

Comparison of Chemical Approaches for Assessing Bioavailability of Sediment-Associated Contaminants

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Two chemical approaches, Tenax extraction and matrix solid-phase microextraction (matrix-SPME), were compared to assess the bioavailability of hydrophobic contaminants from sediment. Hexachlorobiphenyl, DDE, permethrin, chlorpyrifos, and phenanthrene were individually spiked into two sediments differing in physical characteristics. Bioaccumulation was determined by exposing the oligochaete, *Lumbriculus variegatus*, to the spiked sediments. The rapidly desorbing fraction from Tenax extraction at 6 h and fiber concentration at 14 d from the matrix-SPME were compared for predicting bioaccumulation. Further, a comparison between laboratory-spiked and field-contaminated sediments was conducted. A regression between the rapidly desorbed sediment concentration at 6 h and the amount bioaccumulated across compounds and sediments described 94% of the variation in the data when phenanthrene was excluded. Phenanthrene was excluded because of complications due to a combination of biotransformation and rapid elimination during the sampling process. Contaminant accumulation by *L. variegatus* also correlated well with matrix-SPME fiber concentrations, accounting for 92% of the variation in the data, again excluding phenanthrene. Both chemical methods provided matrix- and chemical-independent estimations of bioaccumulation for hydrophobic contaminants without extensive biotransformation.

Introduction

Hydrophobic organic compounds (HOCs) are ubiquitous sediment contaminants around the world. The lipophilic nature of these compounds, coupled with their persistence, results in accumulation into biota (e.g., bioaccumulation) potentially leading to direct toxicity to benthic organisms or transfer of the contaminants through food chains to other ecological receptors (1). Currently, assessment of HOC contamination is often conducted using total chemically extractable contaminant concentration. This measurement is unreliable and often poorly predicts toxicity and bioaccumulation due to differing bioavailability of HOCs among sediments. The main alternative approach is to test each sediment sample of interest for toxicity and HOC bio-

accumulation using bioassays. Although this may provide adequate data for assessments, the testing is tedious, very expensive, and only allows testing of a few ecological receptors.

Due to the current lack of reliability and high cost of assessment techniques for HOC-contaminated sediment, it is highly desirable to find a rapid, inexpensive, and reliable technique for assessing bioavailability of HOCs. Although gains have been made toward understanding bioavailability, prediction of HOC accumulation has remained problematic (2, 3). Ultimately, HOCs must desorb from sediment into the porewater prior to being available for uptake by organisms (2). Thus, knowledge of desorption rates and porewater concentrations provide a better metric for organism exposure than does total sediment concentration.

Recently, techniques for measuring HOC desorption from sediment (4–6) and HOC concentrations in porewater (7–9) have been developed. In the first technique, desorption from sediment is measured using Tenax beads as an infinite sink and measuring the rate of mass transfer from sediment to the Tenax (4–6, 10–11). Specifically, the fraction rapidly desorbing (F_{rap}) is thought to be the fraction of contaminant that is bioaccessible (mass quantity of chemical that is or can become available for uptake by an organism through desorption, 12). Previous studies using Tenax to calculate F_{rap} have determined that both the entire contaminant/sediment desorption curve (4) and specific points along the curve (e.g., 6 h, 5) were positively correlated to the bioavailability of sediment-associated HOCs. In the second technique, solid-phase microextraction fibers are directly inserted into the sediment matrix (matrix-SPME) to allow for direct determination of porewater concentrations. Matrix-SPME was successful in predicting the bioavailability of PAHs, PCBs, DDE (7), TNT and its primary metabolites (13–14), and chlorobenzenes (15–16).

The present study compared the suitability of the Tenax extraction (at 6 h) and matrix-SPME (at 14 d) to predict the bioaccumulation of five sediment-associated HOCs for the oligochaete, *Lumbriculus variegatus*. The compounds 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenylchloroethylene (DDE), permethrin (PERM), chlorpyrifos (CHL), and phenanthrene (PHE) were spiked into sediments with differing characteristics. These chemicals represent ubiquitous hydrophobic sediment-associated contaminants and were intentionally chosen from different chemical classes to thoroughly test the Tenax and matrix-SPME procedures and extend the chemical surrogate methods beyond the usual poorly biotransformed nonpolar organic contaminants.

