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Chapter 4

Influence of temperature and origin of dissolved organic matter on the partitioning behaviour of polycyclic aromatic hydrocarbons

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Joris J.H. Hafka, Harrie A.J. Govers and John R. Parsons

*Earth Surface Sciences, Institute for Biodiversity and Ecosystem Dynamics,
Universiteit van Amsterdam*

Abstract

The behaviour of polycyclic aromatic hydrocarbons (PAHs) is affected by dissolved organic matter (DOM) present in pore water of soils and sediments. Since partitioning to DOM reduces the bioavailable or freely dissolved PAH concentration in pore water, it is important to assess the effect of environmental variables on the magnitude of dissolved organic matter to water partition coefficients (K_{DOC}). The objective of this study was to apply passive samplers to measure freely dissolved PAHs allowing depletion from the aqueous phase. The method was applied to determine K_{DOC} at different temperatures for a selection of PAHs with natural DOM of very different origin. Freely dissolved concentrations of (spiked) phenanthrene, anthracene, fluoranthene, pyrene and benzo[*e*]pyrene were determined by exposing polydimethylsiloxane (PDMS) fibers to aqueous solutions containing DOM extracted from freshwater sediments from Finland and The Netherlands. The K_{DOC} values were subsequently calculated at different temperatures (3.2, 20 and 36°C) by including temperature dependent PDMS to water partition coefficients (K_{PDMS}) in a mass balance. Furthermore, the effect of temperature on partitioning of PAHs to PDMS fibers or DOM was assessed by comparing the enthalpy of sorption to the excess enthalpy of dissolution of liquid PAHs. Partitioning to DOM resulted in a decrease of freely dissolved concentrations with increasing DOM concentrations and a large range in log K_{DOC} values at 20°C for benzo[*e*]pyrene was observed (log K_{DOC} = 4.93 - 6.60 L/kg organic carbon). An increase of 10°C in temperature resulted in a decrease of K_{PDMS} by 0.09 to 0.13 log units for phenanthrene to pyrene and a decrease of K_{DOC} by 0.13 log units for pyrene. The calculated enthalpies of sorption were less exothermic than the (negative) excess enthalpies of dissolution as expected for non-specific interactions between PAHs and PDMS or DOM. The bioavailability of PAHs in sedimentary pore waters can be accurately determined by application of PDMS fibers (without requiring negligible depletion) in the presence of natural DOM with different sorption affinity for PAHs. The observed natural variability in log K_{DOC} values for different sediments shows that large differences can occur in freely dissolved PAH concentrations in pore water and properties of DOM should be taken into account in predicting the bioavailability of PAHs. Furthermore, the effect of temperature on the partitioning behaviour of PAHs shows that interactions between PAHs and environmental sorbents are comparable to interactions between PAHs in their pure condensed liquid phase and calculated excess enthalpies can be safely used to directly correct partition coefficients for temperature. The application of PDMS fibers in measuring freely dissolved PAH concentrations can be used to study structural and thermodynamic aspects of PAH sorption to natural DOM as well as other environmental processes such as enhanced diffusion phenomena in pore water that are dependent on the amount (or concentration) of DOM, sorption affinity of DOM and hydrophobicity of PAHs. These environmental factors will therefore give further insight into the site-specific exposure to freely dissolved PAH concentrations in soil and sedimentary pore water.

Introduction

The presence of dissolved organic matter (DOM) in pore water of soils and sediments significantly affects the partitioning behaviour of PAHs [1-3]. This results in decreased bioavailability and bioconcentration of dissolved PAHs due to the presence of DOM in freshwater ecosystems [4], whereas enhanced bioconcentration has also been observed at low DOM concentrations [5]. Reported DOM to water partition coefficients (K_{DOC} ; expressed in L/kg dissolved organic carbon) generally show a variability up to several orders of magnitude either due to the different origins of DOM (terrestrial or aquatic sources) [6] or caused by the uncertainties in the methods used [7, 3] and the way in which DOM is separated from sediments [8]. Furthermore, the variation in K_{DOC} values is dependent on pH and ionic strength [9].

The technique of Solid Phase MicroExtraction (SPME), developed by Arthur and Pawliszyn [10], provides a reliable way to determine freely dissolved concentrations of PAHs in the presence of DOM, provided that DOM is not altered by the way of separation [8] or influenced by time-dependent effects [11]. SPME fibers coated with polydimethylsiloxane (PDMS) have been applied successfully in the past as passive samplers to determine freely dissolved PAH concentrations in the presence of humic acids (HA) and fulvic acids (FA) isolated from water and sediments or from commercial sources [12-14]. The method is called negligible-depletion SPME if the amount of depletion by the SPME fibers is kept below 5 or 10% to prevent disturbance of equilibria between solutes and DOM [15, 13]. In case of significant depletion of the solutes from the aqueous phase, the separate determination of the PDMS to water partition coefficient (K_{PDMS}) for each solute is required [16].

