

Sorption Kinetics of Hydrophobic Organic Compounds in Wetland Soils

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습지 토양에서 소수성 유기화합물의 흡착 동력학. 신원식* · 박제철 (금오공과대학교 환경공학과)

자연습지 토양에서 소수성 유기화합물(염화벤젠 및 페난쓰린)의 흡착동력학을 실험실규모의 회분식 반응기를 이용하여 조사하였다. 단일영역 물질전달모델(one-site mass transfer model, OSMTM)과 두영역 1차속도모델(two compartment first-order kinetic model, TCFOKM)을 사용하여 흡착속도를 분석하였다. OSMTM 분석결과 염화벤젠의 경우 10~75시간 이내에, 페난쓰린의 경우 약 2시간 이내에 각각 길보기 흡착평형에 도달하였다. 염화벤젠의 경우, 표면 토양에서의 흡착평형시간이 하부 토양보다 길게 나타났는데, 이는 토양 유기탄소의 물리화학적 특성의 차이에 기인한다. 그러나, 페난쓰린의 경우 각 토양간에 흡착평형시간의 차이는 없었다. 관련 모델매개변수의 수에서 기대되듯이 변수가 3개인 TCFOKM이 변수가 2개인 OSMTM보다 흡착속도를 더 잘 표현할 수 있었다. 실험결과에 대한 TCFOKM의 곡선맞춤으로부터 얻은 매개변수인 빠른 흡착영역의 분율(f_1)과 빠른 흡착영역과 느린 흡착영역의 1차 흡착속도 상수(k_1 및 k_2)를 얻을 수 있었다. TCFOKM 분석결과 빠른 흡착영역에서의 흡착속도 상수는 느린 흡착영역에서의 흡착속도 상수 보다 큰 것으로 나타났다. 빠른 흡착영역의 분율(f_1)과 흡착속도상수(k_1)는 K_{ow} 값이 증가(페난쓰린 > 염화벤젠)함에 따라 증가하였다. 빠른 흡착영역과 느린 흡착영역에서의 1차 흡착 속도상수는 각각 $10^{-0.1} - 10^{+1}$ 과 $10^{-4} - 10^{-2}$ 의 범위에서 변화하였다.

Key words : sorption, kinetics, chlorobenzene, phenanthrene, and wetland peat soils

INTRODUCTION

Sorption and desorption have been received considerable attention as the most important processes controlling interaction between hydrophobic organic contaminants and soils/sediments. Numerous studies have shown that the fate and transport of hydrophobic organic compounds (HOCs) in soil is highly dependent on sorption/desorption characteristics (Brusseau and Rao, 1989; Ball and Roberts, 1991; Brusseau, 1995; Pignatello and Xing, 1996; Xing and Pignatello, 1997, 1998). Sorption of organic com-

pounds in soils and sediments has long been considered a reversible process in assessing risk and determining remedial endpoints. The currently adopted sediment quality criteria (SQC) are based on equilibrium partition models considering reversible sorption only. However, reversible models were not able to explain the long-term persistence of contaminants at many sites. The existence of a desorption-resistant (or sequestered) fraction of HOCs in soil has been identified (Fu *et al.*, 1994; Hatzinger and Alexander, 1995; Hunter *et al.*, 1996; Kan *et al.*, 1998; White *et al.*, 1999; Chen *et al.*, 1999, 2000) and the quality of organic matter is critical in determin-

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ing the magnitude of the desorption-resistant effect. Desorption of organic contaminants is biphasic including a labile fraction and a highly resistant fraction. Desorption-resistance or "irreversible sorption" has been recognized as an important phenomenon for understanding fate of organic contaminants in soils and sediments, because it significantly affects chemical fate and transport, bioavailability, toxicity, and remediation strategies. Therefore, characterization and quantification of desorption-resistant phase should be fully understood to develop more appropriate sorption-desorption models.

