Effect of Temperature on the Distribution of Polycyclic Aromatic Hydrocarbons in Soil and Sediment

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Abstract: The knowledge of sorption-desorption processes of polycyclic aromatic hydrocarbons (PAHs) in natural solids is essential to predict the fate, transport, and environmental risks of these pollutants. In this study, the effect was investigated of temperature on the sorption-desorption of three PAHs (naphthalene, phenanthrene, and pyrene) in two natural solids with different organic carbon contents. In all cases, the sorption isotherms obtained could be well described by the linear sorption model. The analysis based on the measured isotherms and the corresponding equilibrium partition coefficients (K_p) revealed that (1) the sorption of PAHs increased with organic carbon content of the solid and PAH hydrophobicity in the order: sediment < soil and naphthalene < phenanthrene < pyrene, respectively, and (2) the extent of PAH sorption decreased with increasing temperature from 4°C to 27°C on average by 27.3, 17.0, and 27.4% for naphthalene, phenanthrene, and pyrene, respectively. The enthalpies of sorption (ΔH_s) calculated by van't Hoff equation were negative, relatively small, and in the range of weak forces such as van der Waals forces (0–9 kJ/mol), consistent with hydrophobic interactions and partitioning of the PAHs into soil/sediment organic matter. The desorption of naphthalene and phenanthrene showed significant hysteresis, i.e. great fraction of PAHs was resistant to desorption and somewhat increased with temperature.

Keywords: sorption; desorption; thermodynamic parameters; polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic priority pollutants, ubiquitous in soils, sediments and waters, and have gained much concern due to their toxicity, carcinogenecity and mutagenecity (US EPA 1993). Therefore, the processes that affect the migration and distribution of these pollutants within the soil/sediment-water systems must be understood in order to evaluate any adverse effects on humans and the environment.

The final distribution of PAHs in the soil/sediment-water systems is controlled mainly by sorption-desorption processes (Kan *et al.* 1994; Hwang & Cutright 2002). Sorption is also the primary physico-chemical process affecting the transport, biodegradability, and bioavailability of many hydrophobic organic chemicals, including PAHs, in soils and sediments (Piatt *et al.* 1996; Ortega-Calvo *et al.* 1997; Reemtsma & Mehrtens 1997). The extent of the PAH sorption-desorption in soils and sediments depends strongly on the hydrophobicity of the solute and the total organic carbon content of the soil/sediment (Karickhoff *et al.* 1979; Chiou *et al.* 1998; Reeves *et al.*

2004; Hiller & Bartaľ 2006). Often omitted, yet an important parameter that affects the retention and release of hydrophobic organic chemicals is temperature (ten Hulscher & Cornelissen 1996). Most laboratory measurements dealing with sorption processes are often performed at standard temperature (25°C), which is significantly different from the actual temperatures of surface soils and water-saturated sediments in temperate regions. Thus, the change in the sorption strength with temperature should be incorporated in such applications that include the sorption parameters, such as transport and pesticide leaching models, in order to predict correctly the true extent of mobility and the risk of water contamination by an organic chemical (Paraíba *et al.* 2003).

For most hydrophobic organic chemicals, such as PAHs, the extent of sorption in soil/sediment from water decreases with increasing temperature, i.e. sorption is an exothermic process in nature (Piatt *et al.* 1996; Chiou 2002). However, positive temperature dependencies for sorption of organic chemicals have also been reported (Moreale & van Bladel 1979; Brücher & Bergström 1997). Only few studies have been performed in order to evaluate the effect of temperature on the desorption of „fresh" added PAHs into the soil/sediment. Piatt *et al.* (1996) have observed that the desorption of PAHs from the low organic carbon sediments is favoured as the temperature increases. On the other hand, the temperature effect on the desorption of PAHs significantly increased when considering naturally contaminated soil (Enell *et al.* 2005).

The objective of this study was to extend the recent knowledge of the effects of temperature on sorption-desorption characteristics of three rep-resentative PAHs in soil and sediment using well-controlled batch experiments. Sorption isotherms and desorption from two points of the sorption isotherms were measured at two temperatures, 4°C and 27°C. Based on these data, the enthalpies of sorption were calculated.

MATERIALS AND METHODS

Polycyclic aromatic hydrocarbons

Naphthalene, phenanthrene, and pyrene of purities > 98%, purchased from Supelco (USA), were used as representative PAHs in this study. The physico-chemical properties of the selected PAHs are shown in Table 1.