One of the main factors that affect the K_{DOC} value is the source from which DOM, HA or FA are extracted. Depending on the origin of DOM, a large variability in K_{DOC} of PAHs using different methods has been observed [17-19, 6]. For example, $\log K_{\text{DOC}}$ values for the binding of pyrene with DOM originating from 13 European rivers differed by more than 1 order of magnitude ($\log K_{\text{DOC}} = 3.48\text{-}4.64$ L/kg) [18]. A large variability in K_{DOC} has recently been observed by Niederer *et al.* [6] for the sorption of pyrene ($\log K_{\text{DOC}}$ ranged from 3.07 to 5.02 L/kg at 25°C) to 10 different aquatic and terrestrial HA and FA with an inverse gas chromatography method using coatings of HA and FA on silanized glass beads (stationary phase).

Another factor that affects the partitioning behaviour of PAHs towards PDMS fibers or DOM is the effect of temperature on the aqueous activity coefficients or solubilities of PAHs. The free energy driving the (linear) partitioning process for large apolar compounds like PAHs is largely determined by the excess free energy of dissolution ($G_{\text{w}}^{\text{E}} = H_{\text{w}}^{\text{E}} - TS_{\text{w}}^{\text{E}}$) with a larger contribution of enthalpy (H_{w}^{E}) than of entropy (TS_{w}^{E}), in contrast to the dominance of entropy governing the hydrophobicity of small organic compounds like benzene [20]. In general it is concluded that the effect of temperature on the enthalpy of sorption (ΔH_{sorp}) can be directly compared to the (negative) excess free enthalpy of dissolution (H_{w}^{E}), which is a measure for the deviation from ideal behaviour in the aqueous phase. This is based on the assumption that for

PAHs (as opposed to more polar compounds) the contribution of $H_{\text{DOM}}^{\text{E}}$ or $H_{\text{PDMS}}^{\text{E}}$ to the enthalpy of sorption ($\Delta H_{\text{sorp}} = H_{\text{DOM,PDMS}}^{\text{E}} - H_{\text{w}}^{\text{E}}$) is much smaller than that of H_{w}^{E} . The interactions between PAHs and PDMS fibers or DOM are therefore more nearly ideal than the interactions between PAHs and water [21].

The objective of this study is the application of disposable PDMS fibers to determine K_{DOC} for PAHs in the presence of natural DOM extracted from freshwater sediments of very different origin. We preferred to extract DOM from sediments since water soluble DOM is more representative for sedimentary pore water than commercial HA [22] or base-extraction of HA or FA [23]. As a significant depletion of PAHs by the PDMS fibers occurred, values of K_{PDMS} for fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr) and benzo[*e*]pyrene (BeP) were taken into account in the calculation of K_{DOC} . The procedure applied in the present study is therefore different from most other SPME studies because the negligible depletion condition is not fulfilled [16]. The advantage of the applied method compared to other existing SPME methods is that depletion of freely dissolved PAHs from solutions containing DOM is allowed by including the K_{PDMS} values in a mass balance. The effect of temperature on the partitioning of PAHs between PDMS fibers or DOM and water was measured in the range of 3.2 to 36°C and ΔH_{sorp} values were calculated in order to quantify the influence of H_{w}^{E} on ΔH_{sorp} .

Materials and methods

Chemicals

The inorganic salts used for the preparation of artificial freshwater were all of analytical grade and were obtained from Merck (Darmstadt, Germany). Sodium azide (NaN_3 , 99%) was obtained from Acros Organics (Geel, Belgium). The PAHs Flu (98%), Ant (>98%), Fla (99%), Pyr (98%) and BeP (99%) were obtained from Sigma–Aldrich (Steinheim, Germany) and Phe (>98%) and benzo[*a*]anthracene (BaA, 99%) were obtained from Acros Organics (Geel, Belgium). Acetonitrile and pentane were of glass distilled grade and purchased from Rathburn (Walkerburn, UK).

Sampling locations

Sediments were sampled from a River Rhine sedimentation area, Lake Ketelmeer (KET) in The Netherlands and five freshwater lakes in eastern Finland, Varparanta (VAR), Kuorinka (KUO), Høytäinen (HOY), Kontiolampi (KON) and Mekrijärvi (MEK). The exact locations of the lakes as well as the total organic carbon (TOC) content of the studied sediments are shown in Table 1. Further characteristics of KET and four Finnish lakes (except KON) as well as the procedure of TOC determination have been published elsewhere [24]. Generally, VAR and KUO sediments were predominantly composed of sand, HOY sediment contained a large amount of clay and KON and MEK sediments contained relatively high amounts of organic carbon (Table 1). The sediment from KET was intermediate in textural composition. Samples from the upper part (0 – 30 cm) of the sediments were taken, except for KET sediment (10 – 50 cm). The Finnish

sediments had relatively low levels of contamination by PAHs compared to the sediment from The Netherlands (Table 1). Desorption of natively bound PAHs from KET sediment to extracted DOM was found to be negligible (<5%) compared to the spiked amount of PAHs (see below). The sediments were stored in polyethylene containers at 4°C in the dark prior to use.

Table 1. Characteristics of the sampled sediments

Lake	Notation	Coordinates	TOC ^a (% dw)	PAH content ^b (mg/kg dw)	SUVA (L/g)
Ketelmeer (NL)	KET	52°41' N, 5°45' E	5.51±0.01	25	15.96
Varparanta ^c (FIN)	VAR	62°51'59" N, 29°46'15" E	0.120±0.003	0.007	19.45
Kuorinka (FIN)	KUO	62°37'48" N, 29°23'49" E	1.39±0.07	0.2	6.48
Höytiäinen (FIN)	HOY	62°41'22" N, 29°40'34" E	3.30±0.02	0.9	17.09
Kontiolampi (FIN)	KON	62°43'46" N, 29°51'18" E	55.3±0.42	n.d.	10.49
Mekrijärvi (FIN)	MEK	62°46'00" N, 30°57'42" E	21.03±0.12	2	14.89

^a Standard deviations are calculated for OC contents ($n = 3$; data taken from [24]).

