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Passive Sampling Methods for Contaminated Sediments: Scientific Rationale Supporting Use of Freely Dissolved Concentrations

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Special Series

EDITOR'S NOTE:

This paper represents 1 of 6 papers in the special series "Passive Sampling Methods for Contaminated Sediments," which was generated from the SETAC Technical Workshop "Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments," held November 2012 in Costa Mesa, California, USA. Recent advances in passive sampling methods (PSMs) offer an improvement in risk-based decision making, since bioavailability of sediment contaminants can be directly quantified. Forty-five experts, representing PSM developers, users, and decision makers from academia, government, and industry, convened to review the state of science to gain consensus on PSM applications in assessing and supporting management actions on contaminated sediments.

ABSTRACT

Passive sampling methods (PSMs) allow the quantification of the freely dissolved concentration (C_{free}) of an organic contaminant even in complex matrices such as sediments. C_{free} is directly related to a contaminant's chemical activity, which drives spontaneous processes including diffusive uptake into benthic organisms and exchange with the overlying water column. Consequently, C_{free} provides a more relevant dose metric than total sediment concentration. Recent developments in PSMs have significantly improved our ability to reliably measure even very low levels of C_{free}. Application of PSMs in sediments is preferably conducted in the equilibrium regime, where freely dissolved concentrations in the sediment are well-linked to the measured concentration in the sampler via analyte-specific partition ratios. The equilibrium condition can then be assured by measuring a time series or a single time point using passive samplers with different surface to volume ratios. Sampling in the kinetic regime is also possible and generally involves the application of performance reference compounds for the calibration. Based on previous research on hydrophobic organic contaminants, it is concluded that C_{free} allows a direct assessment of 1) contaminant exchange and equilibrium status between sediment and overlying water, 2) benthic bioaccumulation, and 3) potential toxicity to benthic organisms. Thus, the use of PSMs to measure C_{free} provides an improved basis for the mechanistic understanding of fate and transport processes in sediments and has the potential to significantly improve risk assessment and management of contaminated sediments. *Integr Environ Assess Manag* 2014;10:197–209. © 2014 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals, Inc. on behalf of SETAC.

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INTRODUCTION

Contaminated sediments pose a significant challenge to environmental managers worldwide. One formidable barrier has been the inability of traditional analytical characterization methods and normalization strategies to accurately characterize contaminant mobility and bioavailability. Recent advances in passive sampling methods (PSMs) offer a promising alternative

to support improved risk-based decision making because a fundamentally sound basis for delineating and quantifying sediment contamination is provided. This article focuses on providing the scientific rationale supporting the use of PSMs as the measurement technique and freely dissolved concentration as the measurement endpoint for sediment quality and risk assessment.

When faced with assessing potential impacts from contaminants at a sediment site, certain questions arise, including:

1. Are existing sediment quality guidelines, objectives, or targets being met?
2. Do contaminants in sediments pose a risk to benthic organisms, wildlife, or humans?
3. Do contaminants bioaccumulate to a critical level in key receptors such as fish?
4. Does a given remedial approach reduce risk and can it possibly be further optimized?
5. What observations can be made to confirm that a successful remediation has been achieved?

Passive sampling methods, along with careful planning and proper data evaluation, can help address these questions. Potential risks of adverse biological effects from sediment-associated contaminants are most directly related to concentrations of freely dissolved chemicals (C_{free}) in sediment porewater, not to total contaminant concentrations (C_{total}) in whole or bulk sediments (Figure 1) (Hawthorne et al. 2007; Lydy et al. this issue). The reason for focusing on C_{free} is that it quantifies the effective concentration for diffusive transport and partitioning. This is well documented in the peer-reviewed literature (Reichenberg and Mayer 2006; Lydy et al. this issue), and it has also provided the basis for recent advances in remediation strategies for contaminated sediments (Ghosh et al. 2011; Rakowska et al. 2012). Despite this progress, sediment quality guidelines (SQGs) based on C_{total} are used in most regulatory jurisdictions. The use of C_{total}-based SQGs often overestimates risks from sediment contaminants, because it ignores factors that are known to limit or reduce chemical bioavailability (Gustafsson et al. 1997; Wenning et al. 2005).

