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# Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration and implementation

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## ABSTRACT

This paper provides practical guidance on the use of passive sampling methods (PSMs) that target the freely dissolved concentration ( $C_{\text{free}}$ ) for improved exposure assessment of hydrophobic organic chemicals in sediments. Primary considerations for selecting a PSM for a specific application include clear delineation of measurement goals for  $C_{\text{free}}$ , whether laboratory-based “*ex-situ*” and/or field-based “*in-situ*” application is desired, and ultimately which PSM is best suited to fulfill the measurement objectives. Guidelines for proper calibration and validation of PSMs, including use

of provisional values for polymer-water partition coefficients, determination of equilibrium status, and confirmation of non-depletive measurement conditions are defined. A case study is described to illustrate how the measurement of  $C_{\text{free}}$  afforded by PSMs reduces uncertainty in assessing narcotic toxicity for sediments contaminated with polycyclic aromatic hydrocarbons. The paper concludes with a discussion of future research that will improve the quality and robustness of  $C_{\text{free}}$  measurements using PSMs, providing a sound scientific basis to support risk assessment and contaminated sediment management decisions.

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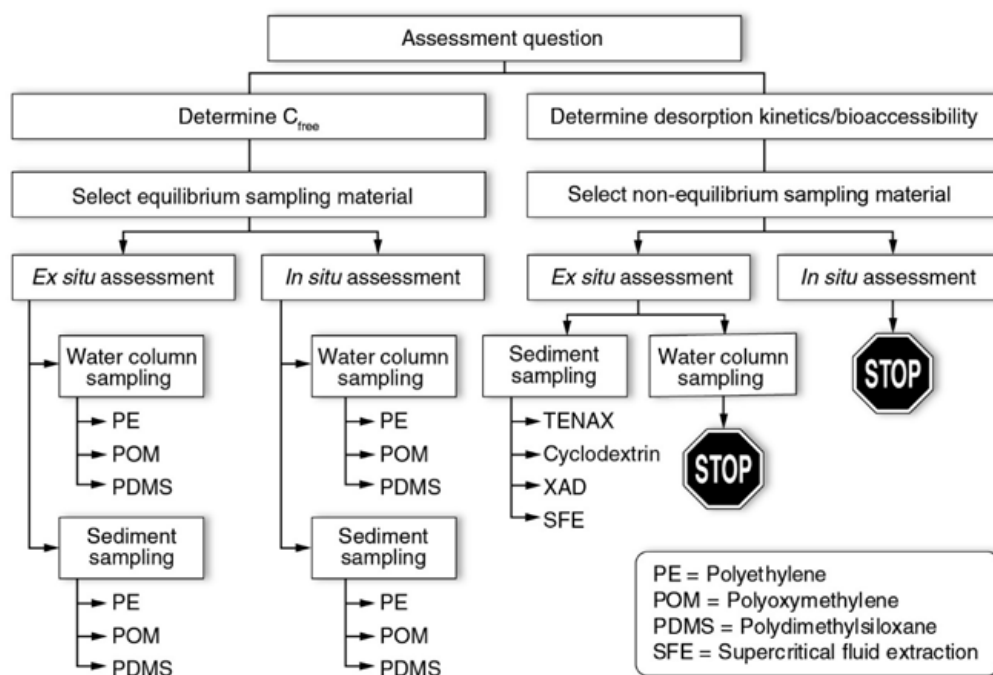
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## INTRODUCTION

Sediments are repositories of past and ongoing discharges of organic and metal contaminants which are potentially available to the aquatic food chain. Assessments of pollutant fate, transport, bioaccumulation, and toxicity of impacted sediments have historically been based on total pollutant concentrations and geochemical properties (e.g., total organic carbon) of bulk sediment (USEPA 2012a). Such assessments have been challenged by a gradually evolving understanding of the complexity of chemical sequestration in sediments and the involvement of various geochemical phases such as black carbon which are often difficult to quantify and accurately characterize (NRC 2003, Ghosh and Hawthorne 2010). Researchers have therefore focused on developing measures that account for bioavailability and better reflect the potential of chemicals to cause impact, be mobilized from, or be degraded in a given sediment. These measures, as illustrated in Figure 1 for hydrophobic organic chemicals (HOCs), typically fall into two broad categories: 1) chemical activity-based bioavailability methods focused on freely dissolved concentrations in pore water ( $C_{free}$ ) and 2) desorption-based methods aimed at determining the bioaccessible fraction of HOCs (Reichenberg and Mayer 2006). While desorption based methods can also be used for assessing potential for bioaccumulation and biodegradation, the focus of this paper is on

chemical activity-based passive sampling methods (PSMs) that target  $C_{free}$  of HOCs in sediment.

In the last few decades, a wide range of methods have been used to measure or estimate  $C_{free}$  in sediment pore water; and these measures have been reported to correlate well with contaminant uptake in organisms and toxicity (Lydy *et al.* In press). Direct measurement methods for pore water have focused on the challenge of removing interference from particulates, especially colloids and losses to glassware. Methods using centrifugation and alum flocculation have shown some success in directly measuring freely dissolved concentrations in pore water (Ghosh *et al.* 2000, Hong *et al.* 2003). Even with these separation techniques, however, accurate measurement of low concentrations of organic chemicals with high octanol-water partition coefficients ( $K_{ow}$ s) remains challenging. Recent work therefore has focused on the development of passive sampling with organic polymers such as polyethylene (PE), polyoxymethylene (POM), or polydimethylsiloxane (PDMS) to accurately measure freely dissolved concentrations of HOCs in pore water or surface water (Figure 1). For pore waters with low interference from dissolved/colloidal organic matter, and especially for less hydrophobic organic chemicals ( $\log K_{ow} < 4$ ), direct measurement using liquid-liquid solvent extraction may also be feasible.



**Figure 1. General flow chart for selecting passive sampling devices for applications involving organic contaminants present in sediments and the overlying water column.**

A method that uses commercially-available PDMS coated solid phase micro extraction (SPME) fibers to extract pore water and estimate  $C_{\text{free}}$  (ASTM D7363-7) has been shown to be a good predictor of toxicity (and lack of toxicity) of polycyclic aromatic hydrocarbons (PAHs) to benthic infauna (Kane Driscoll *et al.* 2009, Kreitinger *et al.* 2007). In this method, sediment is centrifuged to obtain pore water, which is flocculated with alum to remove colloids, resulting in pore water with PAHs that are partitioned between the water ( $C_{\text{free}}$ ) and dissolved organic carbon. Depending on the use of internal standards, the data can be reported for total dissolved concentrations or  $C_{\text{free}}$ . While this method has been used in site assessments to eliminate PAHs as contaminants of concern and to develop clean-up strategies (McArdle *et al.* 2010), a key barrier to wider implementation of this method is that only a few commercial laboratories can perform the measurement currently.

The reader is referred to Lydy *et al.* (In press) for a detailed literature review of passive sampler use in sediment assessments and Mayer *et al.* (In press) for a theoretical description of the rationale behind passive sampling. In the present paper, we provide guidance on the use of passive sampling methods including both laboratory-based *ex-situ* assessments and field-based *in-situ* assessments, along with key research questions and other considerations that influence the selection of particular passive sampling methods. This paper presents guidance on methods for pore water measurement with PSMs, calibration approaches, selection of polymer partitioning parameters, and quality assurance measures. The paper also describes how  $C_{\text{free}}$  data can be used in site decisions and concludes with an illustrative case study.

## Considerations for Using PSMs to Measure

$C_{\text{free}}$

The primary research/investigative question for a site drives many of the choices to be made in the selection of a PSM (and other measures), as indicated in Figure 1. Once established, the two key considerations for selecting a PSM are the choice of polymer type/configuration and whether the technology will be applied *ex-situ* or *in-situ*. These considerations are discussed below.