Soil and sediment

A soil A-horizon (loamy-sand, Albic Luvisol) was collected from an agricultural field near the Zemplínska Šírava water basin, Michalovce district, eastern Slovakia. The sediment sample was taken at 10 cm depth from a stream of the Kyjov brook (eastern Slovakia). The samples were air-dried, crushed, and sieved through a 1 mm mesh before being used in the experiments. Relevant physico-chemical properties of the soil and sediment are given in Table 2. The procedures followed for the soil/sediment characterisation are described in Hiller *et al.* (2006, 2007).

Sorption-desorption experiments

PAH sorption isotherms on soil and sediment were obtained by the batch equilibration procedure

Table 1. Physico-chemical properties of the selected PAHs at room temperature

	Naphthalene	Phenanthrene	Pyrene
Molecular weight (g/mol)	128	178	202
Melting point (°C)	81	100	156
Heat of fusion (kJ/mol)[b]	19.3	18.6	17.6
Molar volume (cm^3/mol)[a]	111	152	159
Solubility parameter (J/mol)$^{1/2}$[b]	41.4	40.1	44.3
Water solubility (μg/cm^3)[a, b]	31.7	1.29	0.135
logK_{ow}[b]	3.36	4.57	5.18

[a]values as cited in Xia and Ball (1999); [b]from Chiou *et al.* (1998)

Table 2. Physical and chemical properties of the soil and sediment used

	OC (%)	C_{HA} (%)	C_{FA} (%)	pH (H_2O)	Clay < 1 μm (%)
Soil	1.212	0.304	0.262	6.32	5.75
Sediment[c]	0.273	0.078	0.040	8.20	12.3

OC – organic carbon content; C_{HA} and C_{FA} – humic and fulvic acid carbon contents, respectively; [c]sediment humic and fulvic acid carbon contents are only rough estimates since humus fractionation by the Kononova and Belcikova method is not reliable if OC is less than 0.5%

using 10 cm^3 glass centrifuge tubes closed with Teflon caps. The predetermined weight of each sorbent (1, 0.3, and 0.05 g for naphthalene, phenanthrene, and pyrene, respectively) was equilibrated with 9 cm^3 of aqueous solutions of PAHs by rotating in an end-over-end shaker for 48 h. Initial PAH solutions, either with four different concentrations for naphthalene (2.2, 7.5, 22.5, 30.3 μg/cm^3) and phenanthrene (0.05, 0.2, 0.5, 1.05 μg/cm^3) or with five different concentrations for pyrene (0.005, 0.01, 0.03, 0.08, 0.115 μg/cm^3), were prepared in the background 0.01M CaCl$_2$ and 100 mg/l NaN$_3$ solution from stock PAH solutions prepared in HPLC-grade methanol. NaN$_3$ was added to prevent biodegradation during the batch experiments. The amount of methanol carrier added from the stock solution was always less than 0.3% by volume. The initial PAH concentrations were selected to cover a wide range of aqueous concentrations of the compound water solubility, approximately 7–96%, 4–80%, and 4–85% for naphthalene, phenanthrene, and pyrene, respectively. After equilibration, the suspensions were centrifuged at 6000 rpm for 20 min, and 3 cm^3 of the supernatant solution was removed using a glass pipette for subsequent analysis by high-performance liquid chromatography (HPLC) as described below. Control samples without soil were also prepared in the same way and used to account for possible losses due to the volatilisation and sorption of PAHs to the glass centrifuge tubes. The average system losses were shown to be consistently lower than 3% of the initial solute concentrations, therefore no correction was required.

Desorption was measured for naphthalene and phenanthrene immediately after sorption from two equilibrium points of the sorption isotherms corresponding to the initial concentrations 22.5 and 30.3 μg/cm^3 for naphthalene, and 0.5 and 1.05 μg/cm^3 for phenanthrene. 7 and 8 cm^3 of naphthalene and phenanthrene supernatant, respectively, were

carefully removed and replaced with the same volume of 0.01M CaCl$_2$ and 100 mg/l NaN$_3$ solution. After shaking for 48 h, the suspensions were centrifuged, and the concentrations of PAHs were determined in the supernatants. This desorption procedure was repeated two times. All sorption and desorption experiments were carried out in duplicates at two temperatures, 4°C and 27°C. To maintain constant temperature during the sorption-desorption experiments, the glass centrifuge tubes were placed in a thermostatic chamber with adjustable temperature. The desorption of pyrene was not studied due to the very low desorption efficiency of this PAH. The desorbed solution concentrations were very low to be analysed accurately by direct injection of aqueous solutions into a reverse-phase HPLC system.