Although causality-based SQGs derived using equilibrium partitioning (EqP) theory attempt to account for bioavailability by taking into consideration relevant sorption phases (e.g., organic C), the ability to reliably predict contaminant partitioning using EqP in field sediments has proven difficult (McGroddy et al. 1996; NRC 2003; Hawthorne et al. 2006). For example, considerable literature has shown that soot carbon and other forms of black carbon in field sediments exhibit orders of magnitude higher sorption than predicted by generic sediment to water partition coefficients (K_d) for natural sediment organic carbon (Gustafsson et al. 1997; Accardi-Dey and Gschwend 2002, Cornelissen et al. 2005). Unfortunately, even multicarbon models that take sorption to black carbon into account can still fail to accurately predict dissolved concentrations or accumulation in benthos in the field (Thorsen et al. 2004; Hawthorne et al. 2007). Thus, the "business as usual" approach in applying empirically or theoretically derived C_{total}-based SQGs in combination with predicted K_d values for assessing risks associated with sediment contaminants, still introduces considerable inaccuracy and uncertainty. Consequently, risks may be overstated at 1 site whereas correctly delineated at another site. For example, in a recent field study of harbor sediments, marked differences in C_{free} of PAHs were observed in 3 sediments despite similar total organic carbon normalized concentrations (Allan et al. 2012). In contrast, C_{free} of polychlorinated biphenyls (PCBs) and organochlorine compounds were in closer agreement with EqP predictions across sites in this same study. Such findings highlight the need to determine C_{free} to improve risk assessment of sediment contaminants.

A growing body of literature shows that PSMs are effective tools for quantifying C_{free} in sediments. For instance, Lydy et al. (this issue) and Peijnenburg et al. (this issue) highlight a number of ways that PSMs have been used in contaminated sediment contexts. Moreover, there is growing consensus that,

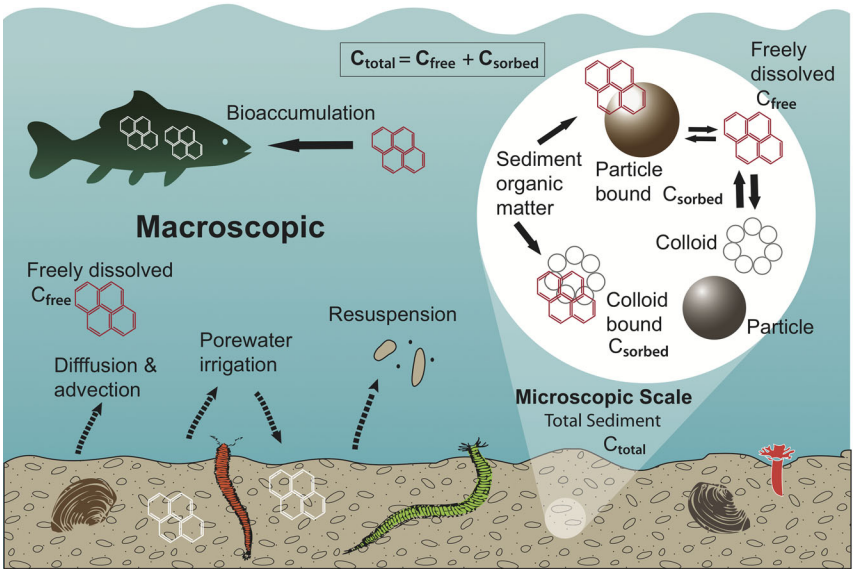

Figure 1. Conceptual view of contaminant cycling in sediment highlighting the central role of freely dissolved concentration, C_{free}.

when applied appropriately, PSMs can help inform sediment management decision making (Greenberg et al. this issue). The objective of this article is to describe the fundamental principles that govern the successful application of PSMs to hydrophobic organic chemicals (HOCs), and to outline some perspectives for future development and applications.

THE IMPORTANCE OF DETERMING EQUILIBRIUM CONCENTRATIONS

The uptake kinetics into the passive sampler are not fully covered in this article, because mass transfer kinetics can involve many processes and steps such as desorption from sediment, convective transport, binding to dissolved organic matter, bioturbation, diffusive mass transfer through the water saturated sediment matrix, mass transfer through biofilm or precipitates accumulated on the passive sampler, and diffusion within the passive sampling polymer. This section focuses on equilibrium sampling and the need for reaching and confirming equilibrium.

