

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5967791>

Desorption of Hydrophobic Compounds from Laboratory-Spiked Sediments Measured by Tenax Absorbent and Matrix Solid-Phase Microextraction

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · SEPTEMBER 2007

Impact Factor: 5.33 · DOI: 10.1021/es0700395 · Source: PubMed

CITATIONS

56

READS

52

4 AUTHORS, INCLUDING:



Jing You

Chinese Academy of Sciences

92 PUBLICATIONS 1,911 CITATIONS

SEE PROFILE



Sari Pehkonen

University of Eastern Finland

6 PUBLICATIONS 166 CITATIONS

SEE PROFILE



Michael J Lydy

Southern Illinois University Carbondale

195 PUBLICATIONS 5,148 CITATIONS

SEE PROFILE

Desorption of Hydrophobic Compounds from Laboratory-Spiked Sediments Measured by Tenax Absorbent and Matrix Solid-Phase Microextraction

JING YOU,[†] SARI PEHKONEN,[†]
PETER F. LANDRUM,[‡] AND
MICHAEL J. LYDY*,[†]

Fisheries and Illinois Aquaculture Center & Department of Zoology, 171 Life Science II, Southern Illinois University, Carbondale, Illinois 62901, and Great Lakes Environmental Research Laboratory, NOAA, 2205 Commonwealth Boulevard, Ann Arbor, Michigan 48105

Tenax extraction and matrix solid-phase microextraction (matrix-SPME) were used to study desorption of hydrophobic contaminants (HOC) from sediments. ¹⁴C-labeled hexachlorobiphenyl, DDE, permethrin, chlorpyrifos, and phenanthrene were individually spiked into sediments differing in physical characteristics. Sequestration of the HOCs into sediment was observed for all compounds, and desorption was described by rapid, slow, and very slow rates. The freely dissolved HOC concentration in the sediment porewater was estimated by matrix-SPME, and serial sampling was used to ensure equilibrium was achieved among sediment, porewater and matrix-SPME fiber. Differences in partitioning of the HOCs between sediment and porewater for the different sediments were reduced by replacing the HOC concentration in sediment with the rapidly desorbing fraction. The significantly lower porewater concentration determined from matrix-SPME, than predicted from equilibrium partitioning theory (EPT), showed that only a small fraction of sediment HOCs were available for equilibrium and the predictability of EPT can be improved with the consideration of sequestration in sediment. A good correlation was noted between sediment concentration in the rapidly desorbing fraction measured by Tenax extraction, and SPME fiber concentration as determined by matrix-SPME. Thus, the two methods both tracked the readily desorbed contaminant equally well though Tenax extraction measures the accessible pool, and matrix-SPME measures the chemical activity of the HOCs.

Introduction

Equilibrium partitioning theory (EPT) was developed to explain the variation in sorption behavior of sediment-associated organic contaminants as a way to determine which fraction of sorbed compound was likely bioavailable (1, 2). This approach described the expected partitioning of hydrophobic organic contaminants (HOC) among various

compartments including sediment organic matter, porewater, and the lipids of an organism, the dominant storage site for HOCs. The result of this theory was a biota-sediment accumulation factor (BSAF) where the concentration in the lipid of an organism was compared to the concentration in sediment organic matter (Figure S1A in the Supporting Information). The partitioning of HOCs among compartments was considered reversible, and it was expected to yield a relatively constant BSAF value even for compounds over a range of hydrophobicities, as represented by the octanol: water partition coefficient (K_{ow}) (3, 4). However, BSAF values determined from field studies revealed up to 2–3 orders of magnitude variability (5) indicating a need to improve our understanding of the partitioning process, and thus bioavailability.

An explanation for the failure of simple EPT to explain the observed partitioning behavior between sediments and organisms was provided with desorption studies that demonstrated that HOCs occupied at least two heterogeneous compartments within sediments (6) (Figure S1B in the Supporting Information). These compartments were described as an amorphous, rubbery organic matter from which HOCs desorb rapidly, and as a condensed, glassy organic matter from which desorption was much slower. A second explanation for the failure of EPT to explain observed partitioning behavior was the finding that slow desorption can be described as a hysteretic diffusion of compounds within sediment particles including intraorganic matter diffusion and intraparticle micropore diffusion (7). Although sequestration, the presence of compartments within the sediment where desorption is slow to very slow, is not fully understood; the influence of sequestration on the fate of HOCs is well documented (6–9). The rapidly desorbing fraction (F_{rap}) is described as the compound attached to the outer regions of sediment aggregates, and it represents the HOC pool that contributes directly to bioaccumulation and bioavailability of HOCs from sediment. Further, bioavailability was demonstrated to decrease with higher degrees of sequestration, often observed as a reduction in F_{rap} (10–16).

A major recent finding is the role of black carbon (BC) composed of soots, chars, charcoal, cenospheres, coke, and the like as major contributors to partitioning behavior of contaminants (17). The contribution of the very strong partitioning of HOCs to these materials is thought to provide an explanation of both desorption and sequestration behavior of compounds in sediments, and thus the major reason for the variation in bioavailability observed by simple EPT (17). However, adjusting for the partitioning of BC in sediments is not straightforward (18). The difficulty results from two sources. The partition coefficients for different types of BC can vary by 23 orders of magnitude (19), and the methods for measuring the amount of BC in sediments do not distinguish the type of BC because they are based on simple oxidation procedures (20, 21). Finally, it is not clear if BC is the only “super sorptive” phase affecting the partitioning and bioavailability of HOCs (19).

Until there are adequate methods to quantify the types of sorptive phases within sediment, and their respective partitioning behaviors so that equilibrium calculations can be accurately made, biomimetic approaches to address the fraction of readily desorbed compound will be the most useful for determining bioavailability. There is a growing interest in using bioavailability in soil and sediment management; however, the application is hindered by the absence of reliable, simple, and cost-effective techniques for site-specific measurements of bioavailability (22). Measurements of

* Corresponding author phone: 618-453-4091; fax: 618-453-6095; E-mail: mlydy@siu.edu.

[†] Southern Illinois University.

