOC). The DOC suspended in the solution is trapped on the SPE-column, and during the soaking and elution stage the PAH are dissolved into the hexane and recovered. The PAH concentrations measured in the aqueous solution are therefore assumed to represent the total PAH content eluted from the sediment, including the DOC-bound fraction. The PAH content of the solid phase was determined using the method described for the total PAH determination.

3. Column Experiments

Glass columns (internal diameter 7 cm, height 30 cm) were packed with a 700 g slurry of harbour sludge and sand. Sand was added to increase the hydraulic conductivity of the sludge. The sand was heated beforehand to 900 °C to remove carbonate and organic matter. For the BMR a 1:1 sludge-sand mixture was used; for the BK sludge a 1:3 mixture was used. Because of the high clay content (Table I) of the BK sample a higher sand content was used. Of each sludge sample two columns were packed which are referred to as BMR-I, BMR-II, BK-III and BK-IV.

The columns were fitted with a coarse glass frit and a 0.7 μm glassfiber filter to prevent the removal of fine solid material during elution. Recently, anaerobic breakdown of several PAH like naphthalene and phenanthrene were described in PAH contaminated sediments (e.g., Coates *et al.*, 1996b; 1997; Zhang and Young, 1997). To reduce anaerobic activity and minimise degradation of the PAH the column experiments were conducted at 4 °C and under dark, strict anaerobic conditions. A constant hydraulic head was maintained at the top of the columns using

TABLE II

Detection limits and average recoveries, with their standard deviation, from aqueous solution for the different PAH using Bakerbond SPE extraction columns and HPLC with fluorescence detection. Recoveries were determined on three individually spiked solutions in the presence of 10 mg kg^{-1} SOM and without DOM

Compound	HPLC	Recovery	
	detection limit	Without DOM	With SOM[a]
	μg L^{-1}	(%)	
Phe	0.002	119.0 ± 3.6	116.9 ± 3.5
Ant	0.0001	97.2 ± 2.6	93.8 ± 2.6
Flu	0.001	100.6 ± 0.8	93.8 ± 0.7
BbF	0.001	78.2 ± 0.3	74.1 ± 0.3
BkF	0.0001	61.3 ± 0.8	72.8 ± 1.0
BaP	0.002	94.0 ± 2.0	103.0 ± 2.2
BgP	0.049	71.7 ± 1.2	55.6 ± 0.9
InP	0.107	94.0 ± 0.7	50.6 ± 0.4

[a] Synthetic DOM (Aldrich, Zwijndrecht NL).

de-aired 0.01 M NaCl solution, resulting in a hydraulic gradient of approximately 1. The freely draining eluate was sampled each one or two week period for about four months. BMR-I was sampled during a period of nine months. The eluate was collected in N$_2$ filled, airtight 250 mL flasks to which 3 mL of a 600 μg L^{-1} benzethonium chloride (Hyamine^{TM}) solution was added to prevent adsorption of the PAH onto the glass walls (Kicinski, 1992). The PAH content in the eluate was determined using the method described for the supernatant of the batch experiments. Detection limits and recoveries for the individual PAH in aqueous solution with and without DOC are listed in Table II. DOC concentrations were measured using a Shimadzu TOC-500 Analyzer and where whenever needed recalculated to dissolved organic matter (DOM). The chloride concentration in the eluate was determined using ion chromatography (Dionex QIC Analyser).

3.1. HYDRODYNAMIC PARAMETER ESTIMATION

The diffusion-dispersion coefficient (D) of the columns was derived from the slope of the chloride breakthrough curve (BTC) assuming chloride to be a non-reactive, conservative tracer. The value of D was then used in a one dimensional, single solute transport model SOLUTE (Wilkens, 1995) together with the measured pore water velocities (Table III) to gain insight in the presence of immobile water. Immobile or stagnant water presents a source/sink for the transported solute as it does not participate in convection. Transfer between mobile and immobile water is by

TABLE III

Physical properties and experimental parameters for the harbour sludge columns

	Height L (cm)	Velocity v (cm d^{-1})	Water content θ (cm^3 cm^{-3})	Pore volume (cm^3)	Bulk density ρ_b (g cm^{-3})
BMR-I[a]	9.2	0.077	0.48	169	1.36
BMR-II	8.7	0.108	0.45	150	1.44
BK-III	8.4	0.430	0.42	134	1.53
BK-IV	8.6	0.374	0.44	143	1.47

[a] For the nine month period.

diffusion, therefore the presence of stagnant water in a column results in so-called transport non-equilibrium (Kookana *et al.*, 1993; Gaber *et al.*, 1995; Beigel and Di Pietro, 1999). The exchange between immobile and mobile water is generally represented by a first order mass transfer coefficient α (d^{-1} – e.g., Domenico and Schwartz, 1990). The presence of immobile water in the columns can have a profound effect on the desorption resulting in non-equilibrium behaviour whenever the sorption sites are located within the immobile water regions (Ball and Roberts, 1991; Gratwohl and Reinhard, 1993; Kookana *et al.*, 1993; Schüth and Gratwohl, 1994; Gaber *et al.*, 1995; Beigel and Di Pietro, 1999).

4. Results and Discussion

4.1. TOTAL PAH-CONTENT

The concentrations of the individual PAH compounds are given in Table IV. PAH concentrations in the BK sample are lower than in the BMR sample. The higher concentrations of the BMR site can be explained by its location near industrial sites and the larger influence of river transported material and contaminants compared to the BK site. Based on the Dutch classification system[*] the BMR sludge falls within the concentration category which has to be stored in permanent harbour sludge depots. Based on the PAH content this sludge exceeds the target value and therefore falls in class 2 which is unsuitable for disposal on land or in open water. On the other hand, the BK sludge does not exceed environmental criteria and can be disposed of in open sea after dredging.

[*] The quality class of a sludge is based on comparison of the concentration of heavy metals and organic compounds with a number of limits. For each compound or group of compounds a target concentration is defined as the desired value (class 1) in addition an upper value (class 2), a critical value (class 3) and an intervention value (class 4) are distinguished.