Although the mechanism of the desorption-resistance or "irreversible sorption" has not yet been determined, several important characteristics of this phenomenon have been identified. HOCs residing in this phase have much higher partition coefficients than would be predicted by the properties of the contaminants and the organic fraction of the soil. In fact, the partitioning of HOCs with widely different octanol:water partition coefficients (K_{ow} s) is very similar in the desorption-resistant phase. In addition, the size of the desorption-resistant fraction appears to be predictable for sediments. An accurate estimation of this desorption-resistant phase is very important in remediation because sequestration (or aging) of contaminants directly related to limited bioavailability (Huang and Weber, 1997).

Several reports have shown that desorption-resistant compartment has a finite maximum capacity (Kan *et al.*, 1998; Chen *et al.*, 1999; 2000). At high solid phase concentrations, the overall desorption is dominated by desorption from the labile fraction exhibiting an apparent linear isotherm. At low concentrations, finite portion of the sorbed compounds resides in desorption-resistant phase. Once the maximum capacity is reached, subsequent sorption and desorption becomes reversible.

An accurate estimation of desorption-resistance may have wide implications on the remediation of HOCs in natural environments. Only a few studies were conducted on the sorption and desorption of HOCs in wetland peat soils (Pardue *et al.*, 1993; Alvord and Kadlec, 1995; Lyon, 1995; Deitsch *et al.*, 1998; Deitsch and Smith, 1999; Chiou *et al.*, 2000). In this paper, sorption characteristics of chlorobenzene and phenanthrene in wetland peat soils with high organic carbon content. Sorption kinetic model para-

eters were determined to explain rate-limited sorption of chlorobenzene and phenanthrene.

In this work, natural wetland soils were used as sorbent. Chlorobenzene and phenanthrene were used as sorbates. Sorption experiments were carried out in a batch-type adsorber and were analyzed using one-site mass transfer model (OSMTM) and two-compartment first-order kinetic model (TCFOKM). The objective of this study is to examine sorption kinetics of HOCs in wetland soils. The results of this study may provide a valuable insight into the fate and transport of organic contaminants in wetlands.

MATERIALS AND METHODS

Soil sampling

Two wetland soils were used as sorbents in this study. The soil properties were determined by Huffmann Laboratories, Inc. (Golden, CO, USA) and are summarized in Table 1. Wetland soils (from surface (0~2 cm) and deeper (10~15 cm) horizons) were obtained from a fresh marsh near Madisonville, LA, USA. Surface soils were assumed to have more recently deposited organic matter than the deeper soils. Since accretion in this marsh is approximately 0.5 cm/year, the top horizon was assumed to be 0~4 years old and the deeper soil was >20 years old. The organic matter age can be inferred using the elemental ratio in the organic matter (Table 1). The H/C, O/C, and C/N ratios were increasing with depth confirming our assumptions of organic matter age of the wetland soils. The use of H/C and O/C ratios has been proposed as a measure of organic matter age related to sorption properties (Garbarini and Lion, 1986; Gauthier *et al.*, 1987;

Table 1. Summary of soil characteristics by Huffman Laboratories, Inc. (Golden, CO, USA). Data indicates percentage per g of dry soil.

Component	Surface soil	Deeper soil
Total carbon (wt %)	27.58	23.14
Hydrogen (wt %)	3.93	3.38
Oxygen (wt %)	23.32	21.52
Nitrogen (wt %)	2.06	1.65
Sulfur (wt %)	1.00	1.01
Ash (wt %)	42.40	52.42
Carbonate carbon (wt %)	< 0.02	< 0.02
Organic carbon (wt %)	27.58	23.14

Table 2. Physicochemical properties of chlorobenzene and phenanthrene used.

Compound	M.W.	Solubility (mg/L)	log K_{ow} *
Chlorobenzene	112.56	497	2.84
Phenanthrene	178.23	1.18	4.46

*Octanol–water partition coefficient

Grathwohl, 1990; Rutherford *et al.*, 1992; Huang and Weber, 1997; Young and Weber, 1997; Perminiva *et al.*, 1999).

