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To cite this article: BO PAN , BAOSHAN XING , WENXIN LIU , SHU TAO , XIUMEI LIN , YANXV ZHANG , HUIISHI YUAN , HANCHENG DAI , XIANMING ZHANG & YANG XIAO (2006) Two-Compartment Sorption of Phenanthrene on Eight Soils with Various Organic Carbon Contents, Journal of Environmental Science and Health, Part B, 41:8, 1333-1347, DOI: [10.1080/03601230600964043](https://doi.org/10.1080/03601230600964043)

To link to this article: <https://doi.org/10.1080/03601230600964043>



Published online: 05 Dec 2006.



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Two-Compartment Sorption of Phenanthrene on Eight Soils with Various Organic Carbon Contents

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Sorption characteristics of phenanthrene (PHE) were studied on eight soils with organic carbon contents spanning over an order of magnitude using phase distribution relationships (PDRs) at 1 h, 48 h, and 720 h contact times. A new algebraic method was employed to describe the sorption characteristics at different time intervals (between 1 h and 48 h, and 1 h and 720 h). It was found that nonlinearity increased with increasing contact time and sorption that occurred in the subsequent time interval following the initial 1 h exhibited stronger isotherm nonlinearity. Sorption coefficients were positively correlated with the organic carbon contents of the soils. Detailed sorption dynamics were also examined on these soils. A two-compartment, first-order model was used to describe the sorption dynamics. The rate constants of the two compartments differed 18–170 times, suggesting the dissimilar sorption behaviors of the mathematically separated compartments. These two compartments were labeled fast and slow sorption compartment according to the rate constants. Calculation showed that the fast compartment accounted for over 80% of the overall sorption at the initial 1 h, while the slow compartment predominated the total sorption in the following 47 h. By combining the discussion of PDRs and sorption dynamics, the contributions of the two compartments to linear and nonlinear sorption were differentiated. The slow sorption compartment made a major contribution to nonlinear sorption and possibly to sequestration of organic pollutants by these soils.

Key Words: Phase distribution relationships; Two-compartment sorption; Sorption dynamics; Phenanthrene; soil.

Received May 4, 2006.

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INTRODUCTION

Sorption is a critical process in modeling the fate and transport of hydrophobic organic chemicals (HOCs) in soils and sediments. Numerous studies have shown that biodegradation and transport of HOCs in the environment were controlled by adsorption and desorption dynamics.^[1,2]

Current sorption concepts consider soil or sediment as a multi-domain sorbent, where different domains contribute to different sorption characteristics, such as nonlinearity, capacity and rate. Multi-domain models are therefore often applied to describe sorption dynamics. A two-compartment, first-order dynamics model, has been widely used due to its agreement with multi-domain sorption theories^[3] and simplicity over other models.^[4] According to the discussion on the model of sorption and desorption,^[5] a two-compartment first-order dynamics model of sorption can be easily derived,^[4] and is presented as follows:

$$\frac{S}{S_e} = f_1(1 - e^{-t/k_1}) + f_2(1 - e^{-t/k_2}) \quad (1)$$

where, S is sorbate concentration in the solid phase ($\mu\text{g}\cdot\text{g}^{-1}$) at time t , and S_e represents sorbate concentration in the solid phase at equilibrium. This model regards soil or sediment as a two-compartment sorbent, and each compartment with distinct sorption rate constant, k_1 and k_2 (h^{-1}). Parameters f_1 and f_2 are the fractions of the two compartments, respectively, and $f_1 + f_2 = 1$.

Because of multiple-sorption domains, the Freundlich equation has been used to describe nonlinear sorption isotherms.^[3] Moreover, Weber and Huang reported that a Freundlich-type model provided a good fit for the nonequilibrium data, namely, phase distribution relationships (PDRs).^[6] Studies on PDRs revealed that sorption nonlinearity increased as the contact time was prolonged, and the total sorption was contributed by more than one compartment. Xing and Pignatello reported that a subtraction method could be used to quantify the amount of sorbate retained by slow compartment.^[7] The subtraction method may provide a way to estimate the contribution of different compartments to total sorption and how the individual compartments affect the overall sorption characteristics. Their study was significant for understanding the sorption over long periods. However, only one mineral soil was used in their work.

The present study examined the PDRs of phenanthrene (PHE) on eight soil samples at three different contact times, and the sorption characteristics at different time intervals were described using the Freundlich equation based on a modified subtraction method introduced by Xing and Pignatello.^[7] The contribution of different sorption compartments at different time periods was determined in a detailed sorption dynamics experiment of these soils and by two-compartment modeling.

