



Toxicological Exposure of Sediment-Bound Hydrophobic Organic Contaminants as a Function of the Quality of Sediment Organic Carbon and Microbial Degradation

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PURPOSE: This technical note 1) relates the importance of the toxicological exposure potential of hydrophobic organic contaminants (HOC) in sediments and dredged material to implementation of public laws and regulations governing environmental risk assessment, 2) summarizes recent peer-reviewed literature on sediment HOC exposure potential in the context of the sorbent quality of sediment organic carbon and microbial degradation, and 3) introduces the practical utility of thermal desorption mass spectrometry with respect to identification and quantification of HOC, measuring HOC release energy, and the compatibility of the development of field-portable direct sampling analytical technologies.

Bioavailability of HOC and Environmental Risk Assessment. The Clean Water Act (Section 404 of PL 92-500) and the Marine Protection, Research, and Sanctuaries Act (also known as the Ocean Dumping Act; Section 103 of PL 92-532) require that sediment-associated contaminants be evaluated for their ability to accumulate and cause toxicity in biota. Jointly, the U.S. Army Corps of Engineers (USACE) and the U.S. Environmental Protection Agency (USEPA) adopted a tiered system to evaluate this bioaccumulation potential (USEPA/USACE 1991, 1998). Definitive bioaccumulation tests require that two different organisms be exposed to sediment for 28 days, and then the HOC body burdens can be determined using standard analytical techniques. From a practical perspective, it is not feasible to test all sediments and dredged material the USACE must manage. It is also apparent that noncontaminated sediments do not warrant bioaccumulation testing, and some sediments are so contaminated that bioaccumulation is a foregone conclusion. The USEPA/USACE (1991, 1998) testing manuals describe a screening level protocol termed Thermodynamic Bioaccumulation Potential (TBP) (McFarland 1995). TBP has been used in Tier 2 evaluations to exclude from further testing sediments from both extremes of the contamination level continuum.

The sorption of HOCs to sediments from water has been simply described. Karickhoff (1981) combined thermodynamic theory (i.e., fugacity) (Mackay and Paterson 1981, 1982) with empirical correlations to derive a systematic procedure for predicting the contaminant - sediment sorptive behavior. In spite of the "high degree of variability and complexity in sediment composition and large number of potential sorptive interactions," Karickhoff intentionally developed a simple mathematical format that required a minimum of measured parameters. He felt a balance must be struck between a complex model few could afford to parameterize and the degree of accuracy and precision required in its application (Karickhoff, Brown, and Scott 1979). Karickhoff showed that for neutral hydrophobic contaminants (i.e., water solubilities less than 10^{-3} M), sorption isotherms in the low loading limit are linear and reversible. The apparent partitioning of aromatic hydrocarbons and chlorinated hydrocarbons between water and sediment (i.e., partition coefficients, K_{ps}) were highly correlated to the organic carbon content of the soils/sediments in his data set. Referencing sorption to the quantity of sediment organic carbon produced an organic contaminant aqueous

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partition coefficient (K_{oc}) that was independent of other bulk sediment/soil parameters. Karickhoff's (1981) "justifiable simplification" found even wider application when he showed K_{oc} could be directly derived from the contaminants' octanol-water partition coefficients. Concurrently, Könemann and van Leeuwen (1980) showed a linear relationship between K_{oc} and the partitioning of a series of chlorobenzenes from sediments to lipid normalized goldfish biomass.

McFarland (1984) synthesized information from Karickhoff (1981) and Könemann and van Leeuwen (1980) and derived a relationship for TBP (McFarland and Clark 1987).

$$TBP = AF(C_S/f_{OC})f_L$$

where

AF = Accumulation factor

C_S = HOC concentration in whole sediment

f_{OC} = Decimal fraction of organic carbon in sediment

f_L = Decimal fraction of lipid in targeted organism

TBP predicts the partitioning behavior of HOC between sediment organic carbon and organism lipid. TBP is based on a thermodynamic model (Mackay and Paterson 1981 and 1982) of the environment as a system comprised of various compartments where contaminants have come to equilibrium through passive processes. At equilibrium, fugacity (i.e., escaping tendency) is equal in all sorptive and solution phases (Mackay 1991). On the basis of fugacity, it is possible to predict the equilibrium distribution of a nonpolar contaminant between any two phases. The two most relevant phases with respect to the bioaccumulation of HOC from contaminated sediment are sediment organic matter and organism lipid. TBP does not require the measurement of aqueous HOC levels and enables correlations to be drawn between HOC body burdens and toxic effects.

Initial TBP predictions, derived from an arbitrarily fixed Accumulation Factor (AF) of 4, consistently overestimated polynuclear aromatic hydrocarbon (PAH) bioaccumulation from contaminated sediments by factors ranging between 41 and 386 (McFarland 1995). Precision and accuracy of TBP predictions were improved to a factor of 10 when empirically derived Biota - Sediment Accumulation Factors (BSAF) from one field reference sediment contaminated with PAH were used to calculate TPB for a second field sediment contaminated with PAH (Clarke and McFarland 2000). That is, field reference derived BSAF were substituted for AF in the original TBP equation. Clarke and McFarland (2000) concluded that TBP was a useful screening tool for eliminating sediments with negligible likelihood of causing unacceptable effects because of bioaccumulation from further testing and tended to generally over estimate HOC bioaccumulation from sediment.

$$BSAF = (C_T/f_L)/(C_S/f_{OC})$$

where

C_T/f_L = the lipid normalized contaminant tissue concentration

C_S/f_{OC} = the organic carbon normalized contaminant sediment concentration

Equilibrium Partitioning and Sediment Quality Guidelines. In the absence of site-specific information, managers must use the best available information. Various models have been proposed to support sediment management decisions (Condor et al. publication pending). The Equilibrium Partitioning (EqP) model (DiToro et al. 1991) has received considerable attention from the USEPA. EqP uses the logic of Karickhoff's fugacity-based model of HOC-sediment partition coefficients (K_p) normalized to organic carbon content (K_{oc}) to predict pore water HOC concentrations, and thus potential aqueous exposure levels (Figure 1). These potential exposure levels, taken together with EPA's Water Quality Criteria databases that relate HOC concentration in water to toxicity, have been used to predict sediment toxicity. Measures of HOC body burdens are not required. This conceptual model, EqP, is the basis for deriving sediment quality guidelines as proposed by DiToro et al. (1991).

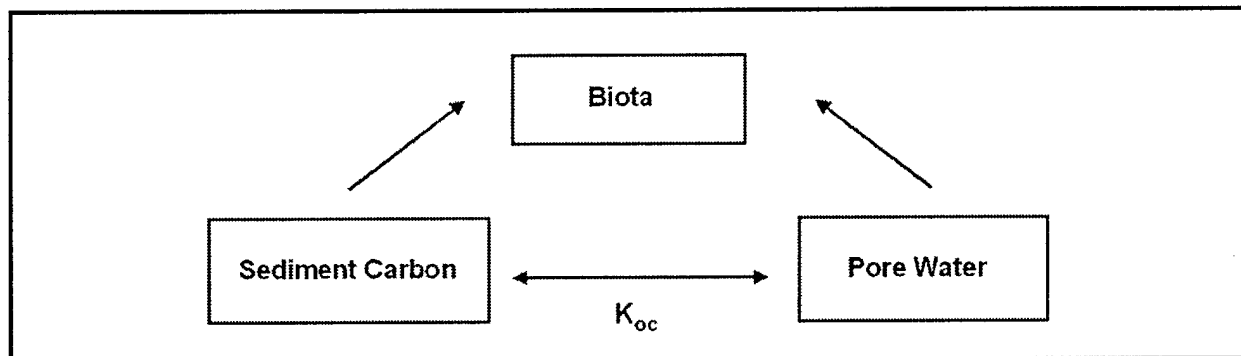


Figure 1. EqP as described by DiToro et al. (1991) is predicated on a model that assumes that equilibrium exists between the contaminant sorbed to sediment organic carbon, pore water, and biota. The partitioning of HOC between sediment organic matter and pore water is predicted from K_{oc} (Karickhoff 1981). Water Quality Criteria databases are used to predict toxicity. Toxicity is not derived from HOC body burdens