### Polymer Type

For HOCs, the polymers most commonly used to determine  $C_{\text{free}}$  are PE, POM, and PDMS. Both PE

and POM are most often deployed as thin sheets with large surface areas. In contrast, PDMS has been most often deployed as a coating on a thin glass fiber (i.e., SPME) or as coatings inside vials. However, other types of silicone polymers or rubbers are available for passive sampling in fiber and thin sheet or film configurations (see Lydy *et al.* In press for a review). Chemical structural differences between PDMS and these other silicones have to do primarily with the dimethyl group being replaced by another hydrocarbon group (e.g., ethyl, phenyl). Furthermore, SPME fibers can be coated with polymers other than PDMS; for example, polyacrylate. All of these polymers are moderately sorbing organic phases that exhibit similar sorption capacities, and have demonstrated the ability to reliably determine  $C_{\text{free}}$  for a wide variety of HOCs (e.g., polychlorinated biphenyls [PCBs], PAHs, and chlorinated pesticides) in both laboratory and field applications (Lydy *et al.* In press). While these commonly used polymers are commercially available, certain polymer configurations, such as custom thicknesses or vial coatings, may not be commercially available and will need to be synthesized in the laboratory or specially ordered.

### *Ex-situ* and *In-situ* Deployments

PSMs can be deployed in the field (*in-situ*) or used in the laboratory (*ex-situ*) assessment of  $C_{\text{free}}$ . Table 1 lists factors to consider when selecting between the *ex-situ* and *in-situ* approaches. The *ex-situ* approach will often be simpler to perform and more acceptable for many sediment research and management applications. The objective of the *ex-situ* approach is to determine  $C_{\text{free}}$  that is representative of equilibrium conditions for the sediment sample under consideration, while maintaining the practicality, relevance, control, and interpretation possibilities (e.g., hypothesis testing) that are afforded by laboratory experiments. In the *ex-situ* PSM approach, sediment samples collected from the field site are transported to the laboratory, where the sampler is added to the sediment and mixed well for a duration typically sufficient for the contaminants to achieve equilibrium between pore water, environmental phases (e.g., colloids), and the polymer. Laboratory-spiked sediments can also be analyzed in this manner. Common *ex-situ* applications include partitioning investigations, sediment toxicity testing, and bioaccumulation assessments (Vinturella *et al.* 2004, Friedman *et al.* 2009, Gschwend *et al.* 2011, Gargervold *et al.* 2010).

**Table 1. Factors to consider when selecting between *ex-situ* or *in-situ* application of passive sampling methods (PSMs).**

Factor	Approach	
	<i>Ex-situ</i>	<i>In-situ</i>
Ability to estimate equilibrium $C_{free}$	Laboratory conditions can be controlled to better attain equilibrium.  Comparison to independent confirmatory methods (e.g., air bridge) can be applied.	Uncertainty can occur; need to use performance reference compounds (PRCs), multiple polymer thicknesses, or time series sampling to confirm equilibrium. Time series interpretation can be impacted by temporal changes in the field.
Spatial scale (e.g., to differentiate between biologically active zones and underlying sediments or contaminant migration through a cap)	Sediments are frequently composited and/or homogenized to avoid concentration variability caused by vertical and horizontal spatial heterogeneity.  Coring followed by passive sampling in intact cores can maintain spatial characteristics if not influenced dramatically by site dynamics.	Fine-scale spatial (vertical and horizontal) patchiness in concentrations can be measured (e.g., identify gradients).  Best approach to capture field conditions.
Contaminant depletion	Mixing (e.g., tumbling of sample) during equilibration period is used to limit localized depletion.	Contaminant depletion may occur in the zone around samplers; use of multiple polymer thicknesses or time series analysis may be used to evaluate depletion.
Statistical design	Multiple treatments and replication are possible; hypothesis testing can be performed.	Multiple treatments, replication, and hypothesis testing are possible, but logistically challenging and expensive.
Ease of experimentation	Experiments are simpler to perform under laboratory conditions.	Expense, achieving experimental and statistical design goals, safety concerns, weather, adverse site conditions, and vandalism.
Ability to capture field conditions (e.g., currents, tidal cycles, groundwater intrusion, sediment-water column fluxes, bioturbation, temperature and salinity change)	Laboratory conditions are frequently standardized, but can be altered to attempt to replicate some field conditions.	Best approach for capturing field conditions.

In contrast, the *in-situ* approach is used when it is critical to capture conditions in the field. In this approach, the polymer is inserted directly into sediments or suspended in the water column above the sediment in the field and left in place for sufficient duration to allow the derivation of  $C_{free}$  (Fernandez *et al.* 2009a,b, 2012; Oen *et al.* 2011; Beckingham and Ghosh 2013; Lampert *et al.* 2013). However, the ability to attain equilibrium and demonstrate that equilibrium has been achieved is often more difficult for the *in-situ* approach as compared to the

*ex-situ* approach (Table 1). *In-situ* approaches may be preferable where it is important to understand groundwater intrusion, currents, bioturbation, depth-varying contaminant pore water concentration profiles, and sediment–water column gradients and fluxes. In general, these conditions are difficult to recreate or model in the laboratory. Groundwater movement can transport contaminants from deeper contaminated sediments to surface sediments (Gidley *et al.* 2012). Uncontaminated groundwater intrusion through sediment and tidal pumping in coastal

regions can reduce pore water concentrations of HOCs (McCoy and Corbett 2009), although the degree of dilution will depend on the time scales of the fresh groundwater movement and kinetics of the release of contaminants from the sediment phase. If the groundwater flow is very slow, the impact on pore water concentrations may not be appreciable.

## CALIBRATION OF PASSIVE SAMPLING MATERIALS

### Mathematical Basis for Passive Sampler Calibration

Calibration of passive samplers involves deriving the concentrations of target analytes in the medium of interest (i.e., sediment pore water) from their concentrations in the passive sampling material. For substances that reversibly sorb to the passive sampling polymer, the mass transfer into or out of the polymer is governed by diffusion within the polymer matrix, diffusion through the external aqueous boundary layer, and desorption and diffusion of contaminant from the sediment solids. For simplicity, this exchange is usually described by a first order kinetic model as described in Lydy *et al.* (In press). This assumes that the passive sampling application does not produce a significant reduction of the analyte concentration in the medium sampled (i.e., depleted) and that  $C_{free}$  is constant over the sampling time.

Figure 2 illustrates data for PCB 153 (hexachlorobiphenyl) fractional uptake in 77  $\mu\text{m}$  POM sheet (Hawthorne *et al.* 2009) from a sediment slurry and a first order model fit to the kinetics data. During the initial period of deployment, the analyte concentration increases in a linear fashion such that  $C_{free}$  can be determined from the slope of the linear increase of the analyte concentration in the passive sampler ( $C_p$ ) over time. For first order uptake, a near-linear response between  $C_p$  and  $t$  is maintained during the initial time period that is less than approximately  $0.5/k_e$  representing 40% uptake of the analyte's equilibrium concentration, where  $k_e$  is the analyte's exchange rate constant between the sampled media and the sampler. The initial linear uptake period is followed by a period of time where the analyte concentration increases in a non-linear fashion with time. Finally, the concentration in the passive sampling polymer reaches a steady-state (i.e.,  $dC_p/dt = 0$ ) and the analyte concentration in the sampler is constant over time. If the analyte does not degrade in the sampling polymer or in the sampled medium, this situation represents a thermodynamic equilibrium (i.e., an equilibrium controlled by the relative affinities of the analyte for the sampling material and the sampled media). This chemical equilibrium is represented by the polymer-water partition coefficient ( $K_{pw}$ ). The time required to reach equilibrium is controlled by  $k_e$ . The time to reach 95% of the analyte's equilibrium concentration is approximately  $3/k_e$ .