Analysis of PAHs

Chemical analyses were carried out by the National Water Reference Laboratory for Slovakia, Bratislava. The concentrations of PAHs in aqueous solutions before and after equilibration were analysed using a reverse-phase HPLC system (Hewlett-Packard model 1100) equipped with a fluorescence detector (Hewlett-Packard 1200). The following chromatographic conditions were used: Supelcosil LC-PAH 57945 column (250 mm length, 2.1 mm i.d.), acetonitrile/5% acetonitrile in water (60:40) eluent mixture for 3 min, followed by a linear gradient to 100% acetonitrile over 17 min, and 5 min isocratic with 100% acetonitrile, at a flow rate of 0.44 cm^3/min, and 15 μl injection volume. The excitation/emission wavelengths for naphthalene, phenanthrene, and pyrene were 220/325, 244/360, and 237/385 nm, respectively. External solution standards were used to establish linear calibration curves for a fluorescence detector. The average uncertainty for the measured concentrations was about ± 5%.

Data analysis

The amounts of PAHs sorbed in the soil/sediment were calculated by the differences between the initial and equilibrium solution concentrations:

$$S_e = (C_i - C_e)\frac{V}{m} \tag{1}$$

where:
S_e – amount of the chemical sorbed in the solid phase (μg/g)
C_i – initial solution concentration of the chemical (μg/cm³)
C_e – equilibrium solution concentration (μg/cm³)
V – volume of the solution (cm³)
m – mass of soil/sediment (g)

A linear isotherm is assumed to model the sorption of hydrophobic organic pollutants in soil/sediment, with the following equilibrium expression (Chiou 2002):

$$S_e = K_p C_e \tag{2}$$

where:
K_p – equilibrium partition coefficient (cm³/g)

As the primary interaction of hydrophobic organic pollutants with soils/sediments is governed predominantly by the soil/sediment organic carbon, the K_p values are related linearly to the organic carbon content of the given soils/sediments by the following equation (Karickhoff *et al.* 1979):

$$K_p = K_{oc} f_{oc} \tag{3}$$

where:
K_{oc} – organic carbon-based partition coefficient (cm³/g)
f_{oc} – weight fraction of organic carbon in the soil/sediment (g/g)

The definition of K_{oc} results from the assumption that organic carbon is the main sorbent of hydrophobic organic pollutants in soil/sediment, if total organic carbon content in the soil/sediment is > 0.1% (Schwarzenbach & Westall 1981). It has been shown that, for a given organic pollutant and particular group of soils or sediments containing organic matter of approximately the same origin and properties, K_{oc} values are nearly constant and differ only within a factor of 3 (Rutherford *et al.* 1992; Kile *et al.* 1999).

In each desorption step, the solution concentration for a given PAH is the sum of the remaining solution concentration plus the PAH amount that desorbed from the solid phase back to the solution.

Therefore, the desorption from the solid phase during the *a*-th desorption step can be calculated as follows:

$$S_d = \left[C_{a,d} - C_{a-1,d}\left(\frac{V - V_r}{V}\right)\right]\frac{V}{m} \tag{4}$$

where:
S_d – amount of the chemical desorbed from the solid phase (μg/g) during the *a*-th desorption step
$C_{a,d}, C_{a-1,d}$ – solution concentrations of the chemical at the end of the *a*-th and (*a*−1)-th desorption steps, respectively
V_r – volume of the supernatant (cm³) removed and replaced by the same volume of 0.01M CaCl₂ and 100 mg/l NaN₃ solution

The percentage of the chemical desorbed was calculated as follows:

$$P_d = \frac{\sum\limits_{a=1}^{2} S_d}{S_e} \times 100\% \tag{5}$$

Enthalpies of sorption were calculated by the difference using an integrated form of the van't Hoff equation (Karickhoff 1984; Chiou 2002):

$$\ln\frac{K_{p,4°C}}{K_{p,27°C}} = \frac{\Delta H_s}{R}\left(\frac{1}{T_{27°C}} - \frac{1}{T_{4°C}}\right) \tag{6}$$

where:
K_p – equilibrium partition coefficient at a given temperature (cm³/g)
ΔH_s – enthalpy of sorption (kJ/mol)
R – gas constant (8.314 × 10⁻³ kJ/K.mol)
T – absolute temperature (K)

The above equation assumes that ΔH_s is constant over the temperature range investigated.