EqP estimates of toxicity are derived from K_{oc} . The accuracy, precision, and general applicability of predictions made on the basis of K_{oc} have been debated in the technical literature since it was first proposed (e.g., Farrington et al. 1983; Rutherford, Chiou, and Kile 1992). The practical ecological and economic consequences of this issue have escalated as applications of the K_{oc} have expanded from a simple description of neutral organics partitioning between water and sediment, through screening tools for estimating bioaccumulation potentials, to potential indicators of sediment toxicity. Some suggest EqP-derived Sediment Quality Criteria could be used in a manner comparable to the USEPA's Water Quality Criteria (USEPA 1993). A review of this issue is beyond the scope of this technical note. The reader is referred to articles promoting the use of EqP model predictions in sediment management decisions (DiToro et al. 1991; Ankley et al. 1996; and Burkhard 1998), and those that argue for more limited use of the models in sediment management

decisions (Iannuzzi et al. 1995; Driscoll and Landrum 1997; Peddicord, Lee, and Engler 1998; O'Connor et al. 1998; van Beelen, Verbruggen, and Peijnenburg 2001; and Condor et al. publication pending). Instead, we will focus the remainder of this discussion on technical issues relevant to two factors that have been acknowledged as being potentially important (McFarland 1984) but that are not taken into account by K_{oc} -based models - HOC sequestration in sediment and microbial degradation of HOC in sediment.

HOC in Sediments. Only a fraction of the HOC that is extractable from sediment with organic solvents (e.g., USEPA Priority Pollutant Analysis) may be biologically available. Luthy et al (1997) characterized matter in soils and sediments as geosorbents. Sediments are heterogeneous at the scale of samples, aggregates, and particles (Figure 2). Structurally and/or chemically different constituents of sediments interact differently with HOC in terms of binding energies and associated rates of sorption and desorption. Complex assemblages of the components can cause complex mass transfer phenomena. The term sequestration refers to some combination of diffusion limitation, adsorption, and partitioning. Sorption and desorption rates for HOC in geosorbents occur on time scales ranging from fast (e.g., minutes to days) to slow (e.g., weeks to years). Although their relative proportions vary greatly, most HOC-contaminated sediment to date have both rapidly and slowly desorbing HOC fractions (Davis 1993). Desorption rate differences are thought to be the result of processes such as intra-aggregate diffusion, releases from micropores, or different forms of geosorbent organic matter.

Two of these proposed geosorbant domains, soft amorphous organic matter and soot, have been particularly important when attempting to predict HOC equilibrium partitioning, and ultimately, exposure, and toxicity. Decaying plant material (Case A in Figure 2) is a major source of sediment organic matter and a major food source for detritivores. This low-density fraction of sediment organic matter from a New York/New Jersey estuary contained 10 times the levels of PAH predicted by organic carbon normalized equilibrium partition coefficients (K_{oc}) (Rockne et al. 2002). This fraction readily released PAH into the aqueous phase and was the controlling factor in whole sediment PAH release. Drifting plant detritus has also been a major contributor to the total annual load of organochlorine contaminants (including polychlorinated biphenyls (PCB)) in the Detroit River (Lovett-Doust et al. 2002). These recent studies are especially important. They demonstrate that plant detritus, a major food source at the base of aquatic food webs, can be the major contributor to HOC Total Maximum Daily Loads, and K_{oc} did not accurately describe HOC partitioning into this trophically important geosorbant. In this common aquatic environmental situation, K_{oc} -based environmental toxicity predictions (i.e., EqP) would not be protective.

K_{oc} -derived predictions of pore water HOC levels from sediments containing soot (Case B in Figure 2) have also been inaccurate (Gustafsson et al. 1997). Socha and Carpenter (1987) compared PAH-contaminated sediments from two sites within Puget Sound. Predicted pore water PAH levels agreed with empirically determined pore water PAH levels (within a factor of 4) at a creosote impacted site. However, no PAH was detected in pore water from a site impacted by combustion products and natural PAH, even though detectable levels were predicted using K_{oc} . McGroddy and Farrington (1995) published similar results on PAH-contaminated sediments in Boston Harbor. Pore water PAH levels were depleted relative to those predicted using partition coefficients. The extent of deviations for individual PAHs varied, but only 0.2 to 5.0 percent of the predicted phenanthrene was actually measured in sediment pore water. PAHs associated with pyrogenically derived soot

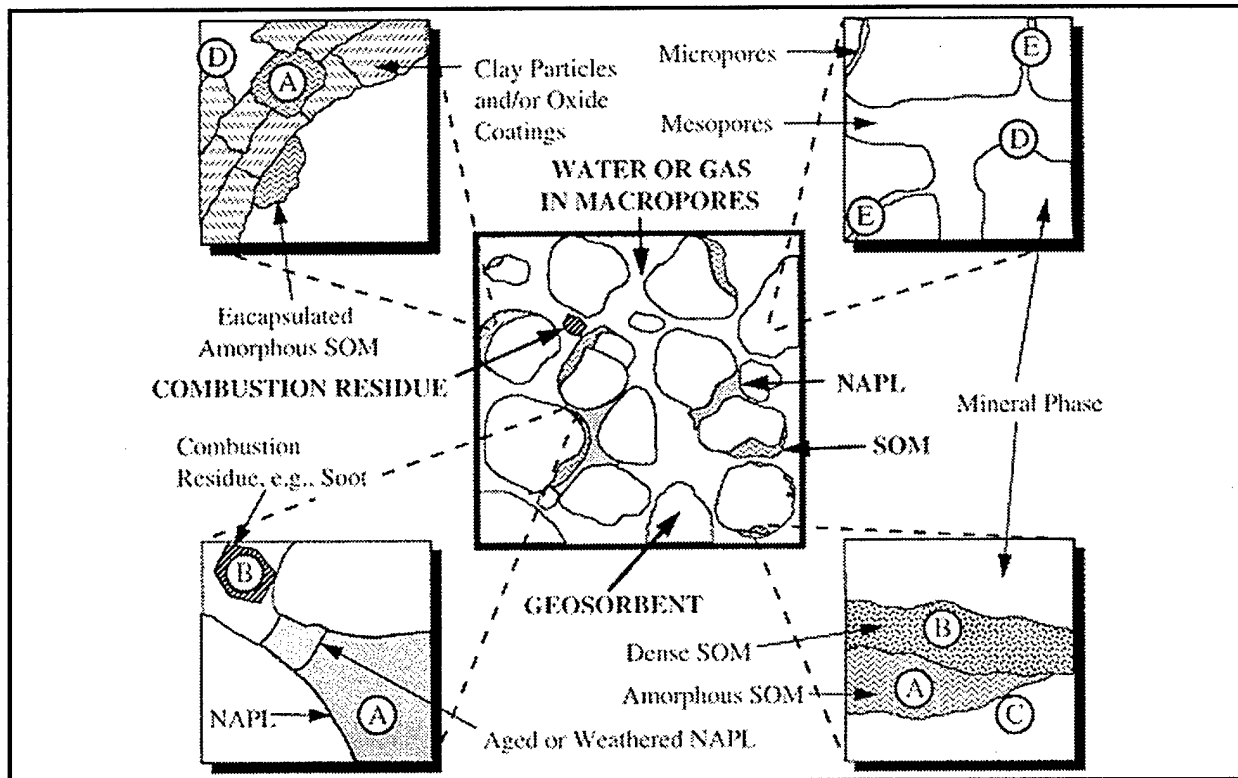


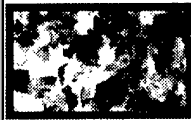

Figure 2. Conceptual model of geosorbent domains. The circled letters refer to representations of the sorption mechanisms described in text. The geosorbent domains include different forms of organic matter (SOM), combustion residue particulate carbon such as soot (Ghosh, Talley, and Luthy 2001), and anthropogenic carbon including nonaqueous-phase liquids (NAPLs). Case A: Adsorption into amorphous or "soft" natural organic matter or NAPL. Case B: Adsorption into condensed or "hard" organic polymeric matter or combustion residue (e.g., soot). Case C: Adsorption onto water-wet organic surfaces (e.g., soot). Case D: Adsorption onto exposed water-wet mineral surfaces (e.g., quartz). Case E: Adsorption into microvoids or microporous (Kyoungphile and Alexander 1998) minerals (e.g., zeolites) with porous surfaces at water saturation <100% (from Luthy et al. 1997)

