CHAPTER 7

ASSESSING BIOAVAILABILITY OF HYDROPHOBIC ORGANIC COMPOUNDS AND METALS IN SEDIMENTS USING FREELY AVAILABLE POREWATER CONCENTRATIONS

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7.1 INTRODUCTION

Sediments are the ultimate sinks for most hydrophobic organic compounds (HOCs) and metals in aqueous systems. These contaminants can then pose a long-term risk to organisms that dwell or interact with the sediments or to higher organisms through the food chain. The starting point for the assessment of sediment toxicity or effects is bulk contaminant concentrations normalized by sediment mass (Chapman et al., 1999). The values are relatively easy to obtain and are useful as an initial screening tool to assess contamination. These values do not take into account important properties of the sediment, such as the concentration of sulfides, iron oxides, and organic contents, which greatly affect metals availability in sediments, or organic sequestering phases, which can reduce organic chemical availability. Hence, the toxic level of contaminants derived from bulk sediment loading has been proven to vary significantly among different sediments (Di Toro et al., 1990; Chapman et al., 1999).

Many studies have demonstrated that the effect of the soil or sediment-associated contaminants on the organism is not controlled by the total concentration of the contaminant, but instead by the fraction that is biologically available (Meador et al., 1995). A review of a number of studies (Di Toro et al., 1991) found that bulk sediment concentrations do not reflect actual exposure of biota and, therefore, provide an unreliable predictor of effects. Simply stated, the organism response, e.g., toxicity or the extent of bioaccumulation, often appears to be less than what would be expected based upon the entire mass of contaminants in the sediment. Better understanding of bioavailability processes and indicators of the contaminants that are available and/or mobile can lead to better and more protective risk estimates (NRC, 2003).

Bioavailable contaminants can be defined as those that directly relate to observed organism effects and may only be a small fraction of the total contaminant concentration. The reduced bioavailability is usually associated with physical or chemical sequestration mechanisms that are not normally or easily overcome by environmental processes including digestion in deposit-feeding organisms. Partitioning into organic phases is the principal mechanism dictating bioavailability for hydrophobic organic compounds (HOCs) while chemical speciation is the primary overriding factor for bioavailability of metals (Maruya et al., 2011). The goal of this chapter is to explore techniques that provide a better indication of the actual risks posed by sediments than simply measuring total concentration. Because the definition of bioavailability used here is based on observed effects in organisms, biological assays represent perhaps the

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best indicator of bioavailability. The challenges to conduct and interpret such assays are the subject of other chapters. The focus of this chapter is on chemical measures of availability; in particular measurements of the freely available concentration of the contaminants in porewater and compare its ability to predict effects in organisms, particularly bioaccumulation or toxicity in deposit-feeding benthic organisms. By focusing on deposit-feeding benthic organisms the emphasis is on exposure and effects that are directly linked to contaminant availability. For example, species that live and feed in the water column are exposed only after mass transfer from the sediment surface or via the food chain, the rate of which may be controlled by physical processes that are not strongly linked to intrinsic availability in the sediments.

Biota-sediment accumulation factors (BSAF), as outlined in Chapter 6, have been used to provide an indication of bioavailability under specific environmental conditions. Environmental factors such as the rate of mass transfer between sediments and water, organism factors such as metabolic processes and the route and rate of uptake, and sediment- and contaminant-specific factors such as sequestration of contaminants, however, lead to BSAFs that are site- and species-specific and subject to substantial uncertainty (Lake et al., 1990; Trimble et al., 2008). As an alternative, abiotic methods using a variety of extraction tests had also been used to measure the readily extractable fraction to mimic bioavailability of HOCs and metals. Dean and Scott (2004) summarized the extraction approaches for assessing sediment bioavailability of HOCs, which includes sequential extraction with different organic solvents, supercritical CO_2 extraction, subcritical water extraction, solid phase sorbents (e.g., TenaxTA, XAD-2) extraction, solid phase micro-extraction (SPME), extraction with membranes dialysis, extraction with gases (gas purging), extraction with temperature (thermal desorption), and in vitro extraction (gastrointestinal). Extraction methods have also been proposed for metals. Dilute acid extractable metals could be a good indication of the bioavailable fraction of metals in sediments because some benthic organisms are ingesting particles and leaching metals by mildly acidic gut fluids (Chen and Mayer, 1999; Lee et al., 2000). Extraction tests for metals include passive extraction with water and neutral salt and aggressive extractions with acids, e.g., 0.1 molar (M) hydrogen chloride (HCl) and disodium ethylenediaminetetraacetate (EDTA) (NRC, 2003).

Different indirect methods as described in the previous paragraph may give different estimates of bioavailability. A more realistic approach would be a direct measurement of exposure concentrations or the bioavailable fraction of a contaminant (Van Der Heijden and Jonker, 2009, cited from Reid et al., 2000). Ideally, a direct measure would allow *in situ* measurement of bioavailability without resorting to extraction or other processing of sediment. There is growing evidence showing that sediment porewater concentration of HOCs, particularly the freely dissolved porewater concentration, represents the highly bioavailable fraction and thus is a good indicator of bioavailability (McElroy et al.,1989; Kraaij et al., 2003; Jager et al., 2000; You et al., 2007). Moreover, free metal ion activity appears to be a better estimator of metal bioavailability and toxicity in soil and sediment (Lofts et al., 2004).

Thus, freely dissolved sediment porewater concentrations are increasingly used as an indication of a highly bioavailable fraction of both metals and organics. The basis for such a conclusion appears to be the relatively static nature of many contaminated sediment deposits, which results in a quasi-equilibrium between organisms, porewaters as a highly bioavailable phase, and solid phases that contain both available fractions and sequestering phases or unavailable species. Contaminants in a sequestering phase may only be available under dynamic conditions that cause release of the contaminants, e.g., oxidation of low availability sulfide phases upon resuspension of sediments (Hong et al., 2011a). Under static conditions, however, the *in situ* measurement of porewater concentrations of contaminants may provide a good indication of available contaminants to benthic organisms even if the route of exposure is via other means, e.g., sediment ingestion. The porewater burden of contaminants may not be the source of organism exposure but may indicate the available contaminants and magnitude of that exposure. This concept is explored further in the next section. Subsequently, assays of freely available contaminants in porewaters will be described and their ability to predict organism effects will be summarized. These assays are of two basic types: prediction of porewater concentration on the basis of models of equilibrium partitioning and direct measurement of porewater concentration; both will be summarized.