Materials and Methods

Chemicals and Instrumentation. Radiolabeled ¹⁴C-HCBP (specific activity 12.6 mCi/mmol), PERM (10.9 mCi/mmol), DDE (12.7 mCi/mmol), CHL (47.7 mCi/mmol), and PHE (14.5 mCi/mmol) were purchased from Sigma Chemical Company (St. Louis, MO) and tested for purity using high-performance 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). Sample counts were corrected for background and quench using the external standards ratio method. Purity was >94% for all compounds.

All experiments were conducted under red light to minimize photodegradation of PHE. Mercuric chloride (Supelco, Bellefonte, PA) was used to inhibit microbial degradation when measuring desorption with Tenax TA (60–

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TABLE 1. Measured Sediment Concentration (C_s , $\mu\text{g/g OC}$) ($n = 3$), Lipid Content (Wet Weight) and Biota Sediment Accumulation Factors (BSAF, g OC/g Lipid) of 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), Permethrin (PERM), Chlorpyrifos (CHL), and Phenanthrene (PHE) for *Lumbriculus variegatus* in Kansas (KS) and Minnesota (MN) Sediments after 14 and 28 d Exposures ($n = 5$) (the Data Are Shown as the Mean \pm SD)

contaminant, sediment	class	log K_{ow}^e	C_s	% Lipid		BSAF	
				14 d	28 d	14 d	28 d
HCBP,KS	PCB ^a	6.72	3.57 \pm 0.31	1.32 \pm 0.19	1.87 \pm 0.15	5.85 \pm 0.72	6.77 \pm 2.99
DDE,KS	OC ^b	6.51	2.81 \pm 0.15	1.50 \pm 0.42	2.29 \pm 0.24	5.31 \pm 0.54	4.50 \pm 2.16
PERM,KS	pyrethroid	6.10	18.1 \pm 0.99	1.57 \pm 0.20	1.93 \pm 0.32	3.37 \pm 0.80	3.02 \pm 0.24
CHL,KS	OP ^c	5.11	6.52 \pm 0.15	1.46 \pm 0.17	1.86 \pm 0.36	6.54 \pm 0.57	1.49 \pm 0.31
PHE,KS	PAH ^d	4.46	11.9 \pm 0.61	1.67 \pm 0.23	1.79 \pm 0.12	0.55 \pm 0.06	0.74 \pm 0.49
HCBP,MN	PCB	6.72	0.71 \pm 0.01	1.38 \pm 0.25	2.36 \pm 0.56	2.14 \pm 0.12	9.44 \pm 7.15
DDE,MN	OC	6.51	0.50 \pm 0.03	1.12 \pm 0.09	2.14 \pm 0.52	2.64 \pm 0.16	2.00 \pm 0.29
PERM,MN	pyrethroid	6.10	2.87 \pm 0.23	1.45 \pm 0.27	2.64 \pm 0.34	3.79 \pm 1.22	2.17 \pm 0.61
CHL,MN	OP	5.11	1.21 \pm 0.06	1.45 \pm 0.14	2.31 \pm 0.43	4.74 \pm 0.54	2.32 \pm 1.12
PHE,MN	PAH	4.46	1.95 \pm 0.10	1.52 \pm 0.09	2.14 \pm 0.52	2.45 \pm 2.81	0.29 \pm 0.16

^a PCB: polychlorinated biphenyl. ^b OC: organochlorine pesticide. ^c OP: organophosphate pesticide. ^d PAH: polycyclic aromatic hydrocarbon. ^e log K_{ow} estimates taken from Verschuere (31) and Laskowski (32).