4.2. EQUILIBRIUM K_{OC}-VALUES

The values of K_d^{eq} for the compounds from the batch experiments were obtained
the presence of DOC in the equilibrium solution into account (Loch, 1996):

$$Q = \frac{K_d^{eq} \cdot C_w}{1 + K_{DOC}^{eq} \cdot C_{DOC}} \; , \tag{1}$$

which, given that $K_d^{eq} = f_{OC} \cdot K_{OC}^{eq}$ and assuming that the partitioning for a compound and organic carbon is the same for DOC and particulate organic carbon (OC), can be rewritten to:

$$K_{DOC}^{eq} = K_{OC}^{eq} = \frac{Q}{f_{OC} \cdot C_w - Q \cdot C_{DOC}} \; , \tag{2}$$

in which K_{OC}^{eq} is the partition coefficient water/particulate organic carbon in L kg^{-1}
taking the presence of DOC into account, f_{OC} is the fraction particulate organic
carbon in the sediment, Q is the amount of PAH in the solid phase in mg kg^{-1},
C_w is the total concentration of PAH in the solution including the amount sorbed
to the DOC in mg L^{-1}, and C_{DOC} is the concentration DOC in the water in kg L^{-1}.
The values for K_{OC}^{eq} are listed in Table IV. The assumption that the log K values for
DOC and OC are equal is not unreasonable as the organic material in the solution
is derived from the organic matter within the sediment. For comparable sediments
from the *Ketelmeer* Lüers and Ten Hulscher (1996) published similar values for
K_{DOC} and K_{OC} for several PAH including compounds used in this study. Because
of the high HPLC detection limits (Table II) no values for K_{OC}^{eq} were obtained
for BgP and InP. In Table IV also K_{OW}-values of the individual compounds and
K_{OC} data for sediments comparable to BMR and BK are presented as found in the
literature.

   In general, the obtained log K_{OC}^{eq} are higher than these literature values. For
the less hydrophobic PAH, Phe, Ant and Flu, the difference with literature values
is larger than for the more hydrophobic compounds BkF and BaP. For Phe, for
instance, generally a value of approximately 4.30 is reported with a range of 0.10
log K units, whereas the values reported here are about 1.0 to 1.5 log units higher.
For the more hydrophobic PAH the difference is on average 0.5 log units when
compared to the data compiled by Mackay *et al.* (1992). The values, however, fall
within the reported log K range for sediments from the *Ketelmeer* (Lüers and Ten
Hulscher, 1996). Sediments from this fresh water lake are comparable in many bulk
sample properties to the studied harbour sludge. The differences in K_{OC}^{eq}-values for
the lighter compounds may be partly explained by the differences in the temperature at which they were determined. Most literature values were determined at
25 °C whereas our values were obtained at 4 °C. Adsorption of most nonionic
hydrophobic compounds decreases with increasing temperature (He *et al.*, 1995;

TABLE IV

Concentration of the different PAHs in the *Beneden Merwede*-river (BMR) and the *Beerkanaal* (BK) sludges, and their distribution coefficient normalised on the organic carbon, K_{OC}^{eq}, at 4 and at 25 °C as calculated using Equation (3). Values for ΔH_s needed in Equation (3) are also listed. For comparison, literature values for K_{OC} of comparible sediments are listed together with the octanol/water distribution coefficient, K_{OW}, for the different compounds

Com-pound	PAH content (mg kg⁻¹)		Experimental log K_{OC}^{eq} at 4 °C (n = 3)[a]		Experimental log K_{OC}^{eq} at 25 °C using Eq. (3)[b]		log K_{OW} at 25 °C	log K_{OC} at 25 °C	ΔH_s kJ mol⁻¹
	BMR	BK	BMR	BK	BMR	BK			
Phe	0.75±0.10	0.15±0.02	5.74±0.08	5.17±0.03	5.70	5.13	4.22–4.48[1]	4.57[1,2]; 4.48[3]	−3.3[4]
Ant	0.44±0.04	0.05±0.01	6.35±0.13	5.97±0.04	6.15	5.77	4.62[1]	4.54[1]; 4.68[2]; 4.53[3]	−15.0[5]
Flu	0.98±0.09	0.17±0.02	6.11±0.01	6.08±0.04	5.76–5.88[c]	5.73–5.85	4.89–5.32[1] 4.65–4.82[4] 5.07–5.65[7]	5.22[1]; 5.23[2]; 5.14[3]	−26.1[6]; −18.3[7]; −17.7[8]
BbF	0.69±0.07	0.15±0.02	6.51±0.09	6.86±0.11	6.03	6.38	5.70–5.74[1] 6.09–6.50[7]	5.75[1]; 6.32[3]	−36.2[7]
BkF	0.36±0.03	0.07±0.01	6.61±0.09	6.90±0.27	6.27	6.56	5.47–6.04[1] 6.22–6.81[7]	6.00[1]; 6.11[2]; 5.45[3]	−25.6[7]
BaP	0.61±0.06	0.07±0.02	6.67±0.06	6.46±0.11	6.26	6.05	5.53–5.99[1] 6.11–6.51[7]	6.04[1]; 6.13[2]; 6.05[3]	−31.3[7]
BgP	0.38±0.06	0.09±0.01	NA[d]	NA	NA	NA	6.20–6.26[1] 6.48–6.96[7]	6.50[1]; 6.22[2]; 6.67[3]	−40.7[7]
InP	0.45±0.09	0.11±0.02	NA	NA	NA	NA	6.38–6.76[7]	7.09[3]	−39.2[7]

[1] Mackay *et al.* (1992); [2] De Maagd *et al.* (1998); [3] Crunkilton and DeVita (1997); [4] Piatt *et al.* (1996); [5] Cornelissen (1999); [6] He *et al.* (1995); [7] Lüers and Ten Hulscher (1996), log K_{OC}-values are recalculated from values reported for 20 °C; [8] reported by Lüers and Ten Hulscher (1996) based on data by He *et al.* (1995).

[a] n = The number of observations; [b] only average value is listed; [c] range results from the range in ΔH_s-values; [d] NA = not analysed.