7.2 SEDIMENT POREWATER CONCENTRATIONS AS INDICATOR OF BIOAVAILABILITY

7.2.1 Hydrophobic Organic Compounds

A study assessing the effect of polycyclic aromatic hydrocarbons (PAHs) on mortality of amphipods (*Hyalella azteca*) provides a good illustration of the relationship between porewater concentrations and toxicity of HOCs (Hawthorne et al., 2007). Bulk sediment concentrations yielded a wide range of toxic response results, making prediction of bioaccumulation unreliable (Figure 7.1a). Extraction approaches improved the ability to estimate sediment toxicity but the best predictor of sediment toxicity was measured porewater concentrations (Figure 7.1b). Porewater measurements show a more well-defined and narrower range of toxicity. Similarly, Lu et al. (2003, 2006) observed a strong correlation ($r^2 = 0.90$) of bioaccumulation of PAHs by oligochaete worms with truly dissolved porewater concentrations from both laboratory spiked sediments and field sediments from the Anacostia River, Washington, D.C. Truly dissolved concentrations are thermodynamically available for partitioning to other phases, e.g., organism lipids and sediment organic carbon, while total porewater concentrations may also include colloidally and fine particulate bound contaminants.

With the ability to more easily measure truly dissolved porewater concentrations via the methods that are discussed herein, additional support for porewater concentration as a predictor of bioavailability has come available. Hereafter, porewater concentration refers specifically to truly dissolved porewater concentration and will be denoted by the symbol, C_{pw}. Kraaij et al. (2003), You et al. (2006) and van der War et al. (2004) have found porewater concentrations to be a good indicator of bioaccumulation in soil and sediment organisms. The ratio of bioaccumulation in tissues (C_t, lipid normalized) of HOCs to porewater concentration, C_{pw}, C_t/C_{pw}, has been found to be approximately given by the octanol-water partition coefficient (K_{ow}), suggesting that bioaccumulation, even via active uptake through ingestion, achieves an equilibrium equivalent to that suggested by passive uptake from the porewater. Experiments supporting this conclusion include the following:

- In Anacostia River (Washington, DC) sediments, the bioaccumulation of PAHs and polychlorinated biphenyls (PCBs) in a deposit feeding freshwater oligochaete, *Ilyodrilus templetoni*, was well predicted by the product of porewater concentration (C_{pw}) and compound octanol-water partition coefficient K_{ow}, (as reported in Lu et al. (2011)). The measured ratio of the lipid- normalized tissue concentration to $K_{ow}C_{pw}$, was 1.08 ($r^2 = 0.76$). The data is shown in Figure 7.2.
- In a sediment from New Bedford Harbor (New Bedford, Massachusetts) diluted with a fresh-water sediment from Brown Lake (Vicksburg, Mississippi), the bioaccumulation of PAHs and PCBs in the freshwater oligochaete, *Ilyodrilus templetoni*, was also well predicted by the product of porewater concentration and K_{ow} (Lu et al., 2011). The use of the sequentially diluted sediment allowed evaluation of a much larger range of

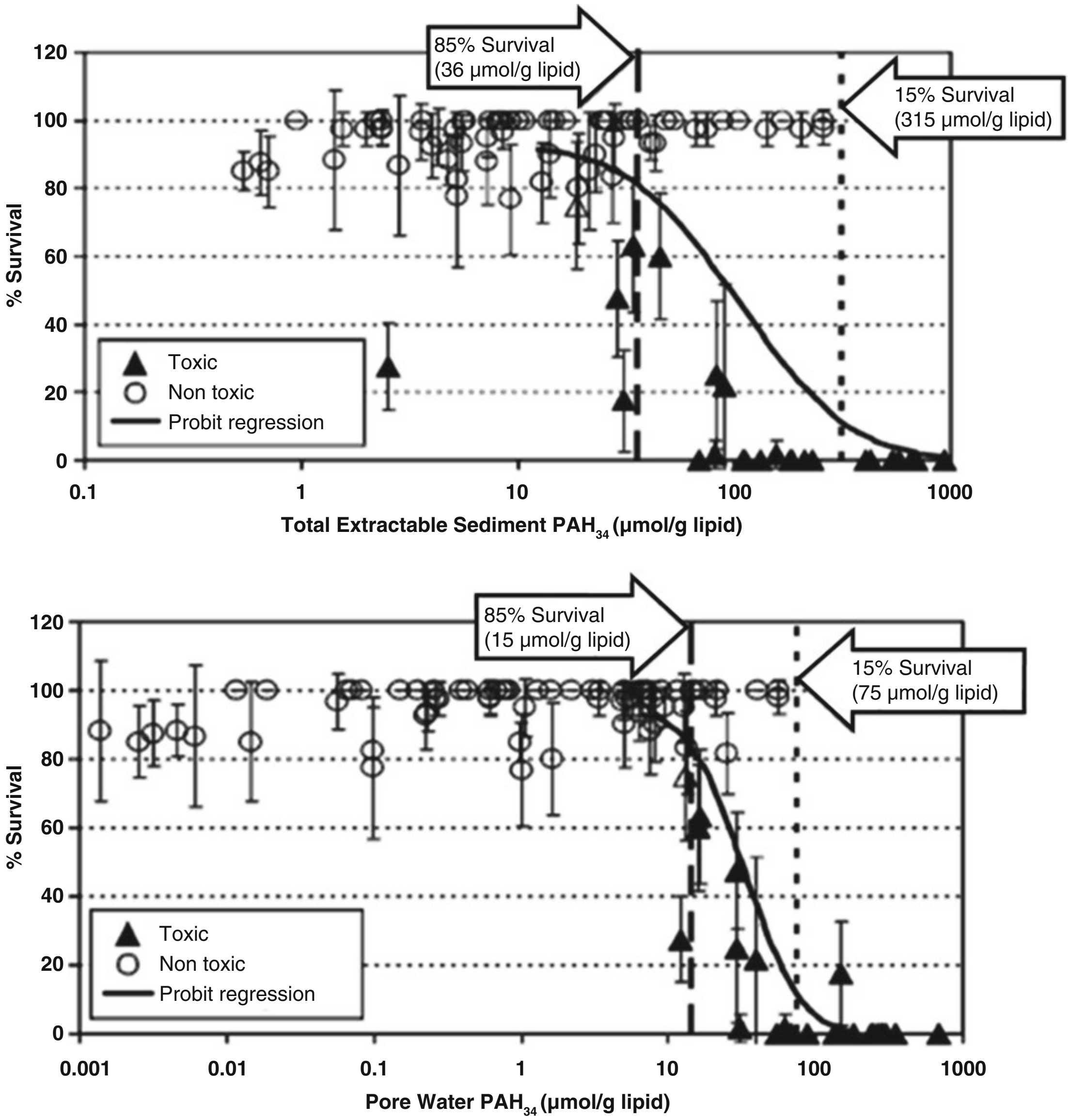

Figure 7.1. Amphipod survival correlates with bulk sediment concentration and sediment pore-water concentrations (reprinted with permission from Hawthorne et al., 2007. Copyright 2007 American Chemical Society).

sediment and porewater concentration than could be evaluated using the fresh sediment. In addition, the dilution with freshwater sediment allowed use of the freshwater oligochaete in the bioaccumulation testing. The measured ratio of the lipid-normalized tissue concentration to $K_{ow}C_{pw}$ was 1.24 ($r^2 = 0.76$).