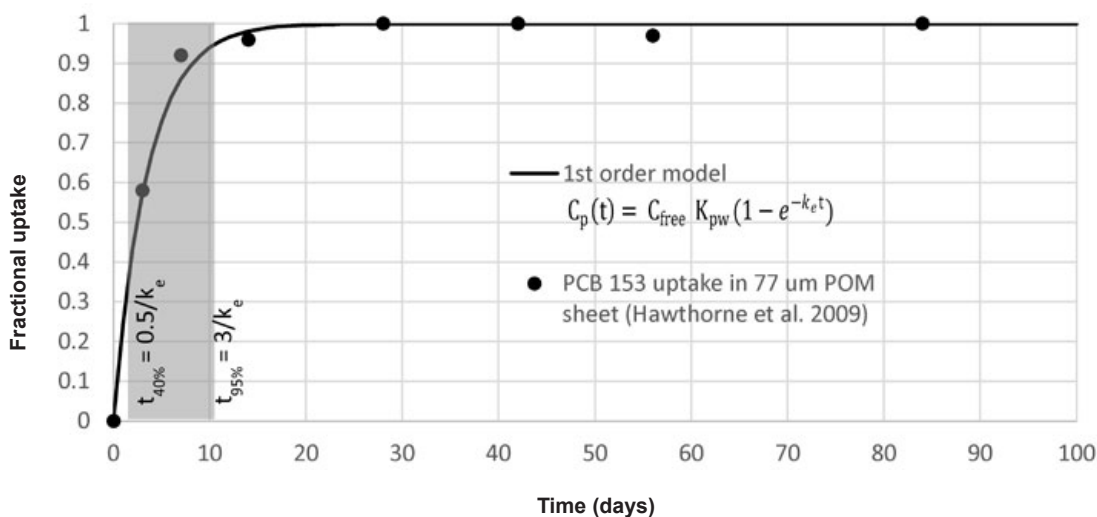


Figure 2. Time course of fractional uptake of PCB 153 (hexachlorobiphenyl) in a 77  $\mu\text{m}$  POM sheet (Hawthorne *et al.* 2009) from a sediment slurry. A first order model fit illustrates the conditions required for equilibrium sampling (i.e.,  $t \geq 3/k_e$ ) and for linear non-equilibrium sampling (i.e.,  $t \leq 0.5/k_e$ ). The intermediate, shaded region illustrates the period when uptake into the polymer is nonlinear.

### Three Basic Passive Sampler Calibration Strategies

Based on the above-mentioned three time phases, three possible passive sampling strategies are possible:

#### Equilibrium Sampling

The first and most commonly used strategy is suitable for substances that can reach equilibrium between the polymer and the sampled media within a realistically short exposure time. For these substances, the deployment time,  $t_d$ , should be equal to or greater than  $t_{95}$  or  $3/k_c$ . The relationship between  $C_p$  and  $C_{free}$  is then given by  $K_{pw}$ , and  $C_{free}$  can be found from  $C_p$  as  $C_p/K_{pw}$ . Equilibrium samplers require relatively fast exchange kinetics and/or sufficient equilibration time. Fast exchange rates can be achieved by keeping the polymer thickness small, thus reducing diffusion distances by mixing the sampler during equilibration. The equilibration times are related to the magnitude of  $K_{pw}$ , with larger  $K_{pw}$  producing longer equilibration times. Equilibrium conditions can be readily, and in most cases, more rapidly attained in well-mixed laboratory systems (i.e., *ex-situ*) than under primarily static field conditions (i.e., *in-situ*). The equilibrium uptake approach is the most convenient approach for determining  $C_{free}$  and has been used with PE, POM, and PDMS (Lydy *et al.* In press, Mayer *et al.* In press).

#### Nonlinear Uptake Rate

A second sampling strategy is based on the non-linear relationship between  $C_p$  and  $t$ , and may be appropriate if deployment times are between  $0.5/k_c$  and  $3/k_c$ . This sampling strategy is used less frequently than the equilibrium approach as it requires more data to relate  $C_p$  to  $C_{free}$  and such data are not always available. Also, more sophisticated data analysis tools such as non-linear regression, curve fitting, and diffusion modeling tools are required to establish the relationship between  $C_p$  and  $C_{free}$ . The use of performance reference compounds (PRCs) to characterize nonlinear uptake falls under this category of sampling strategy and is described in below.

#### Linear Uptake Rate

A third strategy (which is rarely implemented for  $C_{free}$  assessments in sediment) can be used for organic contaminants for which the passive sampler deployment time is much shorter than  $0.5/k_c$ ,

representing sampler analyte concentrations that are small compared to their equilibrium values (Huckins *et al.* 1999). For these substances, the uptake rate of the analyte in the sampling material is determined by the uptake rate constant and the analyte concentration in the sampled medium, and the concentration in the sampled medium is determined from the measured uptake rate divided by the analyte's uptake rate constant  $k_c$ . This sampling and calibration strategy is therefore a function of  $t_d$  and the  $k_c$  of the analyte in the passive sampling device.

### Calibration of the Polymer-Water Partition Coefficient

The most important and commonly used parameter necessary for calibration of PSMs is  $K_{pw}$ . Given the challenges involved in accurately measuring  $K_{pw}$  values, there is practical value in utilizing reliably determined published partition coefficients for commonly used polymers (i.e., PE, POM, PDMS). However, it is important to use the same source of polymer, or to verify that  $K_{pw}$  values for target HOCs are sufficiently close to those described below if using materials from different batches and/or suppliers. A provisional list of  $K_{pw}$  values that are judged to be reliable for the three most commonly used polymers are included in Supplemental Information (SI) Tables SI-1 and SI-2 ([ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13\\_95\\_114SI.pdf](ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_95_114SI.pdf)), and discussed below.

#### $K_{PDMS-w}$ PDMS-Coated Fibers

Values for PDMS-coated glass fibers are based on Smedes *et al.* (2009) for SR-TF (J-Flex Industrial Rubber Produces), and are consistent with a variety of other published and unpublished measurements using Supelco, Polymicro (Difilippo and Eganhouse 2010), and Prime Optical Fibers (Taiwan; Hsieh *et al.* 2011), as well as PDMS sheets from Dow Corning (Midland, MI) and Vizo (Zeewald, The Netherlands; Smedes *et al.* 2009). The  $K_{PDMS}$  variation among these sources is approximately 0.2 log units with up to 0.4 log units for specific compounds listed.

#### PDMS Sheets

For PDMS sheets (AlteSil™) manufactured by ALtecWeb (Cornwall, UK), the values are based upon Smedes *et al.* (2009). The expected variation in  $K_{pw}$  for a given chemical for AlteSil PDMS sheets is  $\pm 0.2$  log units for PAHs and low molecular weight PCBs (Smedes *et al.* 2009). Based on other literature

sources, the expected variation for high molecular weight (HMW) PCBs is  $\pm 0.4$  log units.

$K_{PE-w}$

Values for PE sheets (obtained from Brentwood Plastics) presented are also from Smedes *et al.* (2009). Variation of  $\pm 0.2$  log units is expected for PCBs and 2 to 3 ring PAHs (Adams *et al.* 2007, Booij *et al.* 2003, Cornelissen *et al.* 2008, Fernandez *et al.* 2009a, Perron *et al.* 2009, Choi *et al.* 2013). The few reported  $K_{PE-w}$  measurements for >4 ring PAHs show variability up to  $\pm 1$  log units.

$K_{POM-w}$

Values for commercially available POM sheets (77  $\mu\text{m}$ ; from C S Hyde Company) are presented based on Hawthorne *et al.* (2009, 2011). Variation of  $\pm 0.1$  (with a maximum of 0.3) log units were observed between the two laboratories participating in a comparison (Gschwend *et al.* 2011). Independent measurements presented in Hale *et al.* (2010) for the same POM agree mostly within a factor of 3 or  $\pm 0.5$  log units to those determined by Hawthorne *et al.* (2009).