MATERIALS AND METHODS

Soil Preparation and Characteristics

Eight soils samples that varied in total organic carbon (TOC) content were collected in the northern outskirts of Beijing, which is far from any industrial area. The soil samples were ground and sieved through a 2-mm sieve, and then kept moist and in dark at room temperature (25°C). In the experiments, the soils were wet weighed and the dry weights were calculated by subtracting moisture contents, which were computed based on the weight differences before and after heating the soil samples overnight at 105°C. The moist soil samples were used because it takes too long for sorption to reach equilibrium due to slow wetting of dry soils.^[8] The solid concentration was calculated based on dry soil weight. The TOC content of the soils, measured on a TOC analyzer (TOC 5000A, Shimadzu), spanned over an order of magnitude, from 0.4–7.9% (Table 1). The background concentrations of phenanthrene (PHE) were 20–40 times lower than the least concentration of PHE added to the soil samples for the sorption experiment. The desorption of PHE from the original soil samples in the background solution (0.01M CaCl₂ and 200 mg/L HgCl₂) was not detectable, thus the background PHE in the soil samples was neglected in sorption calculation. Soil samples of 0.2–0.5 g were treated by H₂O₂ to remove most of the organic component, and then analyzed on a particle size analyzer (Malvern 2000, UK) for particle size distribution. Five g of each soil sample were mixed with 10 mL distilled water and the suspension was settled for 0.5 h. The pH values of the supernatant were measured.

Sorption Experiment

The experimental procedure was adapted from Xing.^[9] Briefly, a methanol stock solution of PHE was diluted sequentially to a series of concentrations

Table 1: Soil properties.

Soil samples	moisture (%)	TOC ^a (%)	pH	PHE ^b ($\mu \cdot g^{-1}$)	Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)
1	14	0.4	5.7	0.113	3.3	26.5	36.6	33.6
2	9	0.7	7.8	0.034	2.5	30.1	67.3	0.0
3	12	1.2	6.1	0.002	3.0	30.9	62.7	3.4
4	19	2.9	7.4	nd ^c	2.8	32.3	62.9	2.1
5	22	2.9	7.6	0.018	2.8	34.5	58.1	4.7
6	23	4.4	7.5	0.021	2.2	47.4	43.9	6.5
7	28	4.5	6.4	0.056	2.1	48.0	43.2	6.7
8	27	7.9	7.1	0.071	2.6	34.6	57.1	5.7

^aExpressed as organic carbon percentage in whole soil.

^bExhaustedly extracted on accelerated solvent extractor and analyzed on gas chromatography—mass spectrometer.

^cNot detected.

distributed evenly on a log scale in the background solution. The volume ratio of methanol to water was below 0.1% to avoid any co-solvent effect.^[6] The sorption experiments were conducted in 10 mL centrifuge glass tubes equipped with ground glass stoppers. Soil samples of 0.02–0.1 g (wet weight) were mixed with 10 mL of PHE solution in the tubes that were sealed immediately with a glass stopper. The stoppers were tightly bound to the tubes externally by parafilm, which was not in contact with the PHE solution. The headspace in the tubes was kept to a minimum to reduce solute loss via evaporation. The tubes were kept in the dark and rotated vertically on a rotator at 30 rpm (RD9924CE, Glas-Col lab rotator) during the desired contact times, and then sacrificed for centrifugation at 1000 g for 10 min. The supernatant was poured out carefully to prevent the loss of soil particles, and subjected to solute analysis. The amount of residual water in the soil after centrifugation and decanting was calculated by the weight difference, and the solute in the residual water was taken into account in the calculations. All soil samples including the procedure blanks were run in duplicate. In the dynamics experiment, one-initial concentration sorption dynamics were examined, and the organic carbon normalized final concentrations were in the same range for all the eight soils. Two of the vials of the same condition were sacrificed at the desired contact times, and the solute residual in the solution was measured.

Determination of the Solutes

All aqueous samples were extracted by purified hexane with half volume of the aqueous solution. The water-hexane mixture was shaken vigorously, and two drops of ethanol were added to diminish emulsification. The recoveries of the hexane extraction exceeded 98% for PHE, as shown by our preliminary experiments.

Approximately 2 mL of the hexane solution was used for fluorescence analysis (F-2500, Hitachi) after the water-hexane interface was clear. The parameters of fluorescence photometry were set as follows: slit 2.5 nm, voltage 700 V, emission wavelength 300–450 nm, excitation wavelength 293 nm for PHE. The peak height at 365 nm was used to quantify PHE.

Data Analysis

A PDR method, proposed by Weber and Huang,^[6] was used to investigate nonequilibrium sorption characteristics in this study. The Freundlich equation in this method has a following expression:^[10]

$$S = K_F \cdot (C/C_{\text{scl}})^n \quad (2)$$

where S stands for the solid-phase concentration ($\mu\text{g}\cdot\text{g}^{-1}$), C is aqueous concentration ($\mu\text{g}\cdot\text{mL}^{-1}$) and C_{scl} the supercooled liquid-state solubility of PHE at

25°C (5.97 $\mu\text{g}\cdot\text{mL}^{-1}$). In this model, K_F is a Freundlich sorption coefficient with the same unit as S ($\mu\text{g}\cdot\text{g}^{-1}$), and n the nonlinear factor.