Ten Hulscher and Cornelissen, 1995). The temperature effect can be assessed using (Schwarzenbach *et al.*, 1993):

$$\frac{K_{OC}(T_{high})}{K_{OC}(T_{low})} = e^{\left[-\frac{\Delta H_s}{R} \left(\frac{1}{T_{high}} - \frac{1}{T_{low}} \right) \right]} \,, \tag{3}$$

giving the ratio of the distribution coefficients at the high, T_{high}, and the low, T_{low}, temperature in K. ΔH_s Is the change of enthalpy of the sediment/water partitioning in J mol^{-1} (Dewulf *et al.*, 1999) and R is the gas constant (8.31451 J K^{-1} mol^{-1}). Literature values for ΔH_s found for the individual PAH are listed in Table IV. He *et al.* (1995) found for Flu close correspondence between experimental changes of the log K-values at different temperatures and predicted values by Equation (3). An increase from 15 to 25 °C resulted in a decrease in adsorption of Flu of around 30%. In order to eliminate the temperature effect the obtained log K_{OC}^{eq}-values at 4 °C were converted to values at 25 °C (Table IV). As expected, the log K_{OC}-values at 25 °C are lower than at 4 °C, but for Phe, Ant and Flu they are up to one log K value above literature values. This difference can be explained by the experimental method used to determine the K_{OC}^{eq}-value. Contrary to the literature values, our log K_{OC}^{eq}-values were not obtained after short contact times by addition of the PAH to the sediment samples in the laboratory (e.g., De Maagd, 1996). With short contact times sorption of the PAH on the solid phase is far from complete, resulting in an underestimation of the log K_{OC}^{eq}-value. This effect is apparently stronger for the less hydrophobic compounds than for heavier. In the sludges contact time exceeded the three years storage time of the samples. It may therefore be assumed that these lighter PAH are more strongly bound to the solid phase and have diffused further into the organic matter than can be achieved in the short laboratory contact times of the compounds in an uncontaminated soil or sediment. In the typical batch experiments commonly used to obtain these values, a sample is (vigorously) shaken causing dispersion of the solid phase and an increase in the fraction of DOC in the aqueous phase. This adds to the underestimation of the partition coefficients (Schrap and Opperhuizen, 1992). The method used in this study for measuring the PAH in the aqueous solution includes the DOC-bound PAH. Recoveries in solutions with and without DOC were in close correspondence, with the exceptions of BgP and InP (Table II). Thus, the log K_{OC}^{eq}-values obtained here by the centrifugation method are in our opinion more representative for the partitioning likely to be encountered in field sediments contaminated with PAH.

The log K_{OC}^{eq}-values for the brackish BK sample are generally lower than those obtained for the fresh water sample BMR. This trend is not expected, since theoretically the distribution coefficient of a nonelectrolyte increases with increasing salinity as the solubility of the compound decreases due to the so-called salting out effect (Schwarzenbach *et al.*, 1993). However, this effect is small as Hegeman *et al.* (1995) experimentally determined; they observed an increase for Phe and BgP of less than 0.2 log units of the K_{OC} with a salinity increase from 0 to 35‰.

4.3. Relations between log K_{OC}^{eq} and log K_{OW}

Several authors have reported linear relationships between experimental log K_{OC}^{eq}-values and the corresponding log K_{OW}-values of the PAH compounds (Karickhoff *et al.*, 1979; Chiou *et al.*, 1983; De Maagd, 1996). For the BMR and BK sludge similar relationships are presented in Figure 2 based on the data for the measured log K_{OC}^{eq} recalculated to 25 °C and the literature values for the log K_{OW} given in Table IV. The regression equations are:

$$\log K_{OC}^{eq}(\text{BMR}) = 0.19 \log K_{OW} + 4.99 \qquad r = 0.588$$
$$\log K_{OC}^{eq}(\text{BK}) = 0.59 \log K_{OW} + 2.75 \qquad r = 0.835$$

For both sediments the regression lines are less steep than reported elswhere (Karickhoff *et al.*, 1979; Chiou *et al.*, 1983). De Maagd (1996) found slopes close to one for sediments from the *Ketelmeer* and *Oostvaardersplassen*, two large fresh water lakes in The Netherlands, with comparable organic carbon contents. The differences can be solely attributed to the high values of log K_{OC}^{eq} obtained in our experiments for the smaller, less hydrophobic compounds Phe, Ant and Flu. The overall trend of increasing log K_{OC}^{eq}-values with an increase in hydrophobicity as expressed by the log K_{OW} remains.

4.4. Chloride breakthrough curves

From the measured breakthrough curves of chloride (Figure 3) the diffusion-dispersion coefficient (D) was derived using (Van Beek and Pal, 1978):