Sorbate and chemicals

Radiolabeled [^{14}C] compounds: chlorobenzene–UL– ^{14}C (Sigma, 2.7 $\mu\text{Ci}/\mu\text{mol}$, >98%) and [9, 10– ^{14}C] phenanthrene (ChemSyn Laboratories, 56.7 $\mu\text{Ci}/\mu\text{mol}$, >98%) were used as radiotracers. The [^{14}C] compounds were further diluted with unlabeled ^{12}C stock solutions (1,000 mg/L in methanol) to yield desired concentrations. ^{12}C –chlorobenzene (>99.9%) and –phenanthrene (>96%) were obtained in HPLC grades from Sigma Chemical Co., Inc. The physicochemical properties of chlorobenzene and phenanthrene are listed in Table 2. 200 mg/L of NaN_3 was added to the solution as a bacterial inhibitor. Chemical solutions were prepared before each sorption experiment using the ^{12}C stock solutions and an electrolyte solution containing 1 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1 mM MgCl_2 , and 0.5 mM $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (pH 8.0). The amount of methanol added to the vials was less than 0.1% (v/v) of the liquid so that it did not affect the cosolvent properties of the liquid significantly.

Sorption kinetic study

The sorption experiments were conducted in glass vials with a total volume of approximately 42–mL sealed with Teflon–faced silicone septa (Wheaton). To prevent adsorption of chemicals to the glassware, either carefully cleaned or pre-cleaned, EPA–certified vials (Fisher Scientific) were used. Control experiments were conducted to investigate sorption of chemicals on the surface of the glassware (data not shown). The adsorption of hydrophobic chemicals on the glass surfaces was negligible. Subsamples of the homogenized soil were transferred to the vial (water to soil ratio = 10 : 1, w/w) before the addition of chemical solutions at concentrations of 5 and 50

mg/L for chlorobenzene and 0.1 and 1.0 mg/L for phenanthrene, respectively. After filling the vials with soil sample and the spiking solution, the headspace in the vial was kept minimal. The soil/water mixture was horizontally shaken on an orbital shaker at room temperature. After predetermined time predetermined time intervals (10 min to 240 hours for CB and 1 to 48 hours for phenanthrene, respectively), the vials were collected and centrifuged at 2,500 rpm (about 550 g) for 30 minutes. The aqueous phase equilibrium concentration was analyzed via liquid scintillation. The solid phase equilibrium concentrations were calculated by assuming all concentration changes in solution phase result from sorption onto the solid phase. All experiments were run in triplicate.

SORPTION KINETIC MODELS USED

One–Site Mass Transfer Model (OSMTM)

One–site mass transfer model (OSMTM) (Nzungung *et al.*, 1997) was used to fit sorption of chlorobenzene and phenanthrene in wetland soils. In OSMTM, the sorption rate was represented as a first–order function of the concentration difference between the solution and sorbed phases. All sorption sites were assumed to be kinetically controlled. Sorption and desorption kinetics in the batch reactor are described as follows (Nzungung *et al.*, 1997):

Differential mass balance on a sorbate in a batch reactor is:

$$\frac{V}{M} \frac{dC}{dt} = k(q - K_p C) = k \frac{V}{M} \left((C_0 - C) - \frac{K_p M}{V} C \right) \quad (1)$$

where V and M are the volume of the solution phase (L) and the sorbent weight (g), respectively, and t is time (hr). K_p represents the partition coefficient (L/g), C and q denote the solute concentrations in the solution (mg/L) and in the solid phase at equilibrium (mg/g), respectively, and k is the mass transfer coefficient (hr^{-1}).

At equilibrium,

$$q_e = K_p C_e \quad (2)$$

where q_e (mg/g) and C_e (mg/L) denote the solute concentrations in the solid and aqueous phases at equilibrium, respectively.

The total mass balance in the batch reactor is written as:

$$M(q - q_0) = V(C_0 - C) \tag{3}$$

where C_0 and q_0 are the initial solute concentrations in the solution (mg/L) and in the sorbed phases, respectively. If fresh sorbent is used in sorption, $q_0 = 0$.