particles were suggested as the reason for the discrepancies (McGroddy and Farrington 1995; McGroddy, Farrington, and Geschavend 1996). Paine et al. (1996) showed heavily PAH-contaminated sediments (highest levels of 10,000 mg/kg and mean levels of 150 mg/kg) from Kitimat Arm, at the head of Douglas Channel in British Columbia, did not change benthic community structure, were not toxic to benthic fauna, and generally did not accumulate in the commercially important Dungeness crab. Most of the PAH in this sediment was associated with soot that originated from the washout of a wet air scrubber from aluminum smelter potlines. Aluminum smelter-derived PAH in sediments from Sunndalsfjord, Norway (Næs and Oug 1997; Næs et al. 1999), were present at lower levels (15 mg/kg) than Kitimat sediment but were likewise not biologically available, because they were associated with soot particles. Song, Peng, and Huang (2002) showed that black carbon, a type of soot, comprised between 18 and 41 percent of the total organic carbon of soil and sediment samples collected from Guangzhou, China. The percentage of soot in any particular series of sediment samples can be highly variable because of variability in air and water currents that deposit them in aquatic systems. Sediment particles continually undergo segregation, resuspension, redistribution, and transport as the result of episodic water currents.

Effects of diagenesis and weathering on HOC geosorbents. In addition to the sources of sediment organic matter (e.g., vascular plants, algae, etc.), diagenesis and weathering affect sediment quality characteristics that are correlated to rates of HOC sorption and desorption (Luthy et al. 1997). Some diagenetically aged organic matter (e.g., coal and shale) is compacted, is reduced in the relative amount of oxygen-containing functional groups (reflected in H/O and O/C atomic ratios; Grathwohl 1990), and contains more aromatic carbon rings (measure by UV and IR absorbance) than recently deposited organic carbon. This reduced organic matter has been characterized as hard or glassy (Figure 2). Glassy organic matter strongly binds HOC (Brannon et al. 1998) and is characterized by slow mass transfer rates and nonlinear adsorption kinetics (Haitzer et al. 1999; Lebouf and Weber 2000). Kerogen is a solid, waxy, organic substance produced by the partial decay of organic matter that when heated can produce coal or oil. Kerogen has nonlinear HOC sorption isotherms and high capacity to bind HOC (Song, Peng, and Huang 2002). Little is known about the distribution and importance of kerogen in surface sediments in the context of sequestering HOC. A portion of kerogen and other organic material can also be dissolved in pore water in a form that is not removed by filtration (Gauthier, Seitz, and Grant 1987) and thus greatly affect the apparent pore water HOC concentrations and mechanisms of HOC bioaccumulation.

Technical information on the sorption behavior of HOC, with respect to the quality of sediment organic carbon, is directly relevant assessing adverse effects resulting from exposure to HOC-contaminated sediments and, thus, USACE management of dredged materials. Soxhlet extractable PAH levels in dredged material from a confined disposal facility at Milwaukee Harbor (Table 1) averaged 115 mg/kg, but only 46 mg/kg (i.e., less than half) was biologically available either for microbial degradation (Ringelberg et al. 2001) or bioaccumulation in earthworms (Talley et al. 2002a,b). The empirically determined BSAF for total PAH from Milwaukee Harbor dredged material into the earthworm (*Eisenia fetida*) was quite low (0.08). Five percent of the dry weight mass of Milwaukee Harbor dredged material was coal/coke. Sixty percent of the total extractable PAH was associated with this coal/coke fraction, and almost none of it was biologically available. Biodegradation of the HOC in this material was limited to the approximately the 40 percent of the Soxhlet extractable HOC that was bioavailable (Myers, Bowman, and Myers 2002).

K_{oc}-based predictions. Appropriate use and informed interpretation of the data derived from screening tools are essential for effective sediment management. Sediments have been described where K_{oc}-based predictions have over- or under-estimated bioaccumulation. Karickhoff's "justifiable simplification" of the partitioning behavior of neutral organics between water and sediment has been very useful and will be an even more useful screening tool when the limits on its applicability are more fully understood and appreciated. The environmental distribution and relative abundance of organic matter that sequesters HOC in sediment and the fate of HOC when desorbed from this material are currently not fully known and warrant further study. To gain this perspective, we present and discuss additional tests and environmental parameters that will improve assessments of HOC bioaccumulation potential from sediments.

Table 1 Summary of PAH levels in two density fractions (silt/clay and coal) of Milwaukee Harbor CDF dredged material (Talley et al. 2002 a,b)						
Fraction of Milwaukee CDF Dredged Material	% Dry Wght. of Dredged Material	Total PAH Level (mg/Kg)	Measures of PAH Availability			
			Sequestration Energy	Sorption of HOC to Tenax	Earthworm Uptake	Biodegradation Potential
SILT/CLAY 	95%	80-100 <40%	Low	>85%	High	High
COAL 	5%	10,000 >60%	High	<5%	Low	Low

New testing protocols. A number of new sediment testing protocols have been published that are designed to produce better information on HOC sediment-pore water partitioning, bioaccumulation potential, exposure potential, and/or toxicity. These approaches have been reviewed from a toxicological perspective (Condor et al. publication pending). In evaluating these approaches it is important to realize that while some of these approaches are designed to provide better information on the chemical partitioning of HOC between sediment and pore water, others are designed to produce better data on the transfer of HOC from sediment into biota. All these approaches have their respective merits and disadvantages. For example, Kesley and Alexander (1997) compared mild solvent extractions (e.g., butanol) to contaminant bioaccumulation. While the procedure was simple and fast, no single solvent extraction system produced a reasonable correlation to empirically measured BSAF when different soils and test organisms were used. Weston and Maruya (2002) have suggested that gut fluids from deposit feeding animals are an appropriate extraction fluid for benthic animals that accumulate contaminants via their gut tracks. Standardizing this assay presents some technical challenges, and it may not be the most appropriate approach for contaminants that are taken up mainly through the skin and gills. Concurrent Long-Term Effects of Dredging Operations (LEDO) work units led by Dr. Jim Brannon and Dr. Todd Bridges, U.S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL), Vicksburg, MS, are focused on evaluating these approaches, and there will be no further discussion here.

