
Incorporating contaminant bioavailability into sediment quality assessment frameworks

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ABSTRACT

The recently adopted sediment quality assessment framework for evaluating bay and estuarine sediments in the State of California incorporates bulk sediment chemistry as a key line of evidence (LOE) but does not address the bioavailability of measured contaminants. Thus, the chemistry based LOE likely does not provide an accurate depiction of organism exposure in all cases, nor is it particularly well suited for assessment of causality. In recent years, several methods for evaluating the bioavailability of sediment-associated contaminants have emerged, which if optimized and validated, could be applied to improve the applicability and broaden the scope of sediment quality assessment. Such methods include equilibrium-based biomimetic extractions using either passive sampling devices (PSDs) or measurements of rapidly desorbing contaminant pools, which provide information compatible with existing mechanistic approaches. Currently, these methods show promise in relating bioaccessible chemicals to effects endpoints, including bioaccumulation of hydrophobic organic compounds and/or toxicity due to metals. Using these methods, a bioavailability LOE for organics is proposed based on PSD and equilibrium partitioning theory that can be employed as an independent LOE or in assessing causality in tiered toxicity identification evaluations. Current and future research should be aimed at comparing the performance of PSDs and their relationships with effects concentrations, field validation of the most promising methods, addressing contaminant mixtures, further developing the parameterization of the proposed bioavailability LOE, and providing a better under-

standing of the underlying diagenetic cycling of metal contaminants that lead to exposure, affect bioavailability, and drive adverse outcomes.

INTRODUCTION

The assessment of sediment quality as an important contribution to water quality and the health of the aquatic environment was recognized in the early 1980s (Giesy and Hoke 1990). The approaches for such assessments included attempts to find mechanistic models to evaluate toxicity such as the equilibrium partitioning approach (EqP) as well as a number of empirical approaches (Giesy and Hoke 1990). The most widely used approaches today are empirical and form the basis for the State of California's Sediment Quality Objectives (SQOs) for direct benthic effects (Bay and Weisberg 2008). Although these SQOs are derived using multiple LOEs, the current framework does not directly assess bioavailability nor provide the capability to establish causality. Efforts to improve these two aspects of assessing sediment quality have different driving factors for organic contaminants and metals. The underlying principle that dictates the bioavailability of organic contaminants is their partitioning behavior, which governs their association with sediment components and with accumulation into organisms (Di Toro *et al.* 1991). For metals, the overriding factor is primarily one of chemical speciation, which is driven by aqueous chemistry including pH, hardness, oxygen concentration, and complexing ligands (Ankley *et al.* 1996, Di Toro *et al.* 2001, 2005). Metals do not simply partition to sediments but complex and react with various components, which

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in turn alter the chemistry of the metal. Biological uptake of metals occurs primarily through active and facilitated transport (Lee *et al.* 2000, Luoma and Rainbow 2005). Thus, approaches to assess bioavailability and causality for metals are more complex and will require different approaches than for organic contaminants.

Mechanistic Approaches for Sediment Quality Assessment

A mechanistic approach to characterize the impact of contaminated sediments was initiated in the early 1980s with the development of equilibrium EqP to assess nonionic organic contaminants (NOCs) impacts to benthic biota. After years of effort, a theoretical approach was put forward to the US Environmental Protection Agency (USEPA; Di Toro *et al.* 1991). In theory, EqP addresses bioavailability and ties the effect concentration in sediments to the current water quality criteria (WQC). Principally, this method relies on the partitioning of organic contaminants among the organic carbon (OC) phases in sediment leading to an estimation of freely dissolved interstitial water concentrations that can be compared with WQC. The OC phase was defined initially only as natural OC. However, scientific difficulties with the approach were apparent even before any EqP-based sediment quality guidelines (SQGs) could be implemented. These difficulties primarily involved poor predictions of toxicity driven by the lack of an understanding of the different types of sediment OC and their resulting partition coefficients. For instance, some early work with polycyclic aromatic hydrocarbons (PAH) in embayment sediments demonstrated that the interstitial waters were out of equilibrium based on OC partition coefficients (K_{oc} ; McGroddy *et al.* 1996, Maruya *et al.* 1996). As a result, the bioavailable fraction of PAH was substantially less than was estimated by EqP (Maruya *et al.* 1997). Both studies hinted at the role of “black carbon” (BC) in sequestering the sediment-associated PAH as well as natural OC of non-pyrogenic origin. Eventually, the USEPA released several sediment quality guidelines (SQGs) based on EqP, including values for dieldrin, endrin, PAH mixtures and 34 other organic contaminants (USEPA 2003a,b,c, 2008), with the caveat that additional phases including BC may need to be considered when using the SQGs.

During this time period, a mechanistic model was also established for divalent metals including

cadmium, copper, lead, nickel and zinc and the monovalent metal silver (Ankley *et al.* 1996, USEPA 2005). The initial model relied on the role of sulfides in reduced sediments acting as a reactive phase to bind the divalent metal and thus reduce its bioavailability relative to total pool in the sediment. The relationship suggested that concentrations of weakly extractable metal that exceeded the molar sulfide concentration would be available to organisms. Using this approach, the USEPA established SQGs for divalent metals (USEPA 2005).

Empirical Approaches for Sediment Quality Assessment

While the mechanistic approaches were under development, more immediate needs were identified for assessing sediment quality for regulatory programs. As a result, several empirical approaches relating the total concentration of organic or metal contaminants to toxicological effects were developed. These approaches included the Apparent Effects Threshold (AET), the effects range approach (ERA), and its minor modifications including the development of the threshold effects levels (TELs) and probable effects levels (PELs) as well as others (reviewed by Batley *et al.* 2005). In all cases, the total concentration of an individual contaminant was linked empirically to an adverse outcome regardless of the concentrations of other co-occurring contaminants. It is not likely, however, that each individual contaminant acts independently. Thus, methods were incorporated to calculate a mixture approach, such as a quotient method for determining PELs (reviewed by Batley *et al.* 2005) and more recently using logistic regression and/or maximum probability models (P_{max} ; Field *et al.* 2002). These methods have proven useful for defining the magnitude of toxicity of sediments to aquatic organisms and allows for classification of sediment for regulatory purposes. They do not, however, address the likelihood of effects due to specific chemicals, nor do they account for, or identify those sediments in which altered bioavailability resulted in a discordance between bulk sediment chemistry and effects-based LOEs.

These empirical sediment quality values have generally been developed with a focus on large datasets for specific benthic organisms such as amphipods (e.g., *Hyalloa azteca* in fresh water and *Ampelisca abdita* and *Eohaustorius estuarius* in marine systems). It was recognized that such

approaches may only contain a portion of the information (i.e., toxicity) that can be useful for demonstrating that sediments contain harmful concentrations of contaminants of concern. The first presentation of an approach that included multiple LOEs was the Sediment Quality Triad (Chapman *et al.* 1987). This approach included the use of sediment chemistry, toxicity tests, and benthic community structure data as three legs to support not only the extent of impact but to provide assurance that the impact was due to contaminants and not to habitat or nutrient limitations. This approach was reviewed by Adams *et al.* (2005), who recommended that such approaches provide a more robust evaluation of the state of the sediment. This approach was later embraced by the State of California to develop SQOs. However, such an approach remains limited for identifying causality and does not address contaminant bioavailability, either for individual or classes of chemicals of concern. To date, for example, even when a multiple LOE approach is used, bioaccumulation data is generally not included in the design.