- In sediment from Hunter's Point, California, the bioaccumulation of PCBs in the marine polychaete, *Neanthes arenaceodentata*, was also well predicted by the porewater concentration with a lipid-normalized tissue accumulation divided by $K_{ow}C_{ow}$ equal to 1.17–2.21 ($r^2 = 0.7–0.76$) as reported in Gschwend et al. (2011). The range of slopes primarily reflects uncertainty in porewater concentration measurements in that work.

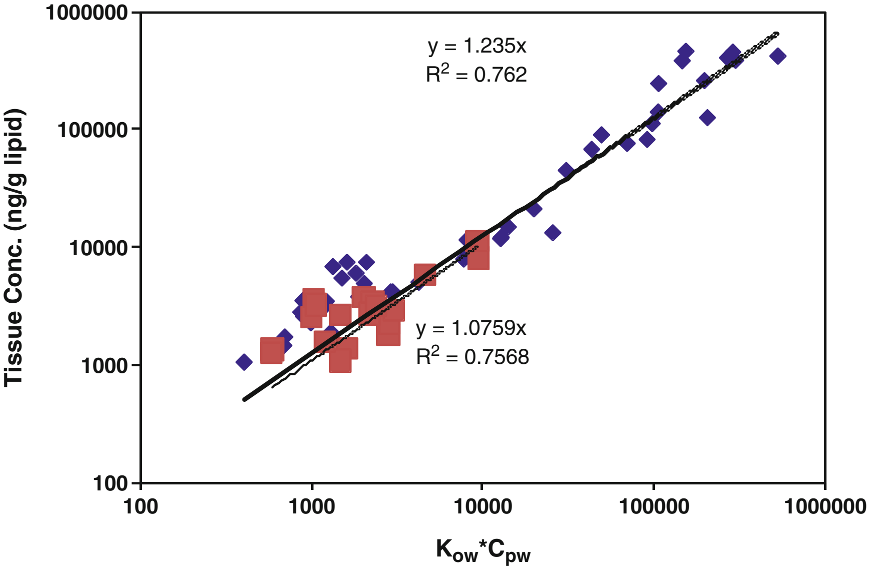

Figure 7.2. Comparison of measured tissue concentrations (lipid normalized) with predictions from porewater concentrations: Anacostia river sediment (*solid square*), sequentially diluted sediments (*solid diamond*). *Solid lines* represent best fit of data ($C_{t,\ measured} = 1.08\ C_{t,\ predicted}$, $r^2 = 0.757$ (Anacostia), $C_{t,\ measured} = 1.24\ C_{t,\ predicted}$, $r^2 = 0.762$ [sequential]). The *dashed line* represents the 1:1 relationship (Lu et al., 2011).

These studies all included deposit feeding organisms that process many times their own weight in sediment every day and thus are likely to attain a state of quasi-equilibrium with the sediment and porewater. Organisms that have less intensive interactions with the sediments are likely to exhibit less bioaccumulation on a lipid normalized basis. Although PAH metabolism is often an issue in oligochaete bioaccumulation studies, the organism *Ilyodrilus templetoni* used in the Anacostia River and sequential dilution experiments was shown to have limited metabolism for PAHs (<15%) (Lu, 2003).

Freely dissolved porewater concentration is also the basis behind the equilibrium partitioning sediment quality benchmarks used as a guideline for protecting benthic organisms in PAH-contaminated sediments (USEPA, 2004). In this approach, porewater concentrations of concern are used to estimate equivalent bulk solid concentrations through equilibrium partitioning (Di Toro et al., 2000; Di Toro and McGrath, 2000). The downfall of the approach, however, is that predictions of equilibrium partitioning do not normally account for the increased sorption due to strongly absorbing organic phases, e.g., black carbon phases (Ghosh et al., 2000), while direct measurement of porewater concentration does reflect the partitioning to strongly sorbing phases.

The conceptual model of uptake from porewater or from digestive juices in the gut of a deposit feeder is shown in Figure 7.3. Uptake of HOCs into deposit feeding organisms involves a two-stage partitioning processes: partitioning into the fluid phases of either porewater or gut juices and partitioning between the fluid phases and the organism lipids. Digestive fluids and porewater both represent intermediate phases for contaminants after desorption from sediment particles. At equilibrium, the four phases – sediment particles, organism lipid, sediment porewater, and organism digestive fluid – are at equilibrium with each other, and equilibrium between any two of these phases can be used to define overall equilibrium as long as the organism cannot effectively process the organic matter responsible for sequestration of

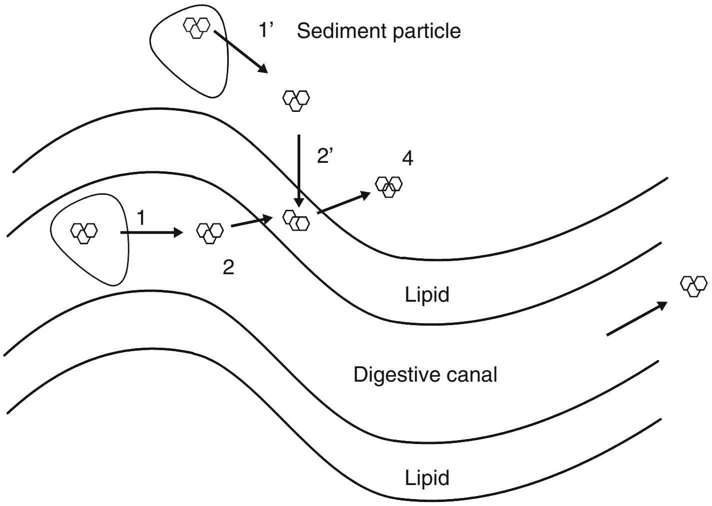

Figure 7.3. Two-stage processes for uptake of sediment-bound organic contaminants into the lipid of the organisms. K_{sw}, sediment-water partition coefficient, and K_{lw}, lipid-water partition coefficient.