^b Sum of the contents of phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, and perylene (data taken from [24]).

^c Varparanta was taken from a shallow shore area in the eastern part of Lake Höytiäinen.

n.d. = not determined

DOM separation from sediment

Artificial freshwater with a relatively low salt content was used to extract organic matter from (wet) sediments. This medium contained the following salts: 58.8 mg/L CaCl₂·2H₂O, 24.7 mg/L MgSO₄·7H₂O, 13.0 mg/L NaHCO₃ and 1.2 mg/L KCl dissolved in Nanopure water (18.3 MΩ; Barnstead International, Dubuque, Iowa, USA). The medium was used in order to simulate freshwater and did not function as an ionic strength buffer. Microbial growth was prevented by adding NaN₃ at a concentration of 65.0 mg/L. A sediment to water ratio of 4:1 (*w/v*) was shaken for 1 h at room temperature with an orbital shaker (200 rpm) to release DOM from sediment (0.08-1.58:1 *w/v* dw). Due to the high OC content of KON sediment, a sediment to water ratio of 1:2 (*w/v*) was used for this sediment (0.02:1 *w/v* dw). The sediment suspension was subsequently centrifuged for 1 h at 7,400 g. After separation of water and sediment, the supernatant was centrifuged for 3 h at 31,000 g to obtain a solution that includes the organic matter that is 'potentially' present in sediment pore water. The centrifugation procedure is preferred here over the conventional procedure of filtration over 0.45 μm as preliminary experiments have shown that filtration artefacts occurred because of membrane fouling. Furthermore, extracts centrifuged for 0.5, 1, 2, 3 and 4 h at 31,000 g resulted in constant DOM partition coefficients for Phe, Fla and Pyr after normalization to TOC indicating that the organic matter had similar partitioning characteristics irrespective of size distribution (data not shown). The pH was adjusted to 7.0 ± 0.1 with small amounts of dilute HCl or NaOH to enable a pH-independent comparison of K_{DOC} values. Concentrations of DOM were measured by high temperature catalytic combustion with a TOC-5000 Shimadzu analyzer ('s-Hertogenbosch, The Netherlands). The decrease in UV absorbance at 270 nm was measured in quartz cuvettes and was subsequently expressed in specific UV absorbance (SUVA = $A_{270} \times 1000 / [\text{DOC}]$; Table 1).

Measurement of free and total PAH concentrations

Freely dissolved PAH concentrations were measured by using disposable PDMS fibers obtained from Poly Micro Industries (Phoenix, AZ, USA). The fibers with a core diameter of 110 μm and a coating of 28.5 μm PDMS were cut into 2 cm pieces ($V_{\text{PDMS}} = 0.248 \mu\text{l}$ PDMS) and thermally cleaned in a glass conditioning unit under a He flow ($\pm 10 \text{ ml/min}$) for 2 h at 250°C. The fibers were exposed to aqueous solutions with a volume of 50 ml in Teflon[®] lined Erlenmeyer flasks spiked with 20 μl (0.04% v/v) of a mixture of Flu, Phe, Ant, Fla, Pyr and BeP dissolved in acetonitrile. Total aqueous concentrations were 13.32 (Flu), 25.69 (Phe), 3.75 (Ant), 9.54 (Fla), 5.16 (Pyr) and 1.87 $\mu\text{g/L}$ (BeP) and were stable in time (verified with liquid-liquid extraction mentioned below). Blank solutions (containing fibers) were spiked with four individual PAH mixtures in equimolar amounts and served as calibration standards by calculating the freely dissolved concentration from the total concentration. Any nonlinear effects due to the presence of PAHs in mixtures were not observed in the partitioning of PAHs to PDMS fibers. The samples were shaken on a rotary shaker (80 rpm) in thermostatted rooms or chambers at 3.2 ± 0.7 , 20.1 ± 0.2 and 36.0 ± 0.1 °C in the dark. Equilibrium times to determine K_{DOC} were 21 days at 3.2°C and 10 days at 20.1°C and 36.0°C. After equilibrium between fiber and water was reached, the fibers were sampled with tweezers and gently blotted dry with a tissue. The fibers were subsequently desorbed in a vial insert with 150 μl of acetonitrile containing 500 $\mu\text{g/L}$ BaA as injection standard. Sample vials were weighed before and after addition of fiber and desorption solvent to correct for small differences in added volumes. Effects of fouling on the PDMS fiber have not been observed in this study, but could be important when commercial PDMS fibers are used due to repeated exposure of the fiber to matrix components (e.g. HA, proteins).

Total PAH concentrations were determined with liquid-liquid extraction and HPLC by shaking 2 ml of sample three times with 3 ml of pentane. The pentane layer was separated from the aqueous layer and evaporated on a water bath held at 60 °C. Before evaporation, a recovery standard of 200 μl of a BaA solution ($c = 500 \mu\text{g/L}$) and 100 μl of 1-octanol were added to the extract. 1-Octanol is added to prevent complete evaporation of the extract and to enhance recovery of three ring PAHs.