Sediment Quality Objectives for California Bays and Estuaries

Since 2002, California has been in the process of developing SQOs as tools to evaluate the condition of the State's bay and estuarine sediments (Bay and Weisberg 2008, State of California 2008). The SQOs are intended to address adverse effects caused exclusively by chemical contamination; thus, other stressors like eutrophication and ship traffic are not meant to be considered. California SQOs are derived using two approaches, one focused on the direct effects to the benthic environment and the other on the indirect effects of contaminated sediments on human health and wildlife resulting from consumption of contaminated seafood (e.g., shell- and fin-fish). This article focuses on aspects of the direct effects approach.

The California Direct Effects SQOs consist of three LOEs for determining if a given sediment station is impaired: sediment chemistry, toxicity, and benthic community effects (Bay and Weisberg 2008; Figure 1). The results of each LOE are combined to reach a determination of sediment condition for benthic health. The magnitude of sediment toxicity is based on both lethal and sub-lethal toxicity tests conducted with a variety of species including amphipods (Bay *et al.* 2007). Benthic community effects are assessed using four different condition indices

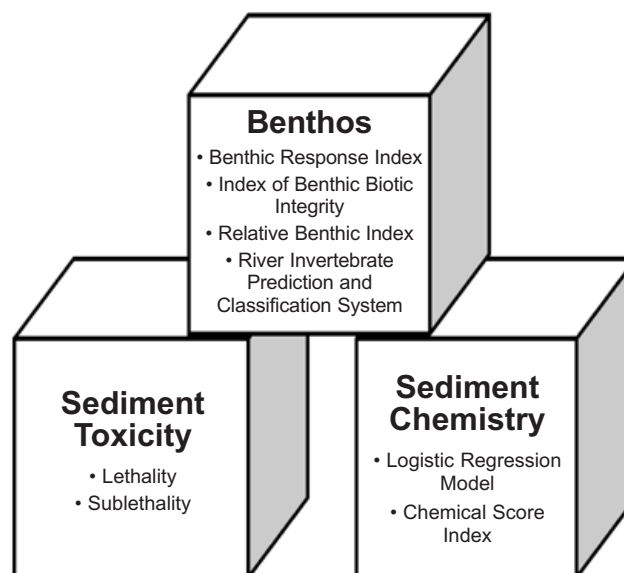


Figure 1. State of California evaluation of sediments for direct effects utilizing three lines of evidence including sediment toxicity, benthic community effects and sediment chemistry (Bay and Weisberg 2008).

(Ranasinghe *et al.* 2007, 2008). The sediment chemistry LOE incorporates measured levels of selected contaminants in bulk sediment to predict sediment toxicity using a logistical regression model (LRM; Field *et al.* 2002, Bay *et al.* 2008) and benthic community impairments using a Chemical Score Index (CSI; Ritter *et al.* 2008). Like other empirical SQGs, the sediment effect concentrations (i.e., concentrations associated with toxicity) are based on correlating effects data versus sediment chemistry. To reach a final assessment of station benthic condition, the score of each LOE is integrated into a matrix of combinations that provide environmental managers with information on the possible impact of contaminants on benthic health (Bay and Weisberg 2008).

While this multiple LOE approach is based on rigorous and scientifically sound principles to determine the likelihood that a sediment station is impaired as a result of chemical contamination, the approach does not directly address whether or not individual chemicals are bioavailable or identify which chemicals are the most likely causal agents. Both the sediment toxicity and benthic community effects LOE results are driven by bioavailable chemicals; that is, for a station to be categorized with a high likelihood of contaminant impact, bioavailable chemicals at sufficiently elevated concentrations must be present. However, like most effects-based

sediment assessment tools, the toxicity and benthic community LOEs do not provide any direct indication of what bioavailable chemical(s) is(are) causing the effect. Further, in the sediment chemistry LOE, contaminant concentrations are measured and then compared to effect concentrations (e.g., lethality, benthic community impairment). However, the measured concentrations are based on total contaminant concentrations (i.e., complete extraction) and not the bioavailable concentrations of contaminants. Consequently, the estimate of adverse effects is primarily correlative and does not identify causality associated with the impairment.

It is widely recognized, however, that measurements of the bioavailable concentrations would provide more specific information in determining which chemicals in sediment may be responsible for observed adverse biological effects. While this type of information may not be critical for answering the question of whether chemical contamination is causing adverse effects to bay and estuary sediments, it is highly relevant later in the California SQO process for informing remediation decisions and/or identifying likely causative toxic agents. For example, within the Total Maximum Daily Load (TMDL) process, there is a diagnostic step (National Research Council 2001), in which the identities of stressors (including chemicals) must be determined to establish the regulated limits imposed by the TMDL. Understanding the bioavailability of chemicals in California's bay and estuarine sediments will address this upcoming need.

In addition to California, Washington and Florida have regulatory frameworks to categorize and manage contaminated sediments. Worldwide, Canada, Norway, and The Netherlands also have such regulatory frameworks in place. Common to these efforts is the goal of setting chemical (or chemical class) specific numeric guidelines; however, as discussed earlier the technical basis for how these guidelines are attained are fundamentally different, ranging from purely theoretical or mechanistic to largely empirical. As a compromise, some frameworks combine components from both approaches. Regardless of their makeup, existing frameworks presently do not incorporate the flexibility to address differential bioavailability of sediment-associated contaminants, a well documented phenomenon that can impart a high degree of uncertainty and variability into the prediction of deleterious effects due to the targeted contaminants.

While uncertainties about the partitioning behavior will always present a challenge for prediction, methods to address bioavailability by defining the uptake, bioaccumulation, and/or toxicity in terms of chemical activity will improve the ability to establish the likelihood of effect or causality for a given chemical (Di Toro *et al.* 1991, Schwarzenbach *et al.* 2003). Thus, methods that provide reliable measures of chemical activity, usually represented as the freely dissolved concentration in sediment interstitial water, of sediment contaminants of regulatory concern to directly understand the exposure of organisms are expected to improve sediment quality regulatory frameworks (Kraaij *et al.* 2003). Moving beyond EqP approaches based on predictions of bioavailability, precise knowledge of the underlying distribution of contaminants in sediments can also allow for the determination of steady state or equilibrium chemical concentrations in benthic organisms and therefore body burden based toxicological risk. This article discusses approaches for determining the bioavailable concentrations of trace organic and metal contaminants in sediments using mechanistic and direct measurement approaches and considers how they may be incorporated into sediment quality assessment frameworks, and as a case example, the development of the State of California SQOs. In addition, the article comments on potential approaches to attempt to address causality.

ADDRESSING BIOAVAILABILITY OF SEDIMENT-ASSOCIATED CHEMICALS

Equilibrium Partitioning of HOCs

The EqP approach is based on a mechanistic model to predict bioavailable concentrations of hydrophobic organic contaminants (HOCs) present in sediments by estimating chemical activity as a surrogate for freely dissolved interstitial water concentration (Di Toro *et al.* 1991):

$$K_{Pi} = \frac{C_{Pi}}{C_{Di}}$$

where K_p is the partition coefficient for chemical i (L/Kg), C_{Pi} is the measured particle concentration of chemical i ($\mu\text{g/Kg}$), and C_{Di} the freely dissolved, and bioavailable, concentration of chemical i in equilibrium with benthic organisms ($\mu\text{g/L}$). In principle, C_{Di} corresponds to the sediment freely dissolved intersti-

tial water concentration of chemical i . Because the majority of HOCs are associated with OC, normalization of K_{Pi} by the sediment's natural OC fraction (f_{OC} ; Kg OC/Kg) results in a more useful parameter known as the OC normalized partition coefficient (K_{OCi} ; L/Kg OC):

$$K_{OCi} = \frac{K_{Pi}}{f_{OC}}$$

Combining the equations above, C_{Di} can be estimated as the freely dissolved concentration:

$$C_{Di} = \frac{C_{Pi}}{K_{OCi} f_{OC}}$$

By assuming that biota are exposed to sediment-associated contaminants in proportion to their chemical activity (or C_{Di}), this concentration can then be compared to a known aqueous effects concentration. For example, C_{Di} can be replaced with the WQC value for a given chemical (i.e., C_{WQCi} ; $\mu\text{g/L}$), and a sediment concentration ($C_{P_{WQCi}}$; $\mu\text{g/Kg}$) that can serve as the basis for a criterion is calculated as:

$$C_{P_{WQCi}} = C_{WQCi} K_{OCi} f_{OC}$$

Using this construct, the USEPA has published four EqP sediment benchmark (ESB) documents for over 60 HOCs (USEPA 2003a,b,c, 2008).

