Passive sampling methods for contaminated sediments: State of the science for organic contaminants

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Abstract

This manuscript surveys the literature on passive sampler methods (PSMs) used in contaminated sediments to assess the chemical activity of organic contaminants. The chemical activity, in turn, dictates the reactivity and bioavailability of contaminants in sediment. Approaches to measure specific binding of compounds to sediment components, e.g., amorphous carbon or specific types of reduced carbon, and the associated partition coefficients are difficult to determine particularly for native sediment. Thus, the development of PSMs that represent the chemical activity of complex compound/sediment interactions, expressed as the freely dissolved contaminant concentration in interstitial water (C_{free}), offer a better proxy for endpoints of concern, such as reactivity, bioaccumulation, and toxicity. Passive sampling methods have estimated C_{free} using both kinetic and equilibrium operating modes and used various polymers as the sorbing phase, e.g., polydimethylsiloxane, polyethylene, and polyoxymethylene in various configurations, e.g., sheets, coated fibers, or vials containing thin films. These PSMs have been applied in laboratory exposures and field deployments covering a variety of spatial and temporal scales. A wide range of calibration conditions exist in the literature to estimate C_{free}, but consensus values have not been established. The most critical criteria are the partition coefficient between water and the polymer phase and the equilibrium status of the sampler. In addition, the PSM must not appreciably deplete C_{free} in the interstitial water. Some of the future challenges include establishing a standard approach for PSM measurements, correcting for non-equilibrium conditions, establishing guidance for selection and implementation of PSMs, and translating and applying data collected by PSMs.

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INTRODUCTION

Contaminated sediments pose a significant global challenge for environmental risk assessment and management. One formidable barrier was the reliable prediction of contaminant bioavailability using traditional analytical methods and contaminant normalization procedures which were often not predictive of the field environment. Recent advances in passive sampling methods (PSMs) offer a promising alternative to support improved risk-based decision making, since the bioavailability of sediment contaminants can be directly quantified. The current paper represents a literature review on PSMs in contaminated sediment analysis for organic contaminants (see Supplemental Information (SI) Table SI-1; ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_075_094SI.pdf) and highlights potential applications as well as technical issues that are currently limiting widespread adoption and application by the user community. The details for the application and current limitations of PSMs are addressed in detail in companion papers for organics by Mayer *et al.* (In press), Ghosh *et al.* (In press) and Greenberg *et al.* (In press), and for metals in Peijnenburg *et al.* (In press).

For decades scientists have recognized that sediments serve as both a sink and source of contaminants in aquatic ecosystems. In addition, the fate, transport, and toxicity of sediment-associated contaminants are influenced by several biological, chemical, and physical processes. Initial efforts to evaluate the impact of sediment-associated contaminants and their role in environmental processes focused on sediment quality thresholds based on bulk or "total" sediment concentrations. These assessments were complicated by the varying compositions among sediments and the different interactions of contaminants with these components. For instance, toxicity of contaminants in sediment exhibited significantly different concentration response curves for the same contaminant among various sediments due to differences in sediment composition (DiToro *et al.* 1991). Research over the past several decades continued to find better approaches to interpret sediment contamination so that factors influencing contaminant exposure were better understood.

Since bioaccumulation is proportional to chemical activity in the exposure environment, better assessments of the bioaccumulation and toxicity of sediment-associated contaminants lies in clearer determination of the chemical activity of contaminants in this complex matrix. An early approach to estimate chemical activity for hydrophobic organic contaminants (HOCs) used organic carbon normalization through an organic carbon interstitial water partition coefficient (DiToro *et al.* 1991). As proposed by this approach, the route of exposure is not important provided the compound of interest comes to equilibrium in all phases and thus represents the chemical activity of the exposure. Thus, measures of chemical activity would predict the maximum exposure for an organism at equilibrium. This approach reduced the variability in predictions of bioaccumulation and toxicity of HOCs among sediments (DiToro *et al.* 1991) suggesting that improved measures of chemical activity would lead to improved assessments. However, attempts to apply this approach, revealed variability among sediments that could not be explained with simple normalization to total organic carbon (TOC) content (USEPA 2012a,b). This variability was controlled by the presence of different forms of organic carbon that had different binding coefficients for HOCs than those proposed for organic carbon in sediment. Included in these materials were fresh plant matter with much lower binding constants (Kukkonen *et al.* 2005) and to a greater extent carbon in more chemically reduced forms (Pignatello and Xing 1996, Luthy *et al.* 1997, Kupryianchyk *et al.* 2011), including soots, chars, and other forms of organic carbon, such as weathered oils with much higher binding constants (Jonker and Barendregt 2006). Because the type of organic matter varies in and among sediments and because it is quite challenging to differentiate between the individual organic carbon components that also cannot be uniquely defined (Ghosh *et al.* 2003, Jonker and Koelmans 2002) or separated, this complication leaves the state of the partitioning among components unknown. An alternative approach that could provide an estimate of the chemical activity measured as C_{free} is the isolation of interstitial water and analytical measurement of the contaminant. For this approach, relatively large volumes of interstitial water are required to meet analytical detection limits for dissolved HOCs (ASTM 2008). The collection and analysis of interstitial water lead to the potential for disturbance of the equilibrium during the separation process (ASTM 2008), and a requirement to account for the binding to dissolved organic carbon (Morehead *et al.* 1986) to obtain accurate determination of C_{free}. As a result, a panel of experts, convened by the National Research Council, determined it was important to find improved methods that would lead to a better understanding of the bioavailability of the contaminants associated with sediment independent of its composition (NRC 2003).