A simple algebraic rearrangement using Eq. (1) and Eq. (3) leads to:

$$\frac{dC}{dt} = k \left[C_0 - \left(1 + \frac{K_p M}{V} C \right) \right] \tag{4}$$

Integration of Eq. (4) yields:

$$\frac{C(t)}{C_0} = \frac{C_e}{C_0} + \left(1 - \frac{C_e}{C_0} \right) \exp \left[\left(- \frac{C_0}{C_e} k \right) t \right] \tag{5}$$

Values of C_e and k were estimated by fitting Eq. (5) to the sorption kinetic data using a non-linear least-squares optimization.

Two Compartment First-Order Kinetic Model (TCFOKM)

Overall sorption can be written as a sum of first-order sorption rate in the fast and slow compartments (Opdyke and Loehr, 1999):

$$\frac{C(t)}{C_0} = f_1 e^{-k_1 t} + (1 - f_1) e^{-k_2 t} \tag{6}$$

where f_1 and $f_2 (= 1 - f_1)$ are the fast and slow sorption fractions (unitless), respectively, and k_1 and k_2 are the sorption rate constants in the fast and slow compartments (hr^{-1}), respectively.

The three model parameters, f_1 , k_1 and k_2 , were determined by using a commercial software package, Table Curve 2D® (Version 5.0, SPSS, Inc.).

RESULTS AND DISCUSSION

Sorption experiments of chlorobenzene and phenanthrene were performed using natural fresh marsh soils. Sorption of chlorobenzene and phenanthrene with time in the wetland soils was depicted in Figs. 1-4. As indicated by a greater reduction in aqueous concentration, $C(t)$, sorption affinity was in the order of phenanthrene > chlorobenzene, mainly due to stronger sorption of more hydrophobic compound as well reflected by octanol to water partition coefficient, K_{ow} of each solute (Table 2).

Sorption kinetics of chlorobenzene

The two parameter OSMTM and three parameter TCFOKM were fitted to the sorption kinetic data and the model parameters of OSMTM and TCFOKM determined from the nonlinear curve fitting are listed in Tables 3 and 4, respectively. OSMTM is based on the assumption that sorption domain in soil is homogenous, while sorption domain of TCFOKM is divided into two regions: fast and slow fractions.

Sorption data of chlorobenzene at different initial concentrations in wetland soils were depicted in Fig. 1 ($C_0 = 5 \text{ mg/L}$) and 2 ($C_0 = 50 \text{ mg/L}$), respectively. As can be seen from Figs and Table 3,

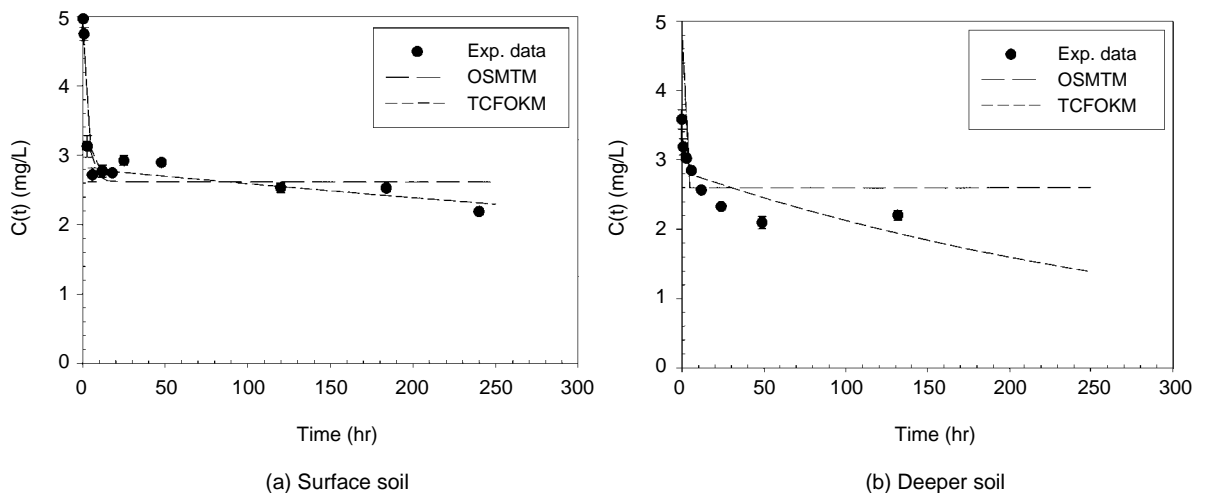


Fig. 1. Sorption kinetics of chlorobenzene in wetland soils. (a) surface and (b) deeper soil. ($C_0 = 5 \text{ mg/L}$)