Application of the EqP model has met with mixed results with several studies having shown that the model was predictive of toxic effects for fluoranthene, DDD, DDE, and DDT (Swartz *et al.* 1990, DeWitt *et al.* 1992, Hoke *et al.* 1994). Application of EqP to mixtures of PAHs also resulted in prediction of toxicity (Swartz *et al.* 1995, Ozretich *et al.* 2000). In contrast, the use of EqP sediment quality guidelines for more than 30 chemicals in sediments from southern California (Vidal and Bay 2005) resulted in a low ability to predict measured toxicity. These authors concluded that the HOCs measured were not likely the cause of amphipod toxicity or that natural OC normalization alone may not have properly described bioavailability in these sediments.

Limitations with the EqP model were becoming apparent by the mid-1990s, perhaps due in part to its consideration of only two partitioning phases (water and solid phase). Specifically, the model did not

consider the quality of particulate organic matter and its influence on partition coefficients (K_P and K_{OC}). Substantial progress has been made demonstrating that one of the major characteristics limiting the two phase EqP model is, as noted earlier, the role of BC such as soot, charcoal and tar, which are formed from the incomplete oxidation of organic substances. This BC has much greater partition coefficients (K_{BCs}), which vary with material type, and can strongly affect the bioavailability of HOCs (Cornelissen *et al.* 2005). To incorporate the potential influence of this "super-sorbing" phase, the equation for C_{WQCi} can be expanded as (Accardi-Dey and Gschwend 2002):

$$C_{Di} = \frac{C_{Pi}}{f_{OC} K_{OCi} + f_{BC} K_{BCi} C_{Di}^{ni}}$$

where f_{BC} is the fraction BC (Kg BC/Kg), K_{BCi} is the BC-water partition coefficient for chemical i (L/Kg BC) and ni the Freundlich nonlinear sorption coefficient for chemical i (unitless). A consequence of ni in the term C_{Di}^{ni} is that a natural log transformation of the equation is needed to establish a likely solution for C_{Di} . Although this equation incorporates both natural OC (f_{OC}) and BC (f_{BC}) to estimate the dissolved and bioavailable concentrations of HOCs, uncertainty still exists around the limited number of K_{BC} values currently available as well as the best method for measuring f_{BC} (Ghosh *et al.* 2000, Currie *et al.* 2002, Jonker and Koelmans 2002, Burgess *et al.* 2004, Kane Driscoll *et al.* 2009).

Despite these uncertainties, the EqP model for HOCs has many advantages including i) addressing bioavailability by defining toxicity in terms of freely dissolved phase concentrations (or more accurately, the chemical activity), ii) focusing on causality by linking the effect concentration to specific WQC, iii) modulating the magnitude of toxicity response by considering the slope of the C_D dose response curve, and iv) the ability to incorporate toxicant additivity to consider multiple contaminants in one assessment assuming a similar mode of action (e.g., narcosis) through the use of toxic units (USEPA 2003a,b,c, 2008).

Equilibrium Partitioning for Metals

Analogously, a mechanistic model for divalent metals including cadmium, copper, lead, nickel and zinc and the monovalent metal silver was developed

to account for binding to sediment (Ankley *et al.* 1996, USEPA 2005). In this model, metals associated with reduced sediments associate primarily with sulfides formed theoretically when the solubility product for a given metal-sulfide pair exceeds the solubility product for iron-sulfide, a common species in anaerobic sediments. If the sulfides, on a molar basis, exceed the combined concentrations of those metals, the metals are considered to be in a non-bioavailable form. The pool of sulfides sequestering the metals are quantified analytically as acid volatile sulfides (AVS; mmoles sulfide/Kg), while the pool of potentially bioavailable metals are called simultaneously extracted metal (SEM; mmoles metal/Kg), which is metal that is extracted by weak acid. Conceptually, the difference between these two quantities on a molar basis (i.e., possible excess metal) serves to indicate whether bioavailable metals are present in the interstitial waters of the sediments:

$$C_{Excessi} \cong SEM - AVS$$

where $C_{Excessi}$ is a latent indicator of the dissolved concentration of metal i associated with the initial SEM pool of the metal after interaction with the co-occurring AVS. At values of $C_{Excessi}$ greater than zero, sediment could potentially contain sufficient bioavailable metals to cause toxicity. In later versions of the AVS model, binding of metals to sediment OC was also included:

$$C_{Di} \cong \frac{AVS - SEM}{K_{oc} f_{OC}}$$

As with the HOCs, the USEPA has developed an ESB for cationic metals and chromium (USEPA 2005). While chromium is not sequestered by AVS due to its low solubility products (K_{sp}) relative to iron, in aqueous solution chromium exists in two forms: Cr^{+3} and the more toxic Cr^{+6} . If the sediments containing chromium are reduced (i.e., contain AVS) the vast majority of chromium will be in the non-toxic Cr^{+3} form (USEPA 2005).

However, a potential difficulty of the AVS-SEM approach is that it does not account for interactions among metals that make up the underlying SEM pool of potentially bioavailable metals. The K_{sp} for the reaction of Zn, Cd, and Cu with sulfides are 2.9×10^{-25} , 1.4×10^{-27} , and 1.3×10^{-36} (Lide 1990), respectively. As an example, if an equi-molar mixture of

Zn and Cd exceeds the available AVS, one would expect that most of the 'excess' SEM would be Zn. In this case, the presence of Zn as part of a mixture with Cd is protective of Cd exposure in that Zn is generally less toxic than Cd. In a similar equi-molar mixture of Cd and Cu, the excess SEM is likely Cd. In this case, the other metal in the mixture, Cu is not protective of Cd exposure. Although each mixture would have the same nominal SEM-AVS, the metal to which an organism is exposed will be quite different based on the underlying binding strength of the specific metals in the sediment.

Other Approaches

More recently, the biotic ligand model (BLM) was introduced to estimate bioavailable metal by taking into account the various ligands that sequester the dissolved metal ions (Di Toro *et al.* 2001, Santore *et al.* 2001). These ligands include dissolved organic carbon (DOC) and inorganic ligands like carbonates, chlorides, and hydroxides as well as competing ions including sodium, calcium and hydrogen. The model considers the site of metal uptake in the organism as the biotic ligand and that at sufficiently high concentrations binding of metal to the biotic ligand results in toxicity. Consequently, the model estimates how much bioavailable metal is available to bind to the biotic ligand relative to its binding to organic and inorganic ligands and/or being replaced by competing ions. While initially designed for water applications, it has been tested in sediment systems with moderate success (Di Toro *et al.* 2001, 2005).