There are multiple methods that have been the focus of research and development over the past few decades to more simply describe the availability of sediment-associated contaminants (NRC 2003, Menzie and Driscoll 2013) and these can be divided into selective depletive (accessibility-based) techniques and equilibrium (activity-based) techniques that are the basis for PSMs. While there is great utility for accessibility-based techniques, such as the use of Tenax extraction (Pignatello 1991), for describing the bioaccumulation of organic contaminants across sediments (Landrum *et al.* 2007, Mackenbach *et al.* 2012, Harwood *et al.* 2013b); the focus of this paper is on PSMs reflecting the objectives of the SETAC technical workshop, where the participants limited the scope to passive samplers as devices that are placed in contact with sediment to assess the chemical activity of the contaminant within the sediment. Passive sampling methods integrate across a range of binding phases and when at equilibrium provide a measure of the chemical activity, which is related to the concentration of freely dissolved contaminant in sediment interstitial water (C_{free}, which in turn is related to the other potential binding phases through specific partition coefficients (Figure 1)). The chemical activity, represented by C_{free}, is the driving force for all chemical interactions with sediment-associated contaminants as the bound forms cannot participate directly in the processes governing bioavailability, diffusive exchange, and environmental reactivity of the contaminant. The bound forms only participate in such chemical interactions as sources governed by the partition coefficients and the sizes of the specifically bound contaminant pools. Having direct measures that lead to estimates of C_{free} eliminates the need for a detailed understanding of sediment composition, both the content and amount of each partitioning phase, and their respective partition coefficients to establish a link to processes, such as bioaccumulation and toxicity (Oen *et al.* 2006; Sun and Ghosh 2008; Zielke *et al.* 2011; Maruya *et al.* 2012, In press).

Through an extensive review of the available literature, the current paper examines the major approaches to assess the chemical activity of HOCs in sediments utilizing passive samplers, summarizes various applications, particularly estimating

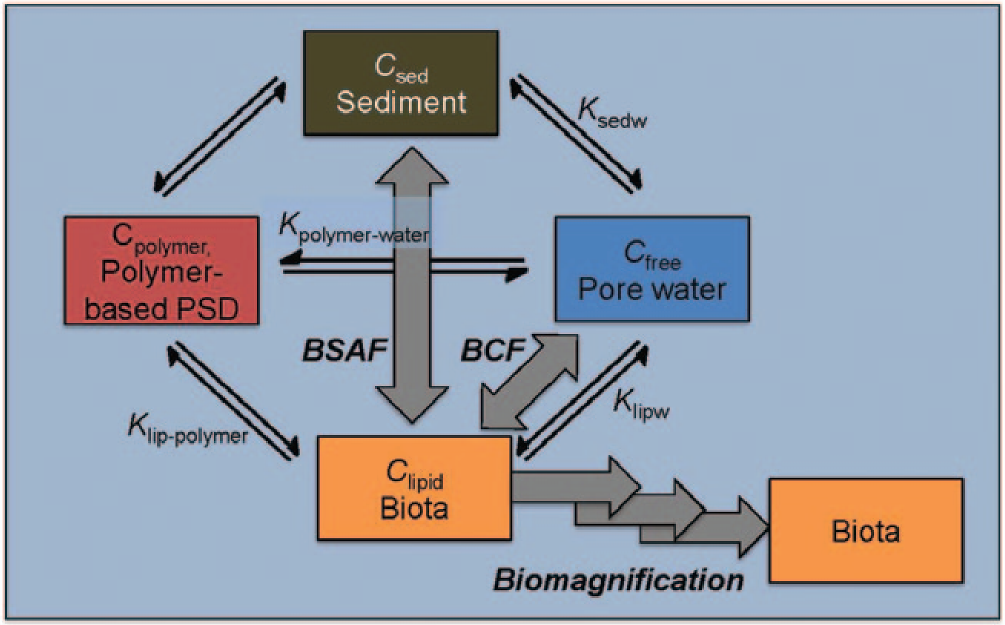

Figure 1. Relationship between sediment, water, biota, and a polymer-based passive sampling device (PSD) at chemical equilibrium. Toxicokinetic processes are denoted with grey arrows and the associated partition coefficients are denoted with the equilibrium arrows. K_{sedw} is the partition coefficient between the binding phases in sediment, usually organic carbon for hydrophobic organic contaminants, and the interstitial water, $K_{polymer\text{-}water}$ is the partition coefficient between the passive sampler polymer and the interstitial water, K_{lipw} is the partition coefficient between organism lipid and the interstitial water, and $K_{lip\text{-}polymer}$ is the partition coefficient between the polymer phase and organism lipid.

bioavailability, to date and highlights technical issues that are currently limiting widespread adoption of PSMs by the user community.

RESULTS OF LITERATURE SURVEY

A summary of available PSM literature and their descriptions is listed in Table SI-1. This summary includes 90 papers describing the application and performance of methods that utilize samplers of different configurations and materials for the assessment of sediment-associated organic contaminants. Of these papers, 82% were based on allowing the PSM to come to chemical equilibrium with the interstitial water and 20% employed kinetic approaches generally using first-order accumulation models to estimate the equilibrium condition with the interstitial water (some studies used both or a combination thereof). Several experimental conditions have been evaluated including *ex situ* (field sediment brought back to the laboratory and tests conducted, 61%), *in situ* (PSM's placed in the field, 20%), and laboratory-spiked sediment (41%) with some overlap between *ex situ* and *in situ* studies. These papers measured C_{free} (84%), bioaccumulation (34%), toxicity (18%), degradation (5%), remediation (5%), and/or polymer-water partition coefficients (1%). Of these studies, 10% utilized performance reference compounds to correct for non-equilibrium conditions. About half of the papers used sheets or films split between polyethylene and polyoxymethylene to make the measurements and a similar fraction used coated fibers with the dominant polymer phase polydimethylsiloxane (PDMS). The papers were also about equally split between examining polycyclic aromatic hydrocarbons (PAHs) and chlorinated hydrocarbon contamination with several other compound classes also included. The following sections address these studies in greater detail, and the paper concludes with a description of current technical limitations, which impede broader adoption for contaminated sediment assessment and management.