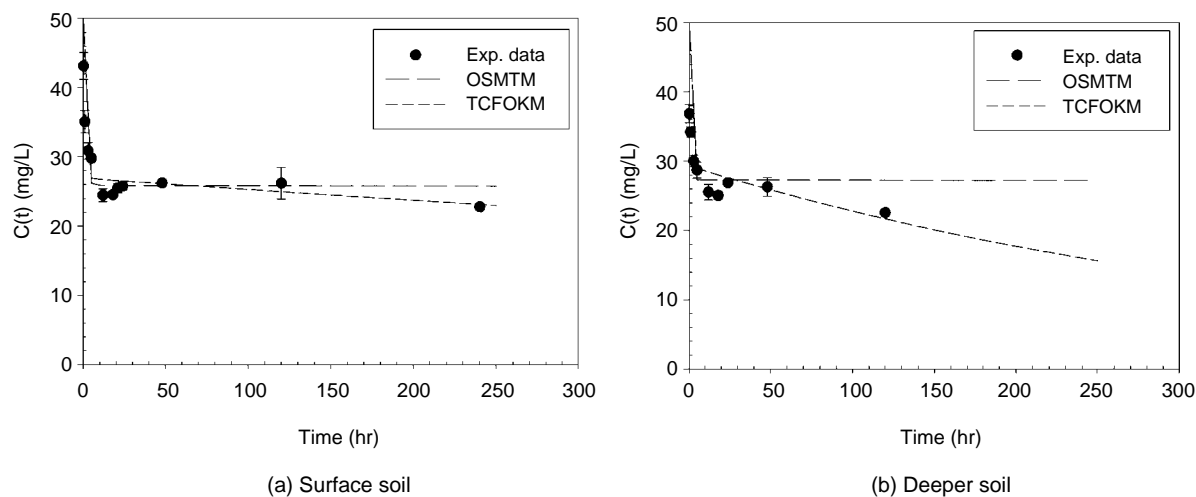


Fig. 2. Sorption kinetics of chlorobenzene in wetland soils. (a) surface and (b) deeper soil. ($C_0 = 50$ mg/L).

Table 3. One-site mass transfer model parameters for sorption of chlorobenzene and phenanthrene in wetland soils.

Compound	Soil	C_0 (mg/L)	C_e (mg/L)	k (h^{-1})	Equilibration time (hr)	R^2
CB	Surface	5	2.62 ± 0.12	0.178 ± 0.052	75	0.919
		50	25.88 ± 0.83	0.441 ± 0.111	35	0.859
	Deeper	5	2.59 ± 0.16	2.557 ± 1.312	10	0.445
		50	27.34 ± 1.25	2.511 ± 1.139	10	0.486
Phen	Surface	0.1	3.36×10^{-4} ($\pm 2.25 \times 10^{-5}$)	0.122 ± 0.012	1	0.643
		1.0	5.50×10^{-2} ($\pm 7.86 \times 10^{-3}$)	0.974 ± 0.240	2	0.421
	Deeper	0.1	4.58×10^{-3} ($\pm 5.92 \times 10^{-4}$)	0.926 ± 0.219	2	0.359
		1.0	5.42×10^{-2} ($\pm 2.67 \times 10^{-3}$)	0.798 ± 0.055	2	0.972

Number in parenthesis indicates the standard deviation.

apparent sorption equilibria were observed within 35 to 75 hours for surface soil and 10 hours for deeper soil, respectively. In other words, a substantial portion of the solute was sorbed within 10 to 75 hours, followed by a slow sorption over 240 hours of sorption period. Approximately 49% and 47% of chlorobenzene were sorbed in the surface and deeper soil, respectively, at the apparent equilibrium followed by slow sorption in the subsequent period of sorption. The results of OSMTM analysis listed in Table 3 indicate that the sorption rate constant (k) of deeper soil was greater than that of surface soil regardless of initial spiking chemical concentrations. For chlorobenzene, the result of TCFOKM analysis (Table 4) shows that the fast fraction (f_1) is slightly smaller than the slow fraction (f_2). The

sorption rate constant of fast sorption compartment (k_1) was much greater than that of slow sorption compartment (k_2).