the HOC in the sediment and cannot rapidly metabolize the contaminants. In particular, bioaccumulation of partitioning HOCs can be indicated by partitioning between the sediment porewater and organism lipids even though the primary route of uptake is from sediment ingestion. Effectively, bioaccumulation can be predicted by porewater concentrations and lipid-water partition coefficients, or a BCF, even if uptake is via active processing rather than simply passive partitioning. As indicated by the examples above, BCF is well-correlated with K_{ow}. That is:

$$C_{t,\,predict} = BCF^{*}C_{pw} = K_{ow}{}^{*}C_{pw} \qquad \text{(Eq. 7.1)}$$

Please note that the observed relationship between porewater concentration and organism bioaccumulation would not necessarily be expected under dynamic conditions such as fast groundwater upwelling rates or rapid contaminant degradation when sediment, porewater and organism may not be in a state of quasi-equilibrium.

7.2.2 Metals

Porewater concentrations of metals have also been linked to toxicity of benthic organisms. Figure 7.4a shows organism mortality with respect to total cadmium (Cd) concentrations in sediment (Di Toro et al., 1990). Three sediments with different sulfide contents were spiked with a range of dissolved Cd concentrations and mortality of test organisms were evaluated in the sediments. Multiple dose–response curves were obtained from total Cd concentrations in sediments indicating total Cd correlated only weakly with the observed toxicity. During the experiments, free Cd activities in sediment porewater, $Cd^{2+}_{(aq)}$, were measured by ion-selective electrode. From the measurement, the multiple dose–response curves were collapsed into one curve based on free metal ions activity in sediment porewater, which is shown in Figure 7.4b. More interestingly, the overlapped single dose–response curve followed the dose–response curve acquired from water exposure only toxicity tests. This finding suggested that porewater

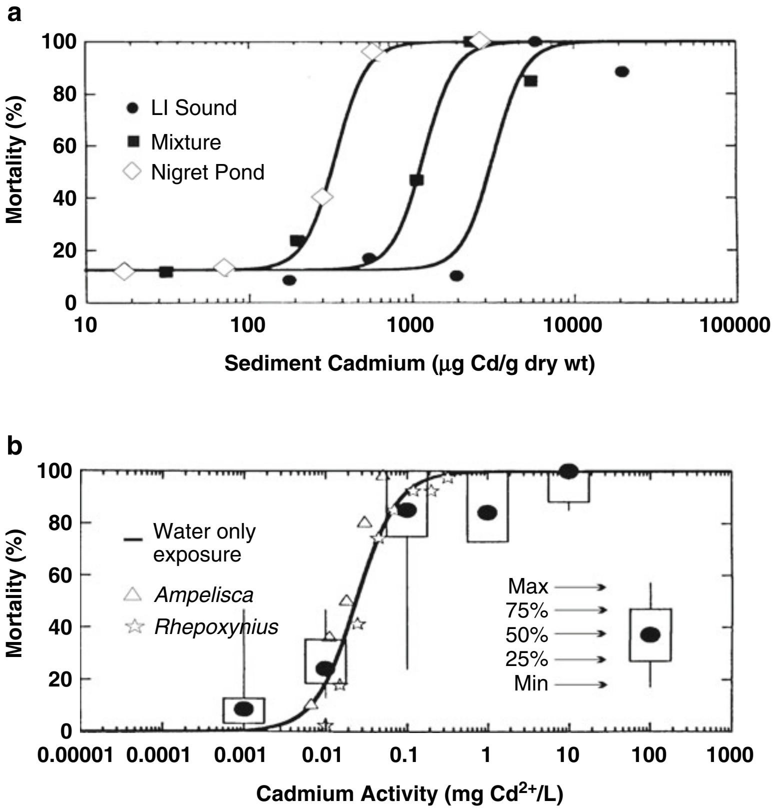

Figure 7.4. Organism mortality (%) versus sediment Cd concentration on a dry-weight basis (a) for three different sediments. Organism mortality (%) versus porewater Cd activity for the same three sediments and for water only exposures (b) (USEPA, 2005).

free metal ion concentration could be a better indicator than bulk solid concentration in predicting the bioavailability and toxicity of metals in sediments. The hypothesis leads to an equilibrium partitioning model (EqP), which estimates the presence of free metal ions and suggests a guideline for metals toxicity in sediments (USEPA, 2005).

7.3 ASSESSING BIOAVAILABILITY WITH EQUILIBRIUM PARTITIONING THEORY

7.3.1 Equilibrium Partitioning for HOCs

It has been demonstrated in Section 7.2 that porewater concentration is a good indicator of bioavailability. This has been recognized by the development of equilibrium partitioning sediment guidelines based on defining bulk sediment concentrations that relate to toxic water concentrations (USEPA, 2004) although, as indicated previously, the use of predicted rather than measured porewater concentrations limits the applicability of the approach. For HOCs, sediment organic carbon is the assumed primary sorption site and sorption is normalized by the fraction organic carbon (f_{oc}) and an organic carbon normalized sediment-water partition coefficient (K_{oc}) ($C_{pw-pred} = C_s/f_{oc}/K_{oc}$). K_{oc} is typically estimated from correlations with K_{ow}. For example, $\log K_{oc} = \log K_{ow} - 0.21$ (Karickhoff et al., 1979) has been widely used to estimate K_{oc} for PAHs. These generic models do not consider the characteristics of the carbon phase and its effect on the partition coefficients and often overestimate the porewater concentrations in actual sediments. The predictions for PAHs by equilibrium partitioning could be 100-times higher than the measurement values (Lu et al., 2011; TerLaak et al., 2006). Although biphasic models were proposed to account for the strong sorption by sequestering carbon phases (Kan et al., 1998; Accardi-Dey and Gschwend, 2002), the uncertainty in determining the partition coefficients to these phases could introduce great errors in estimating the freely dissolved porewater concentrations (Ghosh et al., 2000; Jonker and Keolmans, 2002). Direct measurement of the porewater concentration in the sediments can overcome these limitations and provide a more direct link between water toxicity concentrations and sediment quality.