MODES OF OPERATION, CALIBRATION AND DESIGN CONSIDERATIONS

Passive sampling methods are applied in two operational modes: an equilibrium mode where sufficient time is allowed for the sampler and sediment to reach an equilibrium distribution; and, a kinetic mode that targets a time-specific concentration that must be corrected to the equilibrium condition. In the kinetic mode, the time frame for the sampler exposure, characteristics of the sampler, and the behavior of the contaminants determine the kinetic state of the contaminant in the sampler for a particular experimental condition. The more important characteristics that affect the operating mode include the time to equilibrium, which increases with the polymer-water partition coefficient (K_{pw}) and sampler thickness, which decreases with increased sediment mass contributing to the exposure (Smedes *et al.* 2013). In contrast, the ability to detect contaminants increases with increasing sampler mass. Thus, the optimum characteristics of the sampler represent a trade-off between its ability to reach equilibrium in a given exposure time and the sensitivity of the method for HOCs at low C_{free} concentrations. For applications that involve simultaneous measurement of multiple contaminants over a large range of hydrophobicity, e.g., polychlorinated biphenyl congeners (PCBs), there may be individual compounds that come to complete equilibrium and those for which equilibrium is not achieved within the time allowed for PSM exposure. Furthermore, the detectability of a given contaminant by a PSM will vary based on the physicochemical and partitioning properties of the target analyte(s).

To apply samplers in various applications, they must be pre-calibrated to determine the time required to reach equilibrium and/or the kinetic parameters described by the sampler rate dynamics must be known. In addition, the distribution of the target HOCs between the sediment and passive sampler phase must be determined at equilibrium or a pre-defined exposure time (kinetic mode), while also insuring non-depletive conditions. This is necessary so that equilibrium concentrations can be estimated for the appropriate calculation of C_{free} (Mayer *et al.* 2003, Vrana *et al.* 2005, Ouyang and Pawliszyn 2008, You *et al.* 2011). To reduce equilibration times in laboratory exposures, agitation and/or shaking has been incorporated to enhance mass transport within the aqueous phase and increase mass transfer across the aqueous-polymer interface (Zeng *et al.* 2005, Yang *et al.* 2006, You *et al.* 2007a, Hunter *et al.* 2009, Harwood *et al.* 2012a).

Additionally, the efficiency of the sampling method can vary in relation to the limits of detection (LOD) and sampling equilibration time. For example, due to the relatively small volume of the sampling phase, SPMEs can exhibit a relatively high LOD, especially for the more water soluble compounds (Bao and Zeng 2011, You *et al.* 2011).

Highly hydrophobic compounds have larger partition coefficients to the PDMS sampling phase than more water soluble compounds, which results in larger mass uptake at equilibrium and thus comparatively lower LODs. An effective approach to lower the LODs is to rely on thermal desorption rather than solvent extraction to increase analytical sensitivity or use passive samplers with larger volumes of sampling phase, such as solid-phase microextraction fibers with a relatively thick PDMS coating. However, increasing the thickness (and thus volume) of the sampling phase lowers the surface-to-volume ratio, resulting in longer equilibration times. While not always the case, many currently available passive samplers could take weeks to months for HOCs to reach equilibrium, particularly for highly hydrophobic compounds and under low energy, field conditions (Mayer *et al.* 2000, Gschwend *et al.* 2011).

Passive Sampling Strategies at Equilibrium

Equilibrium partitioning was proposed by DiToro *et al.* (1991) to describe the distribution of contaminants among sediment phases (e.g., sediment organic carbon, sediment interstitial water, and biota lipid), where the chemical activity of the target compound was equal among the three phases. At equilibrium, an expression relating the chemical activity in the aqueous phase, C_{free}, to the activity (expressed as concentration) on the sampler phase (polymer, C_p) can be made using Equation 1:

$$C_{free} = C_p/K_{pw} \qquad \textbf{Eq. 1}$$

where K_{pw} is the polymer-water partition coefficient.

Two requirements are needed for equilibrium sampling with passive samplers (Mayer *et al.* 2000, 2003). First, equilibrium must be reached among the different phases. Second, the sorption capacity of the sampler should be negligible compared to the exposure environment, commonly referred to as a "non-depletive" condition. This will assure accurate measurements of C_{free} in the interstitial water, with no significant disturbance of the original sediment-interstitial water equilibrium condition (Yang *et al.* 2007). Guidance for ensuring the equilibrium and negligible depletion criteria are discussed further by Mayer *et al.* (In press).

Passive Samplers Used in the Kinetic Phase

While it is critical to determine the equilibrium condition of the PSM to attain good estimates of C_{free}, PSMs do not always reach equilibrium. Thus, a method was needed to determine the equilibrium condition and provide an estimate of C_{free}. A two-compartment model, which describes the flux into and out of the sampler, can serve as a method to estimate equilibrium (Equation 2). In a non-depletive equilibration, the difference in chemical activity of the target compounds between the two phases, the source and passive sampler, drives the transport of the compound to the receiving phase (the sampler). In a well-mixed system, the chemical flux into the sampler is controlled by a static aqueous diffusion layer at the interface of the two phases (Bayen *et al.* 2009), diffusion into the polymer controlled by polymer thickness and surface area, and relies on desorption from the sediment being sufficiently fast to maintain C_{free} at or near the original value. The exchange rate constant that reflects these processes (k_e) dictates the time required for equilibrium to be achieved. The solubility capacity of the sampler relative to the water is described by the partition coefficient at equilibrium and is a function of the characteristics of the polymer and the target contaminant (K_{pw}; see Ghosh *et al.* In press). The sampler dynamics can be modeled empirically using an apparent-first-order model:

$$C_p(t) = C_{free}K_{pw}\,(1 - e^{-k_e t}) \qquad \textbf{Eq. 2}$$

where k_e is the exchange constant, which depends on the sampler and target HOC characteristics as well as the experimental (mixing) conditions.