### Correlation of $K_{pw}$ with $K_{ow}$

Correlations with  $K_{ow}$  can be used to extrapolate predicted  $K_{pw}$  values for contaminants in the same chemical class (e.g., specific PCB congeners), but with the caveat that  $K_{ow}$  values should be from a reliable and consistent source as described here. The following correlations relate  $\log K_{pw}$  for PDMS (Smedes *et al.* 2009) and Hilal *et al.*'s (2004)  $\log K_{ow}$  values for PAHs (SPARC estimates) and Hawker and Connell's (1988)  $\log K_{ow}$  values for PCBs:

$$\text{PAH: } \log K_{PDMS-w} = 0.725 \log K_{ow} + 0.479 \quad (R^2 = 0.99)$$

$$\text{PCB: } \log K_{PDMS-w} = 0.947 \log K_{ow} - 0.017 \quad (R^2 = 0.89)$$

The following correlations relate Smedes *et al.*'s (2009)  $\log K_{pw}$  for PE ( $\log K_{PE-w}$ ) and Hilal *et al.*'s (2004)  $\log K_{ow}$  values for PAHs and Hawker and Connell's (1988)  $\log K_{ow}$  values for PCBs:

$$\text{PAH: } \log K_{PE-w} = 1.22 \log K_{ow} - 1.36 \quad (R^2 = 0.99)$$

$$\text{PCB: } \log K_{PE-w} = 1.18 \log K_{ow} - 1.26 \quad (R^2 = 0.95)$$

The following correlation relates Hawthorne *et al.*'s (2009, 2011)  $\log K_{pw}$  for POM and Hilal *et al.*'s (2004)  $\log K_{ow}$  for PAHs and Hawker and Connell's (1988)  $\log K_{ow}$  for PCBs:

$$\text{PAH: } \log K_{POM-w} = 0.839 \log K_{ow} + 0.314 \quad (R^2 = 0.97)$$

$$\text{PCB: } \log K_{POM-w} = 0.791 \log K_{ow} + 1.02 \quad (R^2 = 0.95)$$

Polymers from different suppliers may differ in properties such as the degree of cross-linking, which can impact uptake kinetics and  $K_{pw}$ . Thus, until the selection of polymers is universally standardized, it is advisable for laboratories performing PSM studies to obtain a large quantity (i.e., a multiple-year supply) of one type of polymer, for which partitioning characteristics are available or will be determined. When a new batch is purchased or a new supplier is used, partitioning characteristics should be re-confirmed. This approach is suggested because at this time little information exists on differences in the same polymer obtained from different sources. However, the differences in  $K_{pw}$  between different sources of PDMS and POM are small and this may not pose a significant source of error in assessments when compared to other assessments of bioavailability (i.e., use of default equilibrium partitioning assumptions).

### Calibration of Polymer Exchange Kinetics ( $k_p$ )

Calibration that considers the kinetics of deployment is often challenging, but is needed when equilibrium sampling is not practical. For HMW HOCs, it may take months or more for polymers to reach equilibrium with the sediment pore water when deployed in the field (Tomaszewski and Luthy 2008). Therefore, it is often more practical to employ non-equilibrium sampling techniques in the field rather than wait until equilibrium is established. In this situation, calibration of the passive sampler for mass transfer kinetics is required. Generally, the uptake of HOCs into passive samplers has been shown to be dependent not only on the mass transfer kinetics between the passive sampler and the sediment pore water but also on the compound release rate from the sediment (Fernandez *et al.* 2009a). In addition, kinetics are temperature-dependent and may be affected by biofouling of the membrane surface (Huckins *et al.* 1999). This suggests that the linear uptake assumption may not be sufficiently accurate in some cases and a new calibration study is required whenever the exposure conditions for passive sampling are changed.

To overcome these challenges, Huckins *et al.* (1993, 2002) suggested the use of PRCs to calculate  $C_{ficc}$  from non-equilibrium PSM measurements ( $C_p$ ). PRCs are analytically non-interfering chemicals that

are embedded in the passive sampler prior to environmental exposure (Huckins *et al.* 2002). Examples of surrogate chemicals are stable isotope-labeled or deuterated forms of the analytes of interest, substances with a  $\log K_{ow}$  that is similar to that of the target analytes (Huckins *et al.* 2002, Fernandez *et al.* 2009a), or rare PCB congeners (Tomaszewski and Luthy 2008). A good PRC should i) allow precise measurement of its loss, ii) follow the same kinetics as the target analyte, and iii) not exist in the target environment (Huckins *et al.* 2002, Fernandez *et al.* 2009a). The depletion rate of a PRC during sampler deployment reflects the uptake rates of a target analyte, assuming isotropic exchange kinetics occur (Figure 3). Because of the differences in the compound properties for the PRC and the target analyte, correction is needed to calculate the fractional approach to equilibrium for the target analyte ( $C(t)/C_{(ss)}$ ) from the fractional PRC dissipation ( $1 - C_{PRC(t)}/C_{PRC(0)}$ ) at time  $t$ . In addition, PRC correction becomes difficult if sorption in the surrounding media is concentration dependent. Several approaches for the calibration using PRC data have been suggested (Huckins *et al.* 2006, Tomaszewski and Luthy 2008, Fernandez *et al.* 2009b, Reible and Lotufo 2012).

### Use of Multiple Polymer Thicknesses to Assess Equilibrium

An alternative method for confirming equilibrium involves the application of multiple polymer thicknesses of the sampling material (Mäenpää *et al.*

2011). In this approach, attainment of the same  $C_p$  for different thicknesses confirms that equilibrium has been obtained. This approach is particularly suitable if reaching equilibrium within the deployment time is achievable.

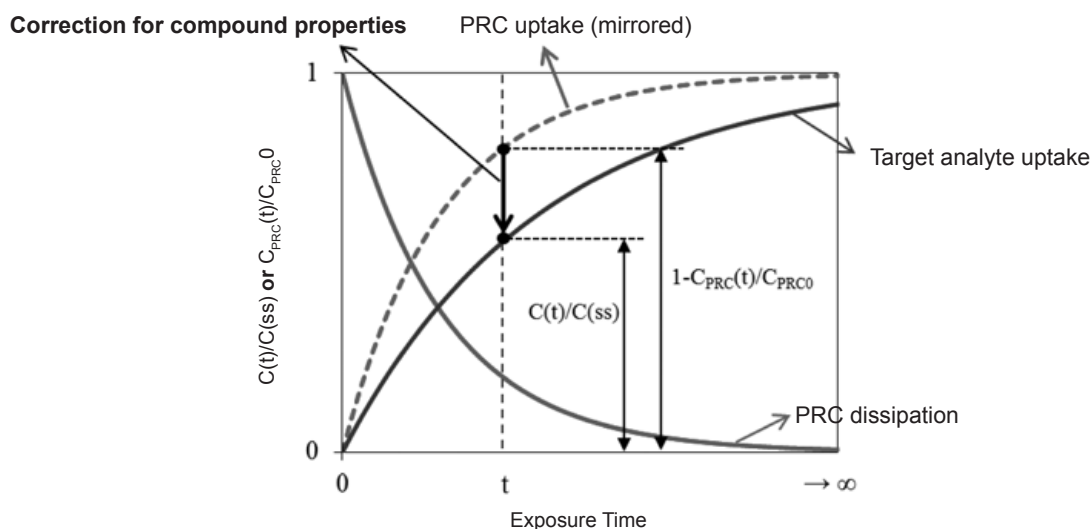
### Temperature and Salinity Corrections

Both temperature and salinity can influence  $K_{pw}$  and mathematical approaches for corrections are available (Schwarzenbach *et al.* 2003) and described in more detail in the SI. Adjustments for temperature and salinity can be performed when it is necessary and viable to validate the data and assess the accuracy of the adjustments. To ensure transparency whenever  $C_{free}$  results are presented, it should be clearly stated if and how corrections for temperature and salinity have been performed. As long as extreme conditions are not expected at the field site, the error introduced by performing *ex-situ* exposures at room temperature is expected to be relatively small compared to other causes of uncertainty and may be within limits acceptable for regulatory purposes (e.g., a factor of two).