[‡] Great Lakes Environmental Research Laboratory.

desorption offer simple chemical methods to determine bioavailability, and several extraction approaches are in development to estimate the bioavailable fraction of HOCs (21). The measurement of desorption using Tenax extraction was developed to measure the quantity of HOCs that can become accessible from sediment (8, 9, 23) (Figure S1C in the Supporting Information). Tenax is used as an infinite sink to maintain a water concentration that is essentially zero during the test allowing the HOC of interest to desorb in proportion to its diffusion and binding limitations. By removing the Tenax at intervals, desorption can be determined including the apparent capacity of different pools including rapidly, slowly, and very slowly desorbing HOC along with the respective desorption coefficients.

A second approach for determining the readily available HOCs from sediments for partitioning process uses matrix solid-phase microextraction (matrix-SPME) (24) (Figure S1D in the Supporting Information). The method was designed as a rapid and economical measure of the HOC porewater concentration at equilibrium. This porewater concentration then represents a measure of chemical activity that would be bioavailable. This measurement is determined by holding polydimethylsiloxane (PDMS) coated fibers in the sediment–water matrix until equilibrium is reached. The concentration in porewater is then calculated based on the PDMS:water partition coefficient.

The objectives of this study were to determine the desorption kinetics of five representative HOCs of differing compound classes, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine, organophosphate, and pyrethroid insecticides from sediments of differing characteristics using Tenax extraction and matrix-SPME. Our previous study (25) compared the utility of the two methods as operationally defined measures of bioavailability for these HOCs. In this paper, the two chemical methods were compared for assessing the readily desorbed and presumably bioavailable fraction of HOCs.

Materials and Methods

Chemicals. ^{14}C -Radiolabeled 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), permethrin (PERM), chlorpyrifos (CHL), and phenanthrene (PHE) were purchased from Sigma Chemical Company (St. Louis, MO) and tested for purity using high-pressure liquid chromatography (HPLC, Agilent Technologies, Palo Alto, CA) followed by liquid scintillation counting (LSC) using a Packard TriCarb 2900TR liquid scintillation analyzer (Packard Instrument Company, Meriden, CT). The HPLC separations were performed with a Zorbax SB-C18 column (5 μm , 4.6 \times 150 mm) using acetonitrile (ACN) and water as a solvent system with a linear gradient of 50–100% ACN in 12 min. Separate fractions were collected and measured by LSC for 10 min using automatic quench control. Chemical structures and other characteristics of the five contaminants are provided in Table S1 in the Supporting Information. To minimize the photodegradation of PHE, all experiments were conducted under red light. Mercuric chloride (HgCl_2) was purchased from Supelco (Bellefonte, PA) and was used to inhibit microbial degradation of the test compounds in sediment. All solvents were pesticide or HPLC grade (Fisher Scientific, Pittsburgh, PA). Moderately hard water (MHW) was prepared following U.S. Environmental Protection Agency methods (26). Scintillation cocktail (Scinti Safe Plus 50%) was purchased from Fisher Scientific.

Tenax TA (60–80 mesh), a porous polymer adsorbent based on 2,6-diphenyl-*p*-phenylene oxide was obtained from Alltech (Deerfield, IL). Prior to use, Tenax was sonicated in triplicate using 10 mL acetone: hexane (1:1)/g Tenax of for 5 min with a Branson 3510 Ultrasonic bath (Branson Ultrasonics, Danbury, CT). After evaporating, the extract was

analyzed by LSC to confirm the background concentrations of the chemicals on the Tenax.

Disposable SPME fiber coated with 10 μm PDMS (Fiber-Guide Industries, Stirling, NJ) had a phase volume of 0.069 μL per cm with a 210 μm core diameter. To protect the fragile fibers, stainless steel envelopes were used in our study. Five centimeter of fiber was cut into ~ 1 cm pieces using a razor and fiber pieces were placed into each 2 \times 1 cm envelope that was made with 110 μm stainless steel screen. Prior to use, the fibers and envelope were rinsed with ACN, ACN–water (1:1) and water, sequentially and dried at room temperature. The 110 μm openings were small enough to retain the fibers, but were large enough for ample contact between the fiber and porewater. Parallel experiments, that exposed SPME fibers for 7 days to each of the contaminants in water with and without envelopes, showed no significant difference in SPME uptake.

Sediments. Dosed sediments were prepared from two uncontaminated reference sediments collected from a small farm pond in Wichita, KS, and Bearskin Lake, in Grand Marais, MN. Total organic carbon (TOC) content of the sediment determined by CHN analysis on an EA 1110 CHN analyzer (CE Instruments, Thermoquest Italia, Milan, Italy) after removing carbonates was 1.31 ± 0.02 and $7.85 \pm 0.18\%$ for the KS and MN sediments, respectively. Other measured physical properties of the sediments were % sand, % silt, and % clay and were 14, 70, and 16% for the KS sediment and 55, 12, and 33% for the MN sediment.

The KS and MN sediments were spiked with the five HOCs at two concentrations (high and low) to examine possible concentration effects and the potential effects of TOC level on desorption (Tenax) and porewater concentrations (matrix-SPME) for each of the HOCs. Sediment was dosed with appropriate quantities of the test compounds in acetone using 100 μL acetone/L sediment. Solvent controls were prepared by adding the same quantity of acetone to the sediments. After dosing, sediments were thoroughly mixed using a stainless steel paddle driven by an overhead motor for 4 h. Sediments were then stored at 4 $^{\circ}\text{C}$ for 7 days and homogenized again prior to use.

Spiked sediment was analyzed in triplicate before and after each experiment to determine HOC concentrations and percent parent compound. Sediment samples (~ 0.05 g wet weight (ww)) were weighed, placed into a scintillation vial, vortexed with 10 mL of scintillation cocktail for 2 min, and counted by LSC after a 24 h holding period. The extraction efficiencies for all HOCs from sediment were 87–100%. The holding period was used to allow ample time for extraction of the ^{14}C -labeled compound from the matrix into the cocktail. Background was subtracted using counts from control sediment samples. Degradation of PERM, CHL, and PHE in sediment was quantified by separating the parent compound from metabolites on HPLC as described in the purity studies (see above).

Determination of Desorption by Consecutive Tenax Extraction. Desorption of the HOCs from sediment was determined using consecutive extraction with Tenax absorbent (8; see the Supporting Information for details). Tenax were continually mixed with sediment and sampled at predetermined intervals throughout the 14 day test. The separated Tenax was extracted with an acetone and hexane mixture and measured by LSC.