However, when such samplers are placed in sediments without mixing, contaminant desorption and diffusion within the sediment may effectively reduce the flux into the sampler requiring longer exposures for the system to return to the original equilibrium state. Such conditions can slow the kinetics affecting the estimates based on kinetics determined from a well-mixed system. To correct for this condition, performance reference compounds (PRCs) that mimic the behavior of target analytes can be added to field-deployed polyethylene samplers to correct for potential non-equilibrium conditions encountered *in situ* (Booij *et al.* 2003, Tomaszewski and Luthy 2008, Fernandez *et al.* 2009a). Further discussion of PRCs can be found in Ghosh *et al.* (In press).

CONFIGURATIONS AND MATERIALS

The two major characteristics that define passive samplers used for measurement of C_{free} are the physical size and shape of the sampler (or "configuration") and the type of polymeric sorbent material used to construct the sampler. There are essentially two configurations used: 1) thin films or membranes cut into sheets or strips; and, 2) coatings. Sheets and strips are homogeneous samplers that vary in thickness and physical dimensions to accommodate the experimental design, while coatings (also of different thicknesses) can be applied to solid supports including glass fibers and glass jars. The polymer sorbing "phase" dictates the sorption affinity (partition coefficient), while the phase volume in combination with the partition coefficient determines the sorption capacity for the device. Some phases including PDMS are commonly employed as coatings, while others, such as polyethylene (PE) and polyoxymethylene (POM), are utilized in sheet form. Typical phase thicknesses range between 25 and 50 µm, but can extend from <10 µm to as thick as 100 µm. Table SI-1 provides a summary of the literature organized by configuration and polymer type and provides the details for the subsequent sections.

Sheet Configurations

Polyethylene

Passive samplers based on triolein-filled low density PE tubes, also known as semi-permeable membrane devices or SPMDs (Huckins *et al.* 1993, Leppänen and Kukkonen 2006, Lyytikäinen *et al.* 2003), were first developed for overlying water, but have been used in sediments to a limited extent. One of the main reasons for the limited use of SPMDs in solid matrices was the relatively long exposure time required for target HOCs to reach equilibrium between the triolein-filled polyethylene tube and the matrix, which led to other issues, such as biofouling. To overcome this shortcoming, polyethylene devices (PEDs) without a lipid reservoir (e.g., triolein) were designed to measure C_{free} (Lohmann *et al.* 2005, Tomaszewski and Luthy 2008). Compared to SPMDs, PEDs have the advantages of shorter equilibrium times and easier cleanup procedures. Finally, PEDs are constructed of inexpensive, commercially available sheets that can be purchased in bulk in many thicknesses (e.g., 25 and 50µm), and are easily fabricated in sheet or strip form to maximize surface area to volume for any sorbent mass. These features result in their ability to potentially measure ultra-low contaminant concentrations of C_{free} (pg/L or lower; Adams *et al.* 2007; Tomaszewski and Luthy 2008; Gschwend 2009, 2010).

Polyoxymethylene

Similar to PE, POM readily sorbs HOCs with partition coefficients similar to PE (Jonker and Koelmans 2001, Janssen *et al.* 2011). A distinguishing feature of POM is that sorption is likely limited to the surface as it has been shown that sorbate diffusion coefficients are orders of magnitude lower than PDMS materials (see below), and also much lower than in PE (see below; Ahn *et al.* 2005; Rusina *et al.* 2007, 2010). The low diffusion coefficients correspond to the higher partition coefficient values observed for thinner materials (Cornelissen 2008a) further supporting the adsorption hypothesis. Thus, PSMs involving POM would in principle need to be calibrated for each thickness of material used due to differences in equilibration times among the different thicknesses. Like PE, a relatively large mass of POM can be applied in sheet configuration, resulting in estimated interstitial water concentrations of HOCs at pg/L levels. Compared to PE, POM has a smoother yet harder surface, which reduces the likelihood of trapping particles, like soots, as well as reducing biofouling (Jonker and Koelmans 2001). This polymer also has a repeating ether group ($-CH_2-O-CH_2-$), resulting in a better affinity for polar compounds compared to PE and PDMS (Endo *et al.* 2011). It is worth noting, however, that the oxygen-containing groups in POM may result in non-equilibrium passive sampling (e.g., adsorption rather than absorption), which could complicate the interpretation of POM data.

Coatings

Coated Fibers (Solid Phase Microextraction)

Solid-phase microextraction (SPME) developed by Arthur and Pawliszyn (1990) utilizes a fused silica fiber with an external polymer coating, typically PDMS, for measuring HOCs. Different coating thicknesses are available, as well as other polymer coating phases (e.g., polyacrylate or PA), allowing the user to select a composition/configuration based on the target analyte(s), the operational characteristics, and the desired performance (Lambropoulou *et al.* 2002, ter Laak *et al.* 2008, Geiger 2010, Reible and Lotufo 2012).

The use of SPME fibers with an integrated syringe assembly allow for direct injection into analytical instruments combining sampling and isolation in one step (Ouyang and Pawliszyn 2008), which greatly decreases the sample preparation time and requires less consumable materials (e.g., extraction solvents) than other sorbents. Disposable SPME fibers can be cut from bulk rolls of fiber optic material into custom lengths and offer the same measurement advantages as manufactured SPME fibers, at a fraction of the material cost. The use of disposable SPME is exemplified by Mayer *et al.* (2000) to calculate C_{free} for organic contaminants in sediment interstitial water. Injection equipment that allows for direct thermal desorption of disposable SPME fibers followed by gas chromatography - flame ionization detection or GC-MS quantification is commercially available and has been applied in design of PSMs (Woods *et al.* 2007).