In contrast to determining the chemical activity of a metal species in sediment, an alternate approach is to focus on its biokinetic uptake and release by organisms (e.g., Luoma and Rainbow 2005). With these methods, one can explicitly account for the underlying geochemistry by quantifying the ingestion rate and assimilation efficiency of different species of metals and estimating the steady state body burden. These methods range from simple measures of the bioaccessibility (solubilization) of metals in simulated gut fluid (e.g., Mayer *et al.* 1996, Kalman and Turner 2007), to highly parameterized models quantifying steady state metal uptake and release rates (e.g., Lee *et al.* 2000, Yoo *et al.* 2004). Two drawbacks associated with these models are the possibility of significant spatial and temporal differences in the uptake and release parameters, even within a species (Rainbow *et al.* 2009), and the

potentially large amount of data required for model initialization, calibration and validation.

CURRENT STATE-OF-THE-ART TO ESTABLISH BIOAVAILABILITY

Much research has recently addressed the need for cost-effective alternative approaches that mimic the uptake and accumulation of sediment-associated contaminants. The last decade has seen the advent of other methods for estimating or measuring the dissolved and bioavailable concentrations of HOCs as well as inorganic contaminants (Huckins *et al.* 1993, 2006; Davison and Zhang 1994; Mayer *et al.* 2003). These so called biomimetic techniques have relied on characterization of desorption kinetics (Cornelissen *et al.* 1997) or determination of freely dissolved concentrations (or activities in the case of metals) in sediment interstitial water (Mayer *et al.* 2000, Blom *et al.* 2002). To be viable, alternatives to currently available conventional techniques (e.g., interstitial water isolation, extraction and off-line instrumental analysis), these approaches need to provide the required sensitivity (e.g., less than ng/L detection limits) for the appropriate metric; that is, mass or fraction desorbed or the freely dissolved concentration of the chemical in question. In addition, alternative methods should reduce the overall cost and turnaround time associated with laborious and time-consuming standard bioaccumulation and/or toxicity tests. While these methods have been previously used to quantify bioavailability and bioaccumulation, their assessment of toxicity is also under development (e.g., You *et al.* 2008).

Characterizing Desorption Kinetics for Organic Contaminants

The availability of sediment-associated contaminants via interstitial water is based upon the net exchange between the particle and aqueous phases. If one assumes that interstitial water is constantly flushing sediment particles, then the steady-state exchange between these phases results in a net removal or “desorption” of contaminant from the particle phase. This desorption phenomenon for HOCs has been well characterized as consisting of a rapid, slow, and very slow time component (Pignatello and Xing 1996). Subsequent work demonstrated that the rapidly desorbing component or fraction (f_r) was the contaminant available to test organisms and that this parameter could be charac-

terized with a single time point extraction (Cornelissen *et al.* 2001). This original work with Tenax[®] resin as the sorbing infinite sink was further expanded to show that EqP could be applied with improved accuracy to establish bioavailability if it were based on measures of f_r (Kraaij *et al.* 2003). Thus, methods that can adjust for the differences in bioavailability lead to acceptable estimations of HOC bioaccumulation that are supported by EqP theory (Trimble *et al.* 2008).

Recently, the use of Tenax extraction for evaluating two different classes of benthic invertebrates, the Great Lakes amphipod *Diporeia* and mixed Great Lakes oligochaetes, demonstrated that bioaccumulation differences were likely related to feeding behavior of the target organisms (Landrum *et al.* 2007). When considering only the oligochaetes, this technique predicted bioaccumulation across species, laboratory and field sediments, and among laboratories so long as biotransformation was not an issue (Figure 2; Landrum *et al.* 2007). Because Tenax extraction can predict the bioaccumulated, absorbed dose, this approach should also permit prediction of expected toxicity. For studies with field sediments, Tenax extraction produced better estimates of toxici-

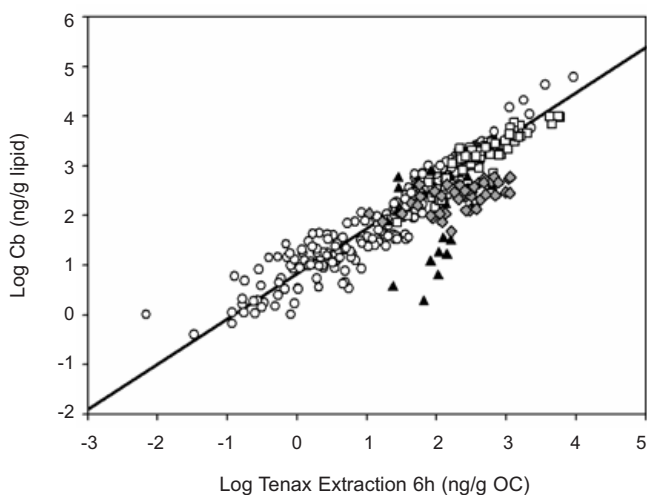


Figure 2. Tissue concentration (Cb) of sediment-associated organic chemicals was correlated with the rapid desorbing fraction as measured with a 6-hour Tenax extraction ($\log [Cb] = 0.912 \pm 0.021 \log [6h \text{ Tenax Extract}] + 0.835 \pm 0.033$, $r^2 = 0.897$, $n = 225$; Landrum *et al.* 2007; open circles). Black triangles represent polycyclic aromatic hydrocarbons in mixed Great Lakes oligochaetes; mixed organics are shown for *Lumbricus rubellus* (gray triangles) and *Limnodrilus* sp. (open squares; ten Hulscher *et al.* 2003). Figure published with permission from the American Chemical Society.

ty of pyrethroids in sediments than exhaustive extraction even when adjusted for the OC content in the sediments (You *et al.* 2008).

Determining Freely Dissolved Concentrations Using PSDs

Passive sampling devices (PSDs) are simple, low cost alternatives to conventional methods for the extraction and chemical analysis of interstitial water that rely on diffusive mass transport and/or preferential sorption to concentrate chemicals of interest. Over the past 20 years, PSDs have been designed and optimized to measure a wide variety of target analytes, including trace metals (Blom *et al.* 2002), HOCs (Stuer-Lauridsen 2005) and organometallics (Aguilar-Martinez 2008). Their potential for providing time-averaged concentrations, spatial and temporal trends, and source characterization in a more cost-effective manner has garnered attention from large collaborative monitoring networks, including the European Union's Water Framework Directive (Allan *et al.* 2006). Passive sampling devices typically target contaminant concentrations among competing phases and can be applied under kinetic or equilibrium conditions. Regardless of mode, laboratory pre-calibration is required to determine uptake rate constants or equilibrium distribution coefficients, usually for each analyte of interest (Mayer *et al.* 2003). Further, PSDs incorporating membranes are prone to fouling which attenuates transport and typically results in underestimation of concentrations in the aqueous phase of interest (e.g., in water column or interstitial water applications; Prest *et al.* 1992, Webb and Keough 2002).

Passive sampling devices have been designed for both *ex* and *in situ* applications. To date, *ex situ* determination of interstitial water concentrations has been the most widely practiced. One example is the EPA-approved Method 8272 that utilizes solid phase microextraction (SPME) for determination of 16 PAHs in remotely collected sediment pore water (ASTM 2007). This method has been shown to adequately predict narcotic toxicity to freshwater amphipods using water only exposures (Kreitinger *et al.* 2007). Similarly, membrane reservoirs (a.k.a. "peepers") directly inserted into sediment have been employed for subsequent off-line determination of trace metals and non-conservative constituents such as nutrients and organic acids. However, their relatively small reservoir volumes are not sufficient for determination of ultra trace level HOCs. Recent advances

have made it possible to quantify very low (<1 ng/L) concentrations of HOCs in sediment interstitial water, using packaging concepts to protect sorptive media such as SPME fibers from damage and biofouling (see Hydrophobic Organic Contaminants below).