RESULTS AND DISCUSSION

Sorption of PAHs in soil and sediment

The isotherms for the sorption of naphthalene, phenanthrene, and pyrene in the soil and sediment are given in Figure 1. The measured sorption isotherms in all experiments fit well to linear isotherm (Eq. (2)) over the range of PAH concentrations in solution used in this study, although some non-linearity of the isotherms for pyrene was observed as revealed by fitting the sorption data to

the Freundlich isotherm. Despite this, the linear isotherm rather than the Freundlich isotherm has been used since it may be difficult to compare the measured sorption data for PAHs with those in the literature if Freundlich exponent values differ or if sorption parameter values (i.e. Freundlich constant values) are derived from different units of S_e and C_e (CHEN *et al.* 1999; CARMO *et al.* 2000). The K_p values and the corresponding organic carbon-based partition coefficients (logK_{oc}) for the soil and sediment studied are given in Table 3. The inspection of the data in Table 3 shows that for a given PAH, the partition coefficient for the soil was almost fourfold of that for the sediment. This difference between the soil and the sediment is an expression of the positive correlations between sorption of PAHs and organic carbon contents of the soils and sediments, as shown by many authors (KARICKHOFF *et al.* 1979; MEANS *et al.* 1980). On the other hand, the K_{oc} values for a given PAH were much less variable between the soil and the sediment than were the corresponding K_p values

(Table 3). This result agrees well with the findings of CHIOU *et al.* (1998) and KARICKHOFF *et al.* (1979). Somewhat higher K_{oc} values for the sediment than for the soil are likely due to a lower polarity of the sediment organic matter. CHIOU *et al.* (1998) and KILE *et al.* (1995) observed that the K_{oc} values for hydrophobic organic pollutants with sediments were about two times higher than those with soils, suggesting that sediment organic matter is in general less polar than soil organic matter. The K_{oc} values at 27°C obtained in this study for all three PAHs are in a good agreement with the values published in the literature and those estimated from the several logK_{oc}/logK_{ow} linear free energy relationships (KARICKHOFF *et al.* 1979; MEANS *et al.* 1980; KARICKHOFF 1981; CHIOU *et al.* 1998; XIA 1998 in ALLEN-KING *et al.* 2002). The findings described above suggest that the sorption of PAHs in the studied solid phases was hydrophobically driven and occurred largely by partitioning (dissolution) into soil/sediment organic matter (CHIOU *et al.* 1979; KARICKHOFF 1984).

Table 3. Equilibrium partition coefficients (K_p), corresponding organic carbon-based partition coefficients (logK_{oc}), and enthalpies of sorption (ΔH_s) for three PAHs in the soil and sediment

	Temperature (°C)	Naphthalene	Phenanthrene	Pyrene
Soil				
K_p (cm³/g)	4	6.95 ± 0.32[a]	147.1 ± 11.0	1 284 ± 94.0
	27	5.28 ± 0.65	116.4 ± 4.6	868.0 ± 78.9
logK_{oc}	4	2.76	4.08	5.03
	27	2.64	3.98	4.86
ΔH_s (kJ/mol)		−8.30	−7.05	−11.80
Sediment				
K_p (cm³/g)	4	2.32 ± 0.11	31.7 ± 3.5	321.0 ± 37.6
	27	1.61 ± 0.28	27.5 ± 1.7	249.3 ± 18.6
logK_{oc}	4	2.93	4.06	5.07
	27	2.77	4.00	4.96
ΔH_s (kJ/mol)		−10.98	−4.21	−7.62
logK_{oc}[b]		2.61–3.11	4.10–4.36	4.64–4.99
logK_{oc}[c]		2.84–3.15	4.12–4.36	4.77–4.97

[a]values in parentheses are 95% confidence intervals; [b]range of measured values from CHIOU *et al.* (1998), MEANS *et al.* (1980) and KARICKHOFF *et al.* (1979); [c]estimated K_{oc} values using the following logK_{oc}/logK_{ow} linear free energy relationships: logK_{oc} = 1.06logK_{ow} − 0.72 (XIA 1998 in ALLEN-KING *et al.* 2002), logK_{oc} = 0.989logK_{ow} − 0.346 (KARICKHOFF 1981), logK_{oc} = 1.00logK_{ow} − 0.317 (MEANS *et al.* 1980), and logK_{oc} = 1.00logK_{ow} − 0.21 (KARICKHOFF *et al.* 1979)