Polymer-Coated Vials and Jars

Glass vials with the interior surfaces coated with a polymer, often PDMS, were developed as an alternative chemical activity-based PSM (Minha *et al.* 2006, Reichenberg *et al.* 2008, Mäenpää *et al.* 2011). With high surface area and relatively thin (0.05 to 16 µm) polymer coatings, the time to achieve equilibrium is reduced compared with thicker passive sampler configurations. Provided exposures are non-depletive, equilibrium can be confirmed by demonstrating that equal concentrations of target analytes are found in the polymer using multiple vials with different coating thicknesses (Reichenberg *et al.* 2008, Mäenpää *et al.* 2011). Coated vials can be used similarly to other polymer-based equilibrium *ex situ* methods as a means of estimating bioaccumulation (Reichenberg *et al.* 2008).

Glass jars coated with ethylene vinyl acetate co-polymer (EVA) have also been used as a passive sampler. Results of equilibration with laboratory-spiked and field sediments were used to estimate C_{free} as a measure of bioavailability of HOCs (Golding *et al.* 2007, 2008; Meloche *et al.* 2009). As with other coatings, EVA worked well to estimate the bioavailability of PAHs and PCBs to marine species (Golding *et al.* 2007, Meloche *et al.* 2009).

Polysiloxane (i.e., silicone rubber) is unique as a passive sampler phase because it has been used both in both coating and sheet formats to estimate C_{free} and bioavailability in marine sediments (Yates *et al.* 2011, Smedes *et al.* 2013). The use of silicone rubber sheets allowed determination of C_{free} for a range of sampler to sediment conditions resulting in an estimate of the K_{oc} for the accessible fraction (Smedes *et al.* 2013). This study showed that for selected PAHs, only a fraction of the total concentration in field sediment was susceptible to desorption and available to contribute to C_{free}.

APPLICATION TO CONTAMINATED SEDIMENTS

Historically, the application of passive samplers for detecting environmental contaminants in the sediment interstitial water began in the laboratory with *ex-situ* applications of PSMs (Lohmann *et al.* 2005, Fernandez *et al.* 2009b). Freely dissolved interstitial water concentrations of HOCs have been determined by placing the passive samplers directly into the sediment (Mayer *et al.* 2000, Conder *et al.* 2003, Vinturella *et al.* 2004, Fernandez *et al.* 2009b, Maruya *et al.* 2009) or through equilibrium solid-phase extractions of sediment slurries with samplers (Kraaij *et al.* 2003, Mayer *et al.* 2003, ter Laak *et al.* 2006, Friedman *et al.* 2009, Witt *et al.* 2009, Friedman *et al.* 2011). Such laboratory-based contaminant interstitial water data can be used to determine spatial characterization of sediment interstitial water, including vertical interstitial water profiles for sediment core samples taken from the field to the laboratory and investigating contaminant bioavailability (Arp *et al.* 2011).

Passive samplers are useful for examining the variables that alter the chemical activity in sediments and can be applied to various matrices and in logistically and technically ‘difficult’ sampling environments (Cornelissen *et al.* 2008). As such, these samplers can be applied at all geospatial scales, using very fine resolution, as demonstrated with the multi-sectional PSMs capable of synchronous measurement in a sediment column (Reible and Lotufo 2012), and across the sediment-water, and water-air interfaces (Bao and Zeng 2011). Ultimately, broad implementation of PSMs depends on their reliability in assessing bioavailability, contaminant mobility, and risk of exposure more effectively than current approaches, e.g., the use of bulk sediment concentrations or simple equilibrium partitioning models.

Further, passive samplers can be placed in the top layer of sediment to calculate composite interstitial water concentrations (Table SI-1; Ghosh *et al.* 2000, Tomaszewski and Luthy 2008, Fernandez *et al.* 2009b, Van der Heijden and Jonker 2009). Measures of vertical interstitial water concentration profiles also reflect the effectiveness of *in-situ* remediation, for example, when assessing sediment capping (Eek *et al.* 2008, Lampert *et al.* 2011, Gidley *et al.* 2012) and amendment treatments (Hale *et al.* 2010, Oen *et al.* 2011). Incorporating vertical interstitial water concentrations with *in-situ* treatment provides information on the effectiveness of remediation with depth. This application is very useful for assessing sediment capping and amendment remediation within the biologically active layer (Hale *et al.* 2010, Oen *et al.* 2011).

When utilizing PSMs in any matrix, it is important to understand their capability to detect chemicals with short residency times. With respect to varying concentrations due to variable emission sources and abiotic or biotic losses, a PSM integrates the concentration over time in accordance with the sampler kinetics. When degradation occurs in sediments, it may not be possible for chemical activity-based approaches to assess the status of the compound. For instance, DDT was not detectable with a larger SPME type sampler compared to a smaller one at low concentrations, perhaps because of the time required to reach equilibrium and the relative stability of DDT in sediment (Maruya *et al.* 2009). The time to equilibrium was also thought to influence the SPME concentrations for fipronil degradation products (Brennan *et al.* 2009). It is thus important to carefully consider and, if warranted, account for the instability of the chemical targeted when estimating calibration parameters for PSM applications (Lao *et al.* 2012). This concern can be partly addressed by suppressing biological activity in *ex situ* applications, with the addition of a biocide, such as mercuric chloride (You *et al.* 2011), or by using techniques that rely on kinetic measures although kinetic approaches can have limited accuracy depending on the system.

