

Sorption and desorption behaviors of PAHs in soil and sediments

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<Abstract>

Batch experiments were conducted to investigate the sorption and desorption behaviors of PAHs (naphthalene, phenanthrene and pyrene) in soils. Three different soils montmorillonite KSF (foc = 0.14%), masato (foc = 0.08%), and diatomite (foc = 0.007%) were investigated. The results of sorption-desorption experiment indicate that the sorption affinity of PAHs was in the order of montmorillonite > masato > diatomite. The Freundlich model was well fitted to the sorption and desorption data. Sorption affinity increased as foc increased. Desorption of PAHs from soils was biphasic composed of reversible and irreversible compartments. Desorption-resistance of phenanthrene in soils was also determined. The biphasic desorption model was used to explain desorption-resistance of phenanthrene in soils. The linear term represents reversible sorption fraction and Langmuinian-type term represents desorption-resistant fraction.

Key words : soil organic carbon, desorption-resistance, Freundlich isotherm, biphasic desorption model.

1. Introduction

The carcinogenic and harmful properties of PAH have led to much interest. Partitioning of these compounds into organic matter in soil is thought to be the main mechanism for their sorption in soil-freshwater systems. Soil organic carbon (SOC) will greatly affect the sorption and subsequent desorption of hydrophobic contaminants. The SOC present in the montmorillonite enabled a relatively easy sorption in comparison to the other two soils. Nonlinear isotherms suggest that the sorption mechanism was a heterogeneous adsorption process occurring on the surfaces of residual organic matter and the bare inorganic minerals in the soils. Our research shows that the capability of sorption in soils is significantly correlated with organic carbon content of the soils. The sorption occurred principally via partition function of organic carbon of soils. Organic matter is the primary sorbent for organic compounds. Partitioning of these compounds into organic matter is considered to be the main

mechanism for their sorption in soil-freshwater systems.

Desorption of phenanthrene from natural soils has been observed to be biphasic, containing reversible and irreversible compartments. Numerous studies have observed that the release of organic contaminants is biphasic, including an equilibrium fraction and a highly resistant (irreversible) fraction. For soil-associated PAHs, the irreversible adsorbed fraction is the greatest concern and uncertainty, because it significantly affects chemical fate, toxicity, risk to human and aquatic life, and efficiency of most remediation technologies. Therefore, characteristics of desorption from the irreversible compartment need to be further understood to develop more useable adsorption-desorption models. Therefore, sorption/desorption study was conducted to determine desorption-resistance of hydrophobic organic compounds in natural soils. Desorption was biphasic with phenanthrene of the sorbed mass residing in the desorption-resistance fraction after several desorption steps. The biphasic behavior of the sorption desorption isotherm was quantified with two terms: a linear term to represent reversible sorption and a Langmuir term to represent irreversible sorption. Batch experiments with phenanthrene were conducted to quantify the effect of soil organic carbon (SOC) on its sorption and desorption behaviors in soils.

2. Materials and Methods

Soils

Three different soils: diatomite, montmorillonite and masato were used in this study. Sieved soil samples were used to obtain a particle size of less than 212 μm . Table I shows the characteristics of the soil samples.

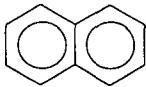
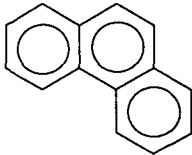
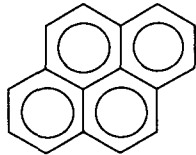
Table 1. Summary of soil characteristics (wt%)

Soil	Total Carbon	Organic Carbon
Montmorillonite	0.144	0.144
Masato	0.124	0.082
Diatomite	0.085	0.007

Chemicals

Radiolabeled [1- ^{14}C] Naphthalene (ChemSyn Laboratories, Inc., 58.4 mCi/mmol), [9- ^{14}C] Phenanthrene (ARC, 55 mCi/mmol) and [4,5,9,10- ^{14}C] Pyrene (ChemSyn Laboratories, Inc., 53.2 mCi/mmol) were used as radiotracer. The [^{14}C] compounds were further diluted with unlabeled PAH (Aldrich, HPLC grade, >96%) stock solution to yield desired concentrations. Sodium azide (200 mg/L) was added to the solution as a bacterial inhibitor. PAH solution was prepared before each adsorption experiment using the ^{14}C stock solution and an electrolyte solution containing 1 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.5mM MgCl_2 . and 1 mM $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Table 2 shows the physicochemical characteristics of the PAHs used.