Determining Metal Ion Concentrations

A number of methods have been developed to measure the free metal ion concentration in surface waters. These include anodic and cathodic stripping voltametry, gel resin techniques (Senn *et al.* 2004), and Donan membrane techniques (Kalis *et al.* 2006). To date, these techniques have not been applied to sediment interstitial waters due to a combination of artifacts associated with sample collection and handling and the fact that free metal ion concentrations are often below analytical limits of detection. One sampling technique that has been used frequently in the study of metals in sediments is diffusion gradient in thin film (DGT) gels (Davison and Zhang 1994). The theory behind DGT gels is that a controlled diffusion gradient is set up within a gel sampler placed in the sediments. The diffusive flux of metals into the gel is related to the concentration of 'labile' metals in the surrounding pore water, which can be calculated using Fick's First Law. An issue with DGT samplers is that they do not sample a distinct geochemical form of a metal, but rather what is operationally defined as "DGT-labile" metal. It is unclear which species of metals comprise this DGT-labile fraction. A recent study in surface waters comparing speciation techniques showed that the concentration of DGT-labile metals are higher than free metal ion concentrations determined from more traditional techniques (Sigg *et al.* 2006). An advantage of the DGT sampler is that it is capable of measuring fine vertical resolution of speciation of metals in surface sediments; for example, showing increases in labile metals at the oxic sediment-water interface (<1.5 mm; Zhang *et al.* 1995). Very few studies, however, have been undertaken to examine the relationship between DGT-labile metals and bioaccumulation (Roulier *et al.* 2008), or the results of *ex situ* acute or chronic toxicity tests.

Hydrophobic Organic Contaminants

Similar to DGT, samplers that employ a diffusion or protective membrane include lipid-filled semipermeable membrane devices (SPMDs; Huckins *et al.* 1993, Hofelt and Shea 1997) or those that contain sorptive disks (Kingston *et al.* 2000) to target

and sequester HOCs. As its name suggests, the polar organic chemical integrative sampler (POCIS) is a recent adaptation of the SPMD designed for polar organics (Petty *et al.* 2004), including pharmaceuticals and other contaminants of emerging concern. However, in the context of sediments, the use of SPMDs is much more limited (Rantalainen *et al.* 2000, Williamson *et al.* 2002) although they have been used in soils (Wells and Lanno 2001) and ground waters (Gustavson and Harlein 2000). Another limitation of SPMDs when used with soils and sediments is the potential for them to act as an infinite sink and deplete the sample of the contaminants of interest from the zone immediately around the sampler. Depletion of target compounds by this type of sampler makes calculating equilibrium dissolved contaminant concentrations (C_{Di}) problematic.

In contrast, samplers that rely on direct sorption of HOCs to a polymeric matrix utilize SPME fibers - glass capillaries coated with a thin polymeric coating ($>10\mu\text{m}$; Arthur and Pawliszyn 1990) - or thin polymer sheets/strips/tubing composed of low density polyethylene (Lohmann *et al.* 2004, Adams *et al.* 2007), polyoxymethylene (POM; Cornelissen *et al.* 2008a,b,c), polysiloxane (silicone) or other polymeric material (Huckins *et al.* 2006). Direct insertion of a SPME fiber into a soil or sediment matrix ("matrix-SPME") has been recently attempted by several investigators (Brennan *et al.* 2009; Trimble *et al.* 2008; You *et al.* 2006, 2007a,b). Polychlorinated biphenyl (PCB) concentration in earthworms were highly correlated with SPME fiber concentrations (30- μm polydimethylsiloxane (PDMS)) co-exposed to sludge-amended, field collected soils (van der Wal *et al.* 2004), which required ~ 20 days to equilibrate. SPME-based samplers have recently been designed specifically for *in situ* applications, incorporating protection from breakage and biofouling of the fragile polymer-coated sorptive fiber for fixed (You *et al.* 2006, Maruya *et al.* 2009) and variable depth (D. Reible, University of Texas, Cockrell School of Engineering, Austin, TX, personal communication) profiling of HOC concentrations. These samplers have been shown to correlate well with total interstitial water concentrations as well as tissue concentrations of invertebrates exposed in controlled lab experiments (Figure 3) and *in situ* (Keith Maruya unpublished data). Examples of the utility of SPME for evaluating bioavailability are growing rapidly to include compounds such as fipronil that can degrade to more toxic degradation products (Brennan *et al.* 2009).

Polyethylene devices (PEDs) are being used more and more frequently in water (Booij *et al.* 2003a, Adams *et al.* 2007, Anderson *et al.* 2008, Morgan and Lohmann 2008) and sediment deployments (Booij *et al.* 2003b; Lohmann *et al.* 2004, 2005; Vinturella *et al.* 2004; Tomaszewski and Luthy 2008; Fernandez *et al.* 2009a,b; Friedman *et al.* 2009) and can be applied similarly to matrix-SPME. Polyethylene devices are inexpensive due to the very low cost of raw materials and simplicity in design

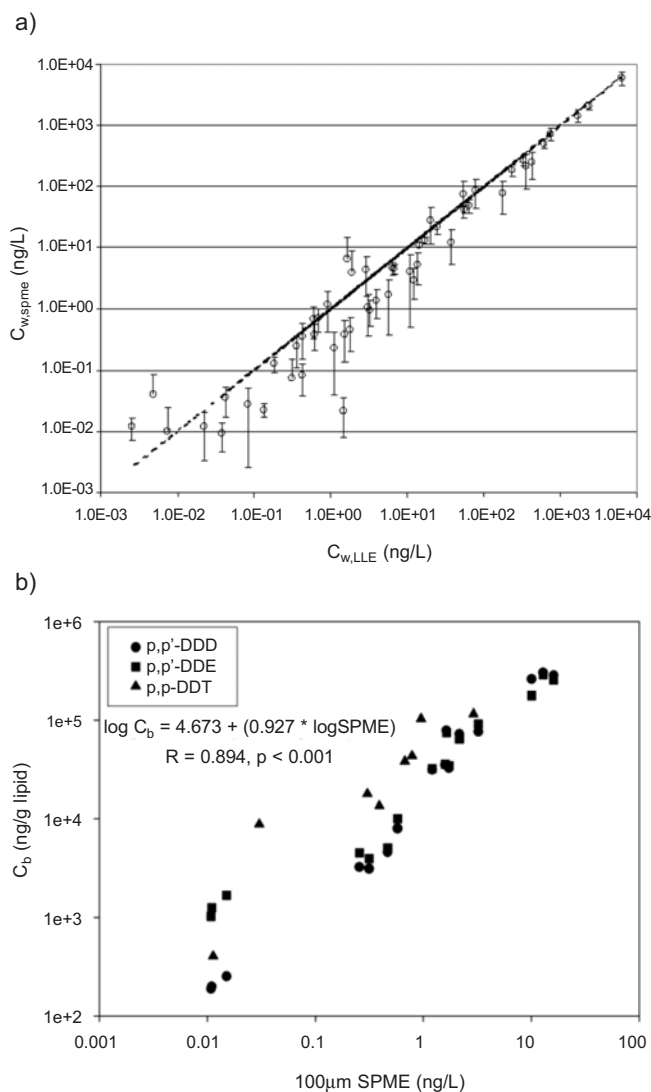


Figure 3. Correlation of bioavailable porewater concentrations measured by SPME ($C_{w,SPME}$) with total porewater concentration measured by liquid-liquid extraction ($C_{w,LLE}$) for 12 model hydrophobic contaminants (a) and lipid-normalized tissue concentrations (C_b) of DDT compounds in *Macoma nasuta* (b). SPME and *M. nasuta* were co-exposed to spiked estuarine sediment in glass aquaria for 28 days. Figure Published with Permission from John Wiley and Sons.

and fabrication. Due to a virtually unlimited sorbent mass/volume, PEDs also afford very high theoretical sensitivity. Evidence of their utility was found in laboratory exposures of whole contaminated sediment where strong relationships between PAH and PCB accumulation were found using PEDs and the polychaete *Nereis virens* (Vinturella *et al.* 2004, Friedman *et al.* 2009). For PCBs, the relationship between PEDs and polychaetes is shown in Figure 4 (Friedman *et al.* 2009).