Bioaccumulation Assessments

Since they are designed to measure the chemical activity of contaminants in sediment, PSMs are appropriate for evaluating the exposure of organisms, usually expressed in terms of bioaccumulation. For instance, the ability of PSM measures of C_{free} to predict bioaccumulation across a range of compounds of differing log K_{ow} demonstrates the potential to address the complex binding that occurs in sediments which influences bioavailability (Figure 2). While PSMs can serve as surrogate estimates of exposure, they are limited in that some important bioaccumulation processes, such as digestive and active processes, including biotransformation cannot be addressed. Thus, the passive sampler may not provide the same magnitude of response as observed in the organism when these conditions dominate bioaccumulation. However, passive sampler concentrations will be proportional to the observed bioaccumulated contaminant in most cases (Conder *et al.* 2005; Bowen *et al.* 2006; You *et al.* 2006, 2007a; Hunter *et al.* 2008; Trimble *et al.* 2008; Harwood *et al.* 2012b). Finally, for non-degrading target contaminants (e.g., PCBs), PSM concentrations on a polymer basis will be similar to organisms concentrations on a lipid basis at equilibrium.

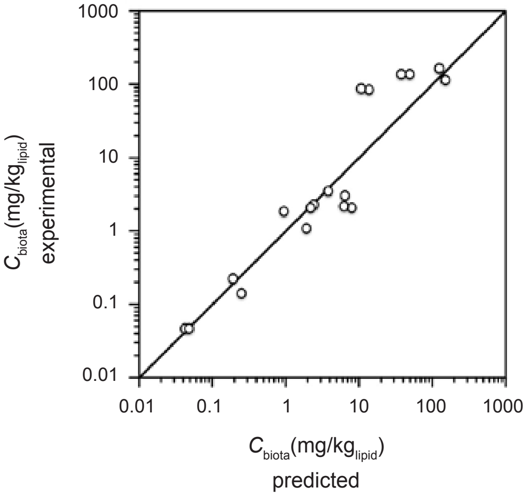

Figure 2. Measured versus predicted steady-state lipid normalized concentrations (Cbiota) in Tubificidae. The estimated steady-state concentrations were calculated from Cbiota = BCF * Cinterstitial water, where the BCF is the bioconcentration factor which was based on literature values that provided a Log Kow model from which BCF values were estimated and the Cinterstitial water was determined with passive samplers. The solid line represents the 1:1 line for 16 organic chemicals with log Kow values ranging from 4.6 to 7.5. Adapted with permission from Kraaij *et al.* (2003).

Both POM and SPMEs have been effectively used to assess bioaccumulation of sediment-dwelling invertebrates. Exposing *Lumbriculus variegatus* to laboratory-spiked compounds in sediments from three river basins demonstrated that POM was a successful technique for estimating bioavailability of sediment-associated contaminants, including those with log K_{ow} values >6 (Sormunen *et al.* 2010). Furthermore, in a comparison of several methods, POM and SPME provided excellent estimates of bioavailability for field-exposed *L. variegatus.* These samplers yielded a 1:1 relationship between equilibrium-predicted bioaccumulation based on

C_{free} and bioaccumulation measured in the field (Van der Heijden and Jonker 2009). The bioavailability of PAHs in Norwegian sediments was investigated using both polychaetes (*Nereis diversicolor*) and gastropods (*Hinia reticulata*) with POM to determine concentrations of PAHs in interstitial water (Cornelissen *et al.* 2006a; Ruus *et al.* 2010, 2013). These studies observed better correlations between C_{free} as determined by POM and tissue concentrations in these species compared to tissue concentrations calculated from total sediment concentrations.

The impact of spatial placement of the sampler to capture bioaccumulation can also be detected with PSMs. A difference between *in situ* and *ex situ* uptake into passive sampling devices and biota for POM samplers depended upon the sediment depth represented by the experimental design. Samplers deployed in the top 0.5 cm *in situ* correlated with *in situ* bioaccumulation data for *Neanthes arenaceodentata,* but were not as well correlated to laboratory bioaccumulation, because the samples used in the laboratory exposures represented an integrated depth sample (Janssen *et al.* 2011). In addition, the passive sampling device was better able to estimate exposure than either exhaustive extraction or mild solvent extraction of bulk sediments, but the variation in predictability was about a factor of 10 (Janssen *et al.* 2011).

Solid-phase microextraction was also found to provide reliable assessments of bioaccumulation (Conder *et al.* 2005, Hawthorne *et al.* 2007, Sormunen *et al.* 2008, Wang *et al.* 2011, You *et al.* 2011, Reible and Lotufo 2012). While most applications have been performed in the laboratory, a recent study with *L. variegatus* and SPME exposed *in situ* at several sites contaminated with PAHs found that SPME effectively predicted the bioaccumulation of the worms within a factor of four by accounting for site-specific bioavailability (Muijs and Jonker 2012). This confirms a previous set of *in situ* exposures with *L. variegatus* and SPME in sediments (Van der Heijden and Jonker 2009). However, due to analytical detection limitations, the SPME as deployed was limited in providing measured values for some PAHs, which were found in worms and sediment from the same system (Van der Heijden and Jonker 2009). In a proof of concept demonstration, Burton *et al.* (2012) deployed benthic organisms and passive samplers in a marine setting and qualitative comparisons were made between the samplers and accumulation in mussels. Similar patterns and concentrations of selected PAHs were found in both media.

There are two concerns directly related to active processes in organisms. First is biotransformation where the prediction by the PSM may overestimate bioaccumulation (Echols *et al.* 2000, Landrum *et al.* 2007), and the second is when feeding behavior can be modified affecting the flux into the organism (Lyytikäinen *et al.* 2003). However, studies have determined PSMs can estimate bioaccumulation and toxicity for biotransformed and toxic compounds (Harwood *et al.* 2012b; 2013a,b; Ding *et al.* 2012a,b). Data collected to date suggests a need for a more complete examination of compounds and conditions once standardized methods are established as discussed in Ghosh *et al.* (In press).