Sorption kinetics of phenanthrene

Sorption of phenanthrene in wetland soils at different initial chemical concentration was presented in Fig. 3 ($C_0 = 0.1$ mg/L) and 4 ($C_0 = 1.0$ mg/L), respectively. As can be seen from Figs and Table 3, apparent sorption equilibria for phenanthrene were observed within first 2 hours for both surface and deeper soil. A substantial portion of phenanthrene was rapidly sorbed within the equilibration time, followed by a slow sorption over 48 hours of sorption period. Approximately 98% and 95% of phenanthrene were

sorbed in the surface and deeper soil, respectively, at the apparent equilibrium followed by slow sorption in the subsequent period of sorption. Unlikely to the observations in chlorobenzene, the result of TCFOKM analysis (Table 4) for phenanthrene shows that the fast fraction (f_1) is much greater than the slow fraction (f_2). Similarly to the results of chlorobenzene, the rate constant of fast sorption compartment (k_1) was much greater than that of slow sorption compartment (k_2).

Comparison of OSMTM and TCFOKM

Comparison of R^2 values of OSMTM (Table 3) and TCFOKM (Table 4) shows that TCFOKM was better fitted to the data than OSMTM for sorption of chlorobenzene and phenanthrene in wetland soils as expected from the number of

parameters involved in each model. The basic assumption of OSMTM is that the sorbent is homogenous and all sorption sites are assumed to be kinetically controlled. Since the wetland soils are highly heterogeneous consisted of mineral, soil organic carbon, debris of dead plants, etc., the applicability of OSMTM to the sorption kinetic data is rather limited. In Table 4, the first-order rate constant (k_1) in the fast sorption compartment increased in the order of chlorobenzene < phenanthrene, which agrees with the order of K_{ow} values. The first-order sorption rate constants in the fast (k_1) compartments were found to vary from $10^{-0.1}$ to $10^{+1.0}$ hr^{-1} , while those in the slow (k_2) compartments were varied from 10^{-4} to 10^{-2} hr^{-1} .

Opdyke and Loehr (1999) discussed that the precision of estimated k_2 is only good when