7.3.2 Equilibrium Partitioning for Metals-AVS/SEM Model

In anoxic sediments, complex biogeochemical reactions often produce reactive sulfide minerals (Rickard and Morse, 2005) that are believed to control the availability of metals. Iron monosulfide is one of the key partitioning phases controlling metal speciation since the phase could precipitate dissolved free metals to insoluble metal sulfide rapidly as follows (Di Toro et al., 1990):

$$M^{2+}{}_{(aq)} + FeS_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + MS_{(s)} \tag{Eq. 7.2}$$

where $M^{2+}{}_{(aq)}$ represents dissolved free metal ions such as Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}; $FeS_{(s)}$ represents iron monosulfide; $Fe^{2+}{}_{(aq)}$ is dissolved ferrous iron; and $MS_{(s)}$is precipitated metal sulfide. As a result, sediments containing more reactive sulfides (e.g., iron monosulfide) than metals would have low porewater free metal ion activity ($M^{2+}{}_{(aq)}$) and metals in sediments would be less bioavailable and toxic because the metals would be bound in insoluble metal sulfides.

Due to the complexities and difficulties in extracting reactive sulfide minerals, operationally defined acid volatile sulfide (AVS) has been used to indicate total sulfide binding. AVS represents sulfides that are evolved from acidified sediment by adding 1 M HCl and includes dissolved sulfides (H_2S, HS^-, S^{2-}), amorphous iron monosulfide ($FeS_{(s)}$), mackinawite ($FeS_{(s)}$), and greigite ($Fe^3S^4{}_{(s)}$). The 1 M HCl also dissolves almost all metals and evolves sulfides from $CdS_{(s)}$ and $ZnS_{(s)}$, but partially from $CuS_{(s)}$ and $NiS_{(s)}$ (Allen et al., 1993; Cooper and Morse, 1998). At the same time, the total metals, such as Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, that are dissolved in 1M HCl are defined as simultaneously extracted metals (SEM) (Allen et al., 1993). Incomplete recovery of Cu^{2+} and Ni^{2+}could underestimate the potential availability of the metal sulfides, but the metals that are not dissolved from 1 M HCl are not likely to be available (USEPA, 2005).

There have been extensive studies that correlate the toxicity and the quantitative differences between AVS and SEM in a variety of anoxic sediments (Di Toro et al., 1990, 1992; Ankley et al., 1996; Berry et al., 1996, 2004; Hansen et al., 1996; Liber et al., 1996) and these efforts lead to the AVS/SEM model (USEPA, 2005). The model assumes if SEM $\leq$ AVS, then all the extracted metals are likely to present as $MS_{(s)}$ and no toxicity would be predicted. However, if SEM $>$ AVS, then toxicity may or may not occur and other binding phases in solid become important. Figure 7.5a, b supports this hypothesis. The paradigm could be viewed, however, as a tool to indicate when there are significant quantities of dissolved metals in the porewater. When AVS $>$ SEM, the presumption is that the metals are not dissolved but present only as the essentially insoluble sulfides and little toxicity is observed as a result.

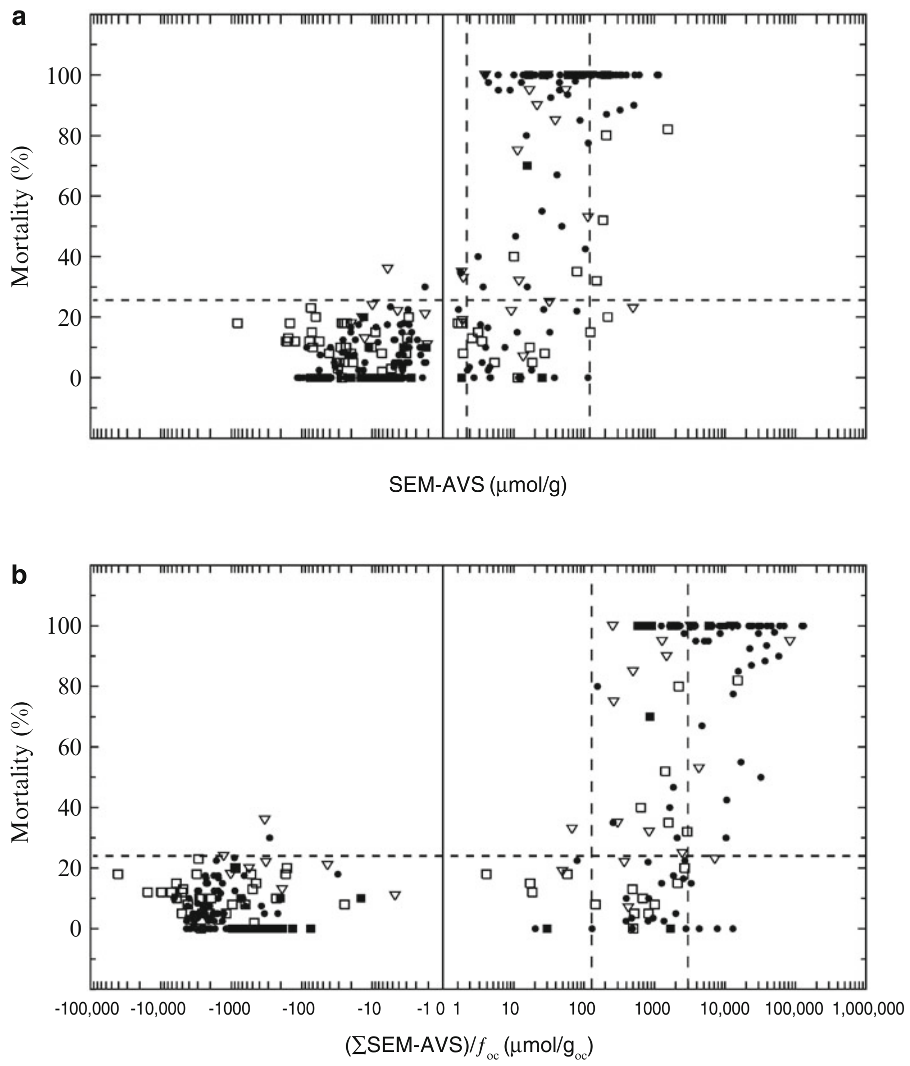

Figure 7.5. Percent mortality versus (a) SEM/AVS and (b) (SEM-AVS)/foc showing effect of organic carbon normalization on SEM/AVS (USEPA, 2005). The data were from laboratory experiments using spiked freshwater and saltwater sediment and from field experiments in freshwater and saltwater. *Vertical dashed lines* are the 90% uncertainty bound limits.