Most studies of pore water-sediment-biomass systems have focused on determining HOC levels in sediments and/or biomass. The low volume of pore water recoverable from most sediments, coupled with the low levels of HOC in most pore waters, presents an analytical challenge with respect to HOC detection limits and the precision and accuracy of these data. Using the fugacity concept, it is not necessary to know pore water HOC levels to predict the HOC levels in biomass. However, a series of studies have shown that the rapidly desorbing fraction of sediment-bound HOC was most likely to become accumulated into biomass (Landrum 1989; Robertson and Alexander 1996, 1998; Tang et al. 1998; Cornelissen et al. 1998; Rockne et al. 2002; Kraaij et al. 2002; McGroddy, Farrington, and Geschwend 1996; Talley et al. 2002; Weber, Kim, and Johnson 2002). Kraaij (2001) demonstrated that the HOC that could readily partition into pore water was a superior predictor of bioaccumulation potential than levels of HOC extractable with organic solvent from the bulk sediments. These data warrant revisiting previously suggested conceptual models (McFarland 1983)

and again evaluating the utility of pore water measurements (or at least measures of the readily desorbable HOC fraction) in predicting HOC bioaccumulation (Figure 3). This approach shows promise because it is a simple model that is independent of bulk sediment measures.

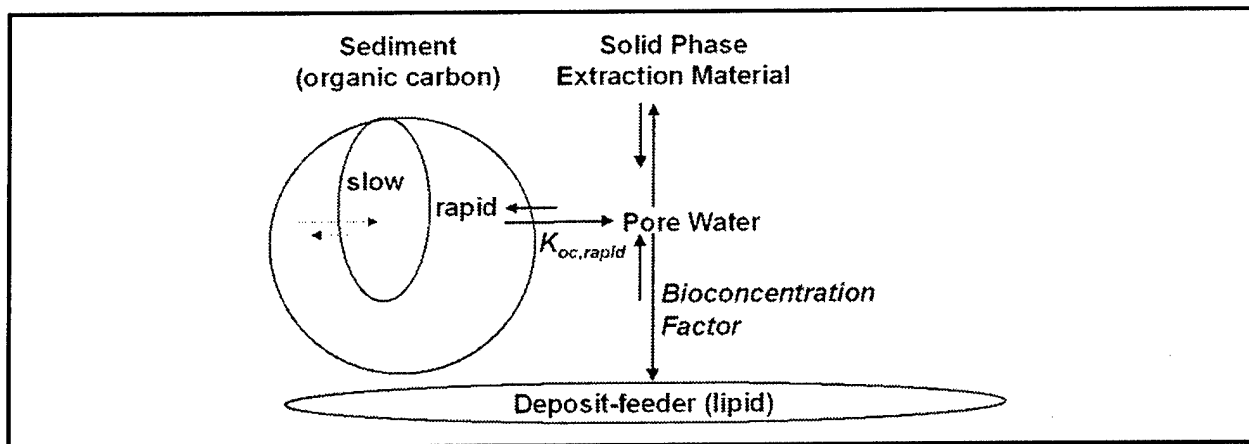


Figure 3. Conceptual model of distribution of hydrophobic organic chemicals in sediment. rap = rapidly desorbing compartment; slow = slowly desorbing compartment; $K_{OC,rap}$ = partition coefficient between rapidly desorbing compartment and pore water (L/kg organic carbon); BCF = bioconcentration factor (L/kg lipid). (Modified from Kraaij 2001)

A number of analytical solutions based on solid phase extraction technologies have been proposed to measure the rapidly desorbed HOC fraction, if not the actual steady-state HOC pore water levels. Cornelissen et al. (2001) developed a simple method to measure the rapidly desorbed HOC whereby Tenax® beads were mixed with sediment, extracted with organic solvent, and analyzed by gas chromatography. They have shown that this functionally defined, rapidly desorbed fraction was useful for predicting the extent to which microorganisms could remediate sediment (Cornelissen et al. 1998). Mayer et al. (2000) used microextraction fibers (200 micrometer polydimethylsiloxane) to measure HOC that could readily partition to pore water. Kraaij (2001) used this analytical method to show that bioaccumulation of HOC in benthic tubificidae can be predicted from measurements of the rapidly desorbed HOC fraction. MacRae and Hall (1998) compared results obtained using polyethylene tube dialysis (PTD) to those obtained using Tenax® and a semipermeable membrane device. In general, the results were similar but the PTD method was able to liberate more PAH from the sediment. Johnson and Weber (2001) used superheated (subcritical) water to measure the slowly desorbing fraction of HOC from geosorbents and used the information to predict long-term rates of HOC desorption from soils and sediments.

Microbial Degradation of HOC in Sediment. Prediction of HOC bioaccumulation from contaminated sediment using K_{oc} -based models does not take into account microbial degradation of contaminants. Microorganisms are champions at recycling chemical elements. They are simple life forms that have minimal metabolic maintenance energy requirements. This enables them to thrive on substrates that do not yield much energy (e.g., HOCs) and may only be available at very low concentrations. Tang et al. (1998) have shown that bioremediation can reduce the levels of pyrene taken up by earthworms by a factor of 10. The rapidly desorbing fraction of sediment-associated PAH is preferentially degraded by microorganisms (Cornelissen et al. 1998), and the rates of biodegradation of the slowly desorbing PAH fraction is limited by the desorption rate (Carmichael,

Christman, and Pfaender 1997). If, as Kraaij et al. (2002) and other researchers suggest, the bioavailable fraction of HOC in sediment is generally equivalent to the rapidly desorbing fraction, then part of the bioavailable (i.e., rapidly desorbing) fraction will bioaccumulate in benthic biota and part will be degraded by microorganisms (Figure 4). Pore water HOC levels will be mainly a function of the fast desorption rate on the supply side and the rate of microbial degradation and partitioning into benthic infaunal lipid on the sink side. HOCs in the rapidly desorbing fraction may overwhelm the capacity of microorganisms to degrade them and render this fraction more likely to accumulate in benthic biota. Fry and Istok (1994) proposed a competitive model for describing the fate of contaminants as they desorb from soils. The slowly desorbing fraction may be effectively scavenged by microorganisms as quickly as it desorbs, thus reducing to negligible the effective dose of HOCs realized by higher benthic species. This effect has been termed biostabilization (Talley 2000). Although this is currently an active research area, there is little published information on the relationships between rates of HOC desorption from sediment, pore water HOC pool size, rates of HOC biodegradation, and rates of HOC accumulation into benthic biota.

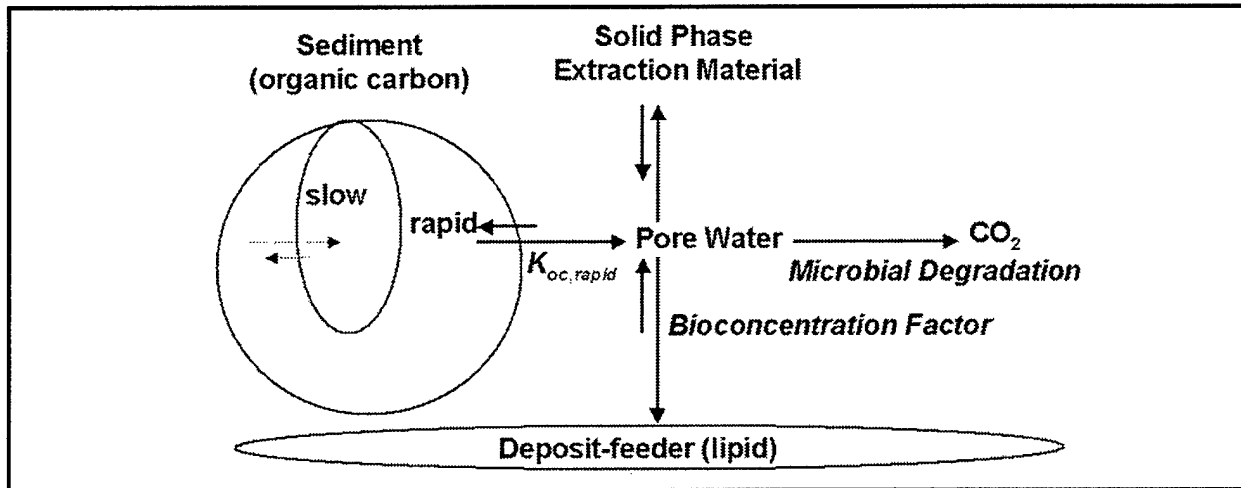


Figure 4. The HOC pore water pool is probably the most biologically available. The Kraaij et al. (2002) conceptual model (modified above) equates HOC in pore water to the rapidly desorbing fraction of HOC from sediment organic matter. Part of the pore water HOC can be taken up into benthic macrofaunal lipid. However, neither Kraaij's conceptual model nor most of those currently proposed take into consideration the ability of sedimentary bacterial communities to mineralize HOC. The factors that determine this competition for the pore water HOC pool between macrofaunal lipid and microbial mineralization are not well understood