Effect of temperature on sorption

The partition coefficient values decreased as the temperature increased from 4°C to 27°C (Figure 1 and Table 3). Therefore, from 4°C to 27°C the sorption of naphthalene, phenanthrene, and pyrene in soil decreased by 24.1, 20.9, and 32.4%, respectively. A similar decrease in the sorption of
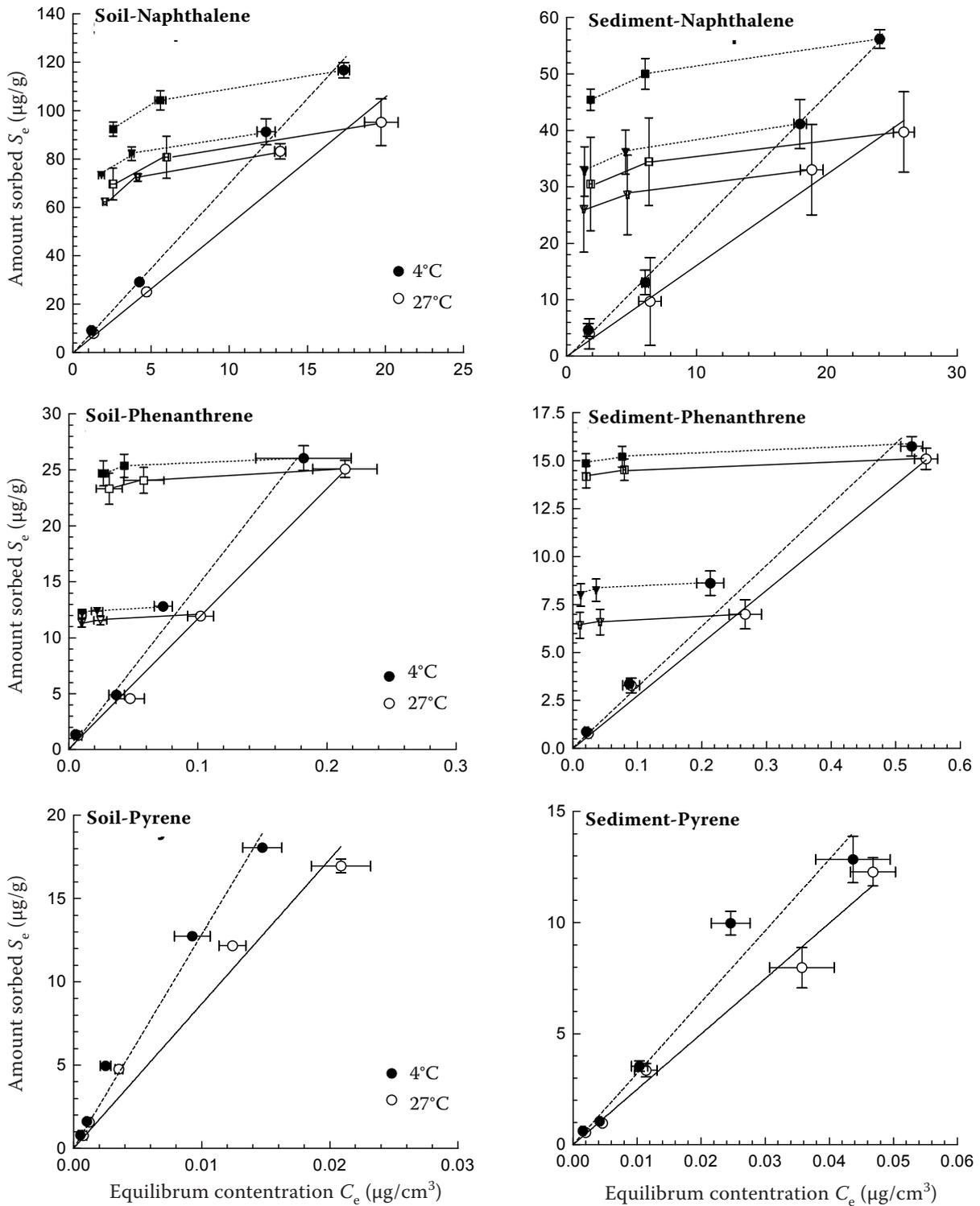

Figure 1. Sorption isotherms of the three polycyclic aromatic hydrocarbons and desorption paths of naphthalene and phenanthrene in soil and sediment at 4 and 27°C. In each desorption step, 78% and 89% of the solutions were replaced with naphthalene- and phenanthrene- free solutions to induce desorption, respectively; error bars represent standard deviations
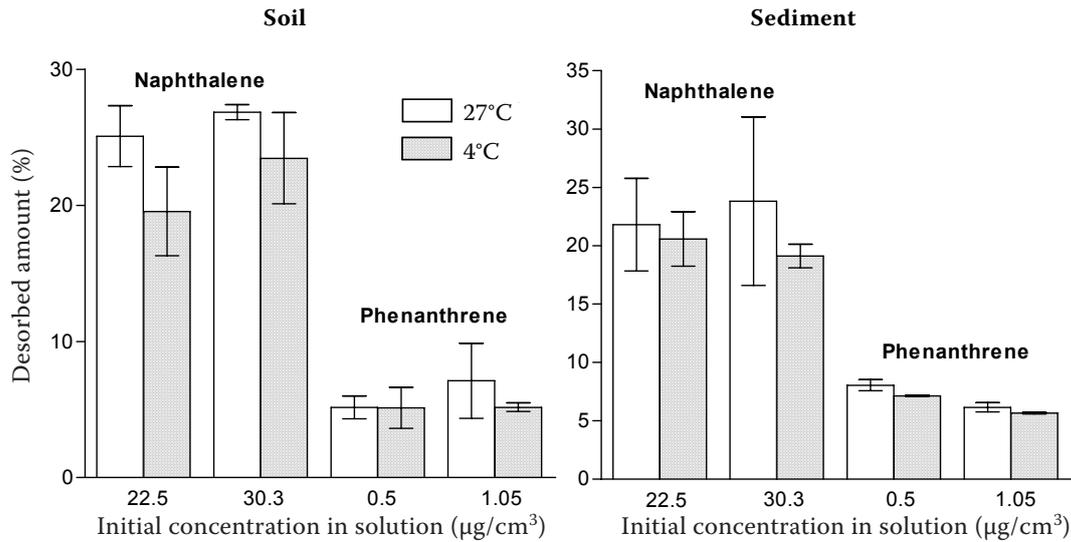
Figure 2. Percentage of naphthalene and phenanthrene desorbed from soil ad sediment at both temperatures and concentrations used; error bars indicate standard deviations