Xing and Pignatello suggested an algebraic method to separate the contribution of slow compartment at equilibrium:

$$S_s = S_e - S_f = S_e - K_{Ff} \cdot C_e^{n_f} \tag{3}$$

where, S_e , S_f and S_s are the overall solid-phase concentration, and the solid-phase concentrations contributed by fast and slow compartments at equilibrium, respectively.^[7] K_{Ff} and n_f are the Freundlich sorption parameters of fast sorption compartment. The calculation concept is presented in Figure 1a.

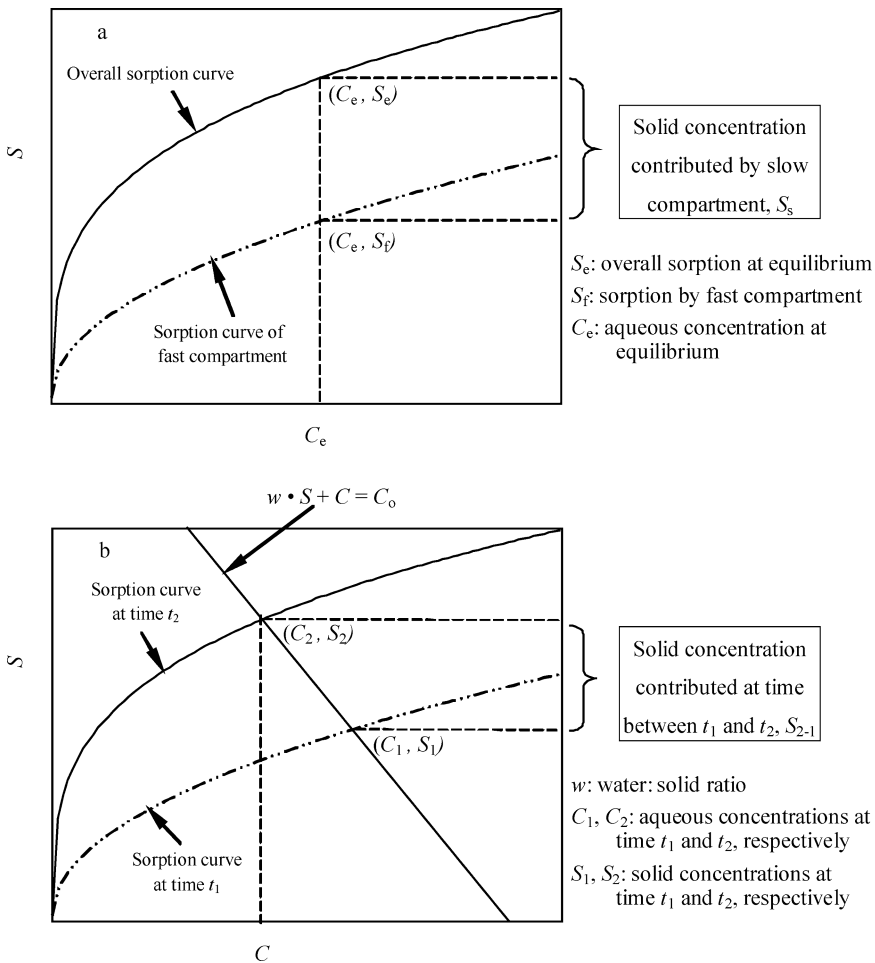


Figure 1: Calculation concepts of solid-phase concentration contributed at a subsequent time interval. Upper panel (a) is the original concept adopted from Xing and Pignatello (1996), and lower panel is the modified calculation of this study. C_0 is the initial input of solute. S and C are the solid and aqueous concentrations, respectively.

This method was proposed to calculate the sorption characteristics of individual compartments at equilibrium. However, it should be noted that sorption of the individual compartments always occurs simultaneously, which cannot be separated by the current experimental technique. Furthermore, operationally, the true equilibrium may not be reached for most sorption experiments. Therefore, the subtraction method was modified to describe the sorption at different time intervals.