In summary, the bioavailable portion of HOC associated with sediments is a subset of that which is solvent-extractable. The rapidly desorbing HOC (aqueous) fraction from sediment is roughly equivalent to the bioavailable fraction. Microorganisms effectively degrade a large, but sediment-specific and variable portion of the rapidly desorbing HOC fraction. The potential for bioremediation of HOC-contaminated sediment is generally limited to the fast desorbing fraction. If the potential rate of HOC biodegradation is greater than the slow HOC desorption rate, then the residual HOC bound in the sediment may present little environmental risk. Data for much of the above are lacking.

Thermal Desorption Mass Spectrometry of HOCs. Within an analysis time of 10 min, thermal desorption mass spectrometry (TD-MS) can provide information on the identity of the

HOCs present in sediment, HOC levels, and the energy with which the individual HOCs are being sequestered. Many common HOCs, such as PAHs, PCBs, and pesticides, are thermally stable, semivolatile organic compounds well suited for TD-MS. For TD-MS analysis, a sample of dried sediment (1-10 mg) is placed in a glass vial, weighed, and then placed on a direct probe (Figure 5). The probe is inserted through a vacuum lock into the ion source of a mass spectrometer and heated according to a specified program. Desorbed HOCs are ionized by electron impact, and the resulting ions are directed into the mass analyzer using electronic lenses.

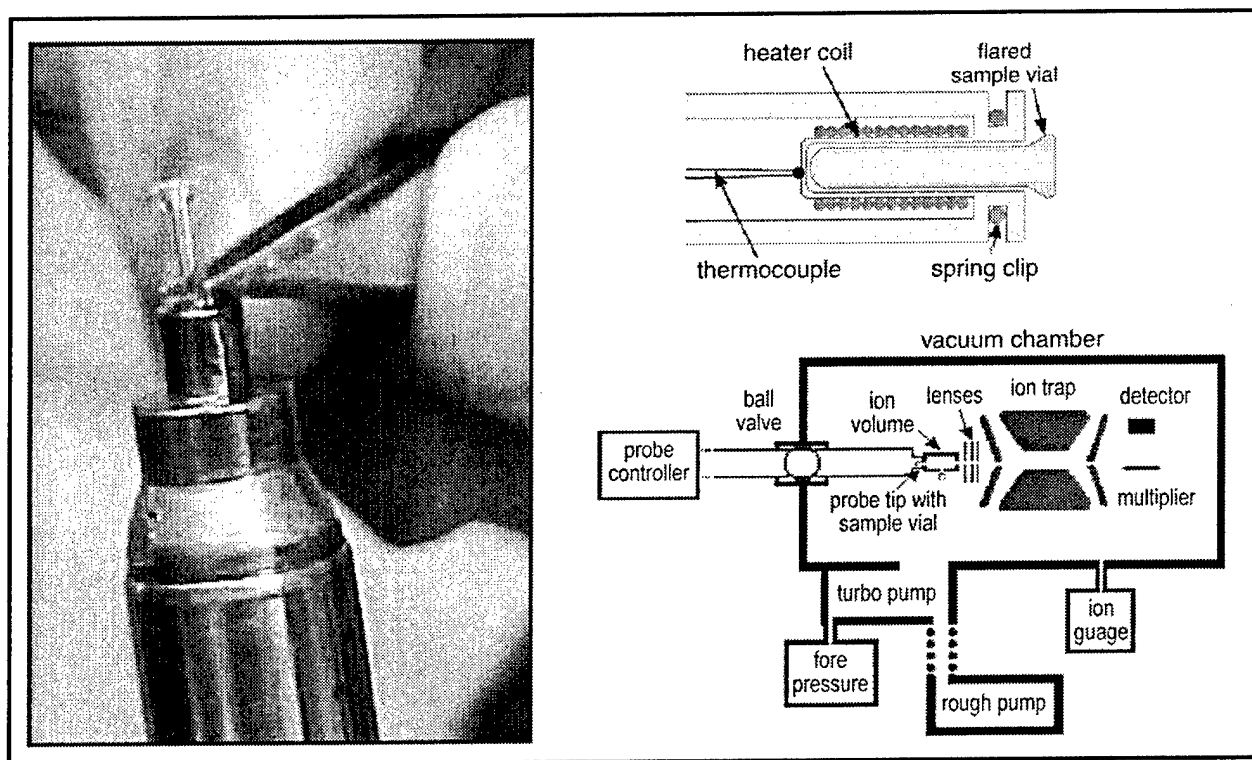


Figure 5. Thermal desorption - mass spectrometry. Milligram quantities of dried sediment are loaded into a glass vial (left) and heated in the direct probe (top right). The probe is inserted through a vacuum lock into a mass spectrometer. Programmed heating of the sample desorbs HOC that are ionized by electron impact and separated in a magnetic field on the basis of mass. Ions of known mass are detected using an electron multiplier

HOCs are identified on the basis of their molecular weight and by mass fragmentography when MS-MS technology is employed. Molecular ion or base peak area is indicative of the amount of a particular HOC thermally desorbed from the sediment. The thermal desorption profile (Figure 6) shows the heat energy required to desorb the particular contaminant and is used to calculate sequestration energy (Talley et al. 2002a (submitted)), which is a measure of how tightly the particular HOC is bound to the sediment.

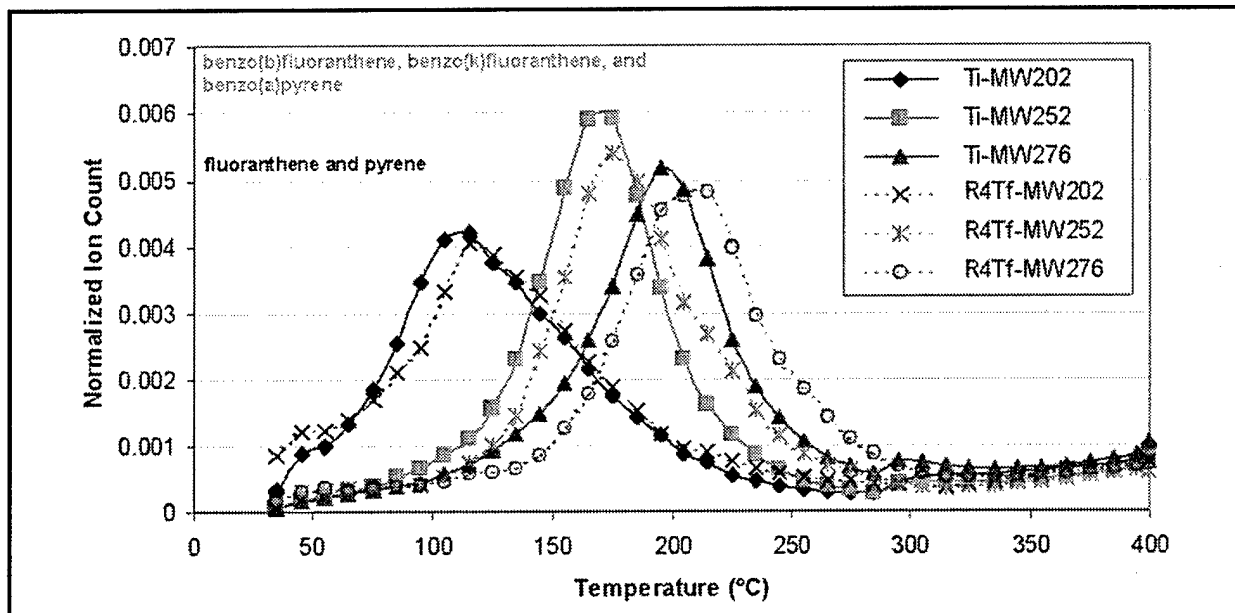


Figure 6. Thermal desorption profiles of molecular ions of selected PAH. Right shifted profiles are the result of removal of the biologically available fraction by microbial degradation. Peak heights can be indicative of PAH concentrations. In this figure, peak heights have been normalized to the largest peak height (Talley et al. 2002a,b)