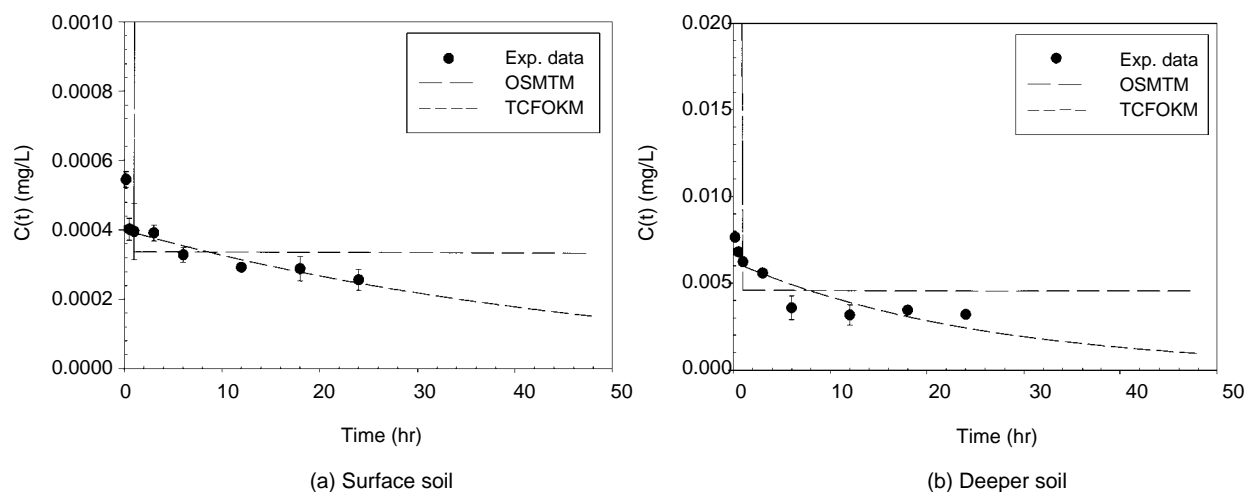


Fig. 3. Sorption kinetics of phenanthrene in wetland soils. (a) surface and (b) deeper soil. ($C_0 = 0.1$ mg/L).

Table 4. Two compartment first-order kinetic model parameters for sorption of chlorobenzene and phenanthrene in wetland soils.

Compound	Conc. (mg/L)	Soil	Fast compartment		Slow compartment		R^2
			f_1	k_1 (h^{-1})	$f_2 = 1 - f_1$	k_2 (h^{-1})	
CB	5.0	Surface	0.439	0.387 ± 0.115	0.561	$8.00 \times 10^{-4} (\pm 5.25 \times 10^{-4})$	0.937
	50	Surface	0.461	1.021 ± 0.255	0.539	$6.16 \times 10^{-4} (\pm 4.25 \times 10^{-4})$	0.889
	5.0	Deeper	0.434	6.166 ± 2.612	0.566	$2.89 \times 10^{-3} (\pm 1.32 \times 10^{-3})$	0.732
	50	Deeper	0.413	5.750 ± 2.141	0.587	$2.50 \times 10^{-3} (\pm 1.11 \times 10^{-3})$	0.737
Phen	0.1	Surface	0.996	38.317 ± 0.840	0.004	$2.00 \times 10^{-2} (\pm 2.75 \times 10^{-3})$	0.972
	1.0	Surface	0.930	19.953 ± 3.876	0.070	$3.07 \times 10^{-2} (\pm 1.79 \times 10^{-2})$	0.648
	0.1	Deeper	0.938	24.411 ± 3.999	0.062	$3.89 \times 10^{-2} (\pm 1.11 \times 10^{-2})$	0.840
	1.0	Deeper	0.945	14.750 ± 0.614	0.055	$4.62 \times 10^{-4} (\pm 3.39 \times 10^{-4})$	0.972

Number in parenthesis indicates the standard deviation.

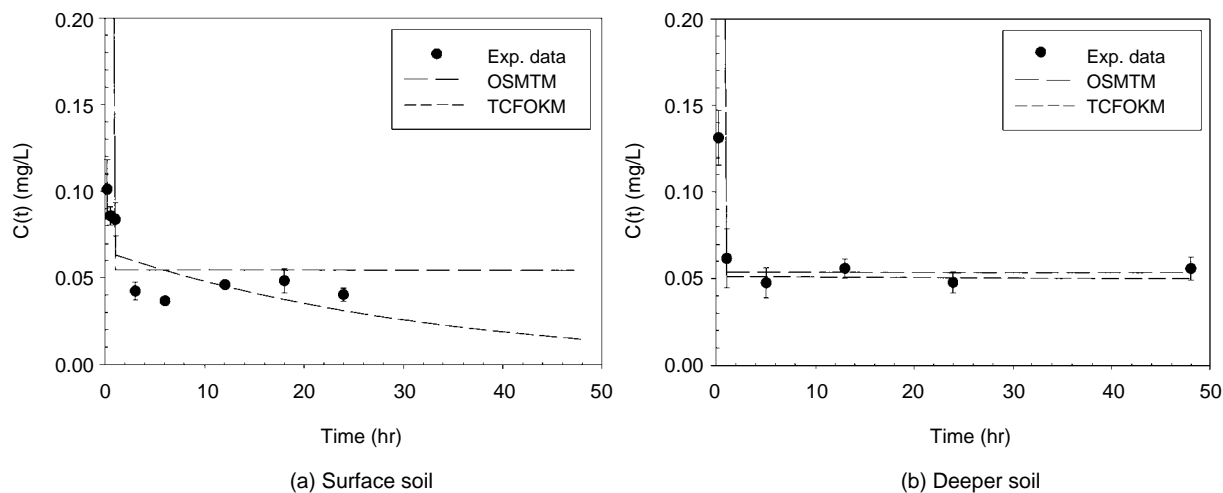


Fig. 4. Sorption kinetics of phenanthrene in wetland soils. (a) surface and (b) deeper soil. ($C_0 = 1.0$ mg/L).

