

Geochemical behaviour of naphthalene, phenanthrene and pyrene in soil: Kinetic and equilibrium sorption studies

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Abstract: The batch experiments were used to determine the sorption properties of three polycyclic aromatic hydrocarbons (naphthalene, phenanthrene and pyrene). One agricultural soil, arenic Fluvi-Gleyic Phaeozem, was used. The experimental sorption isotherms were nonlinear and fitted well to the Freundlich sorption model. Impact of soil contact time on the sorption properties of PAHs was evaluated by measuring the distribution relationships at soil contact time of 2 h, 1, 2 (3 for pyrene) and 21 d. The results indicated that sorption equilibrium for naphthalene, phenanthrene and pyrene was reached within 1, 2 and 3 d, respectively. This suggested more hydrophobic PAHs could exhibit slower sorption kinetics than less hydrophobic PAHs. Water solubility and n-octanol – water partition coefficient were main factors affecting sorption properties of PAHs studied. The effect of nonlinear sorption behaviour of PAHs on the mobility in a soil was also discussed.

Key words: polycyclic aromatic hydrocarbons (PAHs), soil, soil contact time, sorption.

1. Introduction

Many studies indicated that sorption of hydrophobic organic chemicals in soils was not rapid and linear, despite past assumptions to the contrary. Deviations from the sorption linearity and equilibrium have major impacts on contaminant transport and fate models (Appert-Collin et al., 1999; Spurlock et al., 1995). A study by Ball & Roberts (1991) indicated that sorption of perchloroethylene and tetrachlorobenzene was a slow process that could take tens and hundreds of days to reach equilibrium, respectively. They also indicated that sorption of less hydrophobic perchloroethylene was more rapid than more hydrophobic tetrachlorobenzene. Similarly, Xing & Pignatello (1996) showed that Freundlich coefficients could increase 1.3 to 10 times between 1 and 180 d and that sorption isotherms become more nonlinear with increased soil contact time. Conversely, Sharer et al. (2003) observed no increase in chlorobenzene uptake by three soils between 24 h and 14 mo. The results summarized in studies by Luthy et al. (1997) and Pignatello & Xing (1996) indicate that slow sorption of organic chemicals in soils contributes significantly to the overall sorption and that could take a few days to years depending on solute-sorbent system.

Sorption of organic chemicals as polycyclic aromatic hydrocarbons (PAHs) in natural porous solids was often viewed as only linear process (Karickhoff et al., 1979; Means et al., 1980; Schwarzenbach & Westall, 1981). Thermodynamically, the sorption of these compounds is treated as phase partitioning between the aqueous solution and the soil organic matter viewed as an organic phase into which the sorbate is transferred. Rather than an surface adsorption process, sorption of hydrophobic

organic chemicals may be described as an absorption process. This is especially true when concentrations of organic chemicals are sufficient to effectively saturate surface adsorption sites (Chiou & Kile, 1998; Chiou et al., 2000). This concept leads to definition of organic carbon distribution coefficient K_{OC} which is strongly dependent on the solute solubility in water S_w and n-octanol – water partition coefficient of the solute K_{OW} . Thus, it can be expected that K_{OC} value remains constant for a given hydrophobic organic chemical in natural solids with approximately the same nature of organic matter. Many experimental studies have shown that the amount of solute sorbed by soils S only depends on the total soil organic carbon content f_{OC} and on the nature of the solute through K_{OC} and its concentration C : $S = (K_{OC} \times f_{OC}) \times C$. The assumption that K_{OC} is independent of the nature of soil organic matter and the solute concentration in water has been questioned. However, it is believed that the effect of the nature of soil organic matter consisting mainly of humic substances on the K_{OC} is not large (Kile et al., 1999; Rutherford et al., 1992). Similarly, the magnitude of the solute concentration on the K_{OC} of "normal" soils is not large. The observed low-concentration values with such soils usually lie within a factor of three of those observed at higher concentrations, except at extremely low aqueous concentrations ($< 0.01 \times S_w$); (Allen-King et al., 2002).

The objective of this study was to evaluate sorption properties of three representative polycyclic aromatic hydrocarbons in one soil using batch experiments. Distribution relationships for naphthalene, phenanthrene were measured after 2 h, 1, 2 and 21 d and for pyrene after 2 h, 1, 3 and 21 d.