In the first use of this conjunction of data to infer biological availability of sediment bound HOCs, dredged material from the Milwaukee Harbor Confined Disposal Facility was characterized with many factors including bulk particle quality, PAH levels, sequestration levels (by TD-MS), the rapidly desorbed fraction (using Tenax® beads), and two measures of bioavailability - earthworm uptake and microbial biodegradation potential (Talley et al. 2002a,b; Ringelberg et al. 2001). The silt/clay low-density fraction comprised 95 percent of the dry weight of the dredged material and contained less than 40 percent of the Soxhlet-extractable PAH. The majority of this fraction's PAH was biodegradable by microorganisms and could be taken up by earthworms. The higher density coal-derived fraction comprised only 5 percent of the dredged material dry mass but more than 60 percent of the PAH. The PAH from this fraction did not readily desorb onto Tenax® and was not available to microbes or earthworms.

These first results suggest that practical bioremediation could be expected to remove the rapidly desorbing fraction (approximately 50 percent of the Soxhlet-extractable PAH for this confined disposal facility (CDF) material) from entire sediment. This is consistent with the results of a biotreatability study performed on the material (Myers, Bowman, and Myers 2002) and with results on Amsterdam Harbor sediment (Cornelissen et al. 1998). Additionally, both Talley's and Myers's results suggest that the residual tightly bound PAH (approximately 50 mg/kg or 50 percent of the solvent extractable PAH) may not present nearly as much potential for bioaccumulation and toxicity as one would infer from the total Soxhlet-extractable PAH level. The slow or negligible rate of desorption curtails uptake and can enable biodegradation of whatever is slowly desorbed.

In summary, TD-MS can be a very useful analytical tool for rapid characterization of contaminated sediments. It enables rapid determination of the types and levels of HOC present in sediment and the energy with which they are bound. This information can provide a basis for predicting the

bioavailability of sediment-bound HOC and, subsequently, bioaccumulation (Talley and Larson 2000). Most importantly, TD-MS is the basis for the current development of several direct sampling techniques that will enable field portable HOC analysis in near real time (Wise 1998; Palmer, Karr, and Remigi 2000; USEPA 2002). This capability will fundamentally change the approach we use to survey environmental chemical contamination (Crumbling et al. 2001).

OUTLOOK: Our LEDO work unit is designed to fill gaps in our current understanding of the bioavailability of HOC-contaminated sediments and dredged materials. We have selected 10 sediments/dredged materials from ongoing USACE dredging projects (i.e., Housatonic River, New York; Brown's Lake, Mississippi; Waukegan Harbor, Illinois; Milwaukee Harbor CDF, Wisconsin; Kinnickinnic River, Wisconsin; Calumet River, Indiana; New Bedford River, New York; and Indian Harbor, Indiana) for study. After physical, chemical, and microbiological characterization of the sediments/dredged materials, we will measure the rapidly desorbing HOC fraction using solid phase extraction materials, HOC bioaccumulation by *Lumbriculus*, HOC microbial biodegradation potential, and thermal release energy. The resulting data set will be used to compare K_{oc} -based predictions of sediment HOC bioaccumulation and toxicity to those empirically measured, and those predicted using the rapidly desorbed fraction and thermal release energy. We will also evaluate the effect of microbial degradation on the biologically available fraction.

CONCLUSIONS: Environmental risk assessments conducted with models using K_{oc} -derived partition coefficients could be misleading. K_{oc} -derived pore water HOC levels in aquatic plant detritus have underestimated potential exposure concentrations by a factor of 10. On the other hand, no bioaccumulation or toxicity was demonstrated in soot containing sediments with solvent-extractable HOC levels as high as 10,000 mg/kg. The levels of soot and other diagenetically mature, potential HOC super absorbers (e.g., coal and coke) in sediments are expected to be heterogeneous but potentially high in industrialized watersheds. The rapidly desorbed HOC fraction (i.e., that which partitions to solid phase adsorbent within minutes) may provide a quick and simple means of determining the biologically available fraction of sediment HOC. Means to determine what part of the rapidly desorbing HOC microorganisms degrade and what part is accumulated into benthic faunal lipid have yet to be developed.

TDMS can be a very useful tool for USACE dredging operations. TD-MS enables rapid qualitative and quantitative analysis of HOC in sediments and provides a measure of the energy with which they are bound. TD-MS is directly compatible with emerging field-portable, direct-sampling, real-time analytical technologies being developed by the Army for the detection of chemical and biological weapons.

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Notes Collection, ERDC/TN EEDP-04-34, U.S. Army Engineer Research and Development Center, Vicksburg, MS. <http://www.wes.army.mil/el/dots/eedptn.html>

REFERENCES

- Ankley, G. T., Berry, W. J., DiToro, D. M., Hansen, D. J., Hoke, R. A., Mount, D. R., Reiley, M. C., Swartz, R. C., and Zarba, C. S. (1996). "Use of equilibrium partitioning to establish sediment quality criteria for nonionic chemical: A reply to Iannuzzi et al.," *Environ. Toxicol. Chem.* 15(7), 1019-1024.
- Brannon, J. M., Davis, W. M., McFarland, V. A., and Hayes, C. (1998). "Organic matter quality and partitioning of PCB," *Bull. Environ. Contam. Toxicol.* 61, 333-338.
- Burkhard, L. P. (1998). "Comparison of two models for predicting bioaccumulation of hydrophobic organic chemicals in a Great Lake Food web," *Environ. Toxicol. Chem.* 17, 383-393.
- Carmichael, L. M., Christman, R. F., and Pfaender, F. K. (1997). "Desorption and mineralization kinetics of phenanthrene and chrysene in contaminated soils," *Environ. Sci. Technol.* 31, 126-132.
- Chapman, P. M., Downie, J., Maynard, A., and Taylor, L. A. (1996). "Coal and deodorizer residues in marine sediments," *Environ. Toxicol. Chem.* 15, 638-642.
- Clarke, J. U., and McFarland, V. A. (2000). "Uncertainty analysis for a equilibrium partitioning-based estimator of polynuclear aromatic hydrocarbon accumulation potential in sediments," *Environ. Toxicol. Chem.* 19, 360-367.
- Condor, J. M., Landrum, P. F., McFarland, V. A., Meador, J. P., Millward, R. N., Moore, D. W., Shine, J., Word, J. Q., Weston, D. P., Mayer, L. M., Voparil, I., Lotufo, G. R., and LaPoint, T. "Development and application of sediment quality guidelines protective of effects through bioaccumulation" (Publication pending), Pellston Workshops, Pellston, MI.
- Cornelissen, G., Rigterink, H., Ferdinandy, M. M. A., and van Noort, P. C. M. (1998). "Rapidly desorbing fractions of PAHs in contaminated sediments as a predictor of the extent of bioremediation," *Environ. Toxicol. Chem.* 32, 966-970.
- Cornelissen, G., ten Hulscher, T. E. M., Rigterink, H., Vrind, B., and van Noort, P. (2001) "A simple Tenax method to determine the chemical availability of sediment-sorbed organic compounds," *Environ. Toxicol. Chem.* 20, 706-711.
- Crumbling, D. M., Groenies, C., Lesnik, B., Lynch, K., Shockley, J., Ee, J. E., Howe, R., Keith, L., and McKenna, J. (2001). "Applying the concept of effective data to contaminated sites could reduce costs and improved cleanups," *Environ. Sci. Technol.* 405A.
- Davis, W. M. (1993). "Influence of humic substance structure and composition on interactions with hydrophobic organic compounds." Ph.D. Diss., University of Florida, Gainesville, FL.
- DiToro, D. M., Zarba, D., Hansen, C., Berry, D., Swartz, W., Cowan, R., et al. (1991). "Technical basis for establishing sediment quality criteria for non-ionic organic chemical by using equilibrium partitioning," *Environ. Toxicol. Chem.* 10, 1541-1586.
- Driscoll, S. K., and Landrum, P. F. (1997). "A comparison of equilibrium partitioning and critical body residue approaches for predicting toxicity of sediment-associated fluoranthene to freshwater amphipods," *Environ. Toxicol. Chem.* 16, 2179-2186.
- Farrington, J. W., Goldberg, E. D., Risebrough, R. W., Martin, J. H., and Bowen, V. T. (1983). "U.S. 'Mussel Watch' 1976-1978: An overview of the trace-metal, DDE, PCB, hydrocarbon and artificial radionuclide data." *Environ. Sci. Technol.* 17, 490-496.