Like PEDs, thin, rigid POM strips have been deployed in water (Cornelissen *et al.* 2008a), sediment (Jonker and Koelmans 2001, Barthe *et al.* 2008), and both systems (Cornelissen *et al.* 2008b,c). In a comparing POM and SPME uptake of PAHs versus bioaccumulation by freshwater and marine worms (*Lumbriculus variegatus* and *N. virens*), Barthe *et al.* (2008) reported POM underestimated bioavailability in sediments with low levels of contamination, while accurately estimating bioavailability in highly contaminated sediments. Silicone-based samplers have also been evaluated, in part, because polysiloxane is reported to have the largest free volume of common polymers (Huckins *et al.* 2006), which represents the space into which contaminants can move into from the aqueous phase. Advantages of this polymer are tempered by the potential for partition coefficients to

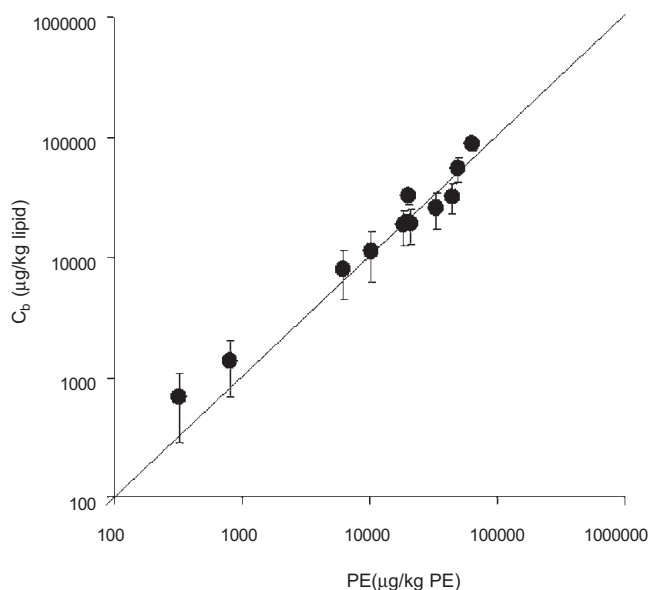


Figure 4. Relationship between PCB uptake by PEDs and bioaccumulation by the marine polychaete *N. virens* (C_b) in 28-day exposures to New Bedford Harbor sediments. Regression resulted in an r^2 value of 0.934 ($n = 12$), based on Friedman *et al.* 2009. Figure published with permission from the American Chemical Society.

increase with increasing contaminant concentrations as the free volume also increases (Huckins *et al.* 2006). Thus far, the silicone samplers have only been applied in water-only deployments (Booij *et al.* 2002, Wenrich *et al.* 2003, Rusina *et al.* 2007, Yates *et al.* 2007). Ethylene/vinyl acetate (EVA) has also been evaluated as a biomimetic PSD (Golding *et al.* 2007, 2008; Tao *et al.* 2008). In one approach, EVA solution is applied to the interior of a vial and allowed to evaporate to a thickness of 0.05 μm (Golding *et al.* 2008). Contaminated sediment is added to the vial and contaminant-EVA equilibration proceeds. Like the PDMS in SPME, the thin EVA film suggests rapid equilibration kinetics. In comparing accumulation of several HOCs using EVA and an amphipod (*Corophium colo*), Golding *et al.* (2008) reported an $r^2 = 0.85$.

Passive sampling devices for HOCs are capable of detecting ng/L and in some cases pg/L levels, particularly for very hydrophobic substances (Zeng *et al.* 2005, Adams *et al.* 2007). Exposure times required for equilibrium samplers without membranes (e.g., SPME or low-density polyethylene (LDPE)) may exceed several weeks for specific analytes (Maruya *et al.* 2009, Adams *et al.* 2007). For very hydrophilic analytes, complete equilibrium is only attainable after several months (ter Laak *et al.* 2008), and thus approximations are required for practical application. Alternatively, pre-loading of surrogates, known as performance reference compounds (or PRCs) within these devices may eliminate the need for lengthy equilibration times while improving measurement accuracy (Huckins *et al.* 2006, Adams *et al.* 2007, Fernandez *et al.* 2009b). As this brief description of PSD methods for HOCs indicates, there is a strong movement being made to further develop and apply these technologies, a trend that is likely to continue with robust comparisons of PSDs and the necessary trials to validate these samplers in the field.

INCORPORATION OF BIOAVAILABILITY INTO SEDIMENT REGULATORY FRAMEWORKS INCLUDING CALIFORNIA'S SEDIMENT QUALITY OBJECTIVES

To incorporate bioavailability into sediment quality frameworks that employ multiple LOEs, such as the California SQO process for direct effects, a line of evidence relating interstitial water concentra-

tions, PSD measurements, or contaminant f_r measurements to known toxic effects concentrations is proposed for HOCs. This so-called “bioavailability LOE” could be employed as an independent LOE that is considered in addition to the others discussed above [e.g., toxicity, benthos and chemistry (Figure 1)] to allow for a designation of sediment station status that includes a consideration of the bioavailability of chemical contaminants of interest. The proposed approach for HOCs is similar to the approach used by the USEPA in their development of ESBs (USEPA 2003a,b,c, 2005, 2008). In this approach, the EqP-predicted bioavailable concentration of an HOC is compared to the matching Final Chronic Value (FCV; $\mu\text{g/L}$) or Secondary Chronic Value (SCV; $\mu\text{g/L}$) from the appropriate WQC or compendium of toxicity values (USEPA 2008), for example:

$$ESB = K_{OC}FCV$$

where the ESB is in units of $\mu\text{g/Kg OC}$ to allow for use with whole sediment contaminant measurements normalized to sediment OC. If the sediment concentration of a given HOC exceeds the ESB value, the contaminant may be bioavailable at concentrations sufficiently high to cause toxicity. For application in the California SQO program, the derivation would be similar. The bioavailability-based SQO would be estimated based on the product of the concentration of contaminant measured on the PSD (C_{PSD}) ($\mu\text{g/Kg PSD}$) and PSD-water partition coefficient (K_{PSD-W} ; L/Kg PSD) divided by a specified toxic effects value (TEV; $\mu\text{g/L}$), the resulting ratio or SQO would be equivalent to the toxic units (TUs; unitless) of the contaminant of interest:

$$SQO = Toxic Units = \frac{C_{PSD}}{K_{PSD-W} TEV}$$

Values for the TEV would be taken as State of California Toxic Rule values (CFR 2000), or alternatively could include USEPA FCVs and SCVs. Under this approach, the magnitude of the TUs could be set to indicate the degree of certainty that a toxic effect is likely to occur. Further, the endpoint for the toxic response could be set at levels of concern (e.g., other than the 50% mortality point and for endpoints other than acute mortality). Note, for some toxic chemicals, the sum of TUs could be considered additive to

address the impact of mixtures. Similarly, PSD or fraction desorbed derived TUs could be used individually or in summation once the relationships are established that would lead to a series of TUs related to specific toxic endpoints. This TU based SQO for the bioavailability LOE could thus be incorporated into the framework described by Bay and Weisberg (2008) for direct effects under the California SQO program.