2. Materials and methods

Soil. Surface soil sample (5–30 cm depth) from a field near Stupava was collected, air-dried and passed through a 2-mm-diameter sieve. Selected properties of soil are listed in Tab. 1. The particle size analysis was determined following the pipette method by Novák. Soil pH was measured in a 1:2.5 (wt:wt) soil-water suspension and a 1:2.5 soil-1 M KCl solution suspension. Organic carbon content was determined using a wet oxidation method by Ľurin. Mineralogical composition of soil clay was determined by X-ray diffraction method.

Solutes. Naphtalene, phenanthrene and pyrene all with purity higher than 97 % were used. Physico-chemical parameters of the selected polycyclic aromatic hydrocarbons are shown in Tab. 2. Primary stock solutions of phenanthrene and pyrene were prepared by dissolving appropriate amount of each chemical in HPLC-grade methanol, and a series of stock solutions of various concentrations were prepared by sequential dilution of the primary stock solutions. Primary stock solution of naphtalene was prepared by dissolving it in a background solution consisting of deionized water (Milli-Q Plus) and 10^{-4} M HgCl_2 to prevent biological activity. Initial aqueous solutions were prepared by mixing a background solution and a desired volume of a stock solution. In all initial aqueous solutions methanol content was less than 1 vol. %.

Sorption experiments. The sorption of the three PAHs was investigated using laboratory batch sorption method. Each batch experiment involved adding soil (4 g of soil for naphtalene and phenanthrene and 1 g for pyrene) and 40 ml of initial aqueous solution into 50 ml glass vials. Glass vials were capped with glass lids and enclosed in aluminium foil to prevent photodegradation. The vials were agitated on a horizontal shaker for 2 h, 1, 2, 21 d (naphtalene and phenanthrene) and 2 h, 1, 3, 21 d (pyrene). An aliquot of soil suspension was withdrawn from each vial at appropriate soil contact time and then added into centrifuge tubes. The soil suspensions in tubes were centrifuged at 10 000 rpm for 5 min and a clear supernatants were taken for analysis. In each set of experiments, 4 blanks without soil were prepared in the same way to estimate loss of solutes. Losses of naphtalene and phenanthrene were ~ 10 % and were taken into account for calculation of sorbed amounts by soil. Concentrations of PAHs in initial aqueous solutions as well as in clear supernatants after sorption were analysed on a reversed-phase HPLC (Hewlett-Packard model 1100, 5 μm , 2.1 \times 250 mm SUPELCOSIL LC-PAH 57945 column or HYPERSIL Green PAH column) with fluorescence detector (Hewlett-Packard 1046A). External methanol solution standards were used to establish linear calibration curves for fluorescence detector. The eluting solvent used was a mixture of acetonitrile and water. The average uncertainty for the measured concentrations was about ± 5 %. All experiments were performed in two replicates. Analysis was carried out by National Water Reference Laboratory for Slovakia, Bratislava.

Data modeling. The amounts of PAHs sorbed by the soil S ($\mu\text{g.kg}^{-1}$) were calculated from the difference

between the initial C_0 ($\mu\text{g.L}^{-1}$) and remaining (equilibrium) C ($\mu\text{g.L}^{-1}$) concentrations in solution $S = (C_0 - C) \times V/m$, where V (L) is the volume of aqueous solution and m (kg) is the weight of soil.

The data were fitted to the Freundlich sorption model $\log S = \log K_F + N \log C$, where K_F ($\mu\text{g}^{1-N} \cdot \text{L}^N \cdot \text{kg}^{-1}$) is the Freundlich sorption constant and N is the Freundlich exponent, an indicator of isotherm nonlinearity.

The sorption distribution coefficient K_D (L.kg^{-1}) for each solute-sorbent combination can be calculated by $K_D = S/C$. The organic carbon distribution coefficient K_{OC} (L.kg^{-1}) is described by $K_{OC} = K_D/f_{OC}$, where f_{OC} is the fraction of organic carbon of the soil ($\text{OC}\%/100$). At a solute concentration of unity, K_D equals K_F and $K_{OC} = K_F/f_{OC}$.

3. Results

The measured distribution relationships with best-fit lines from the Freundlich sorption model for PAHs studied are in Fig. 1. Sorption of naphtalene did not exhibit increases in sorption from 1 to 2 d (Tab. 3), while phenanthrene did show a significant increase in K_D and K_F values between 1 and 2 d of soil contact times (Tab. 3). After 21 d, sorption of phenanthrene showed an increase in K_D compared to the corresponding value at 1 d, but K_D for naphtalene remained unchanged. Sorption of pyrene showed an increase in K_D and K_F values between 1 and 3 d of soil contact times, whereas there was observed no increase in sorption from 3 to 21 d (Tab. 3).