As illustrated in Figure 1b, for a closed system, like the sealed reaction vials in sorption experiments, the total amount of sorbate in aqueous and solid phases is a constant. Therefore two equations could be combined to calculate the contribution of the initial uptake to the overall sorption, as follows:

$$\begin{cases} w \cdot S_1 + C_1 = w \cdot S_2 + C_2 \\ S_1 = K_{F1}(C_1/C_{scl})^{n_1} \end{cases} \quad (4)$$

where, w is the solid/water ratio in sorption experiment ($\text{kg}\cdot\text{L}^{-1}$), and C_1 and C_2 represent the aqueous concentrations ($\mu\text{g}\cdot\text{mL}^{-1}$) at time t_1 and t_2 , respectively. S_1 and S_2 are the solid phase concentration ($\mu\text{g}\cdot\text{g}^{-1}$) at time t_1 and t_2 , respectively. K_{F1} and n_1 denote the Freundlich parameters at time t_1 . Thus, for a given initial concentration, solid-phase concentration difference between t_2 and t_1 could be calculated by:

$$S_{2-1} = S_2 - S_1 = S_2 - K_{F1} \cdot (C_1/C_{scl})^{n_1} \quad (5)$$

The Freundlich equation was used subsequently to establish the relationship between S_{2-1} and C_2 , and the fitted parameters were compared with those of PDRs.

Dynamics fitting was conducted using both one-compartment, first-order and two-compartment, first-order models. The one-compartment model is:

$$\frac{S_t}{S_\infty} = 1 - e^{-t/k} \quad (6)$$

where S_t and S_∞ are the solid phase concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) at time t and at equilibrium, respectively. Parameter k is the overall sorption rate constant (h^{-1}). The two-compartment first order model is as Equation 1. The mathematical fitting was performed using SigmaPlot 2001 for Windows. The adjusted coefficient of determination (r_{adj}^2) was employed instead of a standard coefficient of determination (r^2) in order to compare the goodness of fitting using different numbers of data points. The r_{adj}^2 was calculated as:

$$r_{\text{adj}}^2 = 1 - r^2 \cdot \frac{m - b}{m - 1} \quad (7)$$

where m is the number of data points used for fitting, and b the number of coefficients in the fitting equation.

RESULTS AND DISCUSSION

Phase Distribution Relationships at Different Sorption Times

In this study, the PDRs were examined at sorption times of 1 h, 48 h and 720 h. Typical sorption curves at different contact times and the fitting results are illustrated in Figure 2, and the fitting results of eight soils are listed in Table 2. Nonlinear sorption behavior was generally observed at each contact time, in which, the n values varied from 0.59 to 0.92, depending on contact times and soils (Table 2). The n values decreased as contact time increased for a given soil sample. This phenomenon has been widely reported.^[3,6,11] However, these researchers observed that the K_F value increased also with contact time, whereas in this study, the time dependence of K_F was not obvious after 48 h. It should be noted that the modified Freundlich equation (Eq. 2) employed in this study may result in the K_F values $(C_{sc1})^n$ times higher than in the literatures, where the equation of $S = K_F C^n$ was commonly used. Therefore, one cannot directly compare the K_F values of this study with literature data (as in ref. 6).

On the other hand, consistent with the results presented by Carmo,^[10] K_F s were found to be positively related to the TOC contents of the eight soils (Table 2). The correlation coefficients between K_F and fraction of organic carbon (f_{oc}) were 0.95, 0.96 and 0.88 at 1 h, 48 h and 720 h, respectively.

In addition, the single point sorption coefficient K_d was also found to be positively related to TOC content. In this study, the single point K_d was calculated at $C = 0.01 C_s$ and $C = 0.1 C_s$ (C_s is solubility of PHE in water at 25°C, $1.29 \mu\text{g} \cdot \text{mL}^{-1}$), and their values are presented in Table 2. The K_d varied from 26-1140 $\text{mL} \cdot \text{g}^{-1}$ depending on soils and contact times, which could be explained

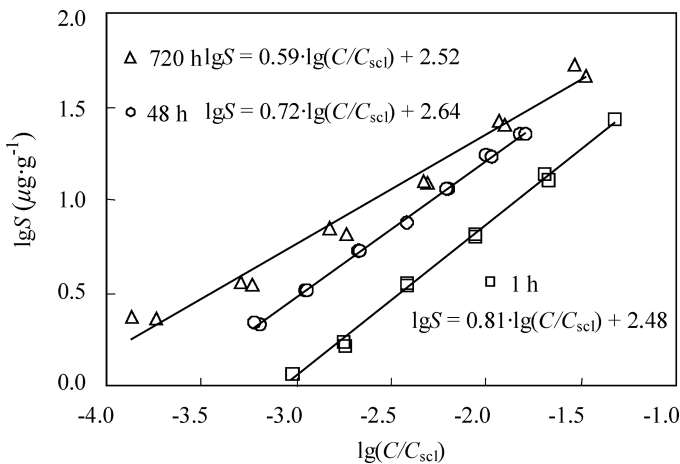


Figure 2: Typical sorption isotherms at different contact times (exemplified by No.5 soil sample). Solid lines are the results of Freundlich equation fitting.

Table 2: The fitted parameters of PDRs.