## APPLICATION OF PSMs IN LABORATORY AND FIELD SITUATIONS

### Pre-Exposure Considerations and Preparations

For assessments performed *ex-situ*, preparations include cleaning/pre-extracting the passive sampler



**Figure 3.** Dissipation and uptake kinetics generally assumed for the performance reference compound (PRC) approach.  $C(t)$  and  $C_{(ss)}$  refer to target analyte concentrations in the passive sampler at time  $t$  and steady state, respectively;  $C_{PRC}(t)$  and  $C_{PRC}(0)$  refer to PRC concentrations in the passive sampler at time  $t$  and 0, respectively.



and glassware, preparing aqueous medium containing at least a biocide, and homogenization of the sediment sample. For *in-situ* exposures, preparations include pre-cleaning the samplers and their carrier devices, loading the samplers with PRCs (if required and possible), and the production of procedural field blanks (i.e., samplers taken into and from the field without exposing them). The different preparation steps are discussed in detail below.

### Selection of Sampling Materials

Figure 4 illustrates various considerations related to the selection of a specific passive sampler for a given application. Considerations include, but are not restricted to:

- Required detection limits. PE and POM sheets generally have lower detection limits than PDMS-coated SPME fibers due to their larger sorptive capacities. While direct injection of an SPME fiber and thermal desorption can reduce detection limits by transferring all sorbed analytes into the analytical instrument, direct injection without analyte cleanup may be impacted by high background noise that increases detection limits. Thus, a relatively large polymer absorptive mass is generally preferable when low detection limits are desired. The mass of polymer needed depends on the detection limit of the chosen analytical method (e.g., GC-ECD or LR-GC/LR-MS versus HRGC/HRMS), anticipated pore water concentrations (more polymer needed for

low concentrations), and  $K_{pw}$ . A quick calculation method for the required polymer mass is provided in the Supplement.

- Equilibration kinetics. Thinner and less sorbing polymers have faster kinetics and PDMS-coated SPME fibers are expected to equilibrate faster than PE and POM sheets, making them preferable for static *in-situ* measurements. PDMS-coated jars with thin layers of polymer have been shown to equilibrate in 14 days (Jahnke *et al.* 2012).
- Sampler fouling. It has been suggested that POM is less prone to fouling by black carbon particles and nonaqueous-phase liquids (NAPLs) than SPME and PE (Jonker and Koelmans 2001; Van der Heijden and Jonker 2009). Housings constructed of biocidal metals (e.g., copper) have been designed to provide structural rigidity and reduce the potential for accumulation of biofilms on the surfaces of deployed polymers (Maruya *et al.* 2009). However, there is a lack of clear understanding on polymer susceptibility to fouling and additional studies are needed to address this issue. Further, the use of PRCs may aid in addressing potential artifacts of fouling.

Assuming fouling and background contamination do not confound measurements,  $C_{free}$  values determined with any of the polymers described should be comparable if equilibrium conditions are attained, and appropriate  $K_{pw}$  and sediment/polymer ratios are used.

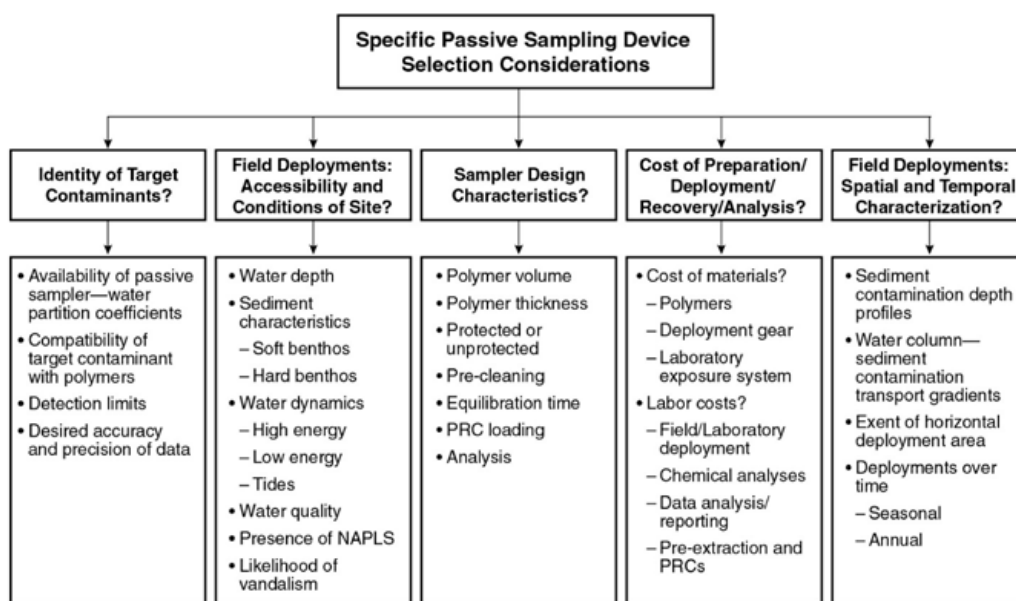


Figure 4. Specific passive sampling device selection considerations. Performance reference compounds (PRCs) are used to correct for non-equilibrium conditions.

The use of commercially-available polymers is advantageous because they are expected to be more uniform and homogeneous and are also available to the general public, which increases the possibilities for standardization. For example, SPME fibers with various thicknesses of PDMS (e.g., 7, 30, and 100  $\mu\text{m}$ ) are commercially available, can be cut to desired lengths, and have been calibrated and utilized in both laboratory and field exposures for several classes of HOCs (Maruya *et al.* 2009).

### Pre-Extraction of Sampling Materials

Prior to exposure, sampling polymers need to be extracted. This pre-extraction and cleaning process ensures that background levels of target contaminants and interfering compounds in the sampling material are minimized. Because of the high absorptive capacity of the materials, they can accumulate ambient chemicals from the atmosphere during transport and storage such that background contamination is introduced easily. Additionally, interfering contaminants might be introduced during the polymer production process. For instance, oligomers are present in many polymers and can interfere with the accurate quantification of target contaminants during the analysis of the final extracts after exposure. Pre-extraction should be performed using appropriate solvents, the choice of which depends on the sampling material and the target compounds. Generally, polar solvents are applied, either alone or in combination with a

nonpolar solvent. The selection of a solvent depends on the resistance of the polymer to the solvent, the polarity of the polymer, and the ability of the solvent to remove oligomers and other background (target) contaminants. For instance, methanol is well-suited for pre-extracting POM, but methanol extraction is insufficient for removing oligomers from PDMS sheets. The pre-extraction processes thus differ too much to generalize among passive sampling devices. Several different approaches have been used, some of which have been listed in Table 2. The pre-extraction solvent, as well as the extraction duration, should be selected carefully after consulting the literature or experts.