$$\frac{D}{v} = \lambda = \frac{L}{4\pi \cdot S^2} \tag{4}$$

where v is the pore water velocity in m d^{-1}, λ is the dispersion length in m, L the length of the column in m, and S the slope of the BTC at $C/C_0 = 1/2$. Values of D for each column are listed in Table V. Using these values the presence of stagnant or immobile water was evaluated, resulting in a fit of the observed data (Figure 3). The fit of the breakthrough curve of BMR was good for 20 to 30% of immobile water and α of 0.01 ± 0.005 d^{-1} (Table V). Indeed the asymmetrical shape of the BTC (Figure 3) indicates the presence of a large portion of stagnant water and a relatively slow mass transfer between the two water regions. Because of the brackish nature of the sample the BTCs of the BK sludge represent elution curves (Figure 3). Therefore the BTCs for BK-III and BK-IV can be plotted as $1 - (C/C_0)$ which enables the use of Equation (4) to determine the slope of the BTC and the subsequent derivation of D. It was not possible to estimate the fraction of immobile water from the BTC of BK-III and BK-IV, but it can be argued that this fraction is negligible as indicated by the absence of tailing in the measured elution curve.
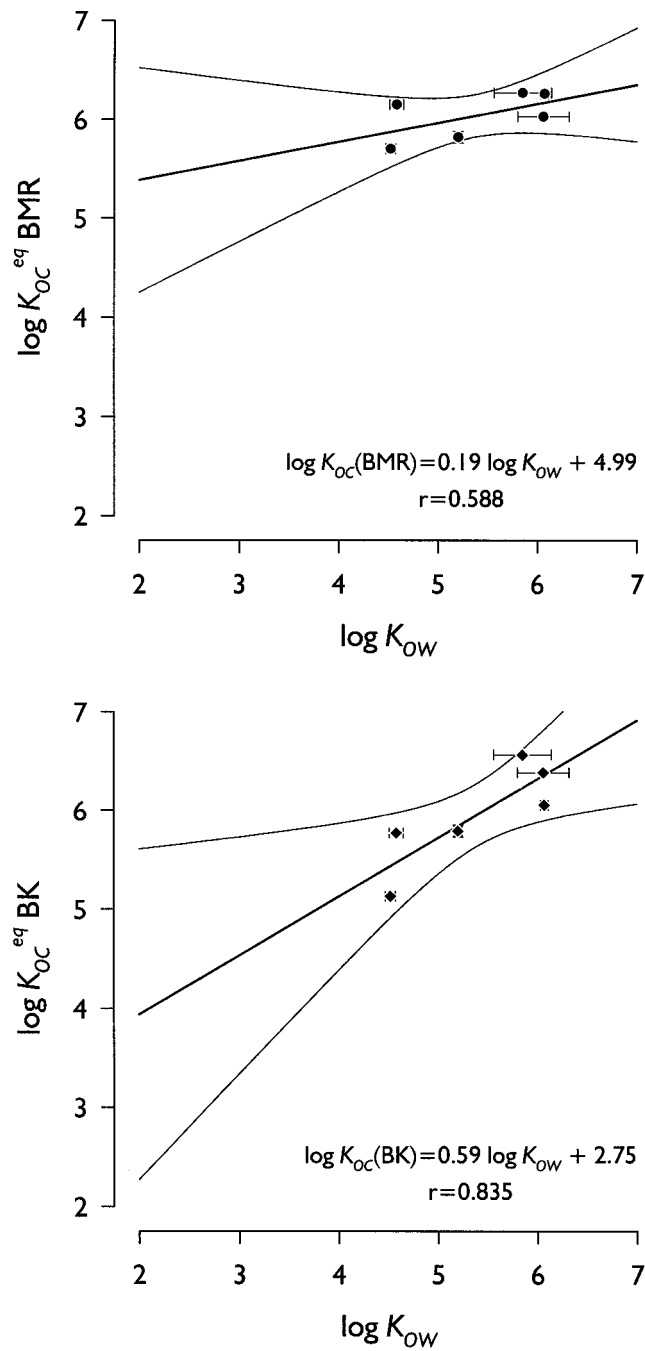
Figure 2. The relationships between the literature log K_{OW} and experimental determined log K_{OC}^{eq} at 25 °C presented in Table IV for; top: the *Beneden Merwede*-river sludge, and bottom: the *Beerkanaal* sludge. For the linear regression lines the relationship, regression coefficient and 95% confidance interval is given.
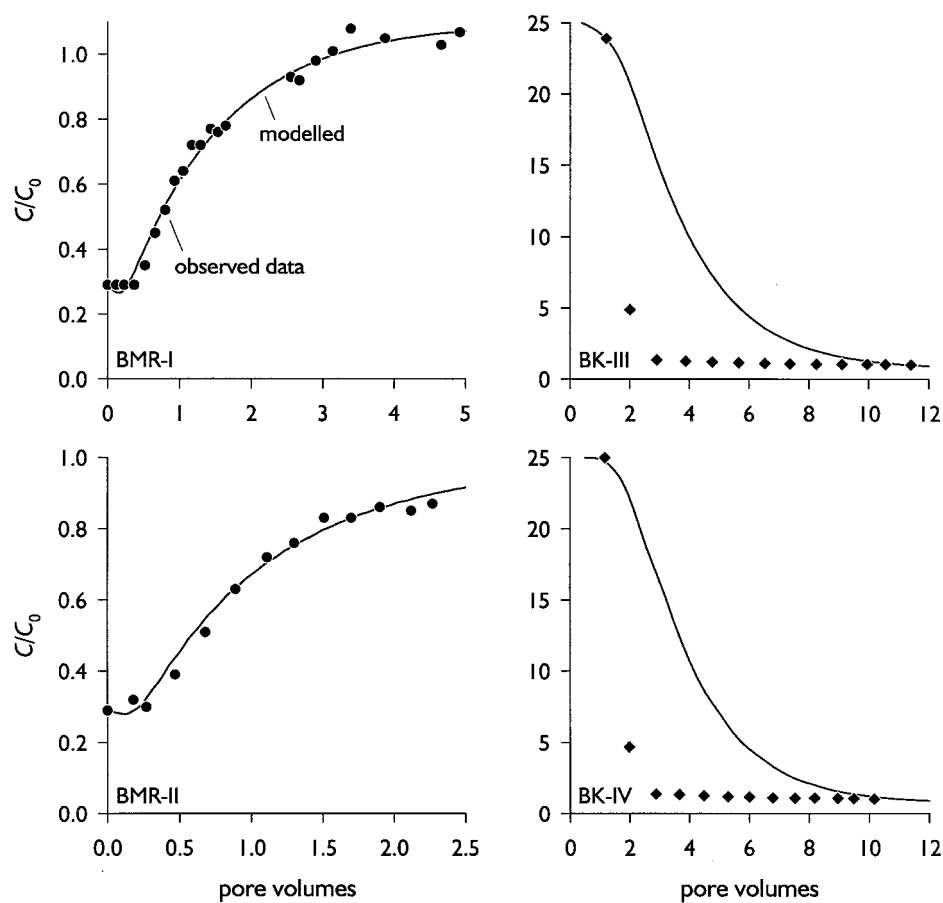
Figure 3. Observed chloride concentrations in the effluent and modelled breakthrough for chloride, left: for the BMR columns, and right: for the BK columns.

TABLE V

Hydrodynamic properties of the columns derived from cloride break-through curves

	D $(cm^2\,d^{-1})$	Immobile water (%)	α (d^{-1})	P_c	λ (cm^{-1})
BMR-I	0.288	~30	0.015	2.3	3.90
BMR-II	0.432	~20	0.010	2.2	3.90
BK-III	0.322	none	–	11.2	0.75
BK-IV	0.265	none	–	12.1	0.71

In addition to the difference in initial Cl$^-$-content of the columns the water regimes in the columns differ. The different regimes are reflected in the column Peclet number ($P_c = vL/D$ – Table V). Peclet numbers smaller than one are indicative for diffusion-dispersion dominated transport, whereas values above ten are found for convection dominated transport (Dunnivant *et al*., 1993; Totsche *et al*., 1997). In the BMR columns a large portion of the water is immobile with a low pore water velocity, whereas the flow regime in the BK columns is convection dominated supporting the assumption of zero immobile water content. The higher pore water velocities are due to the higher proportion of sand that was added to the sludge to increase the hydraulic conductivity of the columns.

4.5. Desorption of PAH

For BMR-I and BMR-II the elution of the individual PAH from the sludge columns is shown in Figure 4. An exponential decrease for the Phe, Ant and Flu concentrations with time was observed in both columns. No significant decrease was found for the hydrophobic compounds BbF, Bkf and BaP during the first four months of the experiment. Thereafter, concentrations for BbF, BkF and BaP dropped below the detection limit. As a result of the relatively high detection limits for BgP and InP (Table II) these compounds could not be detected in any of the eluates. The elution from the BK-III and BK-IV columns of all detected compounds, including the heavier ones, remained more or less constant during the experimental period (Figure 5). The concentrations are lower than those of the BMR columns most likely due to the lower initial concentrations in this sludge (Table IV). BgP and InP were not detected in the eluate of either columns.