PAHs in sediment was also observed. These values compare well with the results of He *et al.* (1995) who reported 25% decrease in the adsorption of fluoranthene on soil with temperature increased from 5°C to 15°C. According to Piatt *et al.* (1996), the decreased sorption of PAHs at higher temperatures was due to increased PAH solubilities in water at higher temperatures. Other investigators also concluded that the aqueous activity coefficient is a major factor controlling the extent of sorption of hydrophobic organic pollutants in soils/sediments with temperature (Karickhoff 1984; Chiou 2002).

The enthalpies of sorption (ΔH_s) calculated by van't Hoff equation are listed in Table 3. It can be seen that all ΔH_s are negative and relatively small. These results are consistent with the generalisation that the sorption of hydrophobic organic pollutants in soil/sediment is an exothermic process (Karickhoff 1984). The magnitude of the sorption enthalpy changes for both soil and sediment is in the range of weak forces such as physical sorption and van der Waals forces (0–9 kJ/mol), which are consistent with hydrophobic interactions and partitioning of the PAHs into soil/sediment organic matter as described above (Karickhoff 1984; Chiou 2002). The enthalpy values obtained in this study are comparable to other ΔH_s for sorption of PAHs in natural soils and sediments. Chilom *et al.* (2005) reported ΔH_s = –6.4 to –24.9 kJ/mol for three PAHs sorbed in soils and sediment. Piatt *et al.* (1996) reported ΔH_s = –3.3 to –14 kJ/mol for

the same PAHs as investigated in this study sorbed in low organic carbon sediment. Wauchope *et al.* (1983) obtained ΔH_s = –7.1 to +3.8 kJ/mol for naphthalene sorbed in a silty loam. However, in sharp contrast, Ran *et al.* (2007) reported much higher negative enthalpy values ranging from –27 up to –64.4 kJ/mol for several PAHs sorbed in surface soils and estuarine sediments with high contents of black and kerogen carbon. The authors suggest that the high negative enthalpy values were due to the extensive sorption of PAHs in several inert, condensed, and aromatic components, such as kerogens, coals, and black carbon, that were present in the studied soils and sediments.

Desorption of PAHs in soil and sediment

The desorption experiments were conducted with naphthalene and phenanthrene from two points of the sorption isotherms at two temperatures, 4°C and 27°C. Plots of the sorption and desorption isotherms for naphthalene and phenanthrene are shown in Figure 1. The desorption data are also shown in Figure 2, where the desorbed amount was expressed as a percentage of the total amount sorbed. It can be seen that the slopes of the desorption isotherms are clearly different from those of the sorption isotherms. For example, when desorption was measured for naphthalene from the equilibrium point of the sorption isotherm corresponding to the initial concentration of 22.5 µg/cm³, only 25.0 and 19.6%

of the sorbed naphthalene actually desorbed from the soil in two steps at 27°C and 4°C, respectively. Similar results were obtained for all other desorption experiments in this study (Figure 2). These findings indicate that a significant hysteresis occurred in the sorption-desorption of the two PAHs, i.e. great fractions of naphthalene and phenanthrene were resistant to desorption even after 2 d soil contact time. To determine the mass balance and to check the occurrence of hysteresis, the soil was extracted by dichloromethane at the end of the adsorption-desorption experiments with phenanthrene at 27°C. The mass balance of > 91% was obtained, suggesting that the hysteresis observed in this study was due to the difference between the sorption and desorption rates (Kan *et al.* 1997). In agreement with this observation, irreversible sorption-desorption of hydrophobic organic pollutants such as PAHs is a commonly observed phenomenon (Kan *et al.* 1994; Hwang *et al.* 2003; Sun *et al.* 2003). For example, Kan *et al.* (1994) found that only 38% of the adsorbed phenanthrene desorbed in a total of 178 days. Recently, a biphasic irreversible adsorption model has been proposed to account for an irreversibly bound portion of the sorbed hydrophobic organic pollutants (Kan *et al.* 1997, 1998). Based on this model, the phenomenon may be due to the occlusion of chemicals by a cooperative conformational changes of the organic matter during the sorption process or due to physical rearrangement of the organic matter phase.