experiments were conducted to near the time of $1/k_2$ that corresponds to 100 to 10,000 hours. An extension of time frame to 10,000 hours would be unrealistic for the sorption of HOCs in wetland soils because most of the fast sorption fractions are sorbed within several hours. Therefore, the precision of k_2 values obtained in this study may be unsatisfactory and only an order of magnitude estimate is useful in interpreting the time frame for the sorption in the slow sorption compartment. However, precision of k_1 in this study would be useful since the time frame in the fast compartment (t_1) is $10^{-0.1}$ to $10^{+1.0}$ hr (i.e., $1/k_1$).

CONCLUSIONS

The sorption kinetics of chlorobenzene and phenanthrene in fresh marsh wetland soils were investigated. Sorption affinity of phenanthrene was greater than that of chlorobenzene mainly due to stronger hydrophobicity as indicated by octanol to water partition coefficient (K_{ow}) of each solute. One-site mass transfer model (OSMTM) and two compartment first-order kinetic model (TCFOKM) were used to analyze sorption kinetics. Apparent sorption equilibria were obtained within 10 to 75 hours for chlorobenzene and 2 hours for phenanthrene, respectively. The relatively rapid equilibration is attributed to stronger sorption of phenanthrene as reflected by the log K_{ow} of the each solute.

Approximately 47~49% of chlorobenzene and

95~98% of phenanthrene were sorbed within the equilibration time and very little was sorbed in the subsequent period of sorption. The three-parameter TCFOKM was better than the two-parameter OSMTM in describing sorption kinetics of chlorobenzene and phenanthrene in wetland soils. The results of TCFOKM indicate that the sorption rate constants in the fast compartment (k_1) were much greater than those of slow fraction (k_2). The sorption rate constants in the fast compartments (k_1) were increasing in the order of increasing K_{ow} (i.e., chlorobenzene < phenanthrene) and rate constants in the fast compartment was much greater ($10^{-0.1} \sim 10^{+1.0}$ hr $^{-1}$) than those in the slow compartment ($10^{-4} \sim 10^{-2}$ hr $^{-1}$).

ABSTRACT

Sorption kinetics of hydrophobic organic compounds (chlorobenzene and phenanthrene) in natural wetland soils was investigated using laboratory batch adsorbers. One-site mass transfer model (OSMTM) and two compartment first-order kinetic model (TCFOKM) were used to analyze sorption kinetics. Analysis of OSMTM reveals that apparent sorption equilibria were obtained within 10 to 75 hours for chlorobenzene and 2 hours for phenanthrene, respectively. For chlorobenzene, the sorption equilibrium time for surface soil was longer than that of deeper soil presumably due to physico-chemical differences

between the soils. For phenanthrene, however, no difference in sorption equilibrium time was observed between the soils. As expected from the number of model parameters involved, the three-parameter TCFOKM was better than the two-parameter OSMTM in describing sorption kinetics. The fraction of fast sorption (f_1) and the first-order sorption rate constants for fast (k_1) and slow (k_2) compartments were determined by fitting experimental data to the TCFOKM. The results of TCFOKM analysis indicate that the sorption rate constant in the fast compartment (k_1) was much greater than that of slow fraction (k_2). The fraction of the fast sorption (f_1) and the sorption rate constant in the fast compartment (k_1) were increasing in the order of increasing K_{ow} , phenanthrene > chlorobenzene. The first-order sorption rate constants in the fast (k_1) and slow (k_2) compartments were found to vary from $10^{-0.1}$ to $10^{1.0}$ and from 10^{-4} to 10^{-2} , respectively.

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