The Freundlich model regressions indicated nonlinear pattern of the measured distribution relationships as showed by Freundlich exponent values less than 1.0. The distribution relationships for all three PAHs were linear at 2 h of soil contact time (Tab. 3). However, they became nonlinear at 1 d of soil contact time and Freundlich exponent values remained unchanged after 1 d. When there was no longer observed a change in sorption of PAHs studied, the measured distribution relationships could represent equilibrium sorption isotherms (Fig. 2).

There seems to be agreement between organic carbon distribution coefficients K_{OC} obtained from K_D at relatively high solute concentration in water ($> 0.01 \times S_w$) and those estimated from the solute's K_{OW} value according to the regression equations of Karickhoff (1981), Karickhoff et al. (1979) and Xia (1998 in Allen-King et al., 2002) (Tab. 3, Fig. 3). The obtained data indicated that the sorption of PAHs was positively correlated to the solute's K_{OW} values and negatively correlated to their water solubilities (Fig. 2).

4. Discussion

Effect of soil contact time

The results indicated that there was somewhat an effect of solute's properties on the sorption equilibrium. The K_D and K_F values for phenanthrene and pyrene showed a significant increase from 1 d to 2 d and 3d, respectively and remained constant at 21 d. On the other hand, the K_D and K_F values for naphtalene were

Tab. 1. Physical and chemical properties of the agricultural soil.

Class	Clay (%)	Silt (%)	Sand (%)	Texture	pH _{H2O}	pH _{KCl}	OC (%)	Main clay minerals
Arenic Fluvi-Gleyic Phaeozem	11	15	74	sandy loam	7.96	7.38	1.19	Illite > Chlorite

Tab. 2. Physical and chemical parameters of the selected PAHs at room temperature.

	Naphtalene	Phenanthrene	Pyrene
Molecular weight (g.mol ⁻¹)	128	178	202
Melting point (°C)	81	100	156
Heat of fusion (kJ.mol ⁻¹) ^b	19.3	18.6	17.6
Molar volume (cm ³ .mol ⁻¹) ^a	111	152	159
Solubility parameter (J.mol ⁻¹) ^{1/2b}	41.4	40.1	44.3
Water solubility (mg.l ⁻¹) ^{a, b}	31.7	1.29	0.135
logK _{OW} ^b	3.36	4.57	5.18

^aValues as cited in Xia & Ball (1999). ^bFrom Chiou et al. (1998).