The principle of equilibrium sampling is to bring a polymer in contact with the sediment for attaining equilibrium of the target analytes (equilibrium criterion), while ensuring that the polymer does not significantly deplete the analyte concentration in the sediment (negligible depletion criterion) (Mayer et al. 2003). The analyte concentrations in the polymer are then measured and translated into C_{free} or alternatively into chemical activity or fugacity (Reichenberg and Mayer 2006; Golding et al. 2008; Gschwend et al. 2011). The main reason for operating sediment sampling methods in the equilibrium regime is that equilibrium partitioning is better defined than the kinetic uptake regime, at least when sampling the complex and heterogeneous sediment matrix. At equilibrium, chemical activity and fugacity are the same in the sampler as in the sediment, and the freely dissolved concentration is well-linked to the concentration in the sampler via a simple partition ratio (Mayer et al. 2000). Another reason for operating such techniques in the equilibrium regime is that equilibrium partitioning is easier to reproduce compared to kinetic uptake, i.e., exhibits better precision. For instance, in an early study, it was shown that relative standard deviations between replicates decreased from 20% to 30% in the kinetic uptake regime to well below 10% when approaching equilibrium (Mayer et al. 2000). In a more recent study, Jahnke et al. (2012) demonstrated that equilibrium sampling of PCBs at trace environmental concentrations yielded excellent precision (average relative standard errors of 2.6%).

Attaining equilibrium or near equilibrium within a practical deployment period can be challenging, because many passive sampling devices (PSDs) require months to years to equilibrate, at least for many HOCs ($\log K_{ow} > 6$) (Hofelt and Shea 1997). An important consideration before deploying an equilibrium sampling device is, therefore, the assessment and optimization of the uptake kinetics while at the same time ensuring that the amount of target analytes in the polymer is sufficient for quantification with available analytical instruments. It is then necessary to distinguish between 2 categories of equilibrium sampling that can be referred to as "in situ" (field-deployed samplers) and "ex situ" (performed on sediments in the laboratory) methods. Field deployment of passive samplers is logistically more difficult but may more realistically reflect environmental conditions and hence may improve accuracy in C_{free} estimates. Generally, it requires dedicated samplers and longer deployment times to achieve in situ equilibration of the sampler (Cornelissen, Pettersen et al. 2008; Witt et al. 2013). In contrast, laboratory based sampling methods (ex situ) normally include constant mixing in closed test systems, which not only reduces equilibration times but also improves reproducibility.

The factors that influence the time to reach equilibrium depend on the physicochemical properties of the target analyte, deployment conditions (temperature, extent of biofouling, etc.) and the sorptive and physical characteristics of the polymer selected. For instance, the polymer surface area to volume ratio (A–V or the reciprocal of the polymer thickness) defines how much polymer volume needs to be equilibrated relative to the surface area that is available for the diffusive mass transfer (Mayer et al. 2003). Uptake kinetics can thus be optimized by choosing a polymer configuration that is characterized by high A–V ratios. An additional strategy is to choose a polymer material with lower K_{pw} values, as this reduces the mass of target compound that must be transferred to the polymer.

Passive sampling kinetics are reduced when mass transfer becomes rate limited by slow diffusion within the polymer (Rusina et al. 2007; Fernandez, MacFarlane et al. 2009), which can be avoided by minimizing polymer thickness and choosing a polymer that provides sufficiently high diffusion coefficients for the target analytes. There are large differences in diffusion coefficients between typical passive sampling polymers. Silicones including polydimethylsioxanes (PDMS), generally provide the highest diffusion coefficients, which are typically 2 to 2.5 orders magnitude higher than for low density polyethylene (LDPE), which in turn is much faster than for polyoxymethylene (POM) (Rusina et al. 2007, 2010). It is not necessarily an advantage to use the polymer with the highest diffusion coefficient, but polymers with low diffusion coefficients can cause the sampler incubation time to be long if equilibration is desired. This criterion will generally be met when sampling with PDMS, because even rather thick PDMS sheets of 0.5 mm were shown to equilibrate internally with PAHs within a few hours (Mayer et al. 2007; Rusina et al. 2007).