The extent of PAH desorption from soil and sediment slightly increased when the extraction temperature increased from 4°C to 27°C (Figure 2), although the differences in desorption for the given PAHs were not statistically significant at the 0.05 probability level. This result agrees well with the findings of Ran *et al.* (2007) and Enell *et al.* (2005) who reported a significant increase in the leached concentrations of several PAHs from aged contaminated sediments with temperature. Enell *et al.* (2005) also concluded that the desorption of PAHs was governed by equilibrium conditions or mass transfer limitations rather than by solubility limitations. This could be a likely explanation of the desorption behaviour observed in this study. In the natural water temperature range (0–35°C), the aqueous solubilities of pure organic chemicals are known to vary by about a factor of 2 (Schwarzenbach *et al.* 1993), while the desorption of naphthalene and phenanthrene from the solid phases used in this study varies only by a factor of 1.20 and 1.15 with temperature, respectively.

CONCLUSIONS

From the experimental data reported here, it is evident that the sorption isotherms for naphthalene, phenanthrene, and pyrene in soil and sediment are practically linear over the concentration range used. Organic carbon-based partition coefficient (K_{oc}) values for the given PAHs were similar to one another and could be estimated from the well-established linear regressions of $\log K_{oc}$ versus $\log K_{ow}$ found in the literature.

The sorption of PAHs in soil and sediment was affected by temperature. The extent of PAH sorption decreased as the temperature increased from 4°C to 27°C. The enthalpies of sorption (ΔH_s) calculated by van't Hoff equation were negative and relatively small, suggesting that partitioning into soil/sediment organic matter was the main mechanism of PAH sorption in the natural solids used. However, the temperature effect on PAH sorption is relatively small, considering the effects of large heterogeneities in physico-chemical properties, occurring commonly in field-scale soil/sediment systems.

The extent of PAH desorption from soil and sediment slightly increased when the extraction temperature increased from 4°C to 27°C, although the differences in desorption for the given PAHs were not statistically significant at the 0.05 probability level. The desorption data confirmed the occurrence of hysteresis in the sorption-desorption of naphthalene and phenanthrene. Only small fractions of the total PAHs sorbed in soil/sediment could be desorbed back to the solution in two steps at both temperatures. Overall, based on the experimental data, the polycyclic aromatic hydrocarbons investigated in this study exhibit a lower mobility in soil/sediment at lower temperature than at higher temperature.

References

Allen-King R.M., Grathwohl P., Ball W.P. (2002): New modeling paradigms for the sorption of hydrophobic chemicals to heterogeneous carbonaceous

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matter in soils, sediments and rocks. Advances in Water Resources, **25**: 985–1016.

Chiou C.T., McGroddy S.E., Kile D.E. (1998): Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environmental Science and Technology, **32**: 264–269.

Enell A., Reichenberg F., Ewald G., Warfvinge P. (2005): Desorption kinetics studies on PAH-contaminated soil under varying temperatures. Chemosphere, **61**: 1529–1538.

He Y., Yediler A., Sun T., Kettrup A. (1995): Adsorption of fluoranthene on soil and lava: effects of the organic carbon contents and temperature. Chemosphere, **30**: 141–150.

Hiller E., Bartaľ M. (2006): Geochemical behaviour of naphthalene, phenanthrene and pyrene in soil: Kinetic and equilibrium sorption studies. Slovak Geological Magazine, **12**: 3–9.

Hiller E., Khun M., Zemanová L., Jurkovič Ľ., Bartaľ M. (2006): Laboratory study of retention and release of weak acid herbicide MCPA by soils and sediments and leaching potential of MCPA. Plant Soil and Environment, **52**: 550–558.

Hiller E., Veselská V., Majzlan J. (2007): Arsenic mobility in stream sediments and impoundment material as evaluated by column and batch experiments. Journal of Hydrology and Hydromechanics, **55**: 223–235.

Hwang S., Cutright T.J. (2002): The impact of contact time on pyrene sorptive behavior by a sandy-loam soil. Environmental Pollution, **117**: 371–378.

Hwang S., Ramirez N., Cutright TJ., Ju L.K. (2003): The role of soil properties in pyrene sorption and desorption. Water, Air and Soil Pollution, **143**: 65–80.