7.4 BIOTIC LIGAND MODEL (BLM) TO ESTIMATE BIOAVAILABILITY OF METALS

The equilibrium-based AVS and SEM model has been successful in predicting metals toxicity in anoxic sediments. The model may not be applicable to sediments where low AVS is expected, i.e., aerobic surficial sediments, and where other mineral and organic phases may control metals availability. In aerobic sediments, the idea that dissolved metals will be precipitated as insoluble metal sulfides is not applicable due to the absence of iron sulfides, which are rapidly oxidized by oxygen with a half-life of a few hours (Burton et al., 2006; Hong et al., 2011a). Thus, suspended and surficial sediment may exhibit greater dissolved metal toxicity and bioavailability. This can also be problematic in the entire biologically active zone of sediments because of localized oxidized microenvironments around burrows of indwelling organisms (e.g., Reible and Mohanty, 2002). Moreover, fluctuations in pH, salinity, and O_2, which are commonly observed in estuarine environments, complicate characterization of the surficial sediments and metals' adverse effect on aquatic life (Chapman and Wang, 2001; Hong et al., 2011b). To predict metal toxicity at the surficial sediments, a more quantitative model is necessary and the Sediment Biotic Ligand Model (S-BLM) has been developed for that purpose (Di Toro et al., 2005).

The bioavailability of metals in water only exposures was initially understood using the Free Metal Ion Activity Model (FIAM) (Morel, 1993), which assumes free metal ion activity is directly related with the toxicity of metals to aquatic organisms rather than total dissolved metals, which include ligands complexed metals. In the BLM (Di Toro et al., 2001), a generalization of the FIAM, toxicity is assumed to occur when the concentration of metal bound to the biotic ligand exceeds the critical body burden for that metal and organism. The metal cation (M^{2+}) complexes to inorganic anions (e.g., OH^-, Cl^-) and dissolved organic carbon (DOC) as well as competes with other cations (e.g., H^+, Ca^{2+}, Mg^{2+}) for biotic ligand binding sites. These reactions account for toxicity variations due to changes in salinity, pH and DOC. Hence, the BLM accounts for the varying bioavailability of metals as a function of varying water chemistry.

BLM has been successful in estimating cupric ion's toxicity to fish in bulk water (Santore et al., 2001) and the Terrestrial BLM (T-BLM) has been developed for assessing metals toxicity in complex soil systems and has estimated toxicities of copper (Cu) and nickel (Ni) on organisms (Thakali et al., 2006a, b). In BLM and T-BLM, DOC and particulate organic carbon (POC) are modeled as fulvic and humic acids, respectively, and metal ion binding to humic substances are modeled by employing Windermere Humic-Aqueous Model (WHAM) V or VI (Tipping and Hurlely, 1992; Tipping, 1998). Recently, sediment BLM (S-BLM) has been developed (Di Toro et al., 2005) to predict metals toxicity in low AVS sediments. The model assumed POC as a dominant metal scavenging phase in sediments, which is similar with T-BLM. Although S-BLM is the most updated model for estimating free metal ion activity in aerobic surficial sediments, the model is considered to be preliminary (Di Toro et al., 2005). Metals oxides, which are neglected in current BLM, are one of the dominant sorption phases for metal sorption as well (Tessier et al., 1985; Wang and Chen, 1997), and these phases should be included to the BLM for better description of metal partitioning to sediment particle.

7.5 PASSIVE SAMPLING FOR MEASURING POREWATER CONCENTRATIONS AND ASSESSING BIOAVAILABILITY

7.5.1 Passive Sampling for HOCs

The sections above have indicated the potential for porewater concentration of HOCs to predict bioaccumulation and hence provide a chemical measure of bioavailability. In the absence of an ability to accurately and consistently predict porewater concentration, however, the most direct way to determine porewater concentration is through direct measurement. The most commonly used conventional method for porewater measurement is centrifugation or filtration, which includes sediment centrifugation or filtration, solvent extraction, solvent exchange, concentration or blowdown, and analysis. However, due to high hydrophobicity of most HOCs and thus very low porewater concentration, especially for HOCs with log

$K_{ow} > 6.0$, an impractical large volume of sample is usually needed to achieve detectable concentrations. Additionally, this approach suffers from incomplete water phase separation (Carr and Chapman, 1995), sorption, or evaporation loss during sample preparation and interference from contaminants associated with colloids and DOCs (Baker et al., 1996). In the presence of colloidal matter, freely dissolved porewater concentration can be estimated by:

$$C_{\text{pw}} = \frac{C_{\text{wm}}}{(1 + C_{\text{DOC}} K_{\text{DOC}})} \qquad \text{(Eq. 7.3)}$$

where C_{wm} and C_{pw} are the measured total and freely or truly dissolved water concentration (milligrams per liter [mg/L]), respectively. C_{DOC} and K_{DOC} are DOC content in water and DOC-water partition coefficient of HOCs. Since K_{DOC} is of the order of K_{ow} (e.g., log K_{DOC} = log $K_{\text{ow}} - 0.58$ by Burkhard, 2000), the difference between the total concentration in the porewater and the truly dissolved concentration can be large for log $K_{\text{ow}} > 6$. Several chemical techniques have been developed to overcome these limitations and detect freely dissolved water concentrations. These approaches include equilibrium dialysis (McCarty and Jimenez, 1985), gas purging (Resendes et al., 1992), alum flocculation to remove colloids (Ghosh et al., 2000), and passive sampling with polymer sorbents. With passive samplers, porewater concentrations can be inferred from the uptake in an easily separable and well-defined synthetic phase, e.g., polymeric sorbents or lipid as used in semi-permeable membrane devices (SPMD) (Huckins et al., 1990). In contrast to SPMD, solid phase microextraction (SPME) using a minimal volume of polymeric sorbents is non-depletive and equilibrium-based sampling of the porewater concentrations is feasible (Maruya et al., 2011).