The PAHs were analysed with HPLC as described elsewhere [25]. The detection limits in acetonitrile and water (calculated back from fiber desorbed PAHs) of the analysed PAHs ranged from 0.19 (BeP) to 2.29 $\mu\text{g/L}$ (Phe) and 10.19 (BeP) to 177.22 ng/L (Phe) in acetonitrile and water, respectively.

Calculation of partition coefficients

In order to take the amount of PAHs absorbed by the fibers into account, K_{PDMS} values were determined by following equilibration in time. At specific time intervals, fibers were sampled (in triplicate) and fiber concentrations were determined using external calibration standards. The calculation of K_{PDMS} values with a two-compartment model assuming first-order kinetics is described elsewhere [25].

Partitioning of constant PAH concentrations to DOM was studied by exposing PDMS fibers (in duplicate) to decreasing concentrations of DOM obtained using the procedure described above. In this method, it is assumed that K_{PDMS} values are known and that the system of fiber and water has reached equilibrium. The K_{DOC} values were determined indirectly by measuring the amount sorbed to the fiber in the presence of DOM. As the fiber-sorbed amount is directly proportional to the freely aqueous PAH concentration (calculated by division of c_{PDMS} with K_{PDMS}), the remainder is assumed to be sorbed to DOM. The K_{DOC} values were subsequently calculated by fitting the freely dissolved fractions ($c_{\text{free}}/c_{\text{total}}$) to the rearranged mass balance equation given below:

$$\frac{c_{\text{free}}}{c_{\text{total}}} = \frac{1}{1 + \frac{V_{\text{PDMS}}}{V_{\text{water}}} K_{\text{PDMS}} + [\text{DOC}] \cdot K_{\text{DOC}}} \quad (1)$$

where c_{free} and c_{total} are the free and total (spiked) PAH concentrations (in mg PAH/L), respectively, V_{PDMS} is the volume (in L) of the PDMS fiber coating and V_{water} is the sample volume (in L). The partition coefficients, K_{DOC} and K_{PDMS} , are expressed in L water/kg OC and L water/L PDMS, respectively, and [DOC] is expressed in kg OC/L. Eq. (1) was fitted with the non-linear regression option in Graphpad Prism, version 3.02 (San Diego, CA, USA). Additionally, partitioning of increasing PAH concentrations to DOM extracted from KON sediment was measured with a linear sorption isotherm for Phe ($c_{\text{water}} = 0.74 - 256.48 \mu\text{g/L}$), Fla ($c_{\text{water}} = 0.13 - 10.10 \mu\text{g/L}$), Pyr ($c_{\text{water}} = 0.11 - 6.97 \mu\text{g/L}$) and BeP ($c_{\text{water}} = 0.29 - 0.87 \mu\text{g/L}$).

Temperature dependence of partition coefficients

Values of K_{PDMS} determined at different temperatures (3.2, 20 and 36°C) were applied in Eq. (1) to calculate the temperature dependent K_{DOC} values for DOM extracted from MEK sediment. Under the assumption that the enthalpy of sorption (ΔH_{sorp}) for the partitioning of PAHs between PDMS fibers or DOM and water is constant over a small temperature range, the ΔH_{sorp} values can be calculated with a linear equation (van 't Hoff plot), that is independent of the units of K_{DOC} or K_{PDMS} :

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H_{\text{sorp}}}{R} \quad (2)$$

where T is the absolute temperature (in K) and R is the gas constant (8.31441 J/mol.K). Thus, the slope, A , of the linear relationship between $\ln K_{\text{PDMS}}$ or $\ln K_{\text{DOC}}$ and $1/T$ results in the enthalpy of sorption, $\Delta H_{\text{sorp}} = -R \times A$. The contribution of entropy to the free energy of sorption was calculated by: $-T\Delta S_{\text{sorp}} = \Delta G_{\text{sorp}} - \Delta H_{\text{sorp}} = -RT \ln K_{\text{DOC}}^x - \Delta H_{\text{sorp}}$, provided that the sorbent has a known or hypothesized molecular structure and the partition coefficients (K_{DOC}^x) are expressed on a mole fraction basis.

Enthalpy and entropy contributions to the free energy of dissolution for solid PAHs at 25°C were converted to the supercooled liquid state by correction with enthalpies and entropies of fusion from Chickos and Acree [26]. The enthalpies and entropies of fusion (ΔH_{fus} and ΔS_{fus}) were corrected from their melting point temperatures, T_{mp} , to 25°C (denoted by superscript '0') with a procedure described by Allen *et al.* [27]. Excess enthalpies, $H_{\text{w}}^{\text{E}} = \Delta H_{\text{sol}}^0 - \Delta H_{\text{fus}}^0$, and entropy contributions, $-TS_{\text{w}}^{\text{E}} = -T(\Delta S_{\text{sol}}^0 - \Delta S_{\text{fus}}^0)$, to the excess free energy of dissolution for supercooled liquid PAHs were subsequently derived by subtracting the temperature corrected enthalpies and entropies of fusion from the enthalpies, ΔH_{sol}^0 , and entropies, ΔS_{sol}^0 , of dissolution for solid PAHs. Literature values for ΔH_{sol}^0 , and ΔS_{sol}^0 were taken from a study of temperature dependent solubility data using a generator-column HPLC method [28].