Contact times	Soil samples	Freundlich equation					Single point K_d^a ($\text{mL} \cdot \text{g}^{-1}$)	
		n	std ^b	$\lg K_F$ ($\mu\text{g} \cdot \text{g}^{-1}$)	std ^b	r^2	$C = 0.1 C_s$	$C = 0.01 C_s$
1 h	1	0.89	0.02	2.01	0.04	0.99	26	34
	2	0.82	0.05	2.07	0.09	0.96	39	584
	3	0.78	0.03	2.24	0.07	0.98	68	113
	4	0.80	0.03	2.53	0.07	0.98	119	187
	5	0.81	0.02	2.48	0.04	1.00	106	165
	6	0.82	0.03	2.55	0.05	0.99	120	183
	7	0.92	0.03	2.84	0.05	0.99	156	187
	8	0.90	0.02	3.10	0.04	1.00	309	386
48 h	1	0.80	0.02	2.17	0.04	0.99	0.96 ^c	0.94 ^c
	2	0.76	0.03	2.29	0.08	0.98	54	86
	3	0.77	0.04	2.43	0.08	0.97	82	142
	4	0.71	0.02	2.68	0.04	0.99	107	182
	5	0.72	0.03	2.64	0.07	0.98	245	478
	6	0.76	0.02	2.79	0.05	0.99	214	405
	7	0.78	0.02	3.03	0.06	0.98	260	453
	8	0.75	0.02	3.17	0.05	0.99	423	708
720 h	1	0.75	0.05	2.24	0.13	0.93	0.97 ^c	0.98 ^c
	2	0.64	0.04	2.01	0.09	0.96	75	132
	3	0.60	0.03	2.16	0.07	0.97	68	154
	4	0.64	0.06	2.56	0.16	0.90	115	292
	5	0.59	0.03	2.52	0.08	0.98	243	563
	6	0.64	0.03	2.58	0.07	0.98	270	698
	7	0.73	0.03	3.01	0.07	0.97	248	562
	8	0.76	0.05	3.12	0.12	0.90	481	897
						563	984	
						0.94 ^c	0.98 ^c	

^a K_d is calculated by $K_F \cdot C^{(n-1)} \cdot C_{\text{sol}}^{-n}$, and C_s is the solubility of PHE in water at 25°C (1.29 $\mu\text{g} \cdot \text{mL}^{-1}$).

^bStandard deviation of fitted parameters.

^cCorrelation coefficients between K_d and f_{oc} .

well by TOC contents, indicated by the correlation coefficients between K_d and f_{oc} (Table 2). Organic carbon normalized sorption coefficients K_{oc} ($K_d = K_{\text{oc}} \cdot f_{\text{oc}}$) are depicted in Figure 3. It can be seen that, at a given time, lower aqueous concentration had higher K_{oc} values due to nonlinear sorption. Obviously, the difference of K_{dS} between 48 h and 720 h was not significant, indicating that sorption occurred mainly during the initial 48 h. The $\log K_{\text{oc}}$ values fell in the range of 3.9 and 4.2 for different aqueous concentrations at 48 h and 720 h, which were comparable to the literature data ($\log K_{\text{oc}}$ of PHE: 4.31 ± 0.49).^[12]

Sorption Characteristics After Initial Sorption

In the current study, some modifications were made on the subtraction method used by Xing and Pignatello^[7] to describe the sorption characteristics after initial sorption. The difference between 48 h and 720 h was not distinct