80 mesh, Alltech, Deerfield, IL). The disposable matrix-SPME fiber was coated with 30 μm of polydimethylsiloxane (PDMS; Supelco) and had a phase volume of 0.132 μL per cm of fiber with a 110 μm core diameter. All solvents were pesticide or HPLC grade (Fisher Scientific, Pittsburgh, PA). Moderately hard water (MHW) was prepared following U.S. EPA methods (17). Scintillation cocktail (Scinti Safe Plus 50%) was purchased from Fisher Scientific.

Sediments. Dosed sediments were prepared from two uncontaminated reference sediments collected from Wichita, Kansas (KS) and Bear-Skin Lake, Minnesota (MN). Total OC content of the sediment was determined by CHN analysis after removing carbonates using a CHN analyzer (CE Instruments, Thermoquest Italia, Milan, Italy). KS soil was 14% sand, 70% silt, and 16% clay, and had a total organic carbon (TOC) content of 1.31 \pm 0.02%. It was sieved at 0.5 mm and mixed with water to produce sediment with a dry/wet ratio of approximately 60%. MN sediment had a grain size distribution of 55% sand, 12% silt, and 33% clay and had a TOC content of 7.85 \pm 0.18%. The dry/wet ratio was approximately 20%. Sediments (1800 g of dry KS sediment and 400 g of dry MN sediment) were dosed with each test compound using acetone (100 μL acetone/kg sediment) as a carrier. A solvent control was prepared by adding the same quantity of acetone carrier to control 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 d and homogenized again prior to use.

Total sediment HOC concentration was determined in triplicate before and after each experiment (Table 1). A weighed sample of sediment (\sim 0.05 g wet weight (ww)) was placed into a scintillation vial, extracted with 10 mL of cocktail by vortexing for 2 min, and counted by LSC after 24 h. Background radioactivity was determined for the control sediments and subtracted from all samples. Extraction efficiencies for all HOCs from sediments were 87–100%. Degradation of PERM, CHL, and PHE in sediment was quantified by extracting 2 g of wet sediment with 3 \times 5 mL of acetonitrile (ACN). The extracts were decanted, combined, filtered, and evaporated to 1 mL. Separation of the parent compound from degradation products was performed as for the purity studies (see above).

Bioaccumulation Test. Fourteen day and 28 d sediment bioaccumulation tests were performed with *L. variegatus* following a miniature version of U.S. EPA recommended procedures (17; See Supporting Information for details). Exposures were performed with five replicates for each compound in each of two sediments. Two worms from each test were used for lipid determinations following the spec-

trophotometric method of van Handel (18) and the remaining worms were used for tissue residue analysis. Biotransformation of PERM, CHL, and PHE was determined in *L. variegatus*. *L. variegatus* were homogenized with 2 mL of acetone and washed three additional times with 1 mL of acetone. After combining the extracts, 2 mL of the extract was mixed with 10 mL of scintillation cocktail for LSC analysis, while 1.5 mL of extract was evaporated to near dryness and solvent exchanged to 0.5 mL of ACN. The extract was analyzed by HPLC as described for the sediment degradation studies (see above). Biotransformation of DDE and HCBP in *L. variegatus* was previously shown to be negligible (19–20); therefore, no biotransformation assessment was performed for these compounds. For DDE and HCBP, *L. variegatus* were directly placed into 10 mL of scintillation cocktail and sonicated for 40 s using a Tekmar model 501 sonic processor (Cincinnati, OH). Radioactivity was determined by LSC after a 24 h holding period that allowed for extraction of the compounds into the cocktail.

Desorption with Tenax. Desorption of the test compounds from sediment using Tenax adsorbent was performed using the methods similar to Cornelissen et al. (4; see Supporting Information for details). Tenax beads were continuously mixed with sediment in a water slurry and the beads were removed at 6 h for analysis. The beads were extracted with 1:1 acetone/hexane and analyzed by LSC.