There is strong evidence that the SPME approach can produce consistent results with laboratory-exposed organisms regardless of whether they are exposed to field-contaminated or laboratory-spiked sediments (Wang *et al.* 2011, You *et al.* 2011). A relationship between SPME concentrations or the corresponding C_{free} has been correlated to *Lumbriculus* bioaccumulation from sediment for several compounds including PCBs, PAHs, and some pesticides (You *et al.* 2006, 2007b; Trimble *et al.* 2008; Hunter *et al.* 2009; Harwood *et al.* 2012b). Some limitations for the inter-comparison of SPME data from these studies may exist, in part, from an absence of a standard approach for evaluating the data, since some studies focused on bioconcentration factors (Vinturella *et al.* 2004, Muijs and Jonker 2012), while others reported lipid normalized body residues (You *et al.* 2006). These methods, which link bioaccumulation to exposure in terms of the chemical activity, are expected to produce consistent predictive relationships. However, standardization and comparative studies would lead to improved confidence in the method for management application (see Greenberg *et al.* In press).

Toxicity Assessments

Although fewer in number compared with studies that have addressed bioaccumulation, (Table SI-1), examples in the literature illustrate that toxicity assessments using PSMs can be accomplished through several approaches. For example, the sampler can provide a measure of C_{free} in interstitial water that can be compared with water quality criteria (Maruya *et al.* 2012). This approach was employed for evaluating the toxicity of sediment-associated PAHs and comparing the toxic response of *Hyalella azteca* to the number of toxic units calculated from the SPME-determined C_{free} which were based on the U.S. EPA sum toxic unit model (Kreitinger *et al.* 2007). Similarly, the toxicity of pyrethroids was found to be independent of sediment characteristics when the toxic response was based on C_{free}, once again determined using SPME (Xu *et al.* 2007, Harwood *et al.* 2013a). Finally, it is possible to develop a direct application of the passive sampler concentration by determining the relationship between the sampler concentration and the response endpoint, such as mortality for individual species (Conder *et al.* 2004 a,b; Zielke *et al.* 2011; Rosen *et al.* 2012; Harwood *et al.* 2013a). Evidence that the above approaches are interchangeable has been demonstrated in two papers, where chironomids and amphipods were exposed in water only solutions (Ding *et al.* 2012 a,b) and the ability to apply the values to sediment was demonstrated (Ding *et al.* 2013).

Comparative and Integrated Studies

There are relatively few studies that compare C_{free} measurements in sediment interstitial water using multiple different PSMs. Most of these studies reported agreement in estimates of C_{free} to within a factor of three. When POM and PDMS tubing were compared to assess bioaccumulation of native PAHs in *N. virens* for marine sediments and *L. variegatus* for freshwater sediments, biota sediment accumulation factors (BSAFs) calculated for the worms were compared to BSAFs calculated based on the values of C_{free}; the resulting values were found to vary within a factor of two for POM and by a factor of 20 for the PDMS tubing (Barthe *et al.* 2008). A second study compared SPME-PDMS and POM to assess bioaccumulation of PAHs in *L. variegatus* in both laboratory and field exposure scenarios (Jonker and Van der Heijden 2007). Bioconcentration factors (BCFs) derived from field and laboratory exposures with SPME were similar in magnitude; in addition, BCF values derived from POM and SPME were also comparable. In a subsequent study, Van der Heijden and Jonker (2009) investigated the bioavailability of sediment-associated PAHs to *L. variegatus* exposed *in situ* at three locations, utilizing POM and SPME to determine C_{free}. The best agreement was observed for *in situ* SPME and laboratory-based POM estimates of C_{free}. A more recent study compared *in situ* bioaccumulation in aquatic worms and application of SPME at several sites contaminated with petroleum hydrocarbons, to *ex situ* application of POM on samples collected from these sites (Muijs and Jonker 2011). The *in situ* SPME appeared less suitable for predicting bioaccumulation of oil constituents than the lab-based POM application, which allowed prediction to within a factor of three of measured worm tissue concentrations.

One of the first inter-laboratory exercises focused on analytical variability between 13 laboratories and 1 reference laboratory. For each tested sample, participants were instructed to expose field-collected sediment using silicone rubber PSDs (10µm coated inside bottles), followed by determination of C_{free} for PAHs and PCBs (Smedes *et al.* 2007a, b). The resulting PAH water concentrations were within a factor of two between the participating laboratories and the reference laboratory; however, due to the lower concentrations used, higher variability was observed in the more limited data set for PCBs (Smedes *et al.* 2007b). A subsequent exercise compared three different PSMs (SPME-PDMS, POM, and PE) applied to a single PCB contaminated sediment in not-mixed and well-mixed laboratory exposure modes (Gschwend *et al.* 2011). Both PE and SPME-PDMS were evaluated in both exposure modes, whereas POM was applied only in the well-mixed exposure mode. In addition, PSM measurements of C_{free} (for the sum of targeted PCB congeners) were compared with aqueous concentrations determined using an air bridge, an apparatus that produces a water sample with uniform C_{free} reflecting the “true” activity of the sediment sample investigated. The PSM-derived and air bridge C_{free} measurements obtained by conventional extraction methods agreed within 20% for the well-mixed exposures, whereas the PSMs applied in the static mode agreed within a factor of two. The authors also found good correlations (r^2 values ranged from 0.64 to 0.91) for total PCB tissue concentrations in the polychaete *Neanthes arenaceodentata* and PSM data (Gschwend *et al.* 2011).

Passive samplers have also been applied in the static mode to investigate the remedial efficacy of activated carbon-amended sediment (Cho *et al.* 2009, Oen *et al.* 2011). Polyethylene passive samplers pre-impregnated with PRCs were employed to measure C_{free} for PCBs, and produced good correlations between PCB uptake into co-deployed samplers (Cho *et al.* 2009). This work was expanded by comparing PCB interstitial water profile concentrations determined using PE and POM (both impregnated with PRCs) (Oen *et al.* 2011). Similar to previous studies, measured and calculated values of C_{free} were within a factor of two in this study.