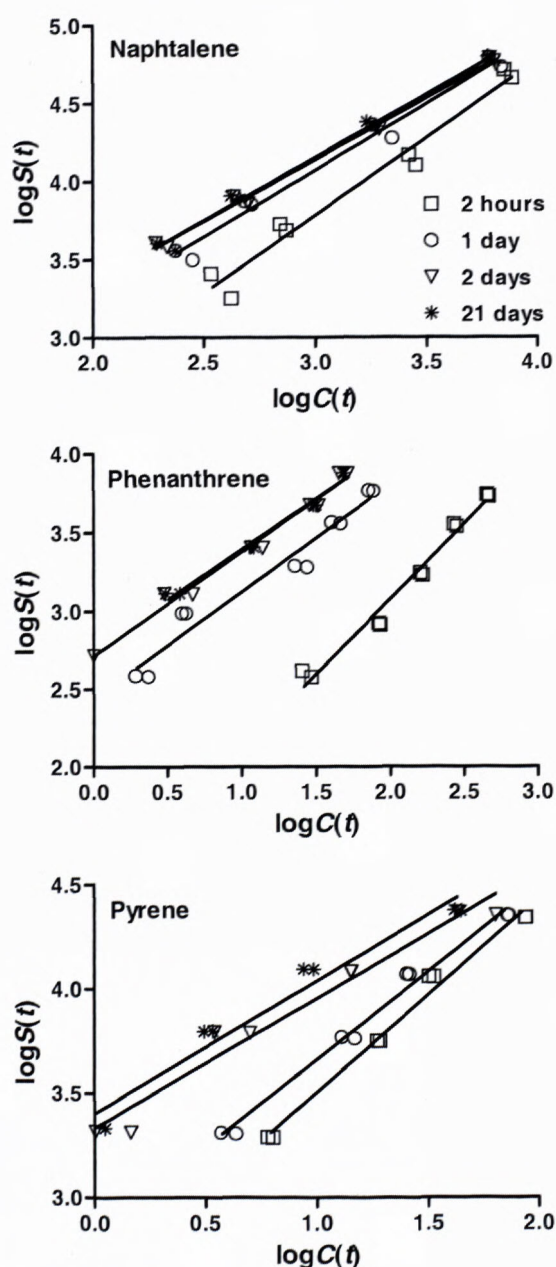


Fig. 1 Measured distribution relationships for naphtalene, phenanthrene and pyrene at different soil contact times.

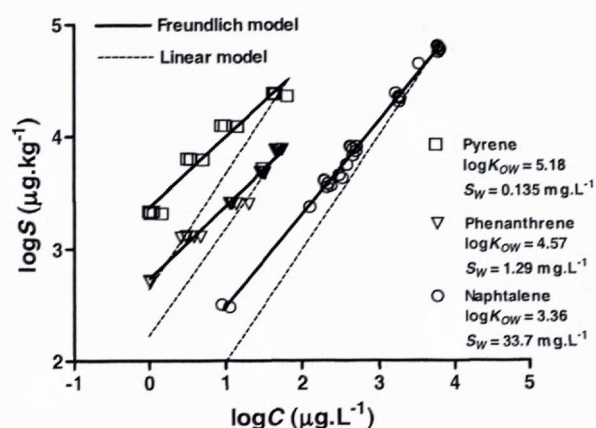


Fig. 2. Sorption isotherms for naphtalene, phenanthrene and pyrene with best-fit lines from the Freundlich sorption model (solid lines). The dashed lines represent the linear sorption model.

unchanged from 1 to 2 d. The limited data set provided here demonstrates that the sorption equilibrium of naphtalene, phenanthrene and pyrene was reached within 1, 2 and 3 d, respectively and that may be correlated to K_D . Naphtalene needs a shorter soil contact time to reach the sorption equilibrium (within 1 d) than phenanthrene and pyrene. Naphtalene has the lowest sorption coefficients and n-octanol – water partition coefficient of the PAHs studied (Tab. 3). Phenanthrene and pyrene have many times higher sorption coefficients and the K_{OW} values and there were necessary longer soil contact times to reach the sorption equilibrium. The results are similar with those of Ball & Roberts (1991) and Wu & Gschwend (1986). They demonstrated that the rate of approach to equilibrium for hydrophobic solutes was inversely correlated to their K_D or K_{OW} . This was attributed to the sorption-retarded pore diffusion of hydrophobic solutes. Brusseau & Rao (1989) showed that solutes with higher sorption coefficients should have slower sorption-desorption behaviour. The solute with higher K_D and K_{OW} equilibrated more slowly than that with lower K_D . On the other hand, Sharer et al. (2003) did not observed such relationships and suggested that specific interactions of the more polar compounds might be an important determinant of sorption kinetic behaviour.

Tab. 3. Sorption distribution coefficients K_D at higher solute aqueous concentrations ($C > 0.01 \times S_w$), organic carbon distribution coefficients K_{OC} and Freundlich parameters for naphthalene, phenanthrene and pyrene sorption by soil.

PAH	Contact time	K_D^a ($L \cdot kg^{-1}$)	$\log K_{OW}$	K_{OC} ($L \cdot kg^{-1}$)		Freundlich sorption model ^d	
				Experimental ^b	Calculated ^c	$\log K_F$ ($\mu g^{1-N} \cdot L^N \cdot kg^{-1}$)	N
Naphthalene	2 hour	6.05	3.36	983 1151 1202	692-1413	0.215-1.40	0.808-1.180
	1 day	11.7				1.12-1.90	0.729-0.978
	2 days	13.7§				1.59-1.95	0.730-0.849
	21 days	14.3				1.48-1.97	0.788-0.888
Phenanthrene	2 h	13.0	4.57	15630 16302	13305-22909	0.897-1.43	0.833-1.080
	1 d	107				2.28-2.60	0.563-0.806
	2 d	186#				2.62-2.81	0.583-0.742
	21 d	194				2.64-2.85	0.561-0.729
Pyrene	2 h	303	5.18	57731 70924	59020-93325	2.42-2.73	0.824-1.040
	1 d	413				2.69-2.95	0.748-0.939
	3 d	687#				3.20-3.46	0.500-0.742
	21 d	844				3.28-3.53	0.511-0.762