Uptake by Matrix-SPME. Matrix-SPME uptake was conducted using the methods described by Conder et al. (13) and modified to fit the current study design (see Supporting Information for details). The fibers were exposed to the sediments for the same length of time as the organisms (e.g., 14 or 28 days) thereby representing a direct surrogate for accessibility. Three sets of five SPME fibers protected in stainless steel envelopes were placed in the sediments prior to adding worms. The fibers were removed at the end of the 14 or 28d exposure, extracted with ACN, and analyzed by LSC.

Data Analysis. Contaminant bioavailability from sediment was expressed as a biota-sediment accumulation factor (BSAF):

$$\text{BSAF} = C_b (\text{lipid-normalized}) / C_s (\text{OC-normalized}) \quad (1)$$

where C_b is the lipid-normalized concentration in *L. variegatus* and C_s is the OC-normalized concentration in sediment. The average sediment concentration measured before and after the exposure was used for calculation, and only the amount of parent compound in the sediment and tissues was used for calculations for PERM, CHL, and PHE.

The bioavailable sediment concentration ($C_{s_{6h}}$) was calculated as follows:

$$C_{s_{6h}} = C_s \cdot F_{6h} \quad (2)$$

Results and Discussion

Bioaccumulation Tests. Bioaccumulation was measured separately after 14 and 28 d exposures at chemical concentrations ranging from 40 to 250 $\mu\text{g}/\text{kg}$ dry sediment (0.50–18.1 $\mu\text{g}/\text{g}$ OC, Table 1). Dissolved oxygen, pH, and conductivity were >5 mg/L, ~ 7.9 , and ~ 320 μS , respectively, and the ammonia level held constant at 0.6–0.8 mg/L N through the tests. No acute toxicity (mortality) was observed for *L. variegatus*. In addition, no significant differences in lipid content were noted for *L. variegatus* exposed in control and spiked sediments and no overt avoidance of the sediment was observed. Thus, bioaccumulation was not complicated by an acute toxic response.

BSAF values varied among compounds and sediments and were generally larger than 1 with the exception of PHE which was very rapidly biotransformed and eliminated from the worms (Table 1). If organism lipid and sediment organic matter had the same capacity for HOCs, then at equilibrium, the expectation would be a BSAF of 1. However, previous work, based on sediment partitioning and bioconcentration factors found a BSAF value of 1.7 (21–22), and suggested that organism lipid has approximately twice the capacity for the HOCs as sediment OC. Here, BSAF values were greater than 1.7, and these higher-than-expected BSAF values may have resulted from two distinct processes.

First, characteristics of the OC may be dominated by plant-derived material that is apparently less sorptive yielding greater bioavailability (23). Super sorptive materials, such as black carbon, do not appear to dominate in these sediments where they are important and affect BSAF in other sediments (24); but, the lower BSAF values in the MN sediment compared to the KS sediment support the contribution of additional sorptive processes that are as important as the increasing OC concentration. The second factor that might have led to the higher BSAF values is the duration of sorption between the compound and sediment. The desorption characteristics measured by Tenax extraction suggested that the compounds are likely at equilibrium in the rapidly desorbed compartment within 7 d (unpublished data), but the full distribution to the slow and very slow compartments, to show the full impact of sequestration, would have required more than 1 yr for equilibrium for some of the compounds. Thus, the observations of high BSAF values may partly result from the relatively short equilibrium time among the various compartments compared to studies that employed field-contaminated sediments.

Another feature of note is the difference in BSAF values between the 14 and 28 d exposures (Table 1). The BSAF values were 16–80% lower at 28 d compared to 14 d except for HCBP. While no significant difference in the HCBP BSAF values for the KS sediment occurred with different temporal exposures, the high variability of the HCBP BSAF in the 28 d exposure in MN sediment prevented a good comparison. The cause for the high variability is unknown at this time. The largest decline in BSAF values occurred for the least hydrophobic compounds, CHL and PHE. The standard toxicological method for *L. variegatus* calls for 28 d exposures (17), however the use of a 28 d exposure is primarily a carry over from previous work on sediment bioaccumulation with marine invertebrates (25). Several studies have noted findings similar to ours where the bioaccumulation of *L. variegatus* declines after peaks in bioaccumulation ranging from 4 to 14 d with laboratory-spiked sediments (26) and some continuous declines with field-collected sediments (27).