Table 2. Physicochemical properties of PAHs.

Compound	Naphthalene	Phenanthrene	Pyrene
Mw	128.17	178.23	202.26
Solubility (mg/L)	31	1.15	0.135
Log Kow	3.30	4.46	4.88
Molecular Structure			

Batch Sorption and Desorption Experiment

Experiments were performed in batch using single-step sorption desorption and sequential desorption. Single-step sorption needs two days followed by desorption. Then the experiment was performed using sequential desorption cycling. A sequential desorption cycle constitutes a series of single-step sorptions followed by sequential desorptions. The sorption and desorption experiments were conducted in amber glass vials with a total volume of approximately 40-ml sealed with Teflon-faced silicone septa. Control experiments were conducted to investigate sorption of chemicals on surface of the glassware. The sorption of PAH on the glass surface was minimal. Predetermined amounts of soils: Diatomite (2g), montmorillonite (0.02g) and masato (0.05g) were used.

Single-Step Sorption and Desorption

Considering the solubility of Naphthalene, Phenanthrene and Pyrene, different concentration solutions: Naphthalene: 1~25 mg/L, Phenanthrene: 0.05~1 mg/L and Pyrene: 0.005~0.1 mg/L were prepared. After filling the vials with soil and the spiking solutions, the headspace in the vial was kept minimal. The soil/water mixture was horizontally mixed at 150rpm in a shaker bath at room temperature. After 2 days, the soil was separated from the solution by centrifugation at 1,500 rpm for 30 minutes and the chemical concentration in supernatant was analyzed via liquid scintillation counter (LSC, EG&G Wallac Co., 1220 Quantulus). Approximately 95% of the supernatant was gently removed using a pipette and re-spiked with electrolyte solution to conduct desorption step.

Sequential desorption

In this experiment we used the left solutions which were the highest concentration solution in single-step sorption and desorption to do the sequential desorption to investigate the desorption-resistance. Method is same with the desorption step. The actual amount of supernatant removed and added was determined gravimetrically. The desorption cycle was repeated until liquid-phase concentration became stable.

3. Sorption and Desorption Models

Single-Solute sorption/Desorption Model

Freundlich model was used to fit the single-solute sorption/desorption of PAH

$$q = K_{FC} \cdot C^N \quad (1)$$

Where C (mg L⁻¹) is the solute concentration in the aqueous solution at equilibrium, q (mg g⁻¹) is the solute concentration in the solid phase at equilibrium, and K_F [(mg g⁻¹)/(mg L⁻¹)^N] and N (dimensionless) are Freundlich parameters.

Biphasic desorption model

The biphasic model is defined as (Kan et al., 1998):

$$q = q^{rev} + q^{irr} = K_p \cdot C + \frac{bQ^0 C}{1 + bC} \quad (2)$$

Where q (mg/g) = total concentration of sorbed compound in the soil phase, q^{rev} (mg/g)=the concentration of sorbed compound in the labile fraction and q^{irr} (mg/g)=the concentration of sorbed compound in the desorption-resistant (non-labile) fraction, K_p = linear partition coefficient (mg/g/mg/L), C = chemical concentration in solution phase (mg/L), and b and Q^0 are the Langmuir site energy and capacity factor for the nonlinear component of DRDM, respectively.

$$q = q^{rev} + q^{irr} = K_{oc} \cdot f_{oc} \cdot C + \frac{K_{oc}^{irr} \cdot f_{oc} \cdot q_{max}^{irr} \cdot f \cdot C}{q_{max}^{irr} \cdot f + K_{oc}^{irr} \cdot f_{oc} \cdot C} \quad (3)$$

where K_{oc}^{irr} = partition coefficient of the desorption-resistant fraction, f = fraction of compound residing in the desorption-resistant compartment, and q_{max}^{irr} = maximum capacity of the desorption-resistant fraction.