Kan A.T., Fu G., Tomson M.B. (1994): Adsorption/desorption hysteresis in organic pollutant and soil/sediment interaction. Environmental Science and Technology, **28**: 859–867.

Kan A.T., Fu G., Hunter M.A., Tomson M.B. (1997): Irreversible adsorption of naphthalene and tetrachlorobiphenyl to Lula and surrogate sediments. Environmental Science and Technology, **31**: 2176–2185.

Kan A.T., Fu G., Hunter M.A., Chen W., Vard C.H., Tomson M.B. (1998): Irreversible adsorption of neutral organic hydrocarbons – experimental observations and model predictions. Environmental Science and Technology, **32**: 892–902.

Karickhoff S.W. (1981): Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere, **10**: 833–846.

Karickhoff S.W. (1984): Organic pollutant sorption in aquatic systems. Journal of Hydraulic Engineering, **110**: 707–735.

Karickhoff S.W., Brown D.S., Scott T.A. (1979): Sorption of hydrophobic pollutants on natural sediments. Water Research, **13**: 241–248.

Kile D.E., Chiou C.T., Zhou H., Li H., Xu O. (1995): Partition of nonpolar organic pollutants from water to soil and sediment organic matters. Environmental Science and Technology, **29**: 1401–1406.

Kile D.E., Wershaw R.L., Chiou C.T. (1999): Correlation of soil and sediment organic matter polarity to aqueous sorption of nonionic compounds. Environmental Science and Technology, **33**: 2053–2056.

Means J.C., Wood S.G., Hassett J.J., Banwart W.L. (1980): Sorption of polynuclear aromatic hydrocarbons by sediments and soils. Environmental Science and Technology, **14**: 1524–1528.

Moreale A., Van Bladel R. (1979): Soil interactions of herbicide-derived aniline residues: a thermodynamic approach. Soil Science, **127**: 1–9.

Ortega-Calvo J.J., Lahlou M., Saiz-Jimenez C. (1997): Effect of organic matter and clays on the biodegradation of phenanthrene in soils. International Biodeterioration and Biodegradation, **40**: 101–106.

Paraíba L.C., Cerdeira A.L., da Silva E.F., Martins J.S., da Costa Coutinho H.L. (2003): Evaluation of soil temperature effect on herbicide leaching potential into groundwater in the Brazilian Cerrado. Chemosphere, **53**: 1087–1095.

Piatt J.J., Backhus D.A., Capel P.D., Eisenreich S.J. (1996): Temperature-dependent sorption of naphthalene, phenanthrene, and pyrene to low organic carbon aquifer sediments. Environmental Science and Technology, **30**: 751–760.

Ran Y., Sun K., Ma X., Wang G., Grathwohl P., Zeng E.Y. (2007): Effect of condensed organic matter on solvent extraction and aqueous leaching of polycyclic aromatic hydrocarbons in soils and sediments. Environmental Pollution, **148**: 529–538.

Reemtsma T., Mehrtens J. (1997): Determination of polycyclic aromatic hydrocarbon (PAH) leaching from contaminated soil by a column test with on-line solid phase extraction. Chemosphere, **35**: 2491–2501.

Reeves W.R., McDonald T.J., Cizmas L., Donnelly K.C. (2004): Partitioning and desorption behavior of polycyclic aromatic hydrocarbons from disparate sources. Science of The Total Environment, **332**: 183–192.

Rutherford D.W., Chiou C.T., Kile D.E. (1992): Influence of soil organic matter composition on the partition of organic compounds. Environmental Science and Technology, **26**: 336–340.

Schwarzenbach R.P., Westall J. (1981): Transport of nonpolar organic compounds from surface water to

groundwater. Laboratory sorption studies. Environmental Science and Technology, **15**: 1360–1367.

Schwarzenbach R.P., Gschwend P.M., Imboden D.M. (1993): Environmental Organic Chemistry. John Wiley & Sons, New York.

Sun H., Tateda M., Ike M., Fujita M. (2003): Short- and long-term sorption/desorption of polycyclic aromatic hydrocarbons onto artificial solids: effects of particle and pore sizes and organic matters. Water Research, **37**: 2960–2968.

ten Hulscher Th.E.M., Cornelissen G. (1996): Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants – a review. Chemosphere, **32**: 609–626.

US EPA (1993): Provisional Guidance for Qualitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. EPA/600/R-93/089. U.S. Environmental Protection Agency. Office of Research and Development, Washington, DC.

Wauchope R.D., Savage K.E., Koskinen W.C. (1983): Adsorption-desorption equilibria of herbicides in soil: naphthalene as a model compound for entropy-enthalpy effects. Weed Science, **31**: 744–751.

Xia G., Ball W.P. (1999): Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. Environmental Science and Technology, **33**: 262–269.

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