The mechanism for BSAF declines could likely come from four sources. The first is potential biotransformation. While this work addressed biotransformation directly and calculated the BSAF only for the parent compound, induction of biotransformation would enhance the apparent elimination rate and reduce bioaccumulation of the parent compound. Thus, the BSAF value could decline with time. For PHE, extensive biotransformation was observed after 28 d (30–70%) and correspondingly low BSAF values were found. Further, the duration of the gut purge, which is recommended to be 6 h, was actually 10 h because of the time required to remove all the animals from the sediment. For highly hydrophobic compounds, the additional purge time would not have a large influence on the body residue due to the overall slow elimination, but for a compound like PHE, which is rapidly biotransformed and readily eliminated (26), the loss during the gut purge could have been approximately 36% based on previously determined toxicokinetics (26). Thus, these factors likely contributed to the overall lower BSAF for PHE reducing our confidence in the PHE data.

The third mechanism that could have created a decline in BSAF between 14 and 28 d would be degradation of compounds in the sediment. Whereas bioaccumulation was based on parent compound reducing the source and therefore the flux into the organism, a compound with a relatively fast elimination rate would show increased loss from and lower bioaccumulation over time. However, the average degradation was minimal over 28 d ($<13.3\%$) except for CHL, which degraded 20%. In addition, due to the relatively high water-solubility of CHL, some compound was lost during water renewals resulting in a loss of 30% based on the overall mass balance of $>90\%$. PHE also showed loss over 28 d, but it was not possible to identify the source of the loss due to an extremely low mass balance (50–70%). Such unexplained loss of PHE in sediment exposure has been observed previously (26). Thus, loss due to transfer during water exchange and some degradation would result in depletion of the labile, bioavailable pool and subsequently reduce the flux into the organism and could have resulted in the observed declines in bioaccumulation.

Finally, reduced feeding with time would reduce exposure. This can be a particular problem with *L. variegatus* which reproduces through architometric reproduction (fragmentation) and ceases feeding after division (28) resulting in lower bioaccumulation (29). To avoid problems of reproduction among the worms that affect the bioaccumulation, evaluations of bioaccumulation with this species should be performed with exposures shorter than 28 d. Thus, to evaluate the utility of the chemical approaches to predict bioaccumulation across compounds and sediments, the 14 d data were used.

Tenax Desorption as a Measure of Bioaccessibility. A linear relationship was found between the measured C_b and $C_{s_{6h}}$ in the two sediments (Figure 1). Because of the possible underestimation of the bioaccumulation for PHE due to biotransformation and excessive loss during the gut purge due to rapid elimination, PHE was excluded from the regression. Generally less variation in bioaccumulation was noted within the KS sediment, excluding PHE for the reasons cited above compared to the MN sediment (Table 2). Variation in the F_{6h} measurements was also observed in the different sediments among chemicals. For example, F_{6h} values for the five chemicals in the high TOC MN sediment were negatively correlated with compound hydrophobicity ($r^2 = 0.91$). In contrast, F_{6h} values from the lower TOC KS sediment were similar for all five HOCs with values of approximately 0.5 regardless of hydrophobicity (Table 2). A strong positive relationship was found between biological and chemical availability ($C_b = 6.77 [1.22] C_{s_{6h}} + 2324 [4568]$, $r^2 = 0.84$ and $\log \text{BSAF} = 1.04 [0.17] F_{6h} + 0.22 [0.07]$, $r^2 = 0.86$) for the