Degradation of PAH under sulfate-reducing, anaerobic conditions in contaminated soil and sediments have been demonstrated for naphtalene (Thierrin *et al*., 1993; Coates *et al*., 1996b; Langenhoff *et al*., 1996; Meckenstock *et al*., 2000), Phe (Coates *et al*., 1996a; Zhang and Young, 1997), and Ant and Flu (Coates *et al*., 1997). Anaerobic breakdown of higher compounds like BaP have not yet been observed (Coates *et al*., 1997; Van Agteren *et al*., 1998). In most of these studies the compounds were rapidly degraded upto 80% within a period of 100–150 days, often after an initial lag period of several tens of days. Generally, microbial activity was stimulated by adding a nutrient mix including trace elements and vitamin solutions and using elevated temperatures upto 30 °C. Coates *et al*. (1997) showed by inoculation of a non-active sediment with an active naphthalene degrading sediment, that prolonged exposure to high PAH concentrations is an important factor in the development of a microbial community capable of degrading PAH. However, the observed decrease of the different PAH compounds in the eluate of the BMR-columns and the more or less constant concentration in the eluate of the BK-columns suggest that there was no degradation of PAH during the column experiments. The presence of Phe in the eluate even after an experimental period of nine months is not consistent with the rapid breakdown observed in degradation
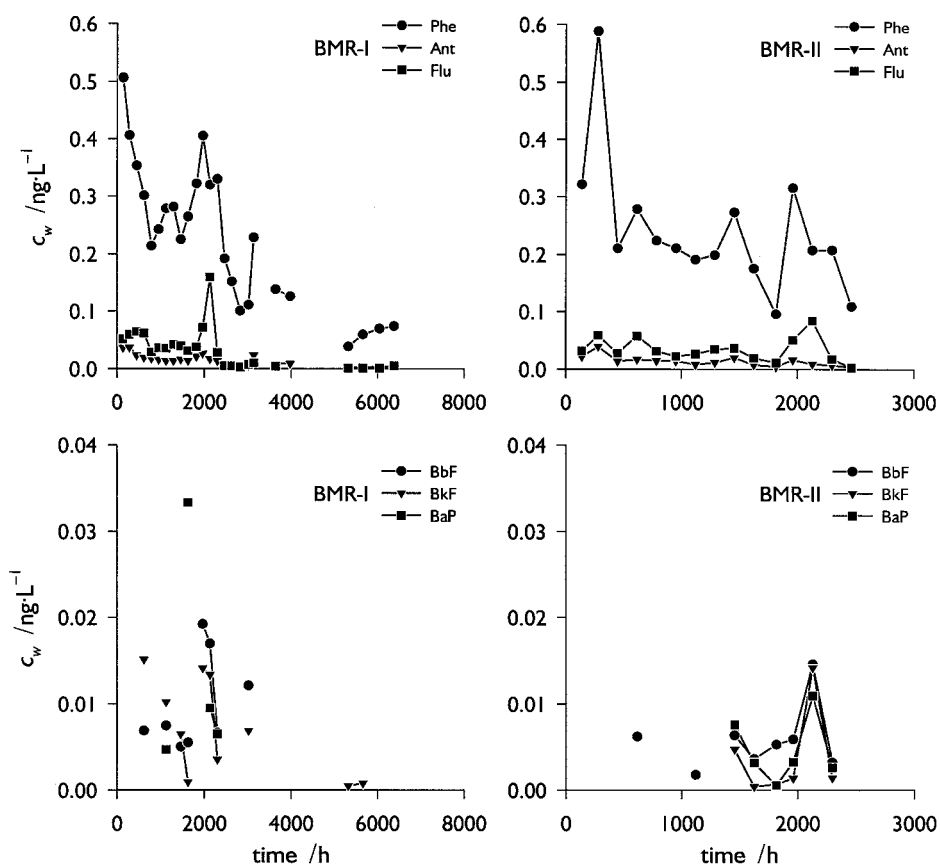
Figure 4. Observed PAH concentrations in the eluate, C_w, over time for; left: BMR-I, and right: BMR-II. No lines are shown during periods in which the compound was not detected in the eluate, or for which no data are available.

studies where Phe is the compound most susceptible for anaerobic degradation. This suggest that microbial activity in our column experiments was minimal due to the low temperature and low nutrient levels at which the experiments were conducted. The microorganisms capable of degrading PAH may be present in both harbour sludges, however, at a lower number and far less active than in the degradation studies reported elsewhere. However, as the eluates were not analysed on the metabolites of anaerobic breakdown of e.g., Phe (Zhang and Young, 1997) the extent of degradation on the obtained results can not be accurately assessed.

The different elution patterns in the columns of the two sludges can be explained by a simple conceptual model (Figure 6). At the start of the column experiment the PAH concentration in the water and solid phase are in equilibrium. During percolation a part of the water is mobile, whereas another part remains stagnant. The concentration in the mobile water can only be replenished by diffusion of the
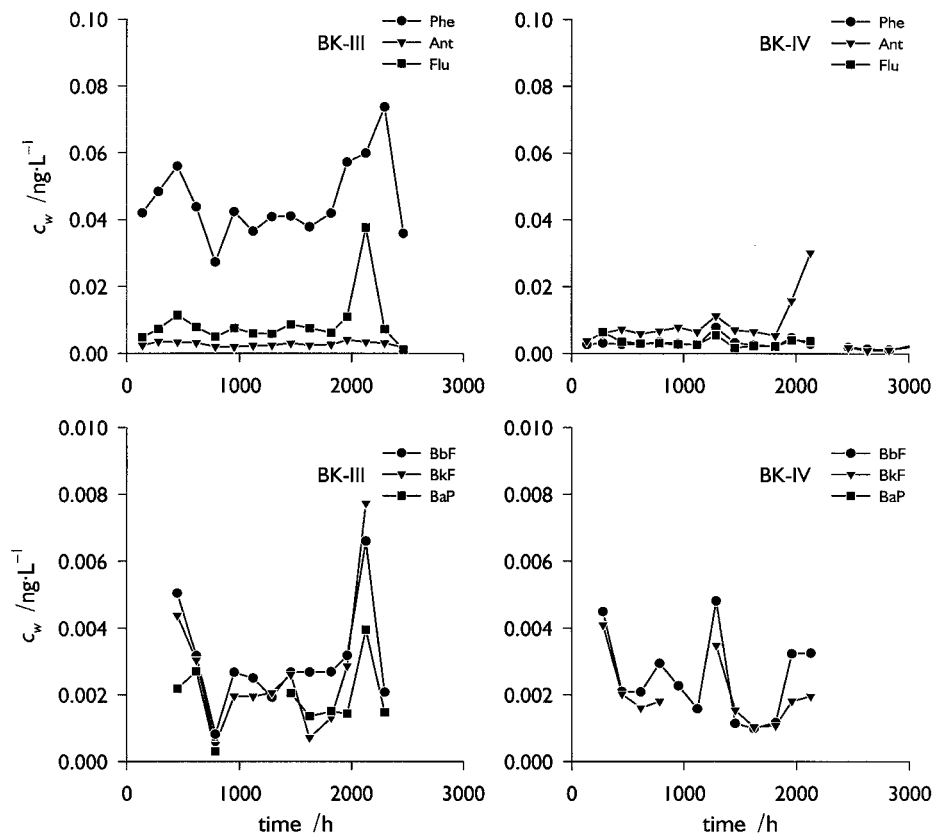
Figure 5. Observed PAH concentrations in the eluate, C_w, over time for; left: BK-III, and right: BK-IV. No lines are shown during periods in which the compound was not detected in the eluate, or for which no data are available.