Results and discussion

Determination of partition coefficients

The fiber equilibration method determined for pyrene at three different temperatures is shown in Fig. 1 and the calculated $\log K_{\text{PDMS}}$ values (Table 2) are in accordance with literature values determined with a fiber depletion method using the same coating thickness of PDMS [29]. For Flu, no value for $\log K_{\text{PDMS}}$ could be calculated at 20.1°C because equilibrium was rapidly achieved and insufficient data points were taken in the initial phase of absorption. Therefore, $\log K_{\text{PDMS}}$ for Flu at this temperature was calculated by dividing fiber and total concentrations determined for all sampling steps.

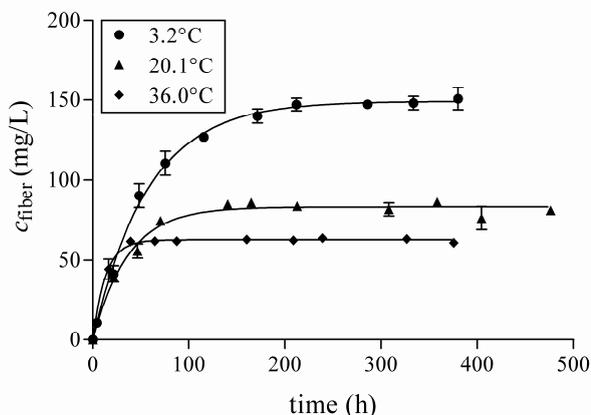


Figure 1. Pyrene concentrations of the polydimethylsiloxane fiber (triplicate samples; standard errors shown; $n = 30$) during equilibration at three different temperatures.

Table 2. PDMS to water partition coefficients ($\log K_{\text{PDMS}}$) for fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr) and benzo[*e*]pyrene (BeP) at three different temperatures

Compound	$\log K_{\text{PDMS}}^{\text{a}}$			$\log K_{\text{PDMS}} \text{ lit.}^{\text{b}}$
	3.2°C	20.1°C	36.0°C	20°C
Flu	3.79±0.03 (32)	3.65±0.03 ^c (30)	3.50±0.09 (30)	n.d.
Phe	4.07±0.03 (32)	3.89±0.10 (33)	3.75±0.09 (30)	3.86±0.03 (52)
Ant	4.19±0.03 (32)	4.00±0.08 (33)	3.89±0.09 (27)	n.d.
Fla	4.55±0.03 (32)	4.37±0.04 (33)	4.17±0.06 (30)	4.40±0.02 (53)
Pyr	4.70±0.03 (32)	4.45±0.05 (33)	4.25±0.05 (30)	4.41±0.04 (55)
BeP	5.69±0.25 ^d (32)	5.42±0.09 (33)	5.08±0.03 (29)	n.d.

^a $\log K_{\text{PDMS}}$ values ± standard errors (number of measurements in parentheses).

^b Data taken from Ter Laak *et al.* [29], $\log K_{\text{PDMS}}$ determined with fiber depletion method.

^c Value determined by dividing fiber and total concentrations.

^d Equilibrium between fiber and water was not reached for this compound.

n.d. = not determined.

The values of K_{PDMS} obtained with the equilibration method were used to determine K_{DOC} with Eq. (1) for Phe, Ant, Fla, Pyr and BeP in the presence of DOM extracted from the sampled sediments (Table 3). Little or no interaction with DOM was observed for the least hydrophobic compound Flu (data not shown), whereas BeP showed the strongest interaction with DOM. In Fig. 2, ratios of free to total concentrations ($c_{\text{free}}/c_{\text{total}}$) of pyrene are plotted at different temperatures showing a non-linear decrease with increasing DOM concentrations from MEK sediment. Freely dissolved fractions in the absence of DOM were invariably below 1 as the residual amount is sorbed to the PDMS fiber (98% for Flu to 44% for BeP at 20.1°C). For most sediment extracts, $\log K_{\text{DOC}}$ values for Flu to Pyr could not be calculated (Table 3) because the freely dissolved fraction did not decrease significantly below the values calculated from the 95% confidence interval of K_{PDMS} values. Significant decreases in freely dissolved concentrations of

Phe, Ant, Fla and Pyr were only observed with DOM from MEK and KON that are both relatively high in sorption affinity compared to DOM from VAR, KUO, HOY and KET. It is therefore suggested that the bioavailability of these PAHs is not affected by DOM present in these latter sediments.

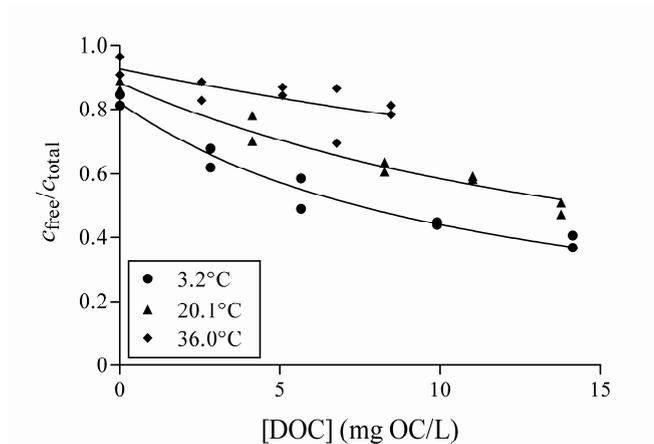


Figure 2. Ratio of free to total pyrene concentrations (duplicate samples; $n = 10$) after partitioning of pyrene to dissolved organic matter from Mekrijärvi sediment at three different temperatures.