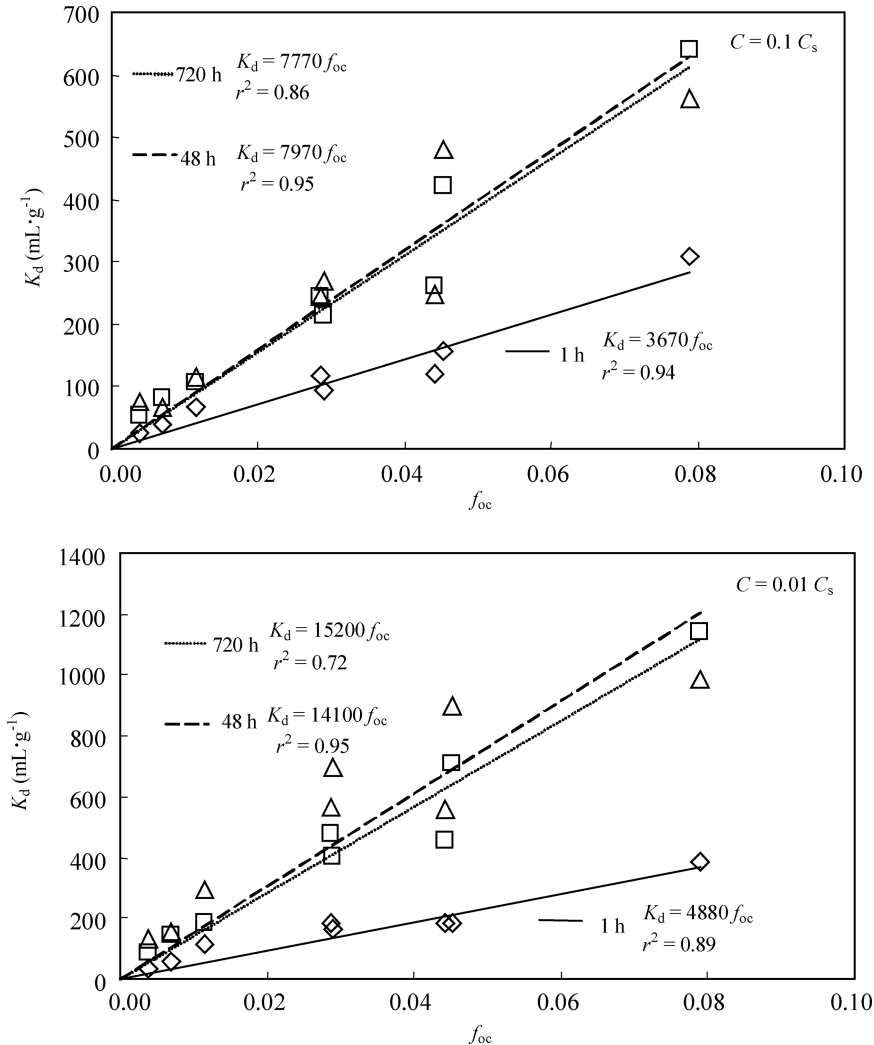


Figure 3: Relationship between (a) single point K_d and f_{oc} at $C = 0.1 C_s$ (b) and $C = 0.01 C_s$ (lower panel). Open diamonds (\diamond), squares (\square) and triangles (Δ) stand for the observed relationship at contact times of 1 h, 48 h and 720 h, respectively.

(see the discussion on single point K_d) and the subtraction for this time interval resulted in large uncertainties. Therefore, the subtraction method was applied only to describe the sorption characteristics of the intervals between 1 h and 48 h, and between 1 h and 720 h in this study. The results are shown in Table 3. Consistently lower n values were observed over the period of 1 h to 720 h for all soil samples, indicating an important contribution of this time period to nonlinear sorption after the initial uptake. In other words, nonlinear sorption may have mainly occurred in the slower sorption process.

Table 3: The Freundlich Fitting results of subsequent sorption intervals of (48⁻¹) h and (720⁻¹) h.

Time intervals	Soil samples	Freundlich equation					Single point K_d^a (mL·g ⁻¹)	
		n	std ^b	lg K_F (μg·g ⁻¹)	std ^b	r^2	$C = 0.1 C_s$	$C = 0.01 C_s$
(48 ⁻¹) h	1	0.76	0.04	1.67	0.07	0.97	20	34
	2	0.73	0.06	1.89	0.14	0.93	37	69
	3	0.70	0.12	1.62	0.24	0.74	22	44
	4	0.73	0.03	2.19	0.07	0.98	73	137
	5	0.71	0.01	2.19	0.03	1.00	79	155
	6	0.84	0.03	2.29	0.08	0.99	60	87
	7	0.73	0.04	2.49	0.10	0.92	147	276
	8	0.68	0.04	2.48	0.36	0.99	175	371
(720 ⁻¹) h	1	0.72	0.08	1.90	0.18	0.86	40	76
	2	0.53	0.07	1.34	0.17	0.81	22	65
	3	0.55	0.04	1.56	0.11	0.93	34	98
	4	0.66	0.09	2.10	0.26	0.80	78	171
	5	0.55	0.03	2.25	0.08	0.97	166	464
	6	0.63	0.05	2.04	0.12	0.94	76	179
	7	0.70	0.04	2.61	0.10	0.96	219	441
	8	0.70	0.08	2.13	0.25	0.85	73	148

a: K_d is calculated by $K_F \cdot C^{(n-1)} \cdot C_{scl}^{-n}$.

b: standard deviation of fitted parameters.

C_s : the solubility of PHE in water at 25°C (1.29 μg·mL⁻¹).

According to the discussion of PDRs by Weber and Huang,^[6] sorption processes may be modeled as three stages (i.e., initial, logarithmic, and apparent equilibrium) derived from different behaviors of three sorption domains (exposed inorganic surfaces, amorphous soil organic matter, and condensed soil organic matter) at different time intervals. Domain III, as the most condensed region, predominated the sorption after the initial fast stage. In addition, the condensed sorbents usually showed the strongest nonlinearity as reported by numerous studies.^[3,13,14] Similarly, this study reveals the relatively strong nonlinearity of a later sorption stage (between 1 h and 720 h).

Furthermore, significant correlation between sorption nonlinearity and resistance to desorption has been also observed.^[15] Accordingly, lower n values for the time interval between 1 h and 720 h probably indicate that resistant sorption may result from slow sorption. Several other studies reported that nonlinear and slow sorption has great relevance with HOCs sequestration and their bioavailability decrease in soils.^[16,17] Therefore, it is of great importance to study the characteristics of later (slow) sorption stages.