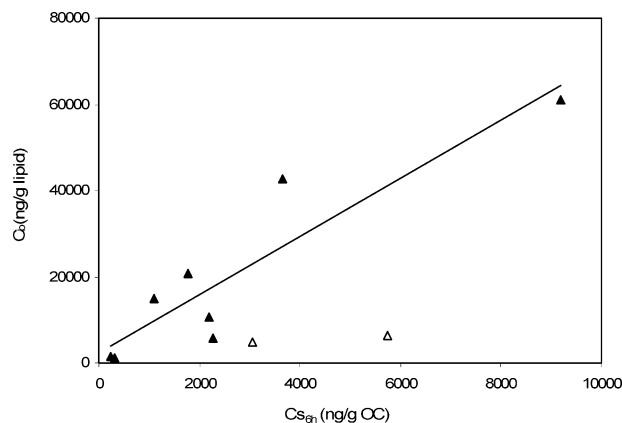


FIGURE 1. Relationship between C_b (ng/g lipid) for *Lumbricus variegatus* and the sediment concentration in the fraction desorbed at 6 h (C_{s6h}) for the five compounds in both sediments. The triangles and dotted line are for C_{s6h} ($C_b = 6.77 [1.22] C_{s6h} + 2324 [4568]$, $r^2 = 0.84$) excluding phenanthrene (PHE). Open symbols represent PHE and solid symbols represent the other compounds.

TABLE 2. Fraction Desorbed in 6 h (F_{6h}) Estimated by Tenax Extraction, Contaminant Concentration in Fiber (C_f) Measured by Matrix Solid-phase Microextraction (M-SPME), and Chemical Residues in *Lumbricus variegatus* (C_b) Measured by 14 d Bioaccumulation Test for of 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), 4,4'-dichlorodiphenyldichloroethylene (DDE), Permethrin (PERM), Chloropyrifos (CHL), and Phenanthrene (PHE) in Kansas (KS) and Minnesota (MN) Sediments ($n = 3$)

contaminant, sediment	F_{6h} (mean \pm SD)	C_f (ng/mL PDMS ^b)	C_b (μ g/g lipid)
HCBP,KS	0.499 \pm 0.017	493 ^a	20.86 \pm 1.96
DDE,KS	0.394 \pm 0.046	620 \pm 17	14.92 \pm 1.14
PERM,KS	0.507 \pm 0.044	1912 \pm 134	61.01 \pm 14.11
CHL,KS	0.559 \pm 0.010	2410 \pm 40	42.67 \pm 3.55
PHE,KS	0.484 \pm 0.010	1807 \pm 50	6.55 \pm 0.64
HCBP,MN	0.155 \pm 0.008	30 ^a	1.51 \pm 0.08
DDE,MN	0.241 \pm 0.007	69 ^a	1.33 \pm 0.06
PERM,MN	0.202 \pm 0.002	198 ^a	10.81 \pm 3.41
CHL,MN	0.395 \pm 0.024	364 \pm 9	5.73 \pm 0.58
PHE,MN	0.643 \pm 0.009	72 \pm 3	4.76 \pm 5.49

^a Three replicates were combined for the measurement due to the low concentration. ^b PDMS = polydimethylsiloxane.

lab-spiked sediments. The slopes and intercepts are given as means [standard deviation].

The lab-spiked data were combined with data from PCB-contaminated sediments collected from Crab Orchard Lake, IL to determine whether C_{s6h} could describe the variation in bioaccumulation data from these diverse dosing regimes (Figure 2). No statistical difference was observed for slope ($t = 0.14$) or intercept ($t = 0.30$) for the relationship between biota concentration and Tenax extractable concentration at 6 h between lab-spiked sediments ($\log C_b = 1.04 [0.06] \log C_{s6h} + 0.71 [0.14]$, $r^2 = 0.95$) and field-collected sediment ($\log C_b = 1.06 [0.19] \log C_{s6h} + 0.62 [0.62]$, $r^2 = 0.83$) ($t_{0.05(2),22} = 2.074$, $P > 0.50$) so the data could be combined. A strong positive relationship was found between biota concentration and Tenax extractable concentration at 6 h between lab-spiked sediments and field-collected sediment ($\log C_b = 1.04 [0.05] \log C_{s6h} + 0.72 [0.14]$, $r^2 = 0.94$). These data support the hypothesis that a single point Tenax extraction can serve as a good surrogate for HOC bioavailability across chemical classes and among sediments. However, it may overestimate the bioaccumulation for chemicals that are easily biotransformed and rapidly eliminated, such as PHE, unless extra care is exercised to account for losses.