One approach to confirm the equilibrium condition is by performing time series measurements to verify no change in polymer concentration with time (Mayer et al. 2003; Cornelissen, Pettersen et al. 2008). Polymer concentrations are plotted against time and a simple exponential equation is then often fitted to the empirical data. It is important to realize that uptake profiles will follow a simple exponential function, only when the mass transfer from sediment to polymer can be approximated by a 2-compartment system, with only 1 rate limiting step and a homogeneous concentration in each compartment. In ex situ sampling, it is often possible to achieve this situation given mixing conditions, the favorable sediment to polymer ratio (as discussed below) and choice of a polymer with high diffusion coefficients for the target analytes. For in situ sampling, it is often not possible to achieve these conditions. Mass transfer limitations within the polymer, local depletion of the sediment adjacent to the polymer or desorption resistance will then lead to biphasic or even more complicated uptake profiles. The fitting of the analytical data then requires more sophisticated models (Adams et al. 2007; Fernandez, MacFarlane et al. 2009).

When deducing the equilibrium status from measured uptake profiles, it is important to be aware of 3 mechanisms that can lead to underestimations of equilibration times. First, analyte uptake can be fast in the beginning and then slow down

when diffusion within the polymer becomes rate limiting. This leads to complex uptake curves, where the slower changing data can be misinterpreted as thermodynamic equilibrium. Second, the establishment of local depletion in the environmental medium during the sampling can slow the overall exchange and make it difficult to determine exact equilibration times. Third, when kinetics are determined in laboratory experiments under depletive conditions, care is required when translating these to nondepletive conditions, because equilibration times are generally shorter for depletive than for nondepletive sampling (Adams et al. 2007).

Alternatively, the equilibrium condition for in situ and ex situ methods can also be confirmed by varying the samplers A–V ratio and verifying that the concentration in all samplers is the same (Mayer et al. 2003; Mäenpää et al. 2011), or by following the elimination of performance reference compounds (PRCs) (Booij et al. 1998; Adams et al. 2007). The common advantage of these 2 approaches is that (near) equilibrium can be confirmed as part of the actual measurements rather than in a parallel kinetic study, which can save time and give additional confidence in the measurements. The specific advantage of varying the A–V ratio is that it simultaneously can confirm the absence of depletion and surface artifacts (fouling, abrasion, and adsorption), while at the same time allowing all measurements to be used for the determination of a precise concentration estimate. Confirmation that polymer concentrations are the same after a fixed deployment period in different samplers constructed of the same polymer but with different thickness may, thus, provide a straightforward, cost-effective technique for assuring the equilibrium criterion has been fulfilled.

Ex situ passive sampling

Ex situ methods are often less labor intensive and less expensive than in situ methods, but this depends on the specific study and the applied methods. Ex situ methods are generally more amenable to standardization and experimental control. However, it must be realized that ex situ methods provide measurements on a sample that is no longer part of the sediment environment, which may limit the ability to reflect the situation in the field, as for example when there is biodegradation, bioirrigation, or flushing due to groundwater discharge.

If passive sampling is performed ex situ, agitation can enhance mass transfer and reduce equilibration times by continuously renewing the sediment at the vicinity of the polymer surface. For example, Jahnke et al. (2012) have recently shown that glass jars with micrometer-thin silicone coatings can provide reduced equilibration times, while providing good analytical sensitivity: equilibrium sampling of PCBs ($5 < \log K_{ow} < 8$) was achieved in less than 2 weeks in the laboratory and yielded measurements of C_{free} in the fg/L to pg/L range.