Estimation of Partition Coefficients between the PDMS Fiber and Water. Partition coefficients between the PDMS fiber and the water (K_{fw}) were measured by exposing SPME fibers in 850 mL MHW spiked with the test chemicals (27; see the Supporting Information for details). To ensure that equilibrium conditions were reached, serial samples were taken over 21 days. Water and fiber concentrations were determined by LSC.

TABLE 1. Spiked Sediment Concentration (C_s , $n = 3$) and Desorption Parameters of 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), Permethrin (PERM), Chlorpyrifos (CHL), and Phenanthrene (PHE) in Kansas (KS) and Minnesota (MN) Sediments at Two Spiking Concentration Levels (high and Low)^a

KS_low C_s (ng/g)	HCBP (42 ± 1.6)	DDE (42 ± 4.2)	PERM (280 ± 14)	CHL (151 ± 2)	PHE (178 ± 14)
F_{rap}	0.4847 ± 0.0491	0.4798 ± 0.0276	0.4782 ± 0.0369	0.5418 ± 0.2008	0.4588 ± 0.0264
k_{rap} (h ⁻¹)	0.3553 ± 0.0471	0.2111 ± 0.0198	0.4393 ± 0.0571	1.5650 ± 9.9914	0.4986 ± 0.0572
F_s	0.2301 ± 0.0431	0.4284 ± 0.0590	0.2832 ± 0.0408	0.1700 ± 6.5365	0.2637 ± 0.0228
k_s (h ⁻¹)	0.0457 ± 0.0191	0.0014 ± 0.0038	0.0403 ± 0.0130	0.0192 ± 0.6381	0.0395 ± 0.0079
F_{vs}	0.2858 ± 0.0434	0.0884 ± 0.0736	0.2383 ± 0.0492	0.3197 ± 6.6816	0.2770 ± 0.0171
k_{vs} (h ⁻¹)	0.0062 ± 0.0009	0.0003 ± 0.0025	0.0058 ± 0.0012	0.0004 ± 0.1345	0.0010 ± 0.0003
COD ^b	0.9996	0.9995	0.9995	0.9778	0.9994

KS_high C_s (ng/g)	HCBP (1500 ± 10)	DDE (1100 ± 40)	PERM (1600 ± 90)	CHL (180 ± 70)	PHE (500 ± 10)
F_{rap}	0.4880 ± 0.0440	0.5963 ± 0.0239	0.5108 ± 0.0311	0.5661 ± 0.0020	0.5562 ± 0.0262
k_{rap} (h ⁻¹)	0.3820 ± 0.0460	0.5687 ± 0.0433	0.4527 ± 0.0410	1.1163 ± 0.2400	0.5235 ± 0.0438
F_s	0.3430 ± 0.0380	0.2476 ± 0.0206	0.3289 ± 0.0272	0.1142 ± 0.0176	0.2683 ± 0.0239
k_s (h ⁻¹)	0.0053 ± 0.0100	0.0580 ± 0.0090	0.0579 ± 0.0079	0.0517 ± 0.0194	0.0512 ± 0.0108
F_{vs}	0.1680 ± 0.0160	0.1560 ± 0.0095	0.1601 ± 0.0102	0.3197 ± 0.0144	0.1753 ± 0.0261
k_{vs} (h ⁻¹)	0.0019 ± 0.0004	0.0015 ± 0.0003	0.0014 ± 0.0003	0.0021 ± 0.0002	0.0065 ± 0.0010
COD ^b	0.9996	0.9998	0.9998	0.9995	0.9998

MN_low C_s (ng/g)	HCBP (53 ± 2.4)	DDE (38.4 ± 2.3)	PERM (226 ± 10)	CHL (101 ± 3.4)	PHE (160 ± 6.3)
F_{rap}	0.1020 ± 0.0229	0.2641 ± 0.0154	0.1585 ± 0.0202	0.5305 ± 0.0616 ^c	0.6397 ± 0.0239
k_{rap} (h ⁻¹)	0.1860 ± 0.0639	0.1685 ± 0.0105	0.2287 ± 0.0384	0.1735 ± 0.0224	0.3934 ± 0.0213
F_s	0.5974 ± 0.0242	0.4809 ± 0.0124	0.5662 ± 0.0171	0.2723 ± 0.0487	0.2922 ± 0.0200
k_s (h ⁻¹)	0.0252 ± 0.0026	0.0270 ± 0.0014	0.0266 ± 0.0020	0.0259 ± 0.0102	0.0482 ± 0.0066
F_{vs}	0.3013 ± 0.0261	0.2555 ± 0.0078	0.2750 ± 0.0178	0.2010 ± 0.0372	0.0744 ± 0.0124
k_{vs} (h ⁻¹)	0.0021 ± 0.0003	0.0009 ± 0.0001	0.0017 ± 0.0003	0.0011 ± 0.0007	0.0030 ± 0.0009
COD ^b	0.9999	1.0000	0.9999	0.9994	0.9999

MN_high C_s (ng/g)	HCBP (2000 ± 110)	DDE (1100 ± 20)	PERM (1000 ± 10)	CHL (290 ± 30)	PHE (600 ± 20)
F_{rap}	0.1282 ± 0.0170	0.2352 ± 0.0376	0.2129 ± 0.0235	0.2695 ± 0.0593 ^c	0.5739 ± 0.0302
k_{rap} (h ⁻¹)	0.0839 ± 0.0103	0.2909 ± 0.0581	0.5016 ± 0.1030	0.8780 ± 0.5082	0.3343 ± 0.0226
F_s	0.4139 ± 0.0153	0.5126 ± 0.0308	0.4283 ± 0.0224	0.3053 ± 0.0494	0.2734 ± 0.0256
k_s (h ⁻¹)	0.0133 ± 0.0014	0.0392 ± 0.0050	0.0353 ± 0.0048	0.0931 ± 0.0279	0.0461 ± 0.0079
F_{vs}	0.4592 ± 0.0257	0.2511 ± 0.0234	0.3541 ± 0.0228	0.4252 ± 0.0264	0.1519 ± 0.0130
k_{vs} (h ⁻¹)	0.0008 ± 0.0002	0.0033 ± 0.0004	0.0022 ± 0.0003	0.0073 ± 0.0006	0.0023 ± 0.0004
COD ^b	0.99997	0.9998	0.9996	0.9994	0.9998

^a The rapidly, slowly, and very slowly desorbing fractions (F_{rap} , F_s , and F_{vs}) and their corresponding rapid, slow, and very slow desorption rate constants (k_{rap} , k_s , and k_{vs}) are shown as the estimated mean ± SD. Desorption data were fitted using triphasic kinetic model with Scientist 2.01 (MicroMath, Inc.). ^b COD, coefficient of determination ^c There is significant difference between high and low concentrations.