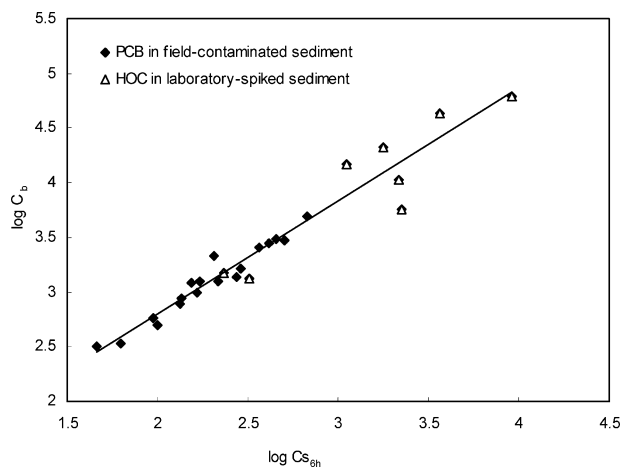


FIGURE 2. Relationship between C_b (ng/g lipid) for *Lumbricus variegatus* and the sediment concentration in the rapidly desorbing fraction (C_{s6h} , ng/g OC) for PCBs in field-contaminated sediments from Crab Orchard Lake and four laboratory-spiked contaminants (2,2',4,4',5,5'-hexachlorobiphenyl, permethrin, 4,4'-dichlorodiphenyldichloroethylene, and chloropyrifos) in two sediments. Solid squares are for the native PCBs and open triangles are the four laboratory-spiked contaminants. Solid line represents regression line for all the data ($\log C_b = 1.04 [0.05] \log C_{s6h} + 0.72 [0.14]$, $r^2 = 0.94$).

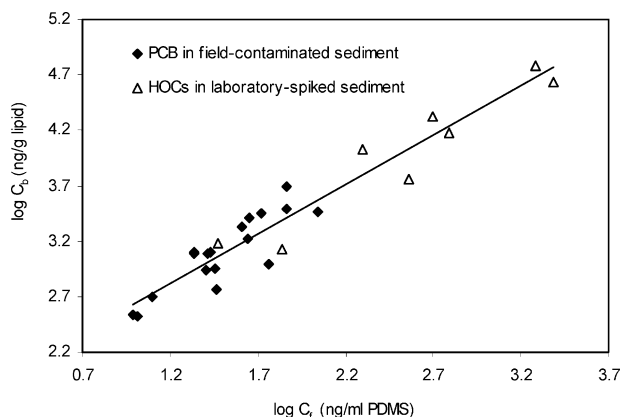


FIGURE 3. Relationship between $\log C_b$ residues in *Lumbricus variegatus* (C_b , ng/g lipid) and solid-phase microextraction fiber (C_f , ng/mL PDMS) for PCBs in field-contaminated sediments from Crab Orchard Lake and four laboratory-spiked contaminants (2,2',4,4',5,5'-hexachlorobiphenyl, permethrin, 4,4'-dichlorodiphenyldichloroethylene, and chloropyrifos) in two sediments. Solid squares are for the native PCBs and open triangles are for the four laboratory-spiked contaminants. Solid line represents regression line for all the data ($\log C_b = 0.89 [0.05] \log C_f + 1.75 [0.11]$, $r^2 = 0.92$).