### Ex-situ (Laboratory) Exposures

#### Exposure Medium

Although wet field sediment with high water content can often be used directly for passive sampling, in many cases, additional clean water may need to be added to allow slurry formation and good mixing. For most HOCs ( $\log K_{ow} > 3$ ), the fraction transferred to the additional water is very small compared to the fraction sorbed to sediments. Adding a biocide is particularly necessary when targeting the  $C_{free}$  of contaminants that are biodegradable (e.g., PAHs). Commonly used biocides include sodium azide or mercuric chloride, applied at concentrations of 25 to 200 mg/L (Fagervold *et al.* 2010; Van der Heijden and Jonker 2009). Furthermore, when adding

**Table 2. Extraction solvents and times commonly applied for pre-extracting passive sampling polymers. POM = polyoxymethylene; PE = polyethylene; PDMS-SPME = polydimethylsiloxane-solid phase microextraction.**

Polymer	Target Compounds	Pre-extraction Solvent	Extraction Time (h)	Reference
POM	PAHs (HPLC, GC-MS), PCBs (GC-ECD, -MS)	Hexane, Methanol, Acetonitrile	2	Jonker and Koelmans 2001; Hawthorne <i>et al.</i> 2009, 2011
		Hexane, Methanol	2	Jonker and Koelmans 2001; Hawthorne <i>et al.</i> 2009, 2011
	Oil (GC-FID)	Hexane/Acetone	6	Muijs and Jonker 2011, 2012
PE	PCBs, PAHs, DDTs, PBDEs, triclosan	Dichloromethane, Hexane, Acetone	24	Fernandez <i>et al.</i> 2009a,b, 2012; Perron <i>et al.</i> 2009, 2013
PDMS-SPME	PAHs (HPLC)	Methanol, Water, Acetonitrile	3	Muijs and Jonker 2011, 2012
	Oil (GC-FID)	Heptane	3	Muijs and Jonker 2011, 2012
	PAHs, PCBs, other semivolatiles	Thermal desorption	0.5	ASTM D7363-7; Reible and Lotufo 2012
Silicone rubber	PAHs, PCBs	Ethyl acetate	100	Smedes <i>et al.</i> 2009

aqueous media to freshwater sediments, a salt like calcium chloride (e.g., 0.01 M) is often added to maintain a natural ionic strength (Van der Heijden and Jonker 2009). In estuarine and marine studies, the exposure system should be designed to mimic natural salinities using natural or artificial seawater.

### *Sediment Homogenization*

The sediment sample under investigation is usually either mechanically or manually homogenized prior to the introduction of the sampler to reduce data variability. In addition, samples may be sieved to remove coarse particles that might potentially damage the sampler (SPME fibers are more fragile than other materials). This should be limited to coarse sieving (e.g., 500  $\mu\text{m}$ ) for removal of non-sorbing constituents like stones, since potentially any manipulation may cause changes in the sediment composition, leading to a matrix that does not fully reflect the *in-situ* conditions to which the ultimate risk assessment should apply. To ensure homogeneity, it is also recommended that sufficiently large subsamples of sediment material be used in each exposure system, as this may help to limit variation caused by small-scale heterogeneity.

### *Negligible Depletion*

Accurate measurement of existing pore water  $C_{\text{free}}$  requires the use of a sampler volume to matrix ratio that ensures negligible depletion of the matrix or pore water concentration (described as < 1% depletion) when equilibrium is reached. For hydrophobic chemicals, the introduction of a passive sampler will inevitably start depleting the pore water, but desorption from the sediment will replenish the aqueous pool. If the mass that must be transferred in order to replenish the pool is too large, the standard exposure time may be insufficient to reach new equilibrium conditions or chemical transport may take place from domains where the chemicals are bound more strongly. This may result in a measurement performed under conditions that do not reflect the actual *in-situ* conditions. To avoid depletive extractions, the sediment organic carbon-to-sampler ratio should be sufficiently large, as these are the two primary absorptive pools that compete for sorption of the hydrophobic contaminants. As a general rule (assuming sediment organic carbon and polymer matrices have similar partitioning characteristics), a ratio of 1:100 polymer mass to sediment organic carbon mass should reduce any depletion to an acceptable value of

< 1%. As described below, this ratio can be refined for sediment and polymer-specific conditions if more accurate estimate of chemical-specific  $K_{\text{oc}}$  and  $K_{\text{pw}}$  values are available:

$$(M_p * K_{\text{pw}}) / (M_{\text{oc}} * K_{\text{oc}}) = (1/100)$$

where,  $M_p$  is the mass of polymer, and  $M_{\text{oc}}$  is the mass of sediment organic carbon.

If detection limit issues and other logistical considerations such as lack of prior accurate estimates of  $K_{\text{oc}}$  or  $M_{\text{oc}}$  do not maintain the depletion at <1%, it may be possible to correct for the potential depletion as described in Fagervold *et al.* (2010). Such corrections are feasible when the depletion is still small (<10%) and within the range for which a linear relationship for partitioning characteristics of the sediment organic matter can be assumed. Also, when the goal of the  $C_{\text{free}}$  measurements is to assess site-specific native partition constants (e.g.,  $K_{\text{oc}}$ ), the decreased matrix concentrations can be measured and accounted for in the partitioning calculation.

### *Equilibration Conditions*

During equilibration in *ex-situ* sampling, mixing is required to enhance exchange of chemicals among the sediment, water, and sampler phases. Equilibration in static systems is slow, especially for hydrophobic chemicals, and thorough mixing using a shaker, orbital mixing table, or other device is recommended. For PE and POM, shaking regimes of 100 to 150 rpm have commonly been applied, whereas for SPME a more gentle agitation (e.g., on a rock and roller apparatus) is needed to not damage the fragile fibers. In well-mixed systems, the thicknesses of aqueous boundary layers surrounding the sampler and the sediment particles are reduced, which enhances the equilibration kinetics.

As the methods discussed here are targeting the equilibrium  $C_{\text{free}}$  of chemicals, it follows that care should be taken to measure the concentrations at (or near) thermodynamic equilibrium. As a general rule, for dynamic *ex-situ* exposures, four-week equilibrations are generally applied when assessing  $C_{\text{free}}$  with SPME, PE, or POM (Gschwend *et al.* 2011, Jonker and Koelmans 2001, Hawthorne *et al.* 2011). Even for the most hydrophobic contaminants such as PCBs and HMW PAHs, this exposure time yields (near) equilibrium concentrations (Maruya *et al.* 2009, Hawthorne *et al.* 2011). Using vials and SPME fibers containing a thin PDMS coating (e.g., 10- $\mu\text{m}$  PDMS), full equilibration can be achieved within a

shorter period of time (e.g., two weeks; Jahnke *et al.* 2012). In case of uncertainty about the equilibration status or if shorter exposure times are warranted, equilibrium conditions should be demonstrated by including a time series of exposures (i.e., exposures of various lengths of time) or by using samplers of different thicknesses. At equilibrium, samplers of different thicknesses should yield the same  $C_{\text{free}}$  values. Alternatively, PRCs can be used to demonstrate equilibrium conditions (discussed below). Although this approach has been applied *in-situ*, *ex-situ* applications are still rare (Gschwend *et al.* 2011, Oen *et al.* 2011).

### ***In-situ* (Field) Deployment**

#### *Spatial Coverage to Address the Extent and Heterogeneity of Contamination*

Because of the relatively small size of passive samplers and because they sample microscale environments (at most several mm surrounding the static sampler), samplers deployed *in-situ* (e.g., SPME fibers) can be prone to very small-scale heterogeneity although the pore water can be an integrative medium in a dynamic sediment environment. As with bulk solid sampling, compositing can more accurately represent average values within a zone. If small-scale heterogeneity is suspected or known to be large, sampling designs may need to include spatial pooling of samplers or results, in order to obtain a spatially representative measurement. Conversely, measuring the spatial heterogeneity of  $C_{\text{free}}$  on a very small scale may be of interest, depending upon the question being asked (e.g., high resolution of the depth distribution of contaminant).

#### *Characterizing Depth Profiles*

Passive samplers can be deployed *in-situ* to characterize the depth profiles of contaminants in pore water (Fernandez *et al.* 2009b, Lampert *et al.* 2013, Beckingham and Ghosh 2013). Although sediment core profiles can also be studied in the laboratory, laboratory evaluation may not adequately characterize site-specific processes such as the effect of groundwater upwelling or hyporheic exchange. However, adequate interpretation and understanding of depth profile data may require additional extensive measurements of contaminant concentrations and total organic carbon and black carbon profiles with depth. If correctly measured and interpreted, depth profiles of  $C_{\text{free}}$  can provide useful information on chemical gradients and potential directions of the

diffusive fluxes of contaminants (Mayer *et al.* In press). Several recent papers have reported *in-situ* depth profiles using POM, SPME, and PE (Fernandez *et al.* 2009b, Oen *et al.* 2011, Lampert *et al.* 2013, Beckingham and Ghosh 2013). In these studies, passive sampler strips (POM or PE) or SPME fibers were either exposed directly, encased in a mesh, supported in aluminum frames, or placed in hollow perforated copper tubes. Copper tubes or mesh provide the additional benefit of reducing biological growth on the sampler. Under these static conditions, kinetics are expected to be retarded, and care must be taken to ensure the equilibrium status of the samplers is understood (e.g., by adding PRCs).