Measurement of Porewater Concentration by Matrix-SPME. Sediment porewater concentrations were measured with matrix-SPME. Serial sampling was conducted to ensure the chemical reached equilibrium among sediment, porewater, and fiber, and detailed information is presented in the Supporting Information.

Modeling and Data Analysis. Desorption Kinetics by Tenax Extraction. Tenax extraction data were modeled using both biphasic and triphasic desorption models assuming no significant readsorption (8, 9). Though both models fit the data well with coefficient of determinations (COD) > 0.99, the triphasic model showed a slightly better fit across all sediments and compounds with an average COD of 0.9997 ± 0.0002 compared to 0.9956 ± 0.0028 for the biphasic model. Therefore, a triphasic model was used.

$$S_t/S_0 = F_{rap} (e^{-k_{rap}t}) + F_s (e^{-k_s t}) + F_{vs} (e^{-k_{vs} t}) \quad (1)$$

$$F_{rap} + F_s + F_{vs} = 1 \quad (2)$$

Where, S_t and S_0 represent the amount of sediment-sorbed

chemical at time t (h) and time zero, respectively. F_{rap} , F_s , and F_{vs} are the fraction of chemical in the rapidly, slowly, and very slowly desorbing fractions at time zero and k_{rap} , k_s , and k_{vs} are the corresponding desorption rate constants (h⁻¹), respectively. Data were fit with Scientist 2.01 (MicroMath Inc., St. Louis, MO).

Partition Coefficient Between the PDMS Fiber and Water. The fiber and water partition coefficient (K_{fw}) was estimated by the HOC concentration on the fiber and the HOC concentration in the water after equilibrium was reached in the water-only exposure system using the following equation.

$$K_{fw} = C_{f,eq}/C_{w,eq} \quad (3)$$

Where, $C_{f,eq}$ and $C_{w,eq}$ are the HOC concentration in the fiber and the water at equilibrium, respectively.

Freely Dissolved Chemicals in Porewater. Five sampling times were used during the matrix-SPME experiment to ensure that equilibrium was achieved. The uptake and elimination of the HOCs by the PDMS fiber from sediment

TABLE 2. Partition Coefficients between PDMS Fiber and Water ($\log K_{fw} \pm SD$) for 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), Permethrin (PERM), Chlorpyrifos (CHL), and Phenanthrene (PHE) Measured in Water-Only Exposure Experiments ($n = 3$) and Compared with Literature Values

chemical	$\log K_{fw}$	$\log K_{fw}$ (lit.)
HCBP	6.01 ± 0.04	5.84 ± 0.08 , 6.16 ± 0.09^a , 5.67 , 6.01^b
DDE	5.68 ± 0.06	5.73 ± 0.09 , 5.88 ± 0.05^a , 5.26 , 5.39^b
PERM	5.59 ± 0.04	no previous studies available
CHL	4.18 ± 0.01	no previous studies available
PHE	3.77 ± 0.03	3.48 ± 0.09^a , 3.25 , 3.45^b

^a $\log K_{fw}$ for 15 μ m PDMS coating exposed after 3 days and six weeks according to Mayer et al. (32) ^b $\log K_{fw}$ values for 7 μ m and 100 μ m PDMS coating according to Paschke et al. (27)

was determined by fitting the data to a first-order one-compartment model as follows:

$$C_{f,t} = C_f(1 - e^{-k_e t}) \quad (4)$$

Where, $C_{f,t}$ and C_f represent HOC concentration on the fiber at time t (day, hour) and at equilibrium, and k_e is the elimination rate constant. The elimination rate constant was used to predict the time to reach 90% of the equilibrium concentration in the fiber and equals $\ln(10)/k_e$. The freely dissolved concentration of HOC in porewater (C_{pw}) was derived from C_f measured from the matrix-SPME experiment, and K_{fw} was measured from the water-only SPME experiment according to the following equation:

$$C_{pw} = C_f/K_{fw} \quad (5)$$

Bioaccessible HOC Concentration in Sediment. The potentially bioaccessible HOC concentration in sediment (C_{srp}) was calculated as follows:

$$C_{srp} = C_s \cdot F_{rap} \quad (6)$$

Where C_s is the HOC sediment concentration and F_{rap} is the rapidly desorbing fraction.

Equilibrium Partitioning between Porewater and Sediment. Matrix-SPME measured porewater concentration was used to calculate the apparent sediment–water partitioning coefficient ($K_{oc,app}$), based on OC normalized sediment concentration $C_{s,oc}$, according to the following equation:

$$K_{oc,app} = C_{s,oc}/C_{pw} \quad (7)$$

While, the partition coefficient between the rapidly desorbing fraction and porewater ($K_{oc,rap}$) was calculated according to Kraaij et al. (35).

$$K_{oc,rap} = [(C_{s,oc} \cdot F_{rap})/C_{pw}] \quad (8)$$

Statistical comparisons were made with a paired sample t test, with a p value <0.05 indicative of a significant difference using SPSS software, version 13.0.