In situ passive sampling: Corrections for deviation from equilibrium

The investigator may also choose to use in situ passive sampling to better characterize true field exposures. For in situ passive sampling, it can be difficult to ensure that the passive sampler actually reaches equilibrium with the sediments in which they are deployed. Consequently, it is then necessary to extrapolate the accumulated contaminant concentrations in the passive samplers to the concentrations they would have reached had they been allowed to reach equilibrium with their surroundings. The PRC approach allows for such disequilibrium corrections while assuming that the rates of sorption and desorption for the PRC and the native analytes of interest are the same. Kinetic models involving physically based, 1-dimensional Fickian diffusion (Fernandez, Harvey et al. 2009) or empirically based, first-order kinetics (Booij et al. 2003) can be used to correct for disequilibrium. PRCs also allow for correction of sampling-specific factors, which affect the contaminant mass transfer into the polymer. Such factors include temperature, the thickness of a depleted layer and biofouling of the polymer surface. Although stable isotope labeled analogs are preferred, nonlabeled structural analogs that are not present in the sampled matrix may also be used as PRCs (e.g., unusual PCBs congeners when sampling for PCBs). PRC-based calibration has been successfully used for disequilibrium corrections in field passive sampling of sediments (Booij et al. 2003; Tomaszewski and Luthy 2008; Fernandez, Harvey et al. 2009; Fernandez, MacFarlane et al. 2009; Oen et al. 2011). The application of PRCs for disequilibrium correction requires additional effort, but can ultimately be integrated within gas chromatography–mass spectrometry (GC-MS) analysis to reduce time and costs because measurement, equilibrium confirmation and disequilibrium correction can be done with only 1 sampler at each location. As in the case for ex situ equilibrium sampling, the goal of the in situ approaches using PRCs is to obtain equilibrium polymer concentrations (C_p) estimates suited to calculating C_{free}. In situ sampling can in theory provide better accuracy because fate processes that are operative in the field are taken into account. However, in situ sampling is often operated in the kinetic regime and correcting for nonequilibrium conditions can then be associated with additional error that affects both precision and accuracy of in situ sampling derived C_{free} measurements. In situ equilibrium sampling combines the advantages of sensing freely dissolved concentrations in the field with the more simple equilibrium sampling principle (Witt et al. 2013). However, such in situ equilibrium sampling requires generally rather long equilibration times, which in turn asks for faster equilibrating field samplers. Additional practical guidance on the trade-offs and selection of ex situ versus in situ sampling approaches is discussed by the US Environmental Protection Agency (USEPA 2012) and Ghosh et al. (this issue).

Negligible depletion and other validity criteria

The reason for operating equilibrium sampling techniques in the negligible depletion mode is not to perturb chemical activity in the sample that is being measured by introduction of the passive sampler. The negligible depletion criterion was initially introduced for solid phase microextraction (SPME) in aqueous solutions, where it was formalized that for instance less than 5% of the unbound molecules should be taken up by the SPME sampler to not interfere with the other equilibria in the aqueous solution (e.g., sorption to organic matter) (Kopinke et al. 1995; Vaes et al. 1996). This was achieved by keeping the phase ratio between water and polymer well above the polymer to water partition coefficient. For equilibrium sampling in sediment, it is often acceptable to temporarily deplete the aqueous concentration and then to use the sediment matrix as a partitioning donor to buffer the chemical activity during the sampling (Mayer et al. 2000; Zeng and Noblet 2002; Reichenberg and Mayer 2006). However, it is then necessary to ensure that only a small fraction of the sorbed analyte is released from the matrix, to avoid desorption resistance in confounding the equilibrium sampling measurement. Using a polymer mass

that is 100 times lower than the organic carbon mass in the sediment sample is a simple rule of thumb to ensure negligible depletion and also to avoid desorption resistance problems. Much larger polymer masses relative to the organic carbon content of the sample have been used in some studies (Jonker and Koelmans 2001), which might have led to significant depletion and subsequent underestimations of freely dissolved concentrations. Unfortunately, such limitations will not be detected with traditional time series measurements, and special attention is necessary to ensure that the negligible depletion criterion is met. As in the case for checking the equilibrium conditions discussed earlier, the negligible depletion condition can also be confirmed by varying the samplers A–V ratio and verifying that the concentration in all samplers is the same (Reichenberg et al. 2008; Jahnke et al. 2012). The negligible depletion issue is fundamentally different for in situ sampling. The infinite bath condition is generally satisfied, and depletion becomes then an issue on the microscale where local depletion at the vicinity of the sampler can limit the uptake into the sampler.

There are 3 additional conditions to be met for equilibrium sampling. First, the analytes retained on the sampler must be absorbed into the polymer rather than being adsorbed on to the polymer surface because all subsequent calculations are based on phase partitioning considerations. This absorption condition can, again, be confirmed by varying the samplers' A–V ratio and by verifying that the concentration in all samplers is the same (Reichenberg et al. 2008). Second, the enrichment into the polymer must follow a linear isotherm, meaning that a single partition ratio characterizes the enrichment of the analytes within the full concentration range. Such concentration independent partitioning is very well established for PDMS due to its wide use in GC columns, SPME fibers and many sorptive enrichment techniques (Vaes et al. 2000; Seethapathy and Gorecki 2013). Concentration independent partitioning has also been shown for other passive sampling polymers (Hawthorne et al. 2011), and is likely not a very critical assumption as long as adsorbents are avoided. Third, the polymer must retain its partitioning properties when immersed in the sample matrix. This was recently shown by Jahnke and Mayer (2010) to be the case for PDMS in a wide range of complex matrices including sediment.