SPME for hydrophobic organic contaminants involves the insertion of a small volume of polymer sorbent into the sediments, withdrawal after a period of time (preferably after achieving equilibrium), and measuring the contaminants sorbed to the polymer. The achievement of equilibrium allows the estimation of porewater concentration with the ratio of the concentration in the sorbent, $C_{sorbent}$, and a polymer sorbent-water partition coefficient, $K_{sorbent\text{-}water}$, as shown in Equation 7.4.

$$C_{pw} = \frac{C_{sorbent}}{K_{sorbent-water}} \qquad \text{(Eq. 7.4)}$$

Non-equilibrium exposures must be corrected for the kinetics of uptake. In SPME, the amount sorbed to the polymer does not significantly modify equilibrium in the soil-water system due to the small mass absorbed. Polyoxymethylene (POM) (Jonker and Koelmans, 2001), polyethylene (PE) (Fernandez et al., 2009a; Cornelissen et al., 2008), and polydimethylsiloxane (PDMS) (Lampert et al., 2013; Maruya et al., 2009; Mayer et al., 2000) are three polymer sorts that have been widely used to measure porewater concentrations of HOCs. POM and PE are normally used in thin (25–100 micrometers [μm]) bulk layers while PDMS is coated in a thin layer (10–30 μm) on glass fibers. The term "solid phase microextraction" (SPME) has been most often applied to the use of PDMS, but use of POM and PE are essentially equivalent extraction processes. PDMS is available as a thin coating (10–30 μm) on a variety of glass capillaries of various sizes (110–1,000 μm). The capillary can be of arbitrary length and can be coiled in long, continuous lengths. The cylindrical shape is convenient for insertion into sediments and the availability of thin layers with modest sorption capacity (compared to the slightly more sorbing POM and PE) speeds equilibration kinetics. The length can be segmented to achieve the desired vertical resolution or to provide sufficient sorbent volume to meet detection limit requirements. Costs of fabricating the PDMS-coated glass fibers range from approximately $1 per meter (m) (for commercial available optical fibers) to $10–25/m (for specially fabricated coated fibers). Only 1–5 centimeters (cm) of this fiber is necessary for detection of HOCs at sub-nanogram per liter (ng/L) concentrations and, therefore, the cost of the PDMS is negligible compared to the chemical analysis. In addition, the analysis method demonstrated herein generally requires no special extraction or sample processing procedures and the analysis cost is equal to or less than conventional water sample analysis costs.

These three sorbents have similar but not identical sorption capacities for HOCs (Gschwend et al., 2011). Gschwend et al. (2011) compared porewater concentrations of selected PCB congeners by three polymer samplers with the results obtained using air bridges. All sorbents were capable of measuring porewater concentration and were essentially equivalent at equilibrium. Sorbent-water partition coefficients reported by Gschwend et al. (2011) were:

$$\begin{aligned} LogK_{PDMS-water} &= 1.06 LogK_{ow} - 1.16 \qquad && r^2 = 0.94 \\ LogK_{PE-water} &= 1.00 LogK_{ow} - 0.287 \qquad && r^2 = 0.96 \\ LogK_{POM-water} &= 0.791 LogK_{ow} + 1.018 \qquad && r^2 = 0.95 \end{aligned} \tag{Eq. 7.5}$$

Passive sampling with polymer sorbents has extremely low detection limits due to the high sorbent-water partition coefficients of HOCs. Another promising feature of passive sampling is that only freely dissolved water concentrations are measured because only a very small amount of HOC is extracted with passive sampling, and the extraction does not influence the existing equilibrium between the bound and free form of a chemical (Van der War et al., 2004). The big challenge for passive sampling especially for *in situ* measurement of porewater concentrations is the uncertainty in the time required for equilibration. The equilibrium time is largely defined by the time required to replenish the zone that is depleted of the contaminants by sampler, which is controlled by the hydrophobicity of compounds, sorption capacity of the sorbents, and the dynamic conditions at the sampling sites. Different methods have been used to correct the disequilibrium of passive samplers. A common method is preloading the sorbent with performance reference compounds (PRCs), such as deuterated PAHs or C-13 labeled versions of the contaminants of interest, that desorb (Huckins et al., 2002; Fernandez et al., 2009b) that desorb and indicate the rate of sorption of a similarly hydrophobic compound. This approach requires that sorption in the surrounding sediments is linear and reversible. An alternative means is through using two different size sorbents (with different intrinsic kinetics) or measurement of concentrations over at least two different time periods. In either case, the ratio of the two concentrations can be used to fit a model of sorbent uptake. If the sorbent in the thin layer is assumed two dimensional and if the kinetics of exchange are controlled by the surrounding medium rather than internal diffusion in the polymer sorbent, the loss of PRCs can be predicted by the first of Equation 7.6 and the uptake of HOCs can be modeled by the second of Equation 7.6.

$$\begin{aligned} M_{PRC}(t) &= M(0)\left[\exp\left(\frac{RDt}{L^2K^2_{sorbent-water}}\right)\operatorname{erfc}\left(\frac{\sqrt{RDt}}{LK_{sorbent-water}}\right)\right] \\ M_{ads}(t) &= K_{sorbent-water}C_{pw}L\left[1-\exp\left(\frac{RDt}{L^2K^2_{sorbent-water}}\right)\operatorname{erfc}\left(\frac{\sqrt{RDt}}{LK_{sorbent-water}}\right)\right] \end{aligned} \tag{Eq. 7.6}$$

Here L is the volume-to-surface ratio of the sorbent, t is time, and RD is an effective transport parameter (product of retardation factor and diffusion coefficient) for the medium surrounding the sorbent. RD would normally have to be fit to data whether it is desorption of PRCs, a time series of uptake, or the ratio of uptake in sorbents with two different volume-to-surface area ratios. The effective diffusion coefficient is only a weak function of compound if molecular diffusion controls (e.g., inversely proportional to the square root of molecular weight) and independent of compound if an effective diffusion process such as tidal motion or advection controls mixing external to the sorbent. Since the retardation factor is generally linear with octanol-water partition coefficient, RD should be linearly related to K_{ow}.

Besides predicting bioaccumulation through porewater concentrations, passive sampling has also been used as a direct biological surrogate since tissue concentrations show strong linear correlation with sorbent concentrations (You et al., 2006; van der War et al., 2004; Friedman et al., 2009). Hydrophobic organic contaminant accumulation by *Lumbriculus variegatus* (C_b, nanograms per gram [ng/g] lipid) correlated well with the matrix-SPME fiber concentrations (C_f, nanograms per milliliter [ng/mL] PDMS) accounting for 92% of the variation in the data (You et al., 2006). With well-designed samplers that can be successfully deployed in the field (Lampert et al., 2013; Reible and Lu, 2011; Maruya et al., 2009), passive sampling with SPME can be used to assess *in situ* bioavailability of HOCs.

7.5.2 Passive Sampling for Metals

Centrifugation, dialysis, suction filtration and other methods have also been traditionally used to collect porewater for dissolved metals analysis, although these methods have suffered from various sources of errors, such as operator inexperience, insufficient sample size and change of oxidation states during processing (Bufflap and Allen, 1995; Mason et al., 1998). More difficulties arise from extremely low metals concentrations on the order of ng/L as well as from sharp porewater metal concentration profiles, which may vary on the scale of millimeters due to complex biogeochemical redox reactions (Zhang and Davison, 1995).