Table 3. DOM to water partition coefficients ($\log K_{\text{DOC}}$) for phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr) and benzo[*e*]pyrene (BeP) at three different temperatures

Sediment	Temp. ^a (°C)	[DOC] ^b (mg/L)	$\log K_{\text{DOC}}^c$ (L/kg)				
			Phe	Ant	Fla	Pyr	BeP
KET	20 (8)	45.49	-	-	-	-	5.47±0.07
VAR	20 (12)	21.80	-	-	-	-	4.93±0.11
KUO	20 (10)	35.54	-	-	-	-	5.14±0.03
HOY	20 (11)	10.00	-	-	-	-	5.74±0.07
KON	20 (10)	51.01	4.74±0.01	4.92±0.01	5.41±0.02	5.53±0.01	6.60±0.01 ^d
MEK	3.2 (10)	14.13	4.29±0.11	4.50±0.10	4.91±0.05	5.03±0.04	-
MEK	20.1 (10)	13.77	4.17±0.08	4.36±0.05	4.75±0.03	4.76±0.04	6.23±0.05
MEK	36.0 (10)	8.46	-	-	-	4.59±0.08	5.67±0.03

^a Number of measurements in parentheses.

^b Maximum DOM concentration.

^c $\log K_{\text{DOC}}$ values ± standard errors. Blank entries denote instances where freely dissolved fractions did not decrease significantly below the 95% confidence interval of the PDMS to water partition coefficient

^d Determined with sorption isotherm.

The $\log K_{\text{DOC}}$ value of BeP for DOM from KON sediment could not be determined due to a fast decrease in the freely dissolved fraction with increasing DOM concentrations and was therefore determined with a (linear) sorption isotherm at constant DOM concentrations, see Table 3 ($\log K_{\text{DOC}} = 6.60$; $n = 8$; $r^2 = 0.9956$). The sorption isotherms for other PAHs were also linear over the range of measured PAH concentrations. The $\log K_{\text{DOC}}$ values determined with this method deviated by maximally +0.09 log units (all $n = 10$) from the values reported in Table 3 for Phe,

Fla and Pyr. The calculation of an average K_{DOC} value from single point determinations for the partitioning of Pyr to DOM from MEK sediment and propagation of errors in K_{PDMS} and [DOC] resulted into a log K_{DOC} value of 4.75 ± 0.06 L/kg ($n = 8$), equal to the log K_{DOC} value reported in Table 3.

For DOM extracted from KON sediment, the log K_{DOC} values of Phe, Pyr and Fla determined with PDMS fibers were compared to log K_{DOC} values determined with equilibrium dialysis using a sediment to water ratio of 1:1 (w/v) and an identical pretreatment procedure of DOM (Personal Communication J. Akkanen, Joensuu University, Finland). The log K_{DOC} values determined with equilibrium dialysis showed slightly higher values for Phe (log $K_{\text{DOC}} = 4.91 \pm 0.02$ L/kg) and Pyr (log $K_{\text{DOC}} = 5.68 \pm 0.05$ L/kg) and a similar value for Fla (log $K_{\text{DOC}} = 5.41 \pm 0.03$ L/kg). This direct comparison shows that the depletion of PAHs from the aqueous phase by PDMS fibers is correctly described with first order kinetics. Furthermore, the determination of equal K_{DOC} values both with a mass balance and a sorption isotherm for DOM extracted from KON sediment validates the use of the mass balance procedure that incorporates the sorption of PAHs by PDMS fibers.

Structure-activity relationships

The log K_{DOC} values determined for the sediments of MEK and KON (both $n = 5$) gave the following relationships with the logarithmic value of the n -octanol to water partition coefficient (K_{ow}):

$$\begin{aligned} \log K_{\text{DOC}} (\text{MEK}) &= 1.306 (\pm 0.128) \log K_{\text{ow}} - 1.858 (\pm 0.658) \\ r^2 &= 0.972; \text{SER} = 0.156 \end{aligned} \quad (3)$$

$$\begin{aligned} \log K_{\text{DOC}} (\text{KON}) &= 1.176 (\pm 0.090) \log K_{\text{ow}} - 0.608 (\pm 0.465) \\ r^2 &= 0.983; \text{SER} = 0.110 \end{aligned} \quad (4)$$

where SER is the standard error of regression. The log K_{ow} values were taken from Burkhard [7]. The slopes of these relationships are similar to the slope of the log K_{DOC} -log K_{ow} relation derived from literature values by Burkhard [7] for the partitioning of PAHs to naturally occurring DOM ($n = 33$):

$$\begin{aligned} \log K_{\text{DOC}} &= 1.18 (\pm 0.13) \log K_{\text{ow}} - 1.56 (\pm 0.72) \\ r^2 &= 0.58; \text{SER} = 0.73 \end{aligned} \quad (5)$$