^aValues at $C > 0.01 \times S_w$ from best-fit parameters of the Freundlich sorption model. ^b $K_{OC} = K_D / f_{OC}$, where f_{OC} is the fraction of organic carbon (OC%/100). ^cValues from K_{OC} - K_{OW} correlations $K_{OC} = 0.989 \log K_{OW} - 0.346$ (Karickhoff, 1981), $K_{OC} = 1.00 \log K_{OW} - 0.21$ (Karickhoff et al., 1979) and $K_{OC} = 1.06 \log K_{OW} - 0.72$ (Xia, 1998 in Allen-King et al., 2002). ^d95 % confidence interval. §No significant increase in sorption from 1-day sample. #Significant increase in sorption from 1-day sample.

Equilibrium sorption behaviour

The equilibrium uptake of naphthalene, phenanthrene and pyrene by soil was affected by their hydrophobicity as reflected by the organic carbon distribution coefficients K_{OC} (Tab. 3, Fig. 2). This is well documented when the K_{OC} ratios for particular solute-solute combination to the corresponding K_{OW} ratios were compared:

$$K_{OC}^{Pyr} / K_{OC}^{Naph} = 60.9, K_{OC}^{Phen} / K_{OC}^{Naph} = 13.5,$$

$$K_{OC}^{Pyr} / K_{OC}^{Phen} = 4.51 \text{ vs. } K_{OW}^{Pyr} / K_{OW}^{Naph} = 66,$$

$$K_{OW}^{Phen} / K_{OW}^{Naph} = 16, K_{OW}^{Pyr} / K_{OW}^{Phen} = 4.07.$$

Many studies emphasized that the sorption of hydrophobic organic solutes was well positively correlated to n-octanol – water partition coefficient (Karickhoff, 1981; Karickhoff et al., 1979; Means et al., 1980; Seth et al., 1999). There was also agreement between organic carbon distribution coefficients K_{OC} obtained from K_D at relatively high solute concentration in water ($> 0.01 \times S_w$) and those estimated from the solute's K_{OW} value according to the regression equations of Karickhoff (1981), Karickhoff et al. (1979) and Xia (1998 in Allen-King et al., 2002); (Tab. 3, Fig. 3).

From the results presented in Fig. 2 and Tab. 4, it is evident that equilibrium sorption isotherms are nonlinear with N values ranging from 0.62 to 0.82 and that the Freundlich sorption model fits the equilibrium sorption data much better than the linear model. The observations are consistent with those of Carmo et al. (2000), Huang et al. (1997), Hwang et al. (2003), Toul et al. (2003) and Weber et al. (1992), but contradict linear behaviour observed by Karickhoff (1981), Karickhoff et al. (1979) and Means et al. (1980). Moreover, the results shown in Fig. 2 directly contradict the fact that linear isotherms are common at solute concentrations below 50 % of the solute water solubility S_w (Karickhoff, 1984). The linear sorption model has been widely accepted. According to

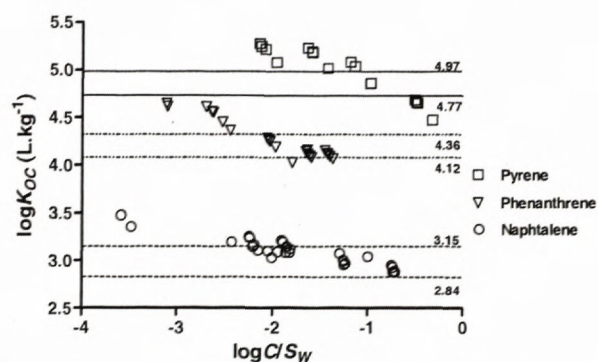


Fig. 3. The observed dependence of individually measured values of K_{OC} on the equilibrium solute concentration expressed by a ratio of equilibrium solute concentration to solute water solubility. The horizontal lines represent K_{OC} values predicted from K_{OC} - K_{OW} correlations by Karickhoff et al. (1979) and Xia (1998 in Allen-King et al., 2002).