Results and Discussion

Tenax Extraction. Previous studies have found that HOCs distribute in a heterogeneous manner within sediments and bioavailability of HOCs is directly proportional to F_{rap} measured with Tenax extraction (11–16). Most studies, however, have focused on two chemical classes, PAHs and PCBs. The present study expanded the compound list to include several pesticides, and examined two sediments with different TOC levels (KS = 1.31% and MN = 7.85%). The effects of chemical concentration on desorption were also

TABLE 3. Spiked Sediment Concentration (C_s) and Porewater Concentration (C_{pw}) for 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), Permethrin (PERM), Chlorpyrifos (CHL), and Phenanthrene (PHE) in Kansas (KS), and Minnesota (MN) Sediments. The Data Are Shown as the Mean \pm SD ($n = 3$).

chemical, sediment	high concentration		low concentration	
	C_s (ng/g dw)	C_{pw}^a (pg/mL)	C_s (ng/g dw)	C_{pw}^b (pg/mL)
HCBP, KS	1635 ± 60	16.6 ± 1.3	45.3 ± 1.3	0.84 ± 0.02
DDE, KS	695 ± 17	44.9 ± 3.0	33.5 ± 1.7	3.4 ± 0.6
PERM, KS	1434 ± 20	29.9 ± 1.2	211 ± 5.5	11.1 ± 3.0
CHL, KS	55.1 ± 4.9	nd ^c	50.2 ± 3.4	nd ^c
PHE, KS	391 ± 13	532 ± 8.1	163 ± 3.3	166 ± 13.8
HCBP, MN	3120 ± 17	3.2 ± 0.4	na ^d	na ^d
DDE, MN	812 ± 29	5.2 ± 0.5	na ^d	na ^d
PERM, MN	1152 ± 5.5	3.6 ± 0.4	221 ± 31.7	0.97 ± 0.05
CHL, MN	312 ± 156	101 ± 7.5	88.4 ± 6.0	27.2 ± 1.8
PHE, MN	613 ± 17	110 ± 12.9	198 ± 6.5	28.0 ± 1.6

^a C_{pw} is from data fit with a first-order one-compartment uptake model using Scientist 2.01 (MicroMath, Inc.). ^b C_{pw} was the measured porewater concentration (at the lower concentration) at 12 h for PHE and 14 days for the remaining compounds. ^c nd, not detected. ^d na, not analyzed.

examined by dosing different concentrations of the five HOCs into sediments. A triphasic desorption model worked well to describe the desorption data for all compounds. The HOC sediment concentrations and desorption parameters are listed in Table 1 and desorption curves are shown in Figure S2 in the Supporting Information. With the exception of a significant difference in F_{rap} for CHL in MN sediment at different concentration levels, F_{rap} was not significantly different for all HOCs regardless of concentration, which contrasted with the observed concentration-dependent desorption noted previously (14, 29, 30). This difference may result from the shorter sediment–chemical contact time (7 days) used in the present study. The relatively high water solubility of CHL (Table S1 in the Supporting Information) may be the reason for the low mass balance in the Tenax desorption tests, which in turn produced inaccuracies in the F_{rap} estimates for CHL. Though F_{rap} showed variation for CHL in MN sediment at two concentrations, the fractions desorbed at 6 h (F_{6h}) were similar with F_{6h} of 0.418 ± 0.040 and 0.395 ± 0.024 for high and low concentrations, respectively. While F_{rap} was similar among compounds (~ 0.5) in the KS sediment, F_{rap} was smaller and inversely proportional to compound hydrophobicity in the MN sediment (Table 1). The lower values for F_{rap} in the MN sediment reflect the higher TOC content that suggests higher sorption capacity. A previous study with sediment from this site also found low fractions of F_{rap} as compared to other sediments even some with much higher TOC content suggesting some difference in sediment composition that contributed to this observation (31). However, the difference could not be accounted for by black carbon for this sediment (31). Planar compounds such as PAHs exhibit enhanced sorption to black carbon (19), and the similar F_{rap} values for PHE in both sediments suggested that black carbon is most likely not present in the MN sediment.

Partition Coefficient Between the PDMS Fiber and Water. To measure K_{fw} , serial samples were collected for up to 21 days to ensure the chemical had reached equilibrium between water and fiber. PHE reached equilibrium with the fiber within 1 day, and CHL and DDE reached equilibrium within 3 days. It took more than 14 days for HCBP and PERM to reach equilibrium. The K_{fw} values for HCBP, DDE, and PHE (Table 2) were comparable with those from the literature (27, 32), even though the thickness of the PDMS coatings and equilibrium times were different. To our knowledge, K_{fw}

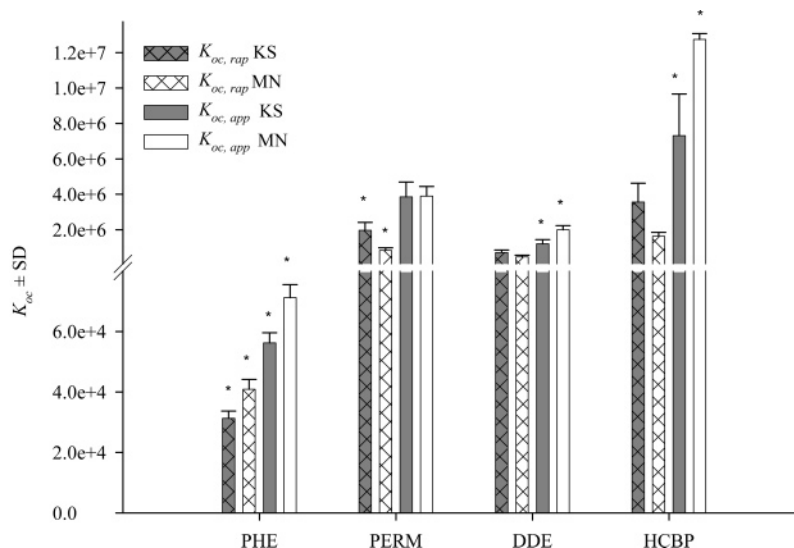


FIGURE 1. Comparison of partition coefficients between sediment and porewater ($K_{oc,app}$) and between the rapidly desorbing fraction and porewater ($K_{oc,rap}$) for 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), permethrin (PERM), and phenanthrene (PHE) from Kansas (KS) and Minnesota (MN) sediments. $K_{oc,app}$ is equal to the organic carbon normalized sediment concentration divided by the porewater concentration, while $K_{oc,rap}$ is equal to the organic carbon normalized chemical concentration in the rapidly desorbing fraction divided by the porewater concentration. The asterisk (*) denotes significant difference between KS and MN sediments.

values for PERM or CHL have not previously been determined; therefore, direct comparisons with literature values were not possible. Nevertheless, the relationship found between $\log K_{fw}$ and $\log K_{ow}$ across studies [$\log K_{fw} = 1.03 \log K_{ow} - 0.90$, $r^2 = 0.98$ in this study, $\log K_{fw} = 1.01 \log K_{ow} - 0.91$, $r^2 = 0.99$ by Mayer et al. (32), and $\log K_{fw} = 1.03 \log K_{ow} - 0.90$, $r^2 = 0.98$ by Paschke et al. (27)] supports the results for PERM and CHL.