To overcome these difficulties, passive sampling techniques have also been widely used for metals (Greenwood et al., 2007). Diffusive gradient in thin film (DGT) devices are one alternative that determines labile metal concentrations in aquatic systems (Zhang and Davison, 1995). The DGT probe employs a series of layers including a filter membrane, a diffusive hydrogel, and a resin gel in a plastic unit. The filter side is exposed to the environment after which dissolved metals diffuse through the hydrogel and are accumulated in the resin gel, which acts as a sink. Assuming that steady-state diffusion in the hydrogel layer of thickness, ΔZ_{gel}, at diffusivity, D_{gel}, controls the rate of uptake into the sorbing resin at its base, the concentration in the porewater is given by the mass accumulated in the resin, m_{resin}, over a time, Δt, as shown in Equation 7.7:

$$C_{pw} = \frac{m_{re\sin}\Delta z_{gel}}{\mathrm{D}_{gel}\Delta t} \qquad \text{(Eq. 7.7)}$$

This device can achieve millimeter resolution profiling of metals in sediments and low detection limits by concentrating metals in resin gel (Zhang et al., 1995). The technique has been used to detect various trace levels of ionic species by employing different types of resins and diffusive layers (Zhang and Davison, 1995; Dočekalov and Diviš, 2005; Clarisse and Hintelmann, 2005; Li et al., 2006, 2009). DGT probes have been applied to a variety of soil and sediment to measure porewater metal concentrations and to study remobilization kinetics of metals (Nowack et al., 2004; Ernstberger et al., 2005).

Figure 7.6 shows AVS/SEM and DGT measured porewater zinc (Zn) and Cd concentrations in Anacostia River sediment, which was exposed to aerobic salt water for 120 days in the laboratory (Hong et al., 2011b). The AVS profiles were characterized as decreased concentrations at the surficial sediments and relatively constant concentrations ≤ 2 cm. Based on the AVS/SEM model, the sediments <2 cm are expected to be nontoxic and dissolved metals concentrations should not be detected. In the upper centimeter, the segment averaged AVS was approximately equal to SEM and so dissolved metals and increased metal toxicity might be present. The vertical profiles of $Zn_{(aq)}$ and $Cd_{(aq)}$ measured by DGT probes reflected this and were characterized by elevated concentrations in the surficial sediments followed by <1 microgram per liter (μg/L) concentrations in the deeper anoxic sediments. These observations

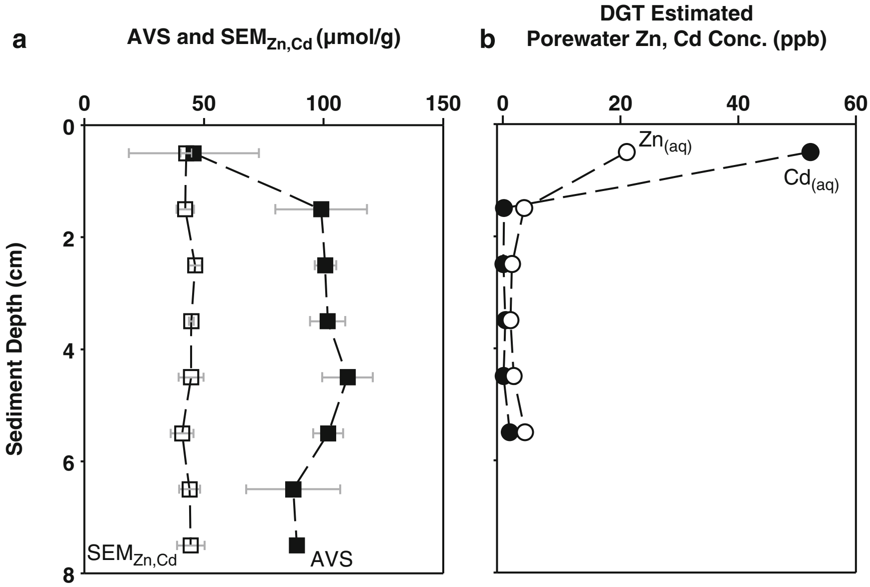

Figure 7.6. Vertical profiles of (a) AVS and SEM in sediments and (b) porewater Cd and Zn concentrations measured by DGT probes (Hong et al., 2011b).

suggested that a bulk measurement of AVS and SEM would not capture the potential metals' availability due to poor resolution in the surficial sediments (Chapman et al., 1998) but that the higher resolution *in situ* passive sampling techniques would better capture the bioavailable fraction of metals in sediments.

DGT is a robust *in situ* passive sampling technique; however, care should be taken when deploying the probe in sediments. In well-mixed bodies of water, the concentration of metals in the aqueous phase can be directly estimated from the mass of metals accumulated in the resin (Zhang and Davison, 1995). However, in soil and sediments, DGT perturbs the local concentration and thus reduces porewater metal concentrations below the equilibrium value near the probe (Nowack et al., 2004; Ernstberger et al., 2005). To overcome these limitations, a modeling approach – the DGT induced fluxes in soil and sediments (DIFS) model – has been used to estimate porewater metal concentrations and to understand the dynamic response of soil and sediment during DGT deployment (Harper et al., 1998, 2000; Lehto et al., 2008). The DIFS model requires a relatively complex numerical simulation for assessing porewater metals kinetics in solid matrices and contains several parameters that must be assessed for interpretation of experimental data.

7.6 SUMMARY

Bioavailability of contaminants is an important factor in sediment and soil remediation and risk assessment. Bulk sediment concentration is not a reliable predictor of exposure and risk; sediment porewater concentration, however, provides a good indicator of readily available contaminants and often describes bioavailability quantitatively. There are several ways to assess bioavailability of HOCs and metals in sediment including equilibrium partitioning predictive methods, extractive methods, and direct porewater concentration measurement. Direct measurement of freely dissolved porewater concentrations are better correlated to bioassays, such as bioaccumulation and toxicity testing. Passive sampling techniques with SPME for HOCs and the DGT probe for metals are efficient tools to measure freely dissolved porewater concentrations because they eliminate the problems associated with colloidally-associated contaminants and the analytical problems associated with detection of low pore-water concentrations. Such passive sampling methods are expected to become increasingly helpful in better characterizing the bioavailability and toxicity of HOCs and metals in contaminated sediments. Although passive samplings are less helpful in assessing future conditions, they help improve the predictive capabilities for bioavailability in sediment.

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