#### *Temporal Variability*

Short-term temporal variations cannot be determined effectively using pore water passive samplers, due to the requirement of a relatively long period of exposure time to reach equilibrium conditions. As discussed above, this is typically in the range of a few weeks (or months in the field). Passive samplers are more effective at assessing time-averaged conditions in the field over the period of deployment. However, annual changes, seasonal changes, or changes brought about due to episodic events can be measured. To ensure proper interpretation of results, it is critical to consider additional parameters, such as the net sediment deposition rate, loss of sediment from the area, episodic disturbances (e.g., resuspension events), and changes in bulk sediment concentrations over time. Also, it is important to be able to distinguish sampling errors and site heterogeneity from temporal effects. In such cases, the use of temperature-specific  $K_{\text{pw}}$  values may be important when assessing and comparing  $C_{\text{free}}$  measured during different seasons (i.e., at different temperatures).

#### *Validation of Equilibrium Conditions*

*In-situ* exposures of passive samplers in field sediments generally should be considered static or semi-static (due to some tidal-, current- or wind-induced pore water and sediment movement). In particular for such exposures, it may take relatively long periods of time to reach full equilibrium conditions. In order to enhance the kinetics, the use of thin polymers or polymer coatings (on SPME) is recommended (see above) although the latter may result in reduced detection limits. Still, it is important to demonstrate the existence of equilibrium conditions. Investigation of the equilibrium status can be

performed as described above for *ex-situ* exposures, although including a time series of exposures may be laborious and costly under field conditions. Although PRCs have proven successful in water-only exposures (Huckins *et al.* 2002, 2006; Fernandez *et al.* 2012; Perron *et al.* 2013a,b), this approach in static sediment-water systems is still being developed (e.g., Tomaszewski and Luthy 2008; Fernandez *et al.* 2009a,b, 2012; Gschwend *et al.* 2011; USEPA 2012b). One study with POM was recently performed successfully by Oen *et al.* (2011), but studies on the utility of PRCs for use with PDMS and POM have been limited so far (Reible and Lotufo 2012). Alternatively, equilibrium in the field can be established by performing two different thickness samplers (Reible and Lotufo 2012) or by time series deployment (Tomaszewski and Luthy 2008), staggering the removal schedule of individual samplers over a period within which the establishment of equilibrium can be expected. Assessment of equilibrium for *in-situ* exposures can be time-consuming and costly and should be considered at the beginning of the planning process for passive sampler deployment.

### Quality Assurance/Quality Control Guidelines

As with every analytical method, analysis, or experiment, quality assurance/quality control (QA/QC) precautions should be taken when performing measurements of  $C_{\text{free}}$ . Because there are many guidance documents available that describe analytical QA/QC, the following sections focus on guidelines that apply specifically to PSMs. These typically include thorough cleaning procedures, processing of (field) blanks, the development and application of reference materials, and the use of dark glassware when targeting photodegradable compounds such as PAHs. As with other analytical methods, replication (e.g., at least triplicate measurements) is also highly recommended.

### Blanks

Various types of blanks (i.e., solvent blanks for *ex-situ* experiments and passive samplers transported to and from the field, without deploying them for *in-situ* exposures) should be used to correct for the presence of any residual, analytical background concentrations or contaminants introduced during any step in the deployment and recovery procedure. Reliable corrections are possible if blanks are replicated, and, at least, triplicate blank measurements with every exposure are recommended. It is desirable for blanks

to be as low in contaminants (target and otherwise) as possible, as correcting for blank concentrations that constitute a substantial fraction of concentrations in samples will lead to unreliable results. Thorough cleaning of samplers and glassware with solvents, and reducing sampler exposure to air, will help to accomplish this goal. Field blanks should, however, be exposed to the air at the site for a period similar to that of total air exposure for deployed samplers. The rationale for this is that media such as PDMS can absorb contaminants from vapors and dusts during deployment and retrieval, and simply taking field blank passive samplers along on the trip without actually exposing them is not a true representation of incidental field exposure. General rules for blank corrections are not widely available, and corrections typically rely on expert judgment and experience.

### Analysis of Reference Materials

To evaluate the accuracy of any results, the inclusion of a reference sediment sample is recommended. The results of the analysis of this sample should be compared to the existing database for this sample (e.g.,  $C_{\text{free}}$  as determined with passive samplers), as obtained by several laboratories or developed by a reliable source (e.g., U.S. National Institute of Science and Technology [NIST] standard reference materials [SRMs]). Based on repeated analyses, quality criteria should be set for acceptable deviations from the mean. If the results do not meet these criteria, the analyses should be assessed for problem sources and then repeated. SRMs for  $C_{\text{free}}$  measurements do not yet exist, but initiatives are being undertaken.

### Interlaboratory Comparison Exercises

Distribution of reference materials among laboratories performing  $C_{\text{free}}$  measurements would allow for the determination of inter-laboratory variability in PSM measurements, which benefits the quality of the results and the robustness of the measurements. So far, very few interlaboratory studies have been reported; only recently have three different laboratories assessed the bioaccumulation of PCBs in a polychaete by three different PSMs (i.e., SPME, POM, and PE) and found general agreement but with considerable variability among PSMs (Gschwend *et al.* 2011). Interlaboratory comparability and data quality would also benefit from standardization of sampling materials (e.g., the type and supplier of a passive sampling polymer) and

establishment of a gold standard data set of passive sampler  $K_{pw}$  values for each of the specific polymers (see previous section). The calculated values of  $C_{free}$  from the application of passive samplers are dependent on the value of the partition coefficient applied, as mentioned above. A first step towards a standard dataset was recently made for POM, for which  $K_{pw}$  values for PAHs and PCBs were determined by different laboratories (Hawthorne *et al.* 2011). The use of standard polymers and partition coefficients will undoubtedly minimize the differences in  $C_{free}$  assessments obtained by multiple laboratories.

### *Instrumental Analysis*

The remaining variation in results will most likely originate from analytical issues, caused by the calibration of analytical equipment and handling (i.e., cleaning, extraction) of the passive sampling materials. The quality of chemical analyses (e.g., GC/MS, GC/ECD, HPLC/MS) should be established by using internal calibration standards. Internal standards should be compounds not existing in the samples or being used as PRCs, whereas calibration standards should span the full concentration range of the target compounds in the sample extracts while preferably falling in the linear calibration range of the instrument used. Furthermore, the solvent in which the standards are prepared should be the same as that of the extracts. This implies that a solvent exchange may be required after the extraction of the sampling materials, as extraction solvents are not always suitable as injection solvents. The completeness of the solvent exchange should be confirmed, to ensure that remaining fractions of unwanted solvents do not adversely affect the analytical equipment or the quality of the results.

### *NAPL-Containing Sediments*

Some contaminated sediments contain NAPLs such as oil or coal tar that may foul passive samplers and affect the final results. NAPLs will typically have high concentrations of organic contaminants (e.g., PAHs). Most importantly, NAPL fouling on passive samplers will lead to over-estimations of  $C_{free}$  if the NAPL is not properly removed from the sampler (Van der Heijden and Jonker 2009). In addition to visual observations, indications of NAPL fouling may include increased variability in  $C_p$  measurements or resulting  $C_{free}$  estimates that are well above the aqueous solubility of the target compound(s). If NAPL appears to be present in a

sediment sample or on a passive sampler, it should be recorded so that the resulting  $C_{free}$  will be recognized as potentially affected by artifacts. For sites where NAPL is an issue, a useful QA/QC step would be to test the effectiveness of pre-analysis removal of NAPL fouling.