Matrix-SPME. The matrix-SPME technique was introduced to measure the freely dissolved HOC concentration in sediment porewater (24). Because of the negligible absorption capacity of the PDMS phase on the SPME fiber compared to the bulk sediment, the temporally depleted HOC from the porewater was renewed quickly by HOCs desorbed from the sediment matrix. Hence, the equilibrium between porewater and sediment should be readily reestablished. Less than 0.9% of chemical in the sediment was taken up by the fiber, which fulfilled the less than 5% requirement for a negligible depletion technique (33). After equilibrium was achieved among the fiber, porewater, and sediment, C_f and C_{pw} were derived from the amount of HOC on the SPME fiber.

The freely dissolved concentration of HOCs in porewater in MN and KS sediments were measured with the matrix-SPME approach. A first-order one-compartment model fit the data for all of the compounds. In general, equilibrium of the HOCs between the fiber and sediment porewater was reached within 14 days for all compounds. PHE, which was the least hydrophobic of the compounds tested, reached equilibrium between the porewater and fiber within 9 h. The equilibrium curve for DDE is shown in Figure S3 in the Supporting Information. A continuous increase in porewater concentration was observed after the first equilibrium was reached at 14 days for HOCs in KS sediment and a similar phenomenon was reported for fiber uptake of PAHs from field-contaminated sediment (34). The existence of multiple equilibria helps support the hypothesis that the HOCs distributed in multiple compartments with different desorption kinetics in the sediment. The relatively short test period (28 days) used in this study may be the reason why the second equilibrium did not occur in the MN sediment where a longer time (75 days) may be required to reach this second equilibrium. Equilibrium times for the HOCs extracted

by SPME fiber from the KS sediment were comparable to those from water (obtained from the K_{fw} experiment). This supported the hypothesis that in the matrix-SPME experiment, the temporally depleted HOC reservoir in the porewater was refilled quickly by HOCs desorbed from the sediment matrix though the complexity of the sediment slurry may have slowed down the diffusion of the HOCs. This is consistent to the assumption of Ter Laak et al. (34) that the rate-limiting step is not the exchange between sediment and porewater, but between fiber and porewater.

Serial samples were taken to ensure sediment, porewater, and fibers were at equilibrium; therefore, the calculated water concentration should represent the freely dissolved HOC concentration in the sediment porewater (Table 3). Loss of chemical was observed, especially for CHL, during the equilibration process and such losses may account for the observed decline in fiber concentration for CHL after apparent equilibrium. Such degradation and loss could affect observed partitioning of total contaminant in sediment because the material in the rapidly desorbed fraction has been shown to be the material that can degrade through bacterial processes (35). The significant drop of CHL in KS sediment made the quantification of porewater concentration difficult, thus CHL was excluded from the comparison between the two methods.

Partitioning Between Porewater and Rapidly Desorbing Fractions. Assuming a homogeneous distribution of HOC in sediment, EPT suggests that K_{oc} equals the quotient of organic carbon normalized C_s and C_{pw} and is independent of sediment characteristics. However, the sequestration process in sediment can complicate this relationship. Rather than the total sediment concentration, C_{srap} was suggested to equilibrate with C_{pw} (36, 37). Compared to the apparent OC based sediment–water partitioning coefficient ($K_{oc,app}$) calculated from total sediment concentration, Kraaij et al. (36) introduced a term $K_{oc,rap}$ that describes partitioning process between rapidly desorbing fraction of the sediment and the porewater to remove the influence of sequestration on the equilibrium between sediment and porewater. Figure 1 compares the calculated K_{oc} values for KS and MN sediments spiked with high concentration HOCs. $K_{oc,app}$ values were significantly greater for PHE, DDE, and HCBP in MN sediments than that in KS sediment even though the sediment

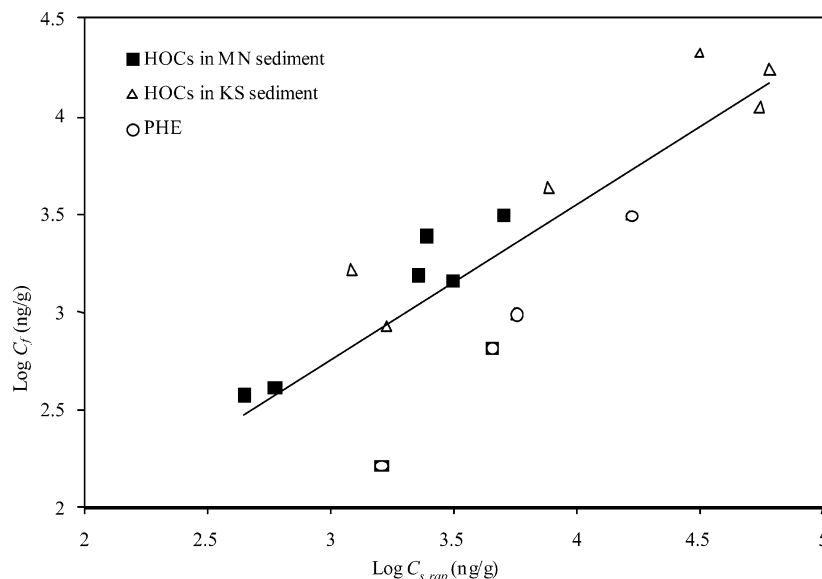


FIGURE 2. Relationship between the HOC concentration in the rapidly desorbing fraction ($C_{s,rap}$) measured by Tenax extraction and the fiber concentration (C_f) measured by matrix solid-phase microextraction for 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), permethrin (PERM), chlorpyrifos (CHL), and phenanthrene (PHE) at different concentrations in Minnesota (MN) and Kansas (KS) sediments. The solid line represents the relationship between C_f and $C_{s,rap}$ ($C_f = 0.79 (0.13) C_{s,rap} + 0.38 (0.47)$, $r^2 = 0.73$).

concentration was normalized to OC to eliminate the OC effect. When $K_{oc,app}$ was replaced with $K_{oc,rap}$, the difference in K_{oc} values determined in KS and MN sediments was reduced for HCBP and DDE (Figure 1). There was no significant difference for F_{rap} of PHE between the two sediments, thus the conversion to $C_{s,rap}$ had no effect on the variation of K_{oc} values. Underestimation of C_{pw} of PERM in KS sediment may be the reason for the observed opposite trend to the other HOCs. $K_{oc,rap}$ determined with high concentration PERM in MN sediment ($8.3 \pm 1.2 \times 10^5$) was similar to that calculated from low concentration PERM in KS ($7.0 \pm 1.9 \times 10^5$) and MN sediment ($6.2 \pm 0.9 \times 10^5$).