4. Results and Discussion

Single-solute sorption/desorption isotherms

In according to similar observations for a wide range of natural solids (Huang et al., 1997), the isotherms we observed for the soils were all nonlinear. The Freundlich sorption model was used to fit all sorption and desorption equilibrium data. The K_F and N parameters in Eq (1) are the Freundlich capacity coefficient and the site energy heterogeneity factor. Values of the resulting K_F and N parameters, along with their standard deviations, number of observations, and R^2 values, are shown in

Tables 3 and 4. Single-solute sorption isotherms of PAH onto montmorillonite, masato, and diatomite are shown in Fig. 1a, 1b, and 1c, respectively.

Sorption affinity was found to be in the order montmorillonite > masato > diatomite on all the PAH, mainly due to the different soil organic carbon content between the soils (Table 1). Organic carbon content increased in the order montmorillonite (0.14%) > masato (0.0816%) > diatomite (0.0068%). The role of organic matter in soils was similar to that of an organic solvent in solvent extraction, and therefore the partitioning of a neutral organic compound between soil organic matter and water should correlate with its partitioning between an immiscible organic solvent and water.

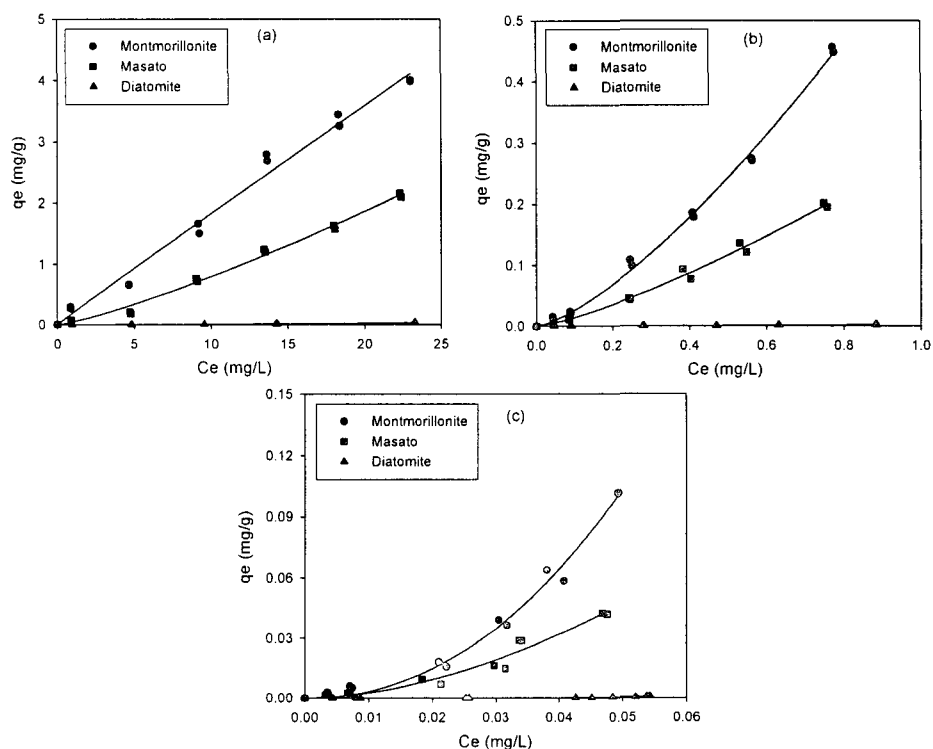


Figure 1. Single-solute sorption of PAHs onto montmorillonite, masato, and diatomite. (a) Naphthalene, (b) Phenanthrene, and (c) Pyrene. Lines indicate Freundlich isotherm.

Table 3. Single-solute sorption model parameters.