The different intercepts in Eqs (3) and (4) indicate a higher sorption affinity of DOM extracted from KON sediment. For DOM extracted from the different sediments, the log K_{DOC} values of BeP span a large range with minimum and maximum values differing by 1.67 log units. The lowest K_{DOC} values are observed for the sandy sediments of KUO and VAR, whereas the more organic-rich sediments of MEK and KON show the highest K_{DOC} values. Intermediate K_{DOC}

values are shown for the sediments of HOY and KET. No significant correlations could be found, however, for $\log K_{\text{DOC}}$ values determined for BeP at 20°C with corresponding properties like UV absorbance at 270 nm or specific UV absorbance (SUVA) as a measure of the aromaticity of the DOM extracts (Table 1 and Fig. 3). It has however been shown in literature that aliphaticity also contributes to the sorption affinity of DOM [30]. Elaborate structural characterization of the DOM extracts used here was however outside of the scope of this study.

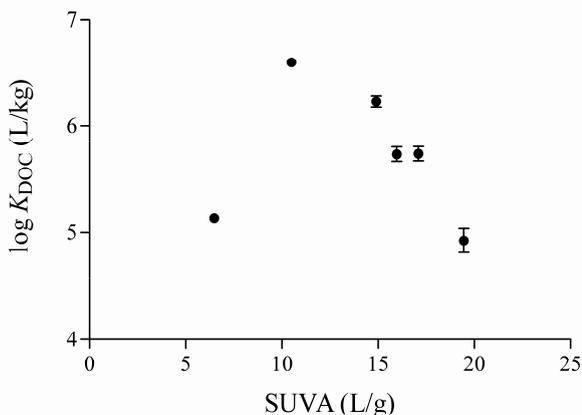


Figure 3. Specific UV absorbance (SUVA) versus dissolved organic matter to water partition coefficients ($\log K_{\text{DOC}} \pm$ standard errors) at 20°C for benzo[e]pyrene of all sediments.

Temperature dependence of partition coefficients

The effect of increasing temperature on the partitioning between fiber and water for Pyr results in decreasing fiber concentrations and shorter equilibrium times (Fig. 1). Consequently, $\log K_{\text{PDMS}}$ values decrease (Table 2) with increasing temperature. With every 10°C increase in temperature, $\log K_{\text{PDMS}}$ values of Flu to Pyr (excluding BeP) decreased by 0.09 to 0.13 log units.

The result of increasing temperature for Pyr in the presence of DOM from MEK sediment shows decreasing interactions with DOM (Table 3 and Fig. 2). At the highest temperature, the freely dissolved fractions of Phe, Ant and Fla did not show a significant decrease in the presence of DOM and $\log K_{\text{DOC}}$ could not be calculated accordingly. At the lowest temperature, the $\log K_{\text{PDMS}}$ value for BeP was subject to error due to insufficient equilibration and sorption of BeP to the glass wall (Table 2). The effect of temperature could therefore only be calculated for Pyr. The $\log K_{\text{DOC}}$ value for Pyr decreased by 0.13 log units with every 10°C increase in temperature.

The enthalpies of sorption (ΔH_{sorp}) to PDMS fibers or DOM from MEK were calculated with Eq. (2) ($r^2 = 0.9925 - 0.9999$). The calculated ΔH_{sorp} values (in kJ/mol) to PDMS are shown in Table 4 and range from -14.70 for Flu to -22.06 kJ/mol for Pyr. These ΔH_{sorp} values show increasing negative (exothermic) values with increasing hydrophobicity of the PAHs studied. Note that the ΔH_{sorp} value for the sorption of Pyr to DOM from MEK sediment is

similar to the ΔH_{sorp} value of Pyr sorption to PDMS. The enthalpies of sorption determined in this study are in a similar range as values determined for the effect of temperature on the partitioning of Phe to polyethylene [31], Fla to (filtered) DOM from KET sediment [1] and Phe, Ant, Fla and Pyr to iron and aluminium oxides [32] where only hydrophobic interactions are involved. The ΔH_{sorp} value of the partitioning of Pyr to polyethylene is however more negative than the value reported for Pyr in this study.

Values for H_w^E and $-TS_w^E$ at 25°C were calculated for the 5 PAHs in Table 4 by subtracting the temperature corrected enthalpies of fusion (ΔH_{fus}^0) from the enthalpies of dissolution (ΔH_{sol}^0). The excess entropy contribution ($-TS_w^E$) to the free energy of dissolution becomes smaller than the enthalpic contribution for larger aromatic compounds as mentioned in the Introduction. The values of H_w^E and $-TS_w^E$ in Table 4 are different from the values reported in Schwarzenbach *et al.* [20] where no correction for temperature was applied. These H_w^E values are higher than the ΔH_{sorp} values (opposite in sign) for the partitioning of PAHs to PDMS or DOM from MEK. The ΔH_{sorp} values are therefore less exothermic than the (negative) $-H_w^E$ values in case of the occurrence of non-specific interactions between PAHs and PDMS or DOM [21]. The excess enthalpy in the DOM or PDMS fiber phase, $H_{\text{DOM,PDMS}}^E$, partially cancels the H_w^E values in the experimental enthalpy of sorption ($\Delta H_{\text{sorp}} = H_{\text{DOM,PDMS}}^E - H_w^E$) amounting to +3.17 (Flu) to +10.72 (Fla) kJ/mol for the sorption of PAHs to PDMS and to +4.88 kJ/mol in the case of Pyr sorption to DOM from MEK sediment. As a result of the errors involved in the regression of $\ln K$ versus $1/T$ with Eq. (2) based on only three data points and in the estimation of excess enthalpies after temperature correction of fusion enthalpies, the interaction between PAHs and PDMS or DOM can be considered comparable to the interaction between PAH molecules in their pure condensed liquid phase ($-\Delta H_{\text{sorp}} \approx H_w^E$) [32]. The H_w^E values can therefore be safely used to correct partition coefficients for temperature as has been done in Cornelissen *et al.* [33].