Freely dissolved concentrations and other measurement endpoints

Instrumental analysis by GC or high-performance liquid chromatography (HPLC) yields the analyte amount retained by the polymer, which is then expressed as an equilibrium concentration (C_p) in the polymer. The sampler polymer can be used as a reference partitioning phase to quantify exposure of target analytes in sediment fate, effect, and monitoring studies. The concentrations in the polymer are much higher than in water, and the partitioning properties of a given polymer are more constant than for both sediment and biota. Furthermore, polymer extraction is much simpler and less subject to interferences. This makes the polymer a preferred reference for both spatial and temporal monitoring of contaminants. For example, time trend analysis is expected to exhibit less scatter and variation on a polymer basis then compared to measurements on water, sediment, or biota.

Although C_p can be used directly as discussed later, these values are traditionally translated into other well defined parameters to support communication in different regulatory or modeling contexts, the most important being C_{free}, fugacity, and chemical activity.

C_{free} can be determined based on C_p and the polymer to water partition coefficient (K_{pw}):

$$C_{free} = \frac{C_p}{K_{pw}}. \quad (1)$$

When using K_{pw} values determined with pure water, this equation yields "freely dissolved concentration in pure water at the chemical activity of the sediment" (Mayer et al. 2000). Freely dissolved concentrations can then be seen as the effective concentrations for diffusion, partitioning, and bio-uptake but have little significance in terms of contaminant mass (Reichenberg and Mayer 2006). It is crucial to apply polymer water partition coefficients in Equation 1, which accurately describe the partitioning during the sampling. Differences in partitioning properties between different types and sources of polymers and also temperature effects can be a main source of error on the eventual C_{free} measurement. This issue is further discussed in the article by Ghosh et al. (this issue).

The fugacity (f) expresses the escaping tendency of the contaminant into ideal gas. Fugacity can be determined based on C_p and the analyte specific fugacity capacity of the applied polymer (Z_p):

$$f = \frac{C_p}{Z_p}. \quad (2)$$

The Z_p can be estimated by dividing the substance-specific K_{pw} by the dimensionless Henry's Law Constant, which describes air-water partitioning.

The chemical activity expresses the energetic level of the contaminants relative to its pure (subcooled) liquid form. The energetic level drives spontaneous processes, including the partitioning of organic substances into the lipid membrane (Reichenberg and Mayer 2006). Chemical activity (a) can be determined by multiplying C_p by an analyte specific activity coefficient (γ_p), or by calculating the ratio of freely dissolved concentration and subcooled liquid solubility (S_L):

$$a = C_p \times \gamma_p \cong \frac{C_{free}}{S_L}. \quad (3)$$

Fugacity and chemical activity are multimedia parameters that give a direct indication of the potential of each analyte for spontaneous processes including diffusion and partitioning.

A fundamentally different strategy for measurements of C_{free} are methods that first separate the water fraction from the bulk sediment (e.g., by centrifugation), then remove the dissolved organic matter from the water (e.g., by flocculation) and finally measure the contaminants remaining in the water phase by SPME (Hawthorne et al. 2005; ASTM 2007). Using this approach, both C_{free} and the total concentration in the solution ($C_{total} = C_{free} + C_{bound}$) can be simultaneously determined with use of internal standards such as stable isotope-labeled compounds (Poerschmann et al. 1997; Hawthorne et al. 2005, 2007). It should be noted that some of these approaches include a physical phase separation step for determining C_{free}, whereas other methods rely on the passive sampling into the SPME fiber to discriminate free and bound forms (Bondarenko and Gan 2009). Using such methods, previous workers (e.g., Fernandez, Harvey et al. 2009) have shown that in situ passive sampling observations, adjusted using PRCs, match such direct measures of C_{free} quite well.