Sorbent	PAHs	KF	N	R2
Montmorillonite	Naphthalene	0.1930±0.0328	0.9754±0.0585	0.988
	Phenanthrene	0.6351±0.0134	1.3857±0.0407	0.997
	Pyrene	59.328±22.767	2.1218±0.1228	0.989
Masato	Naphthalene	0.0464±0.0076	1.2319±0.0563	0.993
	Phenanthrene	0.2872±0.0098	1.3018±0.0601	0.992
	Pyrene	9.9427±5.9284	1.7839±0.1857	0.962
Diatomite	Naphthalene	0.0002±3.87 10 ⁻⁵	1.6060±0.0677	0.996
	Phenanthrene	0.0028±0.0001	1.7467±0.1229	0.983
	Pyrene	84,839.5±890.6	6.3479±0.0458	0.876

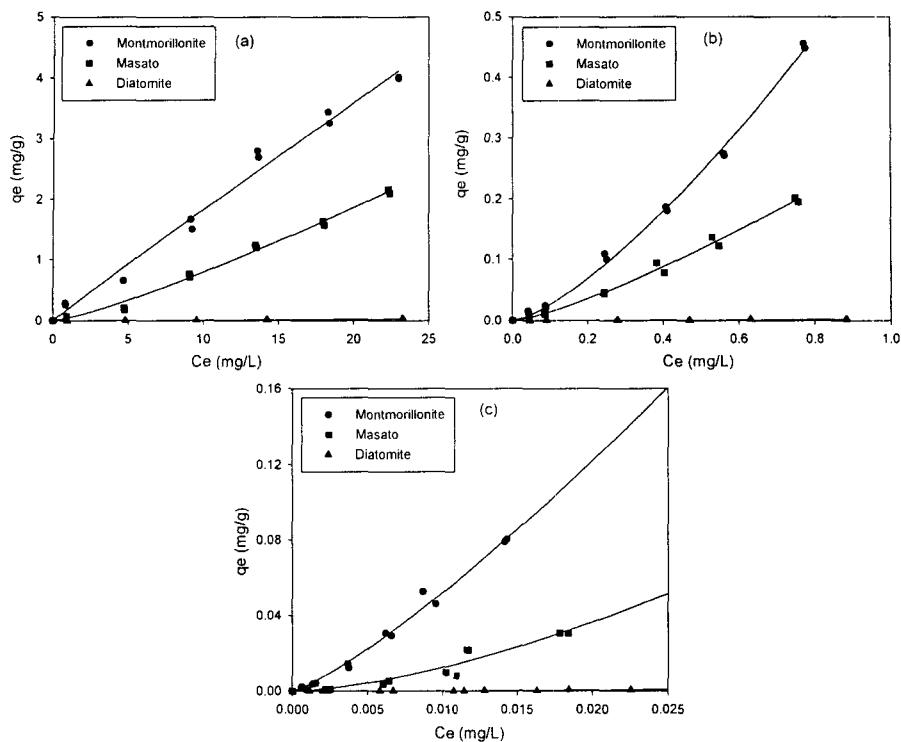


Figure 2. Single-solute desorption of PAHs from montmorillonite, masato, and diatomite. (a) naphthalene, (b) phenanthrene and (c) pyrene. Lines indicate Freundlich isotherm.

Table 4. Single-solute desorption model parameters.

Sorbent	PAHs	K_F	N	R^2
Montmorillonite	Naphthanele	1.8322 ± 0.1144	0.8551 ± 0.1137	0.937
	Phenanthrene	2.2782 ± 0.3588	1.0674 ± 0.0718	0.984
	Pyrene	15.081 ± 4.326	1.2315 ± 0.0642	0.989
Masato	Naphthanele	0.9556 ± 0.0580	0.8593 ± 0.0984	0.949
	Phenanthrene	1.7626 ± 0.3881	1.4928 ± 0.1082	0.983
	Pyrene	16.1866 ± 15.08	1.5591 ± 0.2230	0.926
Diatomite	Naphthanele	0.0065 ± 0.0011	1.4515 ± 0.1953	0.958
	Phenanthrene	0.2484 ± 0.1238	2.9021 ± 0.2741	0.972
	Pyrene	3.2010 ± 5.0722	2.2073 ± 0.4501	0.864

Biphasic desorption

Sequential desorption experiments were conducted with phenanthrene using Tenax bead. In the sequential desorption experiments, the desorption time for Phenanthrene was 1 day. Results indicate that appreciable size of desorption-resistant fraction does exist in the natural soils with low organic carbon content. An irreversible adsorption-desorption isotherm has been proposed by the authors (Kan et al., 1998) to describe the biphasic adsorption and desorption of both the laboratory and field observations. It is proposed that the labile fraction follows a linear isotherm, while the nonlinear behavior associated with the irreversible fraction can be described by a Langmuirian type of isotherm.