Table 4. Thermodynamic parameters at 25°C for the process of sorption, ΔH_{sorp} , of fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla) and pyrene (Pyr) to polydimethylsiloxane (PDMS), polyethylene (PE) or dissolved organic matter (DOM) from Ketelmeer (KET) or Mekrijärvi sediment (MEK), the process of fusion, ΔH_{fus}^0 and $-T\Delta S_{\text{fus}}^0$ and excess molar properties of supercooled liquid PAHs, H_{w}^{E} and $-TS_{\text{w}}^{\text{E}}$.

Compound	ΔH_{sorp} (kJ/mol)	ΔH_{fus}^0	$-T\Delta S_{\text{fus}}^0$	H_{w}^{E}	$-TS_{\text{w}}^{\text{E}}$
Flu, PDMS	-14.70±0.84	17.23	-12.92	17.87	16.29
Phe, PDMS	-16.21±0.48	15.26	-12.24	21.44	15.52
Phe, PE	-18±1 ^a				
Phe, $\alpha\text{-Fe}_2\text{O}_3$	-18.2±1.0 ^b				
Ant, PDMS	-15.27±1.17	22.91	-12.56	24.29	13.05
Ant, $\alpha\text{-Al}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3$	-16±2.8/ -17.2±1.9 ^b				
Fla, PDMS	-18.91±1.65	15.37	-11.58	29.63	10.74
Fla, KET DOM	-18.28 ± 2.81 ^c				
Fla, $\alpha\text{-Al}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3$	-19.5±0.4/ -16.7±3.0 ^b				
Pyr, PDMS	-22.06±0.25	14.42	-9.60	27.18	13.29
Pyr, PE	-29±2 ^a				
Pyr, MEK	-22.30±1.46				
Pyr, $\alpha\text{-Al}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3$	-20.8±0.4/ -20±0.9 ^b				

^a Data taken from Adams *et al.* [31].

^b Data taken from Mader *et al.* [32].

^c Data taken from Lüers and Ten Hulscher [1].

The K_{DOC} values for the sorption of Pyr to DOM from MEK sediment were also converted to mole fraction based partition coefficients ($K_{\text{DOC}}^{\text{x}} = MW_{\text{C}} \cdot N_{\text{C}} / v_{\text{w}} \times K_{\text{DOC}}$) by taking into account the number of carbon atoms (N_{C} with $MW_{\text{C}} = 12.011$ g/mol) of a model structure for DOM from MEK sediment and the molar volume of water ($v_{\text{w}} = 18.0713$ cm³/mol from [34]). It was hypothesized here that DOM from MEK sediment is either represented by the model structure for Suwannee FA from Shin and Moon [35] (DOM1, C₃₇H₄₃NO₂₀; $MW = 821.74$ g/mol) or the model structure for HA from Schulten and Leinweber [36] (DOM2, C₃₄₉H₄₀₁N₂₆O₁₇₃S; $MW = 7760.16$ g/mol). The energetic gain from entropy ($-T\Delta S_{\text{sorp}}$), calculated by subtraction of ΔH_{sorp} from ΔG_{sorp} , is -12.26 ± 1.48 (DOM1) to -17.74 ± 1.48 kJ/mol (DOM2) and contributes less than the enthalpy loss to the spontaneous free energy of sorption. The positive entropy values ($\sim 41.1 - 59.5$ J/mol.K) are due to the loss of structured water molecules surrounding the PAH molecules (hydrophobic effect) and are inconsistent with an adsorption mechanism that is accompanied with a decrease in the entropy of a solute [21].

Conclusions

The bioavailability of PAHs in sedimentary pore waters can be accurately determined by application of PDMS fibers (without requiring negligible depletion) in the presence of natural DOM with different sorption affinity for PAHs. The observed natural variability in $\log K_{\text{DOC}}$ values for different sediments shows that large differences can occur in freely dissolved PAH concentrations in pore water and properties of DOM should be taken into account in predicting the bioavailability of PAHs. Furthermore, the effect of temperature on the partitioning behaviour of PAHs shows that interactions between PAHs and environmental sorbents are comparable to interactions between PAHs in their pure condensed liquid phase and calculated excess enthalpies can be safely used to directly correct partition coefficients for temperature. The application of PDMS fibers in measuring freely dissolved PAH concentrations can be used to study structural and thermodynamic aspects of PAH sorption to natural DOM as well as other environmental processes such as enhanced diffusion phenomena in pore water [37, 25] that are dependent on the amount (or concentration) of DOM, sorption affinity of DOM and hydrophobicity of PAHs. These environmental factors will therefore give further insight into the site-specific exposure to freely dissolved PAH concentrations in soil and sedimentary pore water.

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