Sorption Dynamics

Soil organic matter (SOM) has been considered as the main sink of hydrophobic organic chemicals.^[18] Xia and Pignatello observed the conditioning

effect of the solvent or sorbate on SOM.^[19] They demonstrated that the structure of SOM may be altered by absorbing organic chemicals, and then the sorption properties of SOM can be influenced as a consequence. As discussed earlier on K_d and f_{oc} , TOC content is the most important soil property affecting its sorption capacity. Therefore, solid-phase concentrations, S , were normalized by organic carbon as S_{oc} ($\mu\text{g}\cdot\text{gOC}^{-1}$), and the S_{oc} s were in the same range for comparing the sorption dynamics of PHE on eight soils in this work. The conditioning effect was thus supposed to be in the same range if any. Dynamics data fitting using equations 1 and 6 was based on organic carbon normalized solid-phase concentrations. The overall results are presented in Table 4, and the fitting of dynamics data are illustrated in Figure 4 using soil sample No. 5 as an example. The one-compartment model was not satisfactory to describe the data with longer times due to underestimation of slow sorption, while the two-compartment model showed good fit of the sorption process (Fig. 4). The fitting results were similar for the other seven soils. The two-compartment model (Eq. 1) showed much higher r_{adj}^2 than the one compartment model (Eq. 6), as shown in Table 4.

Current sorption models considered the sorption of HOCs by SOM as a multi-domain process^[20] or more practically two-domain process.^[3] The two-compartment, first-order model (Eq. 1) has been proven to be more appropriate to describe sorption dynamics than other models.^[4] The sorption characteristics of the two compartments could be recognized by the different sorption rate constants. As could be seen in Table 4, the dynamics constants of the two compartments differed 18-170 times in this study, comparable to the literature results of 33-104 times for other geosorbents.^[4]

According to the sorption rate constants, the two compartments could be designated as the “fast” and “slow” compartments, respectively. The fast

Table 4: Fitting results of one-compartment and two-compartment first order models.

Soil samples	m^a	One-compartment first order modeling		Two-compartment first order modeling				
		k (h)	r_{adj}^2	k_1 (h^{-1})	k_2 (h^{-1})	f_1	k_1/k_2	r_{adj}^2
1	18	0.87	0.81	2.40	0.04	0.49	66	0.97
2	18	1.96	0.93	2.78	0.02	0.79	133	0.94
3	18	1.61	0.92	2.92	0.04	0.70	78	0.97
4	18	1.87	0.94	7.24	0.35	0.55	21	1.00
5	17	4.70	0.90	10.55	0.21	0.70	51	1.00
6	18	1.81	0.95	6.23	0.35	0.56	18	0.99
7	18	2.39	0.98	3.69	0.09	0.81	39	0.99
8	18	2.97	0.98	3.48	0.02	0.87	170	1.00

^aNumber of data points used for fitting.

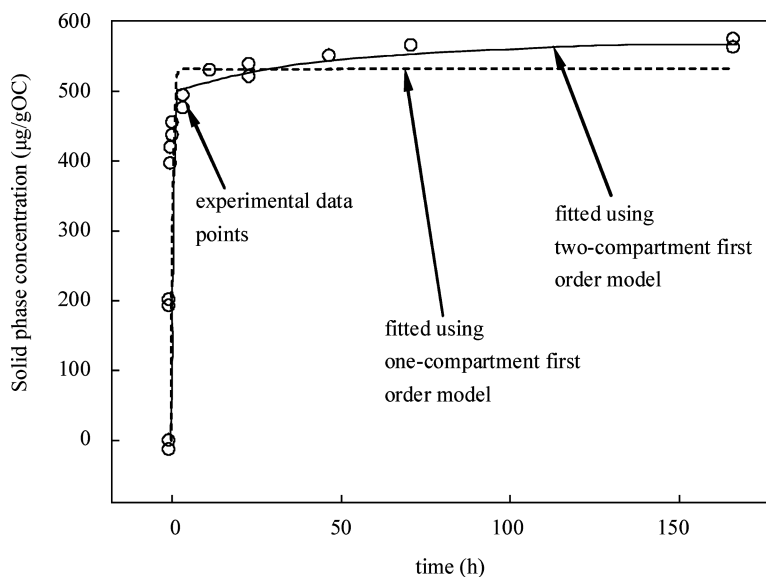


Figure 4: Typical fitting results of sorption dynamics data of No. 5 soil sample (dashed line: fitted using one-compartment first order model; solid line: fitted using two-compartment first order model).