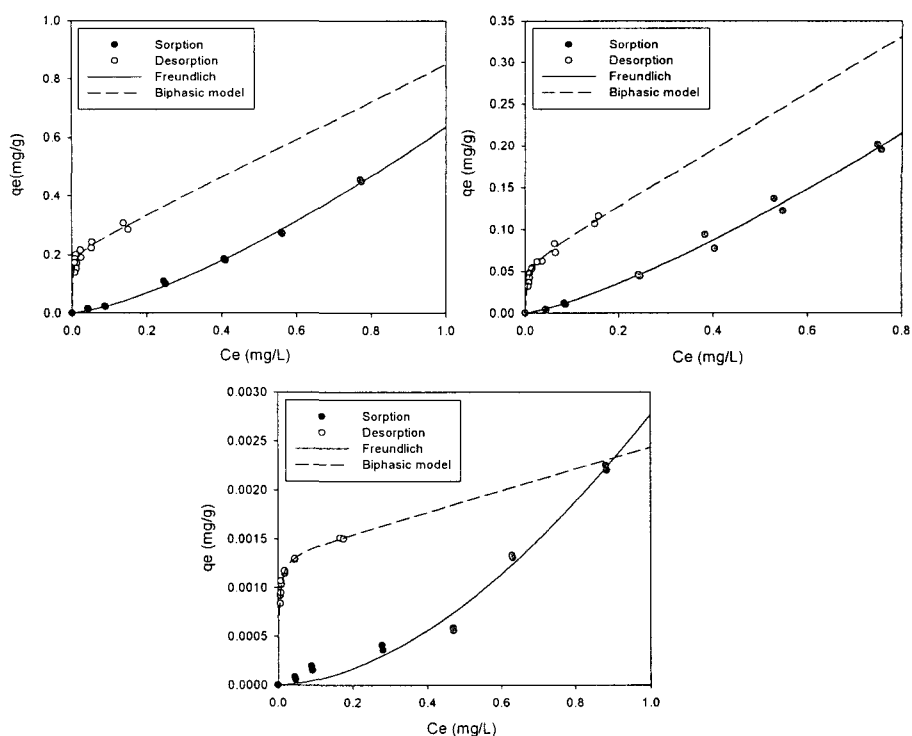


Figure 3. Single-step sorption and sequential dsorption of PAHs in montmorillonite, masato, and diatomite. (a) naphthalene, (b) phenanthrene and (c) pyrene. Solid line indicates Freundlich isotherm and dashed line indicates biphasic desorption model.

In Figure 3, the biphasic desorption model containing both the linear reversible compartment and the nonlinear irreversible compartment was fitted to desorption data. The solid lines in Figure are fitted isotherms using Eq. 1 and the observed K_F and N values from the sorption experiments (summarized in Table 3). The dashed lines are the biphasic desorption models plotted with the K_p , b , and Q values observed in sequential desorption experiments (in Table 5).

Table 5. Biphasic desorption model parameters for PAHs in several soils.

Sorbent	$q_{\max}^{irr} \cdot f$	K_p	$\log K_{oc}$	$\log K_{oc}^{irr}$	b	R^2
Diatomite	0.0013	0.0011	1.21	6.66	310.33	0.953
Masato	0.0608	0.3377	2.62	5.39	201.83	0.980
Montmorillonite	0.2069	0.6428	2.65	5.41	374.54	0.876

5. Conclusions

Soil organic carbon is highly variable in soils. Sorption of organic compounds depends on the soil organic carbon content. The soil organic carbon plays a major role in governing sorption of organics. Biphasic sorption model was used to explain desorption-resistance in natural soils with low organic carbon content. The results of the biphasic sorption model consistently indicate that appreciable desorption-resistance exists in natural soils.

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