this model, soil organic matter is the predominant sorbent in the sorption of hydrophobic organic chemicals by soils. Moreover, the sorption by soil organic matter occurs essentially by partitioning analogous to equilibrium extraction of an organic chemical from water by organic solvent (Chiou et al., 1979; Karickhoff et al., 1979). Linear isotherms are associated with this model and the slope is the linear distribution coefficient $K_{D,L}$, which is constant over the entire solute concentration range as well as K_{OC} . However, there were some limitations for this model as reflected by the equilibrium sorption data. The linear model could explain the equilibrium distributions of PAHs studied only at higher solute concentrations (Fig. 2 and 3). Conversely, the linear sorption model failed to consider the situation in the low relative solute concentrations (ratios of equilibrium solute concentration to solute water solubilities) (Fig. 2 and 3). The PAHs studied exhibited enhanced organic carbon distribution coefficients K_{OC} at low

Tab. 4. The equilibrium sorption data for naphthalene, phenanthrene and pyrene.

PAH	Freundlich sorption model		K_D at $C > 0.01 \times S_w^a$ (L.kg ⁻¹)	K_{OC} at $C > 0.01 \times S_w$ (L.kg ⁻¹)
	$\log K_F$ ($\mu\text{g}^{1-N} \cdot \text{L}^N \cdot \text{kg}^{-1}$)	N		
Naphtalene	1.66 (0.07) ^b	0.822 (0.027)	13.4	1126
Phenathrene	2.73 (0.06)	0.649 (0.05)	188	15798
Pyrene	3.37 (0.08)	0.622 (0.08)	755	63445

^aValues at $C > 0.01 \times S_w$ from best-fit parameters of the Freundlich sorption model.

^bNumber in parentheses is $\pm 95\%$ confidence interval.

relative concentrations ($C/S_w < 0.1$ -0.001) than at high relative concentrations. The observed dependence of individually measured values of K_D and calculated values of K_{OC} ($= K_D/f_{OC}$) on the equilibrium solute concentration for each solute-sorbent system is one of the most striking properties of nonlinear isotherms. K_{OC} values calculated from individual isotherm points decreased appreciably as a function of equilibrium solute concentration (Fig. 3). For example, the K_{OC} value for naphthalene decreased from 2982 L.kg⁻¹ of OC at $C = 8.9 \mu\text{g.L}^{-1}$ to 759 L.kg⁻¹ of OC at $C = 6461 \mu\text{g.L}^{-1}$ and the K_{OC} for phenanthrene decreased from 43782 L.kg⁻¹ of OC at $C = 1.0 \mu\text{g.L}^{-1}$ to 11612 L.kg⁻¹ of OC at $C = 55 \mu\text{g.L}^{-1}$. The observed sorption behaviour of PAHs is inconsistent with that predicated using K_{OC} - K_{OW} correlations. For example, correlations given by Karickhoff (1981), Karickhoff et al. (1979), Means et al. (1982) and Xia (1998 in Allen-King et al., 2002) provided naphthalene's K_{OC} values of 955, 1413, 1096 and 692 L.kg⁻¹ of OC, respectively. K_{OC} values for phenanthrene predicated by these correlations were 14928, 22909, 17783, 13305 L.kg⁻¹ of OC, respectively. While some of these correlation-predicated K_{OC} values agree well with the K_{OC} values measured at higher equilibrium solute concentrations, all are at least 2.5 to 3 times lower than the K_{OC} values observed at lower C (1-10 $\mu\text{g.L}^{-1}$); (Fig. 3).

Nonlinear sorption behaviour of PAHs observed in this study can be in accord with two recent concepts offering possible mechanistic interpretation of observed nonlinear sorption. Whereas one concept is based on the analogy between soil organic matter and synthetic polymers (Huang et al., 2003; LeBoeuf & Weber, 1997; Pignatello, 1998; Xing & Pignatello, 1997), the other looks for explanation in the heterogeneity of the soil organic matter and the presence of small amounts of high-surface-area carbonaceous material with high sorption capacities (Chiou et al., 2000; Karapanagioti et al., 2001; Kleineidam et al., 1999). In the soil organic matter-synthetic polymer analogy, a soil organic matter may comprise two principal domains as synthetic polymers: highly amorphous and swollen organic domain, analogous to a rubbery polymer and condensed, relatively rigid organic matrix, analogous to a glassy polymer (Weber et al., 2001). Sorption by rubbery polymers occurs by partitioning and generally yield isotherms that are essentially linear. Conversely, sorptions by glassy polymers occur by some type of adsorption and generally yield isotherms that are nonlinear and exhibit significantly larger sorption capacities. However, Chiou et al. (2000) and Chiou & Kile (1998) have argued that most of the nonlinearity is due to the presence of small amounts of high-surface-area