PAH out of the immobile water region, thus, assuming the desorption of PAH to be diffusion controlled. In reality desorption most likely consists of two sequential diffusion steps; firstly, diffusion in the solid phase which is most likely the microporous organic matter present in the sediment, and secondly diffusion from the immobile to the mobile water region. Diffusion in the solid phase is generally thought to be a slow process as it is retarded by e.g., resorption on the organic material, interaction with the micropore walls and steric hindrance (Cornelissen, 1999). Diffusion between the different water regions is relatively fast. As the pore water velocity in the column increases, the immobile water film adjacent to the solid phase decreases, reducing the diffusional distance. Therefore, the mobile water is in near-equilibrium with the immobile water because of the small distance to be covered by diffusion, and rapid replenishment of the leached solute. When the immobile water region is thicker as result of a lower pore water velocity the diffusional distance is larger, resulting in non-equilibrium desorption (Figure 6).

The desorption data for the BK columns (Figure 5) basically show an equilibrium release of the PAH as only a negligible fraction of immobile water was present in these columns. The desorption data for the BMR columns show non-equilibrium desorption for Phe, and to a lesser extent for Ant and Flu, owing to the lower pore water velocity and the large fraction of immobile water. For the BMR columns this fraction was estimated to be between 20 and 30% based on the BTC of chloride (Table V). This large fraction is not only caused by the lower pore water velocity but also by the smaller amount of sand added to the sludge than in the BK columns.

Closely related to this conceptual model is the description of non-equilibrium desorption assuming spherical particles (Wu and Gschwend, 1986; Ball and Roberts, 1991; Grathwohl and Reinhard, 1993; Grathwohl et al., 1994). Diffusion controlled desorption from a solid sphere can be described by Fick's second law (e.g., Crank, 1975):

$$\frac{\partial C}{\partial t} = D^{\text{app}} \left(\frac{\partial^2 C}{\partial r^2} + \frac{2 \partial D}{r \partial t} \right) , \tag{5}$$

where D^{app} is the apparent diffusion coefficient in $m^2 \, s^{-1}$, C is the solute concentration in the solution in $g \, m^{-3}$, r the radial distance of the sphere in m, and t the time in s. The analytical solution of the desorption flux q in $\mu g \, g^{-1} \, s^{-1}$ from a spherical soil particle into bulk water with sorption equilibrium at $t = 0$ and with boundary condition $C = 0$ for $t > 0$ (Grathwohl and Reinhard, 1993) is:

$$q = 6 M_0 \frac{D^{\text{app}}}{r^2} \sum_{i=1}^{\infty} e^{\left(-i^2 \pi^2 D^{\text{app}} / r^2\right)} , \tag{6}$$