### **Dealing with Measurement Uncertainty**

Sources of uncertainty in the measurement of  $C_{free}$  is a key consideration when selecting a PSM for a given application. For equilibrium sampling, the primary uncertainties lie in the measurement errors associated with  $K_{pw}$  and  $C_p$ . In most cases, the error associated with  $K_{pw}$  is  $\sim 0.2$  log units compared to  $\pm 20\%$  for analytical determination of  $C_p$  (Lydy *et al.* In press). It is also well documented that the uncertainty for analytical measurements increases as one approaches the analyte-specific instrument detection limit. Practitioners should also be cognizant that a higher maximum uncertainty (factor of up to 10) currently exists for some combinations of HOCs and PSDs. Addition of a third parameter ( $k_e$ ) for nonequilibrium sampling increases the magnitude of uncertainty in  $C_{free}$  determination by PSMs. Moreover, this added uncertainty has the potential to increase the further one operates from equilibrium (Lydy *et al.* In press, Mayer *et al.* In press).

As practical guidance, PSMs offer the best reduction in uncertainty in estimating  $C_{free}$  (a factor of 2 compared to a factor of 10 or more for currently available alternative approaches) when the number of estimated parameters and analytical measurements is minimized, and the sediments under investigation are homogenous. For laboratory-based PSMs, this corresponds to equilibrium sampling of a well-mixed sediment sample that produces a signal well above instrumental detection limits. In contrast, the uncertainty associated with *in-situ* PSM measurements can be much higher, due to small- and large-scale sediment heterogeneity and sub-optimal mass transfer conditions, resulting in non-attainment of equilibrium and the need for correction using PRCs or models.

## **GUIDANCE ON INCORPORATING RESULTS FROM PSMs INTO DECISION MAKING FRAMEWORKS**

As part of the risk assessment of contaminated sediment sites, sediment samples are typically analyzed to determine the likelihood that contamination will result in adverse effects to benthic invertebrates

and higher trophic level organisms. The results of these analyses can be used to develop site-specific measures of exposure as well as measures of biological effects. Resultant exposure-effect relationships can ultimately serve as the basis for risk estimates and remediation plans. However, considerable uncertainty in these relationships can result from an incomplete understanding of bioavailability, which can be highly variable among sites. The use of PSMs to determine and compare  $C_{\text{free}}$  in pore water to observed effects can reduce uncertainty in sediment assessments and management decisions. Examples of the various ways in which PSMs can be used in site assessments are presented in companion papers (Lydy *et al.* In press, Greenberg *et al.* In press, Mayer *et al.* In press).

### Use of PSMs to Estimate Equilibrium Exposure of Sediment-Associated Organisms

The use of PSMs assumes that the chemical activity of an HOC in sediment is directly proportional to its  $C_{\text{free}}$  in pore water (i.e., not associated with particulates or dissolved/colloidal organic carbon), and it has been shown that the  $C_{\text{free}}$  is a good surrogate for bioavailability assessment (Di Toro *et al.* 1991, Lu *et al.* 2011, Gschwend *et al.* 2011, Burgess *et al.* 2013, and citations in Mayer *et al.* In press). Note that this equilibrium partitioning (EqP) approach does not imply that exposure is limited to uptake from pore water, only that the pore water concentration is a better reflection of the chemical activity in sediment which controls chemical uptake through all routes of exposure and ultimate equilibrium distribution between sediment and organism lipid.

### Use of PSMs in Tiered Sediment Assessments

One example of a tiered assessment that uses PSMs is presented in the U.S. Environmental Protection Agency's guidance document on *Equilibrium Partitioning Sediment Benchmarks* (ESBs; USEPA 2012a). The first tier of this approach uses ESBs to assess the likelihood of toxicity to the benthos using an additive toxic unit (TU) model (Figure 5). Concentrations of contaminants in sediment that do not exceed the benchmark (i.e., a sum of TUs of one) are considered protective of sensitive aquatic organisms and require no further consideration based on this line of evidence. Sediments with concentrations that exceed the benchmark may pose a risk to aquatic organisms and may require further

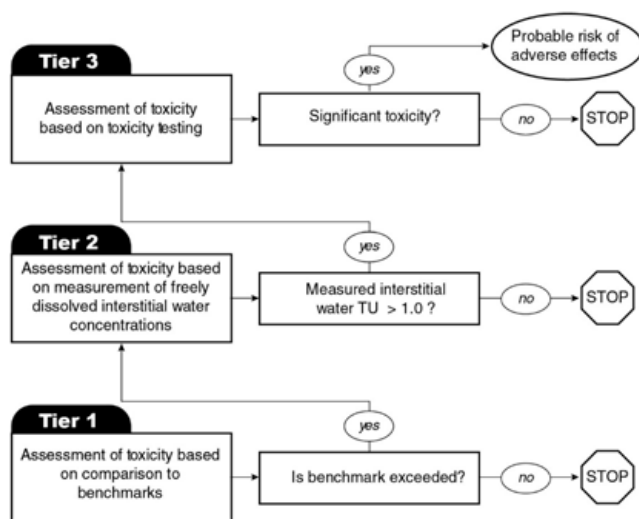


Figure 5. Schematic of a tiered assessment that uses PSMs to measure  $C_{\text{free}}$  for organic chemicals (based on USEPA 2012).

consideration or remediation. In the second tier, passive samplers can be used to measure concentrations of freely dissolved contaminants in pore water. As in the first tier, concentrations in pore water that do not exceed the benchmark are considered protective of benthic aquatic organisms, but concentrations that exceed the benchmark may pose a risk and may require further consideration. Sediment toxicity testing can be conducted in the third tier to verify the findings of the first two tiers. However, it should be recognized that if a whole sediment toxicity test finds significant toxicity, the cause or causes may be toxic chemicals other than those measured in Tiers 1 and 2 (e.g., specific pesticides, ammonium) or by confounding factors such as inappropriate oxygen levels or pH). Results of pore water toxicity identification evaluations can be used in conjunction with other lines of evidence (e.g., chemical analysis, site history information, benthic community analysis) to identify the contaminants of concern at a field site and help focus on the selection of the best remedial alternatives (USEPA 2005). An example of the use of PSMs in developing a site-specific exposure-effect relationship in support of a contaminated sediment site assessment is provided in the supplementary material.

The workgroup concluded that the science of using PSMs for measuring  $C_{\text{free}}$  is sufficiently mature that relatively specific guidance can be provided for their routine use in contaminated sediment site assessments. The use and interpretation of PSMs presents a departure from conventional methods of

site assessments and therefore requires the involvement of trained personnel familiar with the science reviewed in detail in Lydy *et al.* (In press) and Mayer *et al.* (In press). By following this guidance, an environmental scientist or engineer familiar with contaminated sediment management should be able to apply PSMs to incorporate the assessment of  $C_{free}$  as part of their investigation. This endorsement of using PSMs in contaminated sediment site assessments is given while recognizing that there remain a range of scientific issues that need to be addressed in the future to improve the application of PSMs. These improvements will result in the collection of better quality and more robust data, solidifying the scientific basis for environmental management decisions.

Recommendations for future work include:

- Further interlaboratory tests to build greater confidence in the precision of the methods when used by different laboratories
- Development of SRMs that will allow for routine checks of method accuracy by any laboratory
- Further development of the non-equilibrium PSMs in the field and further validation of PRC use in static sediment environments
- Expansion of the list of organic compounds for which  $K_{pw}$  values are reliably measured or predicted from chemical structure
- Peer-reviewed publications of more case study examples where PSMs have been used in site assessments and management decisions
- Continued studies to further demonstrate the predictive capability of passive samplers for toxicity and bioaccumulation assessments.

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## SUPPLEMENTAL INFORMATION

Supplemental Information is available at [ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13\\_095\\_114SI.pdf](ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_095_114SI.pdf).