carbonaceous material (HSACM) with large sorption capacities and non-linear sorption behaviour of Langmuir type. HSACM, such as coal, carbonized woody fragments and soots are commonly present in soils and sediments and may result from fossil-fuel burning or burning of crop residues (Accardi-Dey & Gschwend, 2002; Allen-King et al., 2002; Cornelissen & Gustafsson, 2004; Yang & Sheng, 2003). The nonlinear sorption reported in this study could be attributed to the presence of trace amounts of carbonaceous material. The sampling site of soil sample used likely offers various sources for input of such carbonaceous material: vicinity of highway communications and intensive agricultural activities, e.g. field burning of crop residues. The two concepts presented here can be quite similar when it is considered that high-surface-area carbonaceous material may comprise properties of a glassy polymer.

Effect of nonlinear sorption on the mobility

One consequence of nonlinear sorption is that the mobility of a compound becomes dependent on the concentration. The relative mobility of a solute during equilibrium transport may be described using the retardation factor $R = 1 + (\rho/\theta) \times (\partial S/\partial C)$, where ρ (kg.L⁻¹) is the soil bulk density and θ (L.L⁻¹) is the volumetric water content.

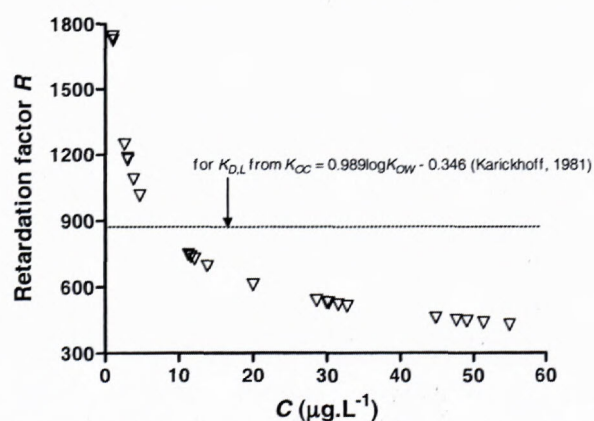


Fig. 4. The calculated change of retardation factor R with changing equilibrium solute concentration for phenanthrene. R is estimated using the idealized equation $R = 1 + (\rho K_F N / \theta) \times C^{N-1}$ (assuming soil bulk density of 1.5 kg.L⁻¹ and volumetric water content of 0.30). The dashed line represents the value of R predicated from $K_{D,L}$ given by K_{OC} - K_{OW} correlation of Karickhoff (1981).

For the linear case, sorption coefficient $K_{D,L}$ is concentration independent, and therefore the retardation factor is also concentration independent. However, for the nonlinear

case, $R = 1 + (\rho K_F N / \theta) \times C^{N-1}$, which shows that the retardation factor is then concentration dependent. In Fig. 4, the dependence of the retardation factor on solute concentration for phenanthrene is plotted. Fig. 4 also illustrates the values of R predicated from $K_{D,L}$ given by the K_{OC} - K_{OW} correlation of Karickhoff (1981). The results show that the relative mobility of phenanthrene is significantly less at lower concentrations than at higher C and as predicated by the linear sorption model.

5. Conclusions

The study presented here demonstrates that the sorption equilibrium of naphthalene, phenanthrene and pyrene was reached within 1, 2 and 3 d, respectively and that may be correlated to K_D . Naphthalene needs a shorter soil contact time to reach the sorption equilibrium (within 1 d) than phenanthrene and pyrene. Naphthalene has the lowest sorption coefficients and n-octanol – water partition coefficient of the PAHs studied. Phenanthrene and pyrene have many times higher sorption coefficients and the K_{OW} values and there were necessary longer soil contact times to reach the sorption equilibrium.

The sorption isotherms of all three PAHs were nonlinear. Our results showed that the use of empirical correlations based on the linear sorption model failed to predict sorption coefficients at low solute concentrations. This is applied to solute concentration levels one order of magnitude or lower than the water solubility of a solute for soils containing mainly humus-like soil organic matter. Moreover, we emphasized the effect of nonlinear sorption behaviour on the mobility of PAHs in soil environment. Therefore, extrapolations of sorption behaviour observed in high solute concentrations in aqueous solution to low concentrations can be a source of considerable errors when estimating sorption-related fate and transport processes for hydrophobic organic chemicals.

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