where M_0 is the initial contaminant concentration in $\mu g \, g^{-1}$ which is assumed constant throughout the sphere at $t = 0$. This analytical solution enables description of the desorption rate by adjusting D^{app}/r^2. Thus, the desorption rate decreases with the particle radius and therefore with the diffusional distance. The desorption flux of the smaller PAH, Phe Ant and Flu, in the BMR columns was described using Equation (6) by fitting the measured fluxes, after proper adjustment of units (Figure 7). Using the modus of the grain size derived from the grain size distribution (Table I) D^{app} was obtained by fitting (Table VI). The derived D^{app}-values are low compared to literature values (Grathwohl et al., 1994). This can be attributed to a diffusional distance due to an immobile water layer adjacent to the sediment particles and aggregates. However, also interaction with the pore walls and steric hindrance determine D^{app}, factors which can vary largely between different soils and sediments (Cornelissen, 1999). Phe could be satisfactorily fitted with Equation (6); the model is less succesful in describing the data of Ant and Flu especially those data points obtained at the end of the column experiments. This is most likely the result of the low concentrations of the compounds in the aqueous solution at the end of the experiment resulting in a relatively large analytical error. However,
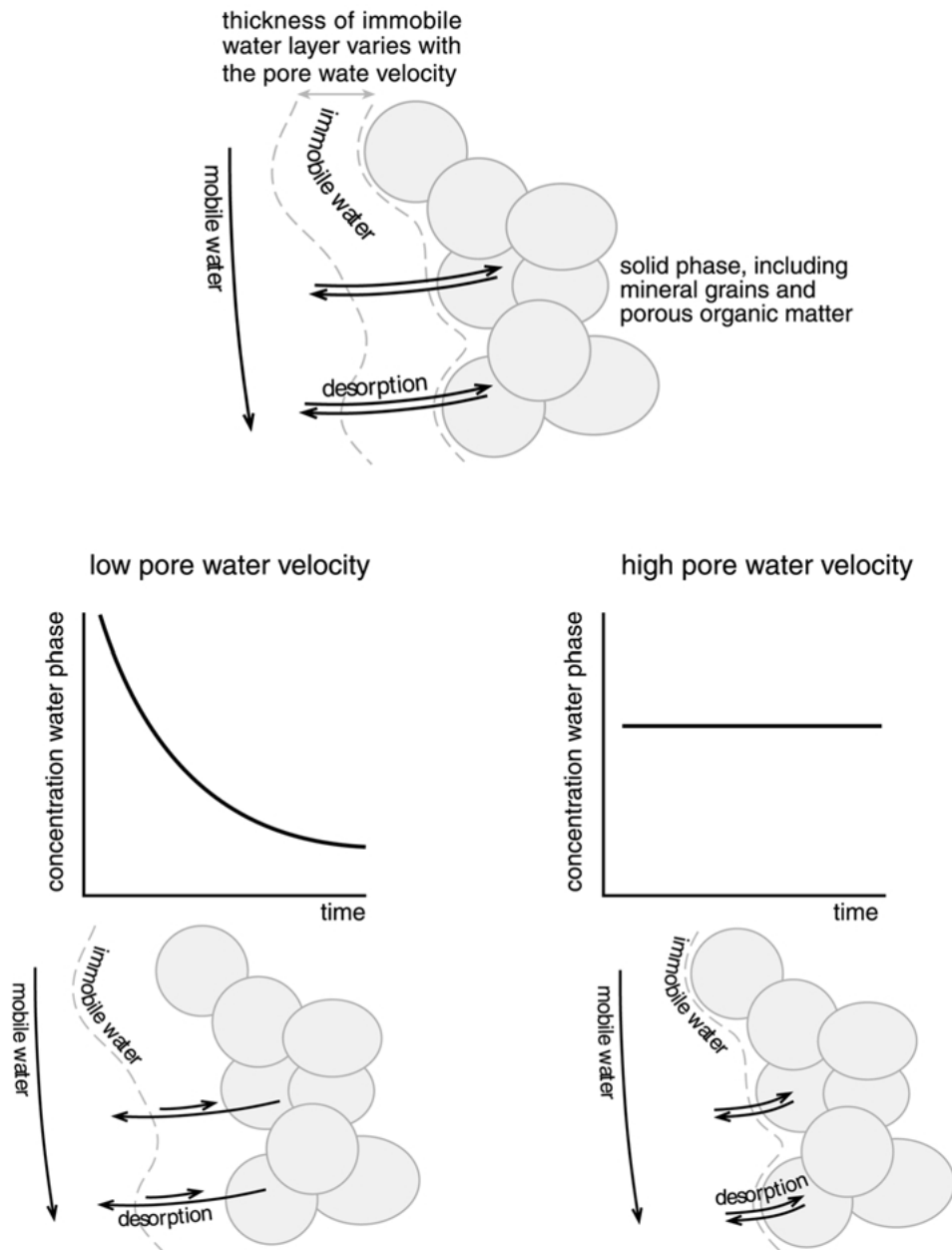
Figure 6. Conceptual model of the desorption of PAH during the column experiments. As desorption is governed by diffusion the path length increases as the pore water velocity in the column decreases. For low pore water velocities this results in a thick immobile water layer resulting in non-equilibrium sorption, whereas at higher pore water velocities the thinner immobile water layer allows for the presence of equilibrium desorption.

TABLE VI

Values for the apparent diffusion coefficient, D^{app}, for Phe, Flu and Ant in the BMR columns obtained by fitting Equation (6)

Compound	D^{app} (cm^2 d^{-1})	
	BMR-I[a]	BMR-II
Phe	0.3×10^{-12}	0.3×10^{-12}
Ant	25.0×10^{-15}	27.0×10^{-15}
Flu	27.0×10^{-15}	25.0×10^{-15}

[a] For the nine month period.

the use of a single value for the grain size where in fact there is a range of values also contributes to the deviation between the modeled and observed desorption as the value for the grain size influences the diffusion length, and thus the D^{app}-value found with the model.

For the individual PAH, apparent partition coefficients (K_{OC}^{app}) values were calculated based on the measured PAH concentrations in the column effluent (Table VII). K_{OC}^{app} is defined analogously to K_{OC}^{app} in Equation (2), however, as in the column experiments sorption equilibrium may be absent it is appropriate to refer to these values as apparent. For the calculation of the K_{OC}^{app}-values also the particulate organic carbon content of the sediments and the DOC concentration in the eluate are taken into account (Figure 8). The association of PAH with DOC increases the apparent solubility of the compound and enhances its transport through a porous medium (Enfield *et al.*, 1989; Abdul *et al.*, 1990; Dunnivant *et al.*, 1992; Maxin and Kögel-Knabner, 1995; Totsche *et al.*, 1997). The DOC concentrations in the eluate of the four sludge columns diminishes exponentially. After approximately 2000 hr or 84 days the concentration in all columns dropped below 5 ppm (Figure 8). Generally, the log K_{OC}^{app}-values for the columns are higher than the equilibrium values obtained from the batch experiments. However, the range of values determined in the column experiment is larger which makes comparison with the batch experiments difficult. The larger range of apparent partition coefficients can be attributed to the differences in DOC concentration in the eluate during the experiment. K_{OC}^{app}-values for Phe, Flu and Ant between the columns with different sediment are in close correspondence with each other. As in the BMR columns equilibrium is absent, K_{OC}^{app}-values for the BMR sludge were expected to be higher than those obtained from the BK columns. However, generally the column distribution coefficients are higher than values obtained by batch experiments (e.g., Grathwohl *et al.*, 1994). In our experiments this effect is less clearly visible due to the large range in the log K_{OC}^{app}-values, and the lower pore water velocities compared to those used in other column studies. For BMR-I and BMR-II no distribution coefficients
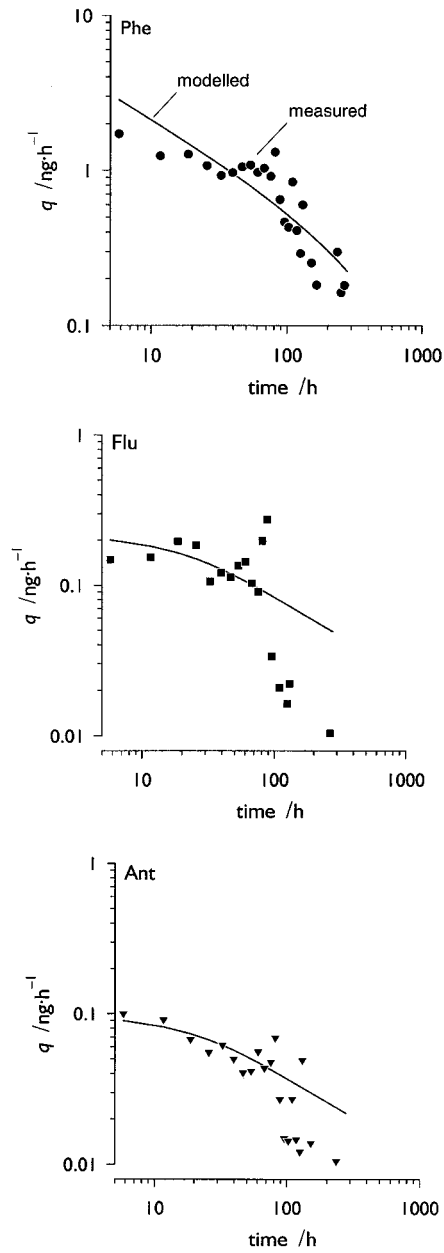
Figure 7. Measured desorption rate in the BMR-I column and the modelled curves using a diffusion limited model for decontamination of spherical particles; top: for Phe, middle: for Flu, and bottom: for Ant.