- Fry, V. A., and Istok, J. D. (1994). "Effects of rate-limited desorption on the feasibility of *in situ* bioremediation," *Water Resource Res.* 30, 2413-2422.
- Gauthier, T. D., Seitz, W. R., and Grant, C. L. (1987). "Effects of structural and compositional variations of dissolved humic materials on pyrene K_{oc} values," *Environ. Sci. Technol.* 21, 243-248.
- Ghosh, U., Talley, J., and Luthy, R. G. (2001). "Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment," *Environ. Sci. Technol.* 35(17), 3468-3475.
- Grathwohl, P. (1990). "Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implication for K_{oc} correlations," *Environ. Sci. Technol.* 24, 1687-1693.
- Gustafsson, O., Haghseta, F., Chan, C., MacFarland, J., and Gschwend, P. M. (1997). "Quantification of dilute sedimentary sootphase: Implications for PAH speciation and bioavailability," *Environ. Sci. Technol.* 31, 203-209.
- Haitzer, M., Abbt-Braun, G., Traunspurger, W., and Steinberg, C. (1999). "Effects of humic substances on the bioconcentration of polycyclic aromatic hydrocarbons: Correlations with spectrometric and chemical properties of humic substances," *Environ. Toxicol. Chem.* 18, 2782-2788.
- Iannuzzi, T. J., Bonnevie, N. L., Huntley, S. L., Wenning, R. L., Truchon, S. P., Tull, J. D., and Sheehan, P. J. (1995). "Comments on the use of equilibrium partitioning to establish sediment quality criteria for nonionic chemicals," *Environ. Toxicol. Chem.* 14(8), 1257-1259.
- Johnson, M. D., and Weber, W. J., Jr. (2001). "Rapid prediction of long-term rates of contaminant desorption from soils and sediments," *Environ. Toxicol. Chem.* 35, 427-433.
- Karickhoff, S. W. (1981). "Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils," *Chemosphere* 10, 833-846.
- Karickhoff, S. W., Brown, D. S., and Scott, T. A. (1979). "Sorption of hydrophobic pollutants on natural sediments," *Water Res.* 13, 241-248.
- Karickhoff, S. (1981). "Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils," *Chemosphere* 10, 833:846.
- Kelsey, J. W., and Alexander, M. (1997). "Selective chemical extractants to predict bioavailability of soil-aged organic chemicals," *Environ. Toxicol. Chem.* 16, 582-585.
- Könemann, H., and van Leeuwen, K. (1980). "Toxicokinetics in fish: Accumulation and elimination of six chlorobenzenes by guppies," *Chemosphere* 9, 3-19.
- Kraaij, R. (2001). "Sequestration and bioavailability of hydrophobic chemicals in sediment," Ph.D. Diss., Univ. of Utrecht, NL. <http://www.library.uu.nl/digiarchief/dip/diss/1960191/inhoud.htm>.
- Kraaij, R., Seinen, W., Tolls, J., Cornelissen, G., and Belfroid, A. C. (2002). "Direct evidence of sequestration in sediments affecting the bioavailability of hydrophobic organic chemicals to benthic deposit-feeders," *Environ. Sci. Technol.* 36, 3525-3529.
- Kyoungphile, N., and Alexander, M. (1998). "Role of nanoporosity and hydrophobicity in sequestration and bioavailability: Tests with model solids," *Environ. Sci. Technol.* 32, 71-74.

- Landrum, P. F. (1989). "Bioavailability and toxicokinetics of polycyclic aromatic hydrocarbons sorbed to sediments for the amphipod, *Pontoporeia hoyi*," *Environ. Sci. Technol.* 23, 588-595.
- LeBoeuf, E. J., and Weber, W. J., Jr. (2000). "Macromolecular characteristics of natural organic matter. 1. Insights from glass transition and enthalpic relaxation behavior," *Environ. Sci. Technol.* 34, 3623-3631.
- Lovett-Doust, J., Lovett-Doust, L., Biernacki, M., Mal, T. K., and Lazar, R. (2002). "Organic contaminant content of plant species in the Detroit River" (in press), *Can. J Fish Sci.*
- Luthy, R. G., Aiken, G. R., Brusseau, M. L., Cunningham, S. D., Gschwend, P. M., Pignatello, J. J., Reinhard, M., Traina, S. J., Weber, W. J., Jr., and Westall, J. C. (1997). "Sequestration of hydrophobic organic contaminants by geosorbents," *Environ. Sci. Technol.* 31, 3341-3347.
- McFarland, V.A. (1983). "Estimating bioaccumulation potential of chemicals in sediment," *Environmental Effects of Dredging Information Exchange Bulletin*, D-83-4, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- McFarland, V. (1984). "Activity-based evaluation of potential bioaccumulation from sediments. Dredging and dredged material disposal," Vol. 1, Am. Soc. Chemical Engineers, New York.
- McFarland, V.A. (1995). "Evaluation of field-generated accumulation factors for predicting the bioaccumulation potential of sediments-associated PAH compounds," Technical Report D-95-2. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- McFarland, V. A., and Clark, J. U. (1987). "Simplified approach for evaluating bioavailability of neutral organic chemicals in sediment." *Environmental Effects of Dredging Technical Notes* EEDP-01-8, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Mackay, D. (1982). "Correlation of bioconcentration factors," *Environ. Sci. Technol.* 16(5), 274-278.
- Mackay, D. (1991). *Multimedia Environmental Models: The Fugacity Approach*. Lewis Publishers Inc., Chelsea, MI, 257 pp.
- Mackay, D., and Paterson, S. (1981). "Calculating fugacity," *Environ. Sci. Technol.* 15, 1006-1014.
- Mackay, D., and Paterson, S. (1982). "Fugacity revisited: The fugacity approach to environmental transport," *Environ. Sci. Technol.* 16, 654A-660A.
- MacRae, J. D., and Hall, K. J. (1998). "Comparison of methods used to determine the availability of polycyclic aromatic hydrocarbons in marine sediment," *Environ. Sci. Technol.* 32, 3809-3815.
- Mayer, P., Vaes, W., Wijnker, F., Legierse, K., Kraaij, R., Tolls, J., Hermens, J. L. M. (2000). "Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid phase microextraction fibers," *Environ. Sci. Tech.* 34, 5177-5183.
- McGroddy, S. E., and Farrington, J. W. (1995). "Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts," *Environ. Sci. Technol.* 29, 1542-1550.
- McGroddy, S. E., Farrington, J. W., and Gschwend, P. M. (1996). "Comparison of the *in situ* and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls," *Environ. Sci. Technol.* 30, 172-177.
- Myers, T. E., Bowman, D. W., and Myers, K. F. (2002). "Dredged material composting at Milwaukee and Green Bay, WI, confined disposal facilities," *DOER Technical Notes Collection* (ERDC TN-DOER-in preparation), U.S. Army Engineer Research and Development Center, Vicksburg, MS.