Passive samplers have also been incorporated into platforms that gather multiple lines of evidence (MLOEs) on sediment quality *in situ*. One such platform is the "SEA ring" (Burton *et al.* 2012, Rosen *et al.* 2012), a polycarbonate carousel that houses various chambers for toxicity and bioaccumulation exposures, PSDs, and other water quality instruments. The SEA ring chamber design allows for exposures in the water column, at the sediment-water interface and in surficial sediment. These platforms were deployed at selected stations in San Diego Bay (Burton *et al.* 2012) with test organisms to assess sediment toxicity including amphipods (*E. estuarius*), polychaetes (*N. arenaceodentata*), mysid shrimp (*A. bahia*) and mussels (*M. galloprovincialis*) to test for toxicity at the sediment-water interface. Bioaccumulation was assessed using mussels (*Musculista senhousia*) and polychaetes (*N. arenaceodentata)* and C_{free} for PAHs were determined using SPME-PDMS. Integration of MLOEs provided by platforms, such as the SEA ring, allow for linkages between field exposure and effects to be investigated and established (Rosen *et al.* 2012).

A large-scale program focusing on validation of PSM systems has highlighted consistency between passive sampling of water in the field, native and deployed mussels and sediment PSMs in the laboratory. Between 2006 and 2007, the International Council for the Exploration of the Sea orchestrated an extensive Passive Sampling Trial Survey involving 12 European and one Australian laboratory. The goal was to investigate sources of uncertainty associated with PSM application and chemical analyses, utilizing marine bivalves to compare HOC uptake by samplers deployed in water and sediment across 31 estuarine and coastal marine locations (Smedes *et al.* 2007a,b). The Passive Sampling Trial Survey was able to confirm environmental validation of passive sampling in water and sediment through multiple replicated parallel analyses of uptake in mussels versus passive samplers, and concentrations in sediments reflecting known contaminant levels. The project also validated the application potential of passive samplers across a wide geospatial scale from cold-temperate to sub-tropical regions.

Research and Application Needs

Drawing upon this review, workshop participants identified three primary focus areas to enable widespread utilization of PSMs for contaminated sediment assessment and management: 1) establish a unifying science-based theoretical framework for applying PSMs that target C_{free} in sediment assessment, addressed in Mayer *et al.* (In press) and Peijnenburg *et al.* (In press) for organics and metals, respectively; 2) provide practical guidance for selection and implementation of PSMs, including standardization of calibration parameters (e.g., partition coefficients), establishment of equilibrium (or correction for non-attainment thereof) and non-depletion and quality assurance/quality control (QA/QC) provisions for reliable estimation of C_{free}, addressed in Ghosh *et al.* (In press); and, 3) describe application of C_{free} measurements using PSMs in sediment risk management decisions, addressed in Greenberg *et al.* (In press).

Despite progress to date, uncertainties still remain relative to PSM selection, equilibration times, fouling impact, and linkage to specific biological endpoints. The most critical criteria to establish the use of chemical activity-based PSMs to provide good estimates of interstitial water concentrations is the availability of accurate values of K_{pw}. Currently there is a shortage of high quality K_{pw} data available, which represents a current challenge for the application of PSMs (see Ghosh *et al.* In press). For organics, the use of PRCs to correct for non-equilibrium conditions due to abbreviated exposure times and/or biofouling clearly requires additional coverage. There is limited discussion on whether or not the use of PRCs is necessary to compensate for realistic environmental concentrations in aquatic environments. This is an area where current standard approaches are missing and guidance should reflect the ever changing state-of-the-art (Mayer *et al.* In press; Ghosh *et al.* In press). Furthermore, there are limited comparisons in the literature among samplers, environmental phases, and laboratories; therefore, improvement in this area is also required prior to widespread implementation of PSMs for regulatory use (see Ghosh *et al.* In press).

The workshop focused on passive sampling methods that lead to measuring/estimating the chemical activity of contaminants in sediment, which is expressed as C_{free}. There are multiple applications identified in the literature for PSM use including determining spatial gradients, bioaccumulation, toxicity, and evaluating remedial efficacy. Studies that illustrate the utility of PSMs for these applications have utilized samplers composed of various polymeric sorbents (e.g., polysiloxanes, polyethylene, polyoxymethylene) configured as thin films (sheets or strips) or coated onto solid supports (e.g., fibers, glass jars). The literature also illustrates that passive samplers have been employed for examining conditions in laboratory-dosed, field-collected, and *in situ* field sediments. The development of these methods has improved the detection of HOCs to the ng/L range and in some cases at pg/L concentrations. For simplicity and robustness of C_{free} measurements, the vast majority of published studies have employed PSMs in the equilibrium operating mode, as opposed to kinetic phase measurement which requires correction to attain the equilibrium condition and/or pre-calibration (i.e., time-dependent) of samplers which are system dependent. The ideal application is to expose samplers until equilibrium is achieved. The design of PSMs represents a trade-off between desired sensitivity (which influences selection of sampler mass/thickness), the practical need to achieve equilibrium within a finite time frame, and the pros and cons associated with *ex situ* and *in situ* applications. While the use of PSMs in sediments has been reported in a wide range of environments from fresh water to marine conditions as well as across different regions, further needs for advancing broader use of PSMs are addressed in upcoming companion papers (Peijnenburg *et al.* In press, Mayer *et al.* In press, Ghosh *et al.* In press, Greenberg *et al.* In press).

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SUPPLEMENTAL INFORMATION

Supplemental Information is available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_075_094SI.pdf.