A second or alternative application for the bioavailability LOE would be for follow up or “second tier” assessments of sediment quality when the baseline multiple LOE framework does not result in a clear cut score/decision. An example of this would be for sediment with very high chemistry score but little to no toxicity or benthic community degradation. The bioavailability LOE could be incorporated into the assessment to demonstrate whether all targeted (or specific suspected) contaminants are present at concentrations at which effects (or lack thereof) would be expected. A third option would be for toxicity identification evaluation (or TIE) studies (USEPA 2007), where a given sediment is deemed to be toxic and/or has degraded benthos, but the causative chemical(s) is (are) unknown. Direct measurement of dissolved contaminants of concern in each case, (i.e. the bioavailable LOE using PSDs); would assist in this determination. This type of TIE application is amenable to real environmental samples, and thus contaminant mixtures as well.

While there is currently research exploring the issue of what constitutes the bioavailable metal, none are sufficiently advanced to make additional recommendations for trace metals of concern at this time beyond those that have been previously proposed (e.g., USEPA 2005).

FUTURE RESEARCH NEEDS TO IMPROVE SEDIMENT QUALITY ASSESSMENTS

The use of biomimetic approaches to better characterize bioavailability shows great promise in sediments where exposure is expected to be more constant than in water. Moreover, the solid phase pool of contaminant should buffer such excursions in exposure particularly for organisms that are infaunal. However, to date the use of a biomimetic approach requires that the PSD reach equilibrium as the kinetics of the devices are not the same as the organisms. Thus, the only condition that can be evaluated at this

point is the steady state accumulation for the organism compared to the equilibrium condition for the PSD or f_r . Conditions that put the PSD or organism at other than steady state may be addressed later when kinetics for each of these media are better defined. Moreover, the toxicity endpoints that could be addressed with these devices are not limited to acute mortality; their inherent sensitivity would allow for comparison to chronic responses, which typically occur at much lower ambient or body residue concentrations (McCarty and Mackay 1993; Hwang *et al.* 2001, 2004; see discussion below). So long as the biomimetic extractant reflects the absorbed dose, then it should allow development of a relationship to an observed endpoint.

Several questions remain as to the degree and scope of PSD effectiveness. Can they be used for a wide variety of contaminated sediments and for all contaminants of regulatory interest? Do they quantify bioavailability with the necessary sensitivity, accuracy and precision? Are they sufficiently predictive of the most relevant biological/ecological endpoints of concern? As important, what is the cost associated with their development and implementation, and how will their measurements/parameters be best incorporated into decision-making frameworks? How do we address contaminant mixtures and metal speciation in these frameworks? Successfully addressing these questions through targeted research and field application will pave the way for the next substantial improvement in SQGs.

Advancement of PSDs

The promising performance and lower unit cost associated with PSDs underscore their utility as a supplemental or alternative sampling strategy for sediment-associated contaminants, particularly those that are bioaccumulative. However, several issues remain with respect to acceptance of PSDs in sediment quality regulatory frameworks. The vast majority of work to date has focused on PCBs, PAHs and legacy organochlorine pesticides (e.g., DDTs and chlordanes), and metals such as copper, zinc and lead. More research is needed to expand the scope of PSDs to include contaminants of emerging concern (e.g., current use insecticides like pyrethroids, fipronil), pharmaceuticals and personal care products, commercial and industrial chemicals, and other potentially toxic metals (e.g., mercury in its organic forms or metal oxy-anions such as arsenic and selenium). This includes the development of equilibrium

or fixed-time partitioning coefficients for target contaminants (and related performance reference compounds) between water and passive samplers. Because freely dissolved concentrations can be extremely low, PSDs must provide the sensitivity concomitant with regulatory goals. Another issue that has not been thoroughly addressed is the measurement precision associated with PSDs. For example, variability in duplicate measurements using SPME can be as high as 50% (Maruya *et al.* 2009), suggesting that a higher degree of replication is needed to reduce measurement uncertainty or evaluate the heterogeneity.

To ensure an acceptable degree of relevance for bioavailability measurements using biomimetic approaches, a comprehensive dataset comparing multiple biological endpoints with PSD measurements or f_r is needed. These biological endpoints should include, as a minimum, LC50s and EC50s for relevant, sentinel organisms (e.g., freshwater, estuarine and/or marine), biota sediment accumulation factors (BSAFs), and critical body residues (CBRs). These matched datasets can be either laboratory generated or field based, as long as they are identified as such. To generate such a dataset, studies with focused objectives and a high degree of quality control should be supported and carried out.

Critical Body Residues and Biomimetic Extractions

A little over two decades ago, the idea of associating the toxicity of HOCs to the accumulated dose was proposed (McCarty 1986) and expanded to demonstrate more clearly the relationship between bioaccumulation and toxicity for different modes of action (McCarty and Mackay 1993). Since that time, many researchers have examined the potential relationship between body residue and toxicity and it has generally been found to improve the interpretation of organism exposure and the resulting toxic response. However, it is clear from the development of toxicodynamic models that the observed toxic response depends on the balance between damage formation and repair (Ashauer *et al.* 2006, Butcher *et al.* 2006). In a workshop held by the Society of Environmental Toxicology and Chemistry in June 2007 (Meador *et al.* 2007), it was clear that additional developments will be needed to bring this approach to full utility. However, interim uses can be made that will improve development of SQGs. For instance, the concept has already been employed by the USEPA

for setting the SQGs for PAH mixtures (Di Toro *et al.* 2000, USEPA 2003c). Based on our understanding of body residue response relationships and the utility of biomimetic extractions, it should be possible to use results from PSDs and/or desorption studies to serve as the dose metric for more reliable toxicity estimates. This approach, undoubtedly, would require careful calibration between the two types of parameters. As an example, toxic units based on pyrethroids evaluated by determining f_r were more accurate for predicting the toxicity of contaminated sediments than using carbon normalized concentrations (You *et al.* 2008).

The use of the body residue approach for evaluation of compounds of similar mechanisms of action may likely be expanded through the concept of additive response for HOCs. From the earlier example, when the contributions of DDT and its metabolites DDD and DDE as a mixture were evaluated using a toxic unit model, the resulting toxic response was determined to be additive (Lotufo *et al.* 2000). However, making body residue measurements in the context of a sediment quality regulatory program could be difficult, particularly in areas where there is substantial toxicity and organism mass may be limited or difficult to obtain. Thus, if an approach is developed that relies instead on a surrogate measurement of bioavailability (e.g., Tenax or a PSD), then it would be possible to improve our ability to interpret sediments with respect to toxicity. To accomplish this, it should also be possible to develop relationships between the PSD concentration at equilibrium and the toxicity to account for both the chemical activity in the sediment and the bioaccumulation potential of the organism, which is the goal of several current research efforts.

It is clear that the use of biomimetic approaches can over-predict the expected accumulation for compounds that are readily biotransformed (Landrum *et al.* 2007). However, this may be used to our advantage since they should reflect the total absorbed dose and thus account for the energy (stress) that organisms must exert to form metabolites. In many cases, the metabolites can contribute to the toxic response and for compounds such as organophosphate pesticides, the metabolites are the active component. Thus, addressing the total absorbed dose might be expected to lead to new insights on the impact of biotransformation on the toxic response. Such an approach would still need to address mixture toxicity, which could perhaps be performed with an addi-

tive toxic unit model as described above (e.g., USEPA 2003c). To date, most mixture work has been performed with the external concentration representing dose, which does not account for nuances associated with toxicokinetics (see McCarty and Mackay 1993). It is thought that removing these additional variables from development of mixture models should improve understanding and prediction. Such new or expanded approaches based on our current knowledge should allow better interpretation of not only the bioavailability of the mixture but also begin to address causality in ways that are not currently possible.