Fate modeling to estimate contaminant exposures

With data on C_{free} of HOCs in sediments, one can gain valuable insights on fate and exposure. First, sediments with higher C_{free} are diffusive sources to surface water and sediments with lower C_{free}. Using passive sampling devices, one can map C_{free} to identify relative "hot spots" and perhaps delineate areas needing remediation. Next, the data allow contaminant transport to be evaluated. For example, the combination of C_{free} in porewater and bottom water can be used to calculate diffusive fluxes between the bed and the overlying water column (Fernandez, MacFarlane et al. 2009). Such sediment–water concentration differences have been examined for PAHs, PCBs, and PCDD/Fs in native sediments (Booij et al. 2003; Cornelissen, Pettersen et al. 2008; Cornelissen, Wiberg et al. 2008; Jahnke et al. 2012).

A recent study has also reviewed the nonequilibrium conditions between sediment and overlying water from different field studies and classes of contaminants using PSM data and implications for risk assessment (van Noort and Koelmans 2012). Eek et al. (2010) used infinite-sink benthic flux chambers and passive samplers to measure the diffusional mass transfer of native pyrene and PCB congener 52 in harbor sediments before and after capping. Measured and calculated fluxes agreed within a factor of 2. Lampert et al. (2011) measured porewater concentrations in thin-layer sand capped laboratory microcosms using PDMS-coated fibers allowing for quantification of vertical concentration profiles that were used to infer contaminant diffusion rates and mechanisms. Similarly, Witt et al. (2009) measured vertical C_{free} profiles for PAHs in sediment cores taken from the Baltic Sea.

Passive sampling methods have also been used to quantify the importance of sediment resuspension for transferring contaminants like PAHs and PCBs from the sediment bed to the water column. Adams (2003) observed a doubling of C_{free} levels in the Hudson River estuary during spring tide resuspension events; this change was not seen during the neap tides when resuspension was much weaker. Friedman et al. (2011) studied the impact of large-scale resuspension of native sediments on the release of PCBs to the water column using passive samplers. The magnitude of increased concentrations depended on resuspension time and the K_{ow} of the congener ranging from 1 to 8 times those found without resuspension.

In summary, PSMs show promise for predicting 1) the direction of contaminant flux based on activity ratios, 2) the magnitude of the flux using in situ studies, and 3) the release or sequestration of contaminants when sediments are resuspended. However, in all cases the attainment of equilibrium conditions during passive sampling needs to be confirmed or corrections for disequilibrium made before drawing conclusions.

BIOACCUMULATION ASSESSMENT

Passive sampling methods have the potential for improving the EqP approach for the prediction of bioaccumulation in benthic animals and subsequent transfer to upper trophic levels. The well documented relationship between sediment–water–biota partitioning and polymer-based passive sampling devices from earlier literature is reviewed by Lydy et al. (this issue). Concentrations in the organisms living in the sediment were predicted as the product of C_{free} and a bioconcentration factor (BCF):

$$C_{biota} = C_{free} \times BCF = \frac{C_p}{K_{pw}} \times BCF. \quad (4)$$

Predicted concentrations of HOCs in worms obtained with this equation generally agreed within a factor of 2 to 3 with actual measured concentrations, which is much better than the typical error of 1 to 2 orders of magnitude related to EqP predictions using generic K_d values (Kraaij et al. 2003; Cornelissen et al. 2005). Similar predictions have been made for a wider range of PAH and PCB congeners and benthic organisms using $f_{lipid} \times K_{ow}$ as a surrogate for the bioconcentration factor. The measured concentrations in biota agreed well with the EqP predictions (Table 1).

Furthermore, Leslie et al. (2002) proposed that polymer samplers can even be used directly to predict bioaccumulation. The partitioning into the polymer was shown to serve as a surrogate phase that directly mimics the bioaccumulation process, which is in contrast to the approach of Kraiij et al. (2003), where passive sampling was used as a sensitive method

Table 1. Ratio of mean measured to predicted bioaccumulation in various benthic organisms using passive sampler derived C_{free} measurements of sediment porewater and equilibrium assumptions for partitioning to biota

Site	Organism	$\frac{C_{biota}}{K_{ow} C_{free}}$	SD	*N*
New Bedford Harbor #1	*Leptocheirus plumulosus*	1.257	0.868	247
	Neanthes arenaceodentata	0.841	1.08	213
	Lumbriculus variegatus	1.66	0.81	322
New Bedford Harbor #2	*L. plumulosus*	1.45	0.82	318
	Maco manasuta	1.18	0.45	144
Elizabeth River #1	*L. plumulosus*	1.2	0.7	10
	N. arenaceodentata	0.9	0.79	11
Elizabeth River #2	*L. plumulosus*	0.617	0.503	18
Average		1.32	0.82	

C_{biota} = lipid normalized, dry weight concentration; SD = standard deviation.
Source: Reible and Lotufo (2012).

to measure C_{free}, which then was multiplied by experimentally derived bioconcentration factors.