Comparison of Tenax Extraction and Matrix-SPME.

Though both methods can estimate the bioavailability of HOC from sediment (25), Tenax extraction and matrix-SPME represent two fundamentally different measures, namely accessibility and chemical activity, respectively (38). Tenax extraction estimates the fraction potentially accessible for desorption, while matrix-SPME directly measures the fraction of HOC in sediment readily available for equilibrium partitioning. To evaluate whether the two fractions are related, C_f was plotted versus $C_{s,rap}$ for the four HOCs spiked in both sediments at two concentration levels (Figure 2). As discussed above, matrix-SPME tests for HCBP and DDE at low concentration in MN sediment were not conducted and no data were obtained for CHL in KS sediment, so they are excluded from the analysis. Figure 2 showed 74% of the variation in fiber uptake among chemicals, concentration, and sediments can be explained as the difference among chemicals readily desorbing from sediment. In addition, uptake of PHE, the only planar compound in the tested compounds, by SPME fiber was lower than in the other compounds (Figure 2). When the PHE data are excluded from the regression, the linearity improved from 0.73 to 0.93. At the same time, a linear relationship was found for PHE in both sediments ($C_f = 1.27 (0.06) C_{s,rap} - 1.82 (0.24)$, $r^2 = 0.99$). Thus, the PHE is an example of a compound that is bioaccessible, but the SPME data would suggest that it is less bioavailable. This is supported by the data from the biological studies (25) where PHE was less available than expected despite attempts to account for biotransformation of the compound in *Lumbriculus variegatus*. The mechanism creating the offset for the PHE between the two methods from the nonplanar compounds is not known at this time.

The results showed that both $C_{s,rap}$ and C_f vary across compounds and among sediments in the same manner. Thus, both methods seem to be equally useful for tracking the readily desorbed compound from different perspectives. This suggests that both approaches should be equally useful for accounting for differences in the bioavailability of HOCs across compound classes and sediments.

Acknowledgments

We thank Duane Gossiaux for measures of sediment organic carbon, Jason Belden, Donald Weston for their reviews of the paper, and Teresa Norberg-King of the U.S. Environmental Protection Agency, Duluth, MN for collecting the sediments. GLERL contribution no. 1428.

Supporting Information Available

Information detailing the experimental methods, chemical approaches for measuring desorption of hydrophobic organic contaminants (Figure S1); desorption of tested chemicals from spiked sediments measured by Tenax extraction (Figure S2); uptake profile of the fiber exposed to sediments spiked with DDE (Figure S3); and, chemical characteristics (Table S1) This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Shea, D. Developing national sediment quality criteria. *Environ. Sci. Technol.* **1988**, *22*, 1256–1261.
- (2) Di Toro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. A.; Paquin, P. R. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* **1991**, *10*, 1541–1583.
- (3) McFarland, V. A. Activity-based evaluation of potential bioaccumulation from sediments. In *Dredging and Dredged Material Disposal*; Montgomery R. L., Leach J. W., Eds.; American Society of Civil Engineering: New York, 1984.
- (4) McFarland, V. A.; Clark, J. U. Testing Bioavailability of Polychlorinated Biphenyls from Sediments using a Two-Level Approach, 6th seminar, February 25–27. In *Proceedings of the US Army Engineer Committee on Water Quality*; Wiler R. G., Ed.; Hydrologic Engineering Research Center: Davis, CA, 1986.
- (5) Tracey, G. A.; Hansen, D. J. Use of biota-sediment accumulation factors to assess similarity of non-ionic organic chemical exposure to benthically-coupled organisms of differing trophic mode. *Arch. Environ. Contam. Toxicol.* **1996**, *30*, 467–475.