- Næs, K., Hylland, K., Oug, E., Förlin, L., and Ericson, G. (1999). "Accumulation and effects of aluminum smelter-generated polycyclic aromatic hydrocarbons on soft-bottom invertebrates and fish," *Environ. Toxicol. Chem.* 18, 2205-2216.
- Næs, K., and Oug, E. (1997). "Multivariate approach to distribution patterns and fate of polycyclic aromatic hydrocarbons in sediments from smelter-affected Norwegian fjords and coastal waters," *Environ. Sci. Tech.* 31, 1253-1258.
- O'Connor, T. P., Daskalakis, K. D., Hyland, J. L., Paul, J. F., and Summers, J. K. (1998). "Comparisons of sediment toxicity with predictions based on chemical guidelines," *Environ. Toxicol. Chem.* 17, 468-471.
- Paine, M. D., Chapman, P. M., Allard, P. J., Murdoch, M. H., and Minifie, D. (1996). "Limited bioavailability of sediment PAH near an aluminum smelter: Contamination does not equal effects," *Environ. Toxicol. Chem.* 15, 2003-2018.
- Palmer, P. T., Karr, D., and Remigi, C. (2000). "Evaluation of two different direct sampling ion trap mass spectrometry methods for monitoring halocarbon compounds in air," *Field Analytical Chemistry and Technology* 4, 14-30.
- Peddicord, R., Lee, C. R., and Engler, R. M. (1998). "Use of sediment quality guidelines in dredged material management," LEDO Technical Note EEDP-04-29, U.S. Army Engineer Research and Development Center, Vicksburg, MS.
- Ringelberg, D. B., Talley, Jeffrey W., Perkins, Edward J., Tucker, Samuel G., Luthy, Richard G., Bouwer, Edward J., and Fredrickson, Herbert L. (2001). "Succession of phenotypic, genotypic, and metabolic community characteristics during in vitro bioslurry treatment of polycyclic aromatic hydrocarbon-contaminated sediments," *Appl. Envir. Microbiol.* 67, 1542-1550.
- Robertson, B. K., and Alexander, M. (1996). "Mitigating toxicity to permit bioremediation of constituents of nonaqueous-phase liquids," *Environ. Sci. Tech.* 30, 2066-2070.
- Robertson, B. K., and Alexander, M. (1998). "Sequestration of DDT and Dieldrin in soil: Disappearance of acute toxicity but not the compounds," *Environ. Toxicol. Chem.* 17, 1034-1038.
- Rockne, K. J., Shor, L. M., Young, L. Y., Taghon, G. L., and Kosson, D. S. (2002). "Distributed sequestration and release of pahs in weathered sediment: The role of sediment structure and organic carbon properties," *Environ. Sci. Technol.* 36, 2636-2644.
- Rutherford, D. W., Chiou, C. T., and Kile, D. E. (1992). "Influence of soil organic matter composition on the partition of organic compounds," *Environ. Sci. Technol.* 26, 336-340.
- Socha, S. B., Carpenter, R. (1987). "Factors affecting pore water hydrocarbon concentrations in Puget Sound sediments," *Geochim. Cosmochim. Acta* 51, 1273-1284.
- Song, J., Peng, P. A., and Huang, W. (2002). "Black carbon and kerogen in soils and sediments. 1. Quantification and characterization," *Environ. Sci. Tech.* 36, 3960-3967.
- Talley, J. W. (2000). "Availability and biotreatment of polycyclic aromatic hydrocarbons in sediment." Ph.D. Diss., Carnegie Mellon University.
- Talley, J. W., Ghosh, U., Tucker, S. G., Furey, J. S., and Luthy, R. G. (2002a). "Thermal programmed desorption (TPD) of PAHs from mineral and organic surfaces," *Environmental Engineering Science* (Submitted).
- Talley, J. W., Ghosh, U., Tucker, S. G., Furey, J. S., and Luthy, R. G. (2002b). "Particle-scale understanding of the bioavailability of PAHs in sediment," *Environ. Toxicol. Chem.* 36, 477-483.

- Talley, J. W., and Larson, S. (2000). "Correlations between chemical extractability, bioavailability, and bioaccumulation of PAHs in marine sediments," *Sediment & Soil Chemistry Session*, Society of Environmental Toxicology and Chemistry (SETAC) Annual Meeting, Nov 12-16, 2000, Nashville, TN.
- Talley, J. W., Tucker, S., Furey, J., Ghosh, U., and Luthy R. G. (2002). "Particle-scale understanding of the bioavailability of PAHs in sediment," *Environ. Sci. Technol.* 36, 477-483.
- Tang, J., Carroquino, M. J., Robertson, B. K., and Alexander, M. (1998). "Combined effect of sequestration and bioremediation in reducing the bioavailability of polycyclic aromatic hydrocarbons in soil," *Environ. Sci. Technol.* 32, 3586-3590.
- U.S. Environmental Protection Agency. (2002). "Volatile organic compounds in water, soil, soil gas, and air by direct sampling ion trap mass spectrometry," Standard Method 8265, Washington, DC.
- U.S. Environmental Protection Agency. (1993). "Sediment quality criteria," Federal Register, FR Doc. 94-1133, Robert Perciasepe, Assist. Admin. for Water, Washington, DC.
- U. S. Environmental Protection Agency/U.S. Army Corps of Engineers. (1991). "Evaluation of dredged material proposed for ocean disposal," Testing Manual EPA 503/8-91/001, Washington, DC.
- U. S. Environmental Protection Agency/U.S. Army Corps of Engineers. (1998). "Evaluation of dredged material proposed for discharge in waters of the U.S.," Testing Manual (Inland Testing Manual) EPA 823-B-98-004, Washington, DC.
- Van Beelen, P. E., Verbruggen, M. J., and Peijnenburg, W. J. G. M. (2001). "The evaluation of equilibrium partitioning method using sensitivity distributions of species in water and soil or sediment," RIVM Report 607220005/2001; www.rivm.nl/bibliotheek/rapporten/607220005.html; Bilthoven, NL.
- Weber, W. J. Jr.; Kim, S. H., and Johnson, M. D. (2002). "Distributed reactivity model for sorption by soils and sediments. 15. High-concentration co-contaminant effects on phenanthrene sorption and desorption," *Environ. Sci. Technol.* 36, 3625-3634.
- Weston D. P., and Maruya, K. A. (2002). "Predicting bioavailability and bioaccumulation using in vitro digestive fluid extraction," *Environ. Toxicol. Chem.* 21, 962-971.
- Wise, M. (1998). "Direct sampling ion trap mass spectrometry," Innovative Technology Summary Report, OST Reference #69, Oak Ridge National Laboratory, TN. <http://ost.em.doe.gov>.
- Yang, R. T., Long, R. Q., Padin, J., and Takahashi, A. (1999). *Ind. Eng. Chem. Res.* 38, 2726-2731.

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