Evaluation of Contaminant Mixtures

Current approaches to evaluate contaminant mixtures in sediments include calculation of quotients of the empirical SQGs assuming that the contaminants are acting in an additive manner without regard to mode of action (Ingersoll *et al.* 2005). An alternative approach uses logistic regression (or P_{\max} model) to identify the compound which empirically provides the maximum contribution to the effect and assumes that it represents the interaction of the compounds in the mixture (Field *et al.* 2002). However, these approaches have not specifically tested the interactions among compounds.

For direct evaluation of mixtures, the dose metric is typically expressed as an external concentration (e.g., in water or sediment) of the individual components. Contaminants are considered to act either additively when they have the same mode of action and act at the same receptor, synergistically when the contaminants act to produce a greater than additive response, or antagonistically when they work to produce a less than additive response. The difficulty in making these assessments is that contaminants show differences in toxicokinetics in the simplest exposure conditions, such as aqueous exposures, and the differences in exposure are even more complex in sediments where issues such as bioavailability must be considered. Some simplification can occur when contaminants are evaluated on a body residue basis. The additivity of PAHs to contribute to the toxic response of organisms from sediments has been developed for an improved interpretation of PAH mixtures in sediments (Di Toro *et al.* 2000, USEPA 2003c). For these compounds, the mechanism of action is the same for acute mortality across the range of PAHs, which is reflected by the similarity of effects concentrations for either single compounds

or mixtures on a body residue basis (Landrum *et al.* 2003). For metal mixtures, the USEPA assumed a similar mode of action for six metals (USEPA 2005). However, even in the case where the mode of action is not the same, mixture toxicity can be evaluated. For instance, the response of *H. azteca* to DDT and its metabolites was found to produce an additive response when using toxic units based on body residues (Lotufo *et al.* 2001). Thus, even in sediment exposures where the bioavailability can be different among contaminants the role of the components in the mixture can be evaluated (You *et al.* 2008). A similar approach using a biomimetic extraction as a surrogate for exposure would also be feasible since these measurements reflect the absorbed dose. However, work to date based on estimation of absorbed dose using the bioavailable fraction has been restricted to HOCs and exposure to larger range of contaminant mixtures including metals will be required to improve future applications.

Understanding Metal Speciation and Temporal Variability *In Situ*

Two methods are commonly used to assess the uptake of metals into benthic organisms: 1) measuring and/or modeling the chemical activity (and thus bioavailability) in sediment and 2) considering the steady state uptake and elimination of metals from multiple routes to measure/predict metal concentration within the organism itself. What is missing is the link between the two methods, which can be defined as an accurate depiction of the underlying diagenetic cycling of metals in sediments. For the biological approaches, one needs to know (or be able to measure) the concentrations of distinct metals species in the sediment. And while current chemical measurement methods may provide a snapshot of metal activity, they do not allow one to consider how speciation and activity may vary in space and time.

Metals are naturally occurring, and as such have distinct biogeochemical cycles governing their environmental transport and fate. This knowledge needs to be better incorporated into the SQG framework for metals. A current means to assess the chemical activity of metals in sediments is the SEM/AVS approach, which uses the concentrations of labile sulfides and metals (and also OC) to estimate a concentration of 'labile' metal in the interstitial water available for uptake and subsequent toxic effects. As described earlier, the mixture of metals making up the SEM pool all have different solubility products,

ligand binding strengths, and rate constants for participation in the myriad of reactions occurring in sediments (especially reaction with reduced sulfides). To date, while some research has been conducted on metals in sediment using geochemical models such as PHREQC or MINEQL (e.g., Bhattacharya *et al.* 2006), very little has been performed to use these models within a bioaccumulation/toxicity framework. Furthermore, the bioavailability of metals in sediments is not a static process. Seasonal variation in AVS levels or resuspension events can alter the speciation and therefore bioavailability of metals (Simpson *et al.* 2000, Campana *et al.* 2009). The exact impacts of these activities depend on the specific metals present and will rely on thermodynamic parameters such as oxidation rates for different metals.

Current approaches for the measurement of metal speciation in surface waters have not been generally applied to sediments due to a combination of methodological or detection limit problems. As a compromise, the DGT sampler has been used in a number of studies. While it can provide valuable information on metal bioavailability, it is not clear what the 'DGT-labile' pool of metal represents. There is clearly a need to be able to adapt water column techniques for use in the sediment environment, either as a direct measure of metal bioavailability or in support of some of the modeling approaches described above.

Field Demonstration

Although less important for *ex situ* techniques (e.g., EPA Method 8272), it is imperative that the most promising *in situ* technologies for incorporating bioavailability into sediment quality assessment be field tested. Robust deployment schemes and reliability of field equipment and/or PSDs must be demonstrated for these technologies to be of practical and consistent utility. Approaches that require complex and expensive equipment may not be well suited to *in situ* applications. In contrast, the simplest, low technology devices such as SPME, POMs and PEDs can be deployed using simple, robust tools (Zeng *et al.* 2004). Reliability of these devices, other than theft or destruction, is generally thought to be a non-issue. Another consideration for incorporating *in situ* PSDs is the degree of spatial and depth (i.e., below the sediment-water interface) coverage required for any given study or site characterization. Devices that can be remotely deployed and retrieved are clearly more cost-effective compared to

those that require human intervention (e.g., divers in subtidal environments). Field demonstrations should also leverage and coordinate with on-going and future studies that assess coastal and/or sediment contamination on local, regional, State and national scales. Examples of such studies include the regional surveys conducted in the Southern California Bight and San Francisco Bay (California), various USEPA monitoring programs (e.g., Environmental Monitoring and Assessment Program (EMAP)), and NOAA's National Status and Trends program that samples and analyzes native bivalves across the nation on a biannual schedule.

Validating the Utility of the Bioavailability LOE

As described in the previous sections, interstitial water concentrations or activities determined by PSDs or the fraction of HOC desorbed can be related to threshold levels of concern to derive a bioavailability SQO (C_{Di}) that can be scored and weighted in multiple LOE sediment quality assessment frameworks. To test the incremental utility of the bioavailability LOE in, for example, the current California SQO framework, spiked laboratory experiments could be designed to confirm the causality of a suspected toxicant that is at a relatively low bulk concentration but that is bioavailable (e.g., a pyrethroid insecticide) vs. another that is present at an elevated bulk sediment concentration but is strongly bound and thus not bioavailable (e.g., a PAH). In the latter case, the bulk sediment chemistry LOE alone would fail to identify the pyrethroid as the cause for concern, and would in all likelihood falsely point to the PAH. Incorporating PSD measurements, on the other hand, would correctly rank the potential effect based on toxic units in the aqueous phase. For several HOCs within the same chemical class, or a suite of contaminants that act via a similar mode of toxicity, the same experimental approach could be used to test for additivity of effect using two or more model toxicants spiked into natural or artificial sediments. Similarly, measurements from *in situ* PSD deployments (see Field Demonstration above) coupled with bioaccumulation and/or *in* or *ex situ* toxicity testing could be compiled for a selected suite of HOCs from several field sites to serve as a validation dataset for incorporating the bioavailability LOE into an existing SQO framework, such as the California case example.

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