- (6) Cornelissen, G.; Rigterink, H.; van Noort, P. C. M.; Govers, H. A. J. Slowly and very slowly desorption organic compounds in sediment exhibit langmuir-type sorption. *Environ. Toxicol. Chem.* **2000**, *19*, 1532–1539.
- (7) Pignatello, J. J.; Xing, B. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* **1996**, *30*, 1–11.
- (8) Cornelissen, G.; van Noort, P. C. M.; Govers, H. A. J. Desorption kinetic of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: sediment extraction with Tenax and effects of contact time and solute hydrophobicity. *Environ. Toxicol. Chem.* **1997**, *16*, 1351–1357.
- (9) Cornelissen, G.; van Noort, P. C. M.; Parsons, J. R.; Govers, H. A. J. Temperature dependence of slow adsorption and desorption kinetics of organic compounds in sediments. *Environ. Sci. Technol.* **1997**, *31*, 454–460.
- (10) Kraaij, R.; Seinen, W.; Tolls, J. Directly evidence of sequestration in sediments affecting the bioavailability of hydrophobic organic chemicals to benthic deposit-feeders. *Environ. Sci. Technol.* **2002**, *36*, 3525–3529.
- (11) Lamoureux, E. M.; Brownawell, B. J. Chemical and biological availability of sediment-sorbed hydrophobic organic contaminants. *Environ. Toxicol. Chem.* **1999**, *18*, 1733–1741.
- (12) Kraaij, R. H.; Ciarelli, S.; Tolls, J.; Kater, B. J.; Belfroid, A. Bioavailability of lab-contaminated and native polycyclic aromatic hydrocarbons to the amphipod *Corophium volutator* relates to chemical desorption. *Environ. Toxicol. Chem.* **2001**, *20*, 1716–1724.
- (13) Kraaij, R. H.; Tolls, J.; Sijm, D.; Cornelissen, G.; Heikens, A.; Belfroid, A. Effects of contact time on the sequestration and bioavailability of different classes of hydrophobic organic chemicals to benthic oligochaetes (*Tubificidae*). *Environ. Toxicol. Chem.* **2002**, *21*, 752–759.
- (14) Leppänen, M. T.; Landrum, P. F.; Kukkonen, J. V. K.; Greenberg, M. S.; Burton, G. A. Jr.; Robinson, S. D.; Gossiaux, D. C. Investigating the role of desorption on the bioavailability of sediment-associated 3,4,3',4'-tetrachlorobiphenyl in benthic invertebrates. *Environ. Toxicol. Chem.* **2003**, *22*, 2861–2871.
- (15) Morrison, D. E.; Roberson, B. K.; Alexander, M. Bioavailability to earthworm of aged DDT, DDE, DDD and Dieldrin in soil. *Environ. Sci. Technol.* **2000**, *34*, 709–713.
- (16) Moermond, C. T. A.; Roozen, F. C. J. M.; Zwolsman, J. J. G.; Koelmans, A. A. Uptake of sediment-bound bioavailable polychlorobiphenyls by benthivorous carp (*Cyprinus carpio*). *Environ. Sci. Technol.* **2004**, *38*, 4503–4509.
- (17) Cornelissen, G.; Gustafsson, Ö.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; van Noort, P. M. C. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation and biodegradation. *Environ. Sci. Technol.* **2005**, *39*, 6881–6895.
- (18) Kukkonen, J. V. K.; Mitra, S.; Landrum, P. F.; Gossiaux, D. C.; Gunnarsson, J.; Weston, D. The contrasting roles of sedimentary plant-derived carbon and black carbon on sediment-spiked hydrophobic organic contaminant bioavailability to *Diporeia* spp. and *Lumbriculus variegatus*. *Environ. Toxicol. Chem.* **2005**, *24*, 877–885.
- (19) Jonker, M. T. O.; Koelmans, A. A. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: Mechanistic considerations. *Environ. Sci. Technol.* **2002**, *36*, 3725–3734.
- (20) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* **1997**, *31*, 203–209.
- (21) Gelinas, Y.; Prentice, K. M.; Baldock, J. A.; Hedges, J. I. An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils. *Environ. Sci. Technol.* **2001**, *35*, 3519–3525.
- (22) National Research Council of the National Academies. *Bioavailability of Contaminants in Soils and Sediments, Processes, Tools, and Application*; The National Academies Press: Washington, DC, 2003.
- (23) Pignatello, J. J. Slowly reversible sorption of aliphatic halocarbons in soils. I. Formation of residual fractions. *Environ. Toxicol. Chem.* **1990**, *9*, 1107–1115.
- (24) Mayer, P.; Vaes, W. H. J.; Wijnker, F.; Legierse, K. C. H. M.; Kraaij, R. H.; Tolls, J.; Hermens, J. L. M. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ. Sci. Technol.* **2000**, *34*, 5177–5183.
- (25) You, J.; Landrum, P. F.; Lydy, M. J. Comparison of chemical approaches for assessing bioavailability of sediment-associated contaminants. *Environ. Sci. Technol.* **2006**, *40*, 6348–6353.
- (26) U.S. EPA. *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates*, EPA/600/R-99/064; U.S. Environmental Protection Agency: Washington, DC, 2000.
- (27) Paschke, A.; Popp, P. Solid-phase microextraction fibre-water distribution constants of more hydrophobic organic compounds and their correlations with octanol-water partition coefficients. *J. Chromatogr. A* **2003**, *999*, 35–42.
- (28) Grathwohl, P. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implications on K_{oc} correlations. *Environ. Sci. Technol.* **1990**, *24*, 1687–1693.
- (29) Braid, W. J.; White, J. C.; Zhao, D.; Ferrandino, F. J.; Pignatello, J. J. Concentration-dependent kinetics of pollutant desorption from soils. *Environ. Toxicol. Chem.* **2002**, *21*, 2573–2580.
- (30) Greenberg, M. S.; Burton, G. A., Jr.; Landrum, P. F.; Leppänen, M. T.; Kukkonen, J. V. K. Desorption kinetics of fluoranthene and trifluralin from Lake Huron and Lake Erie, USA, sediments. *Environ. Toxicol. Chem.* **2005**, *24*, 31–39.
- (31) Kukkonen, J. V. K.; Landrum, P. F.; Mitra, S.; Gossiaux, D. C.; Gunnarsson, J.; Weston, D. Sediment characteristics affecting desorption kinetics of select PAH and PCB congeners for seven laboratory spiked sediments. *Environ. Sci. Technol.* **2003**, *37*, 4656–4663.
- (32) Mayer, P.; Vaes, W. H. J.; Hermens, J. J. M. Absorption of hydrophobic compounds into the poly (dimethylsiloxane) coating of solid-phase microextraction fibers: high partition coefficients and fluorescence microscopy images. *Anal. Chem.* **2000**, *72*, 459–464.
- (33) Vaes, W. H. J.; Ramos, E. U.; Verhaar, H. J. M.; Seinen, W.; Hermens, J. L. M. Measurement of the free concentration using solid-phase microextraction: Binding to protein. *Anal. Chem.* **1996**, *68*, 4463–4467.
- (34) Ter Laak, T. L.; Barendregt, A.; Hermens, J. L. M. Freely dissolved pore water concentrations and sorption coefficients of PAHs in spiked, aged and field-contaminated soils. *Environ. Sci. Technol.* **2006**, *40*, 2184–2190.
- (35) Shor, L. M.; Siang, W.; Rockne, K. L.; Young, L. Y.; Taghon, G. L.; Kosson, D. S. Intra-aggregate mass transport-limited bioavailability of polycyclic aromatic hydrocarbons to *Mycobacterium* strain PC01. *Environ. Sci. Technol.* **2003**, *37*, 1545–1552.
- (36) Kraaij, R.; Mayer, P.; Busser, F. J. M.; Bolscher, M. V. H.; Seinen, W.; Tolls, J. Measure pore-water concentrations make equilibrium partitioning work—a data analysis. *Environ. Sci. Technol.* **2003**, *37*, 268–274.
- (37) ten Hulscher, T. E. M.; van Noort, P. C. M.; van der Velde, L. E. Equilibrium partitioning theory overestimates chlorobenzene concentrations in sediment porewater from lake Ketelmeer, the Netherlands. *Chemosphere*. **1997**, *35*, 2331–2344.
- (38) Reichenberg, F.; Mayer, P. Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. *Environ. Toxicol. Chem.* **2006**, *25*, 1239–1245.

Received for review January 6, 2007. Revised manuscript received May 14, 2007. Accepted June 8, 2007.

ES0700395