TABLE VII

Apparent distribution coefficients, $\log K_{OC}^{eq}$, for the individual PAH based on the measured concentrations in the column effluent at 4 °C. For comparison the $\log K_{OC}^{eq}$-values obtained from the batch experiments at 4 °C are also listed

| Com- | $\log K_{OC}^{eq}$ | $\log K_{OC}^{app}$ | | $\log K_{OC}^{eq}$ | $\log K_{OC}^{app}$ | |
pound	BMR	BMR-I[a]	BMR-II	BK	BK-III	BK-IV
Phe	5.74 ± 0.08	5.32 ± 0.11	5.46 ± 0.19	5.17 ± 0.03	5.45 ± 0.12	5.47 ± 0.23
Ant	6.35 ± 0.13	6.17 ± 0.17	6.73 ± 0.33	5.97 ± 0.04	6.15 ± 0.12	6.21 ± 0.21
Flu	6.11 ± 0.01	6.39 ± 0.28	6.68 ± 0.42	6.08 ± 0.04	6.39 ± 0.37	6.46 ± 0.42
BbF	6.51 ± 0.09	ND[b]	ND	6.86 ± 0.11	6.99 ± 0.49	7.39 ± 0.74
BkF	6.61 ± 0.09	ND	ND	6.90 ± 0.27	6.57 ± 0.37	7.09 ± 0.46
BaP	6.67 ± 0.06	ND	ND	6.46 ± 0.11	6.52 ± 0.22	6.81 ± 0.26

For all columns number of observations (n): $8 < n < 15$.
[a] Values for the nine month period.
[b] ND = Value not determined due to limited data available.

were calculated for BbF, BkF and BaP due to the scattered appearance of their concentrations in the eluate. This scatter can be explained by assuming that most of the PAH desorbing from the BMR sludge is predominantly DOC-bound. Especially, the more hydrophobic PAH – BbF, BkF and BaP – disappear from the eluate when the DOC concentration becomes negligible. The desorption in the BK-III and BK-IV columns remains relatively constant (Figure 5) and the changes in DOC concentrations are not reflected in the desorption of the PAH. The $\log K_{OC}^{app}$-values determined for the hydrophobic compounds, which are close to the $\log K_{OC}^{eq}$-values determined in the batch experiment, support the observation that desorption from the BK columns was equilibrium desorption despite the higher pore water velocity in those columns.

5. Conclusions

Desorption of PAH was studied on two different sludges from the Port of Rotterdam, The Netherlands. Equilibrium $\log K_{OC}$-values obtained from these field contaminated sediments using an ultra-centrifugation method at 4 °C yielded K_{OC} above reported literature values. Temperature correction of the K_{OC} could not account for the observed differences. The differences are attributed to the contact times of PAH in the sediment. The laboratory data reported in the literature were generally obtained after short contact times, thus underestimating the actual $\log K_{OC}$. Our values represent contact times in excess of three years and are therefore more representative for the field conditions. $\log K_{OC}$-values obtained from column elution experiments were slightly above those obtained from the batch experiments. In the BMR columns sorption equilibrium was absent for Phe and to a lesser extend
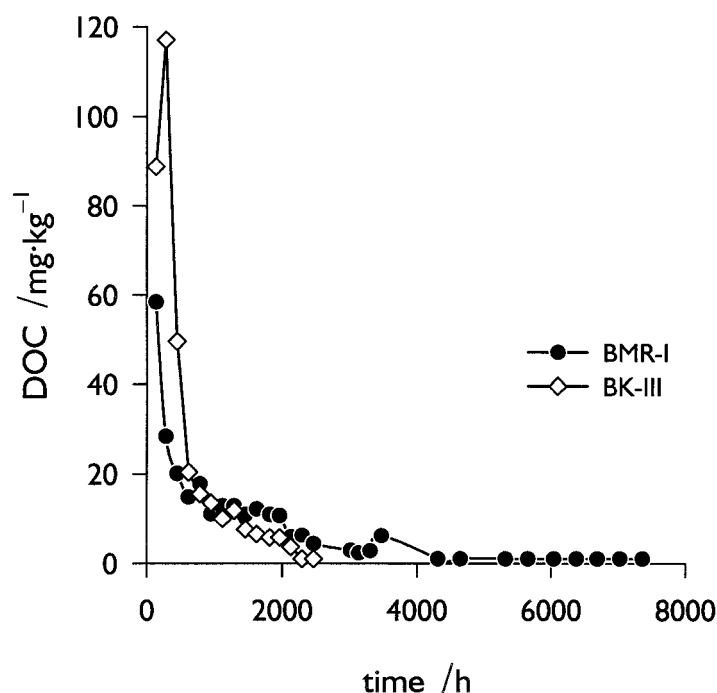
Figure 8. Measured DOC concentrations in the eluate of columns BMR-I and BK-III. The two other columns showed a similar decrease in DOC concentrations.

for Flu and Ant. This is attributed to the presence of a large portion of immobile water in the columns as a result of their smaller sand fraction and low pore water velocities. Also DOC facilitated transport may be contributing to the observed non-equlibrium. Elution in the BK columns occurred at near sorption equilibrium although pore water velocities were higher in these columns. However, due to large water velocity and a large sand fraction almost no immobile water was present in these columns. Assuming that desorption is diffusion controlled and that all sorption sites are covered by immobile water, observed desorption in both materials could be explained. The non-equilibrium desorption observed for phenanthrene, anthracene and fluoranthene in the BMR columns could be satisfactorily described by a diffusion limited model assuming spherical particles.

Acknowledgements

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