Matrix-SPME as a Measure of Bioavailability. Matrix-SPME fibers have produced good relationships between chlorobenzene and PCB concentrations in fibers and oligochaetes at equilibrium (15, 16). Similarly, a positive chemical-specific relationship existed between uptake of TNT and its metabolites by matrix-SPME fiber and *Tubifex* worms (14). Here, a direct correlation was found between accumulation of HOCs by *L. variegatus* and matrix-SPME fiber after 14 d (Table 2, and Figure 3). The regression coefficient was 0.69 across all compounds and sediments, but was significantly improved ($r^2 = 0.90$) by removing the PHE data due to issues described above. Because the fiber and organisms were exposed under the same conditions, influences due to the chemical or biological changes during the test were minimized. It should be noted that most matrix-SPME studies allow the chemicals in the system to reach equilibrium, thereby allowing the chemical activity of the compounds to be quantified. The present study used a different approach.

The fibers were exposed to the sediments for the same length of time as the organisms (e.g., 14 days). The regression slope was less than 1 (Figure 3), because the organisms apparently come to steady-state rapidly, generally within 14 d, whereas the fiber does not reach equilibrium during the 14 d testing period. In a separate study, equilibrium was achieved on the matrix-SPME fiber for all of the HOCs in the KS sediment within 14 days, however, not all HOCs reached equilibrium in the MN sediment (unpublished data). Therefore, the matrix-SPME technique used here measures bioaccessibility of HOCs from sediment as an operationally defined measure of bioavailability and is comparable to the 6 h single Tenax extraction technique.

The main focus of this study was to compare the suitability of chemical approaches to predict bioavailability rather than measuring porewater. Though porewater concentration (chemical activity) was not measured in our study with matrix-SPME due to the short exposure times, a good relationship was found between fiber concentration and biota concentration across chemicals and sediments (including lab-spiked and field-collected). Therefore, matrix-SPME can be used as a surrogate for bioavailability without the need for multiple samplings and allows for simultaneous exposure with organisms, thereby allowing for its potential use for in situ field studies.

The regression for bioaccumulation of laboratory-spiked HOCs ($\log C_b = 0.88 [0.12] \log C_f + 1.76 [0.32]$, $r^2 = 0.90$) was similar to the relationship found for field-contaminated PCBs in sediment collected from Crab Orchard Lake, IL ($\log C_b = 0.99 [0.14] \log C_f + 1.61 [0.21]$, $r^2 = 0.76$), unpublished data). The slopes ($t = 0.61$) and intercepts ($t = 0.45$) of these two regression lines were not significantly different ($t_{0.05(2),22} = 2.074$, $P > 0.50$) and a good fit also was obtained for all HOCs across sediments and chemical classes ($\log C_b = 0.89 [0.05] \log C_f + 1.75 [0.11]$, $r^2 = 0.92$) (Figure 3). Lesile et al. (30) reported a factor of 28 for the concentration difference between organism and SPME fiber concentration in a water-only study, and it is close to the observed factor of 23 in our study ($C_b = 22.9 (1.67) C_f + 1244 (1054)$, $r^2 = 0.89$). Because a single regression fit both the laboratory and field data as well as data from sediments of varying composition, matrix-SPME can be considered a matrix- and chemical-independent predictive technique for bioavailability. From the literature and this work, matrix-SPME appears to provide a good matrix to mimic the bioaccumulation of sediment-associated contaminants across a wide range of organisms and compound classes.

Are Chemical Approaches Good Surrogates for Bioavailability? Suitability of the two chemical approaches, single time point Tenax extraction and matrix-SPME, as surrogates for bioaccumulation was evaluated with five different classes of HOCs from two sediments with different characteristics. Chemical availability measured by both methods was positively related to bioaccumulation across the different chemical classes and sediments extending the use of the methods beyond the usual poorly biotransformed nonpolar organic contaminants usually investigated with such techniques. Both chemical methods could be used as cheaper and easier surrogates of bioaccumulation than traditional bioaccumulation tests as they provided accurate and useful predictions from both field and laboratory data. The single point Tenax extraction at 6 h was the simplest and quickest screen for bioavailability of HOCs from sediment, while matrix-SPME fibers could be exposed simultaneously with organisms to overcome potential exposure bias.

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Supporting Information Available

Information on detailed experimental methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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