As highlighted in the review by Lydy et al. (this issue), the simple approach of measuring C_{free} using PSMs and then estimating bioaccumulation has been applied successfully in an increasing number of studies, including those for complex petroleum hydrocarbons, PAHs, chlorobenzenes, and PCBs (Kraaij et al. 2003; Barthe et al. 2008; Muijs and Jonker 2011; Jahnke et al. 2012). The use of passive samplers as an analytical tool to predict bioaccumulation in laboratory studies may provide conservative estimates if uptake on the sampler is faster than the test organism and the test duration is not long enough to attain equilibrium in biota (Meloche et al. 2009).

The general agreement between the partitioning properties of lipids and polymers used in PSMs is essential for biomimetic extractions, where the polymer actually serves as a partitioning surrogate for the organism (Leslie et al. 2002). Similarity in partitioning properties is not strictly necessary, but helpful, when predicting tissue concentrations as product of C_{free} and BCF. Figure 2 gives a conceptual overview of the described phenomenon. If the log K_{pw} values are plotted against the hydrophobicity expressed as the log K_{ow} (Figure 2A), then there is a linear correlation obtained for all polymers. The regression equations were collated from various literature sources for selected PAHs for illustration. Polymer-specific regressions exhibit similar slopes but different intercepts that reflect the relative partitioning affinity between the polymer and octanol. The variability of experimental K_{pw} is discussed in more detail in the accompanying workshop publication (Ghosh et al. this issue).

As the log–log relationship between K_{pw} and K_{ow} has a slope of close to 1, the resulting lipid-polymer partition coefficients are largely independent of the aqueous activity coefficient (indirectly calculated, see Figure 2B). These relationships also show that the capacity of the polymers is generally similar or somewhat lower than the capacities of the lipids. Lipid–PDMS partition coefficients have been experimentally determined as 14.4 to 62.9 g_{pdms}/g_{lipid} for a range of PCBs and organochlorine pesticides (Jahnke et al. 2008), which is higher than estimated from the above regressions but show a similar independence of hydrophobicity.

More recently Mäenpää et al. (2011) proposed estimating equilibrium concentrations in biota lipids (C_L) as the product of concentration in the polymer and the partition coefficient between the lipid and the polymer (K_{lp}):

$$C_L = C_p \times K_{lp}. \quad (5)$$

This approach circumvents the problems of measuring very high K_{pw} and BCF values that are typically within the range of 10^4 to 10^7 L/kg, whereas K_{lp} values are often in the range of 0.3 to 60 (depending on the polymer, Figure 2B and Jahnke et al. [2008]) and relatively independent of chemical hydrophobicity. Although K_{lp} values are experimentally easier to measure than K_{pw}, measured and published data remain very limited. EqP predictions based on K_{lp} provides also conceptual advantages: it allows one to differentiate between bioconcentration and biomagnification because the experimental lipid-normalized concentration in biota will be larger than C_L if biomagnification applies, or lower if mitigating processes such as biotransformation or nonequilibrium conditions occur. Thus, a comparison of the measured concentration in biota using conventional analysis to that predicted using Equation 5 may serve as a diagnostic tool for evaluating the role of key processes influencing bioaccumulation behavior of a substance (Mäenpää et al. 2011; Jahnke et al. 2012).

For bioaccumulation predictions in more complex food chains that may involve biomagnification processes and both benthic and pelagic organisms, measurement of C_{free} using PSMs may be used to improve site-specific food chain modeling (Gobas and MacLean 2003). For example, a critical model parameter in coupled pelagic–benthic food chain models is the ratio of freely dissolved concentrations in overlying surface water to sediment interstitial water (Burkhard et al. 2003). This application of