compartment possesses a higher rate constant than the slow compartment. As shown in Figure 5, in a relatively short sorption period, such as 1h, the fast compartment reached more than 90% of its own sorption capacity for all the eight soil samples, while the slow compartment only reached below 20% of its sorption capacity for most soils (Fig. 5a). The fast sorption was predominant at short contact time by more than 80% of total sorption (Fig. 5b). The sorption contributed by slow compartment occurred mainly at the longer contact time, e.g. between 1 h and 48 h in this study (Fig. 5c and 5d). Considering the slow sorption compartment, over 80% of its total sorption happened in this later time interval (Fig. 5c) and accounted for 80%–100% of the overall sorption for most of the eight soil samples (Fig. 5d). Therefore, the two compartments controlled the sorption at two different contact times. As the aforementioned discussion on the sorption characteristics of different time intervals, a relatively linear sorption was observed at the initial time interval (1 h) when the fast compartment predominated, while more nonlinear sorption was observed at a subsequent time interval (in the following 47 h). The different contributions of the two compartments to linear and nonlinear sorption were thus differentiated. Although it is difficult to correlate sorption compartments with actual soil components directly with the present experiment, this research emphasized the mathematical recognition and distinct sorption properties of two compartments, thus providing additional support for multi-domain sorption.

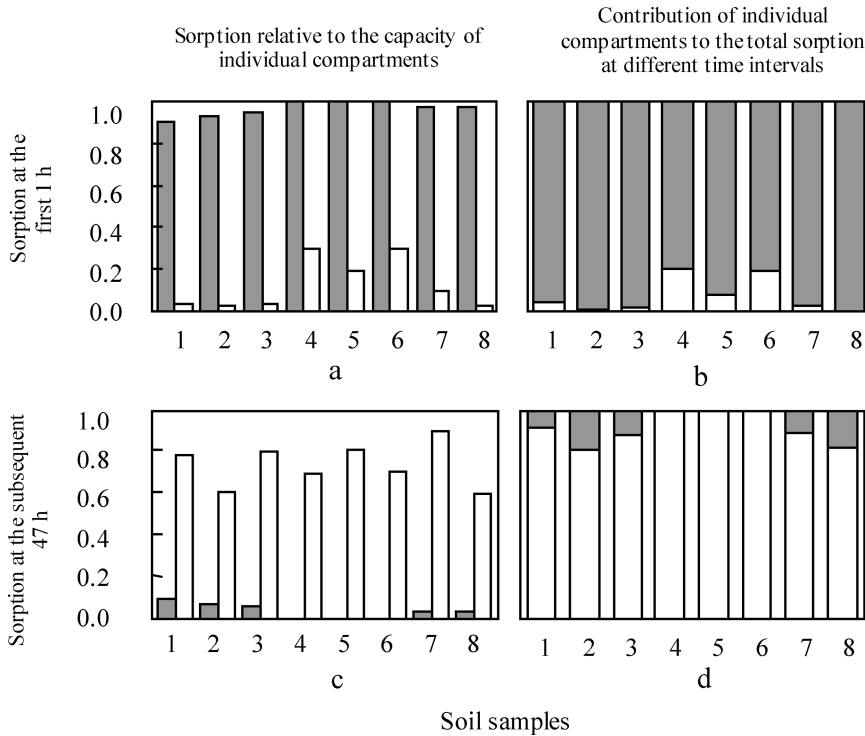


Figure 5: Contribution of two compartments to solid-phase concentration at 1 h and the subsequent 47 h. The black bars (■) stand for the fast compartment and the white bars (□) denote the slow compartment. Left plots (a) and (c) represent the sorption relative to the capacity of individual compartments. Right plots (b) and (d) illustrate the contribution of the two compartments to total sorption at different time intervals.

CONCLUSIONS

Phase distribution relationships (PDRs) of PHE were examined on eight soils that varied in TOC content from 0.4–7.9% at 1 h, 48 h, and 720 h, and nonlinear sorption was observed to increase as the contact time increased. A modified subtraction method showed that the sorption between 1 h and 720 h exhibited the strongest nonlinearity, indicating that sorption occurring over a prolonged period has a major influence on sorption nonlinearity. The direct description of the contribution of the subsequent sorption after the initial fast stage to the overall nonlinearity was thus achieved. Two-compartment first order modeling revealed that the dynamics constants of the two compartments differed by 18–170 times, indicating distinct sorption behaviors in these mathematically defined compartments. Combining the results of PDRs at different time intervals and dynamics modeling, it is concluded that the slow sorption compartment has the major contribution to nonlinear sorption. The slow sorption may be related to soil humin fractions,^[21,14,22] which needs further investigation for

their significance and quantitative relationships for HOCs sequestration and bioavailability in soils and sediments.

ACKNOWLEDGMENTS

Financial support was provided by the National Natural Science Foundation of China (Grant 40428005, 40332015 and 40021101), National Basic Research Program (Grant 2003CB415004), and Federal Hatch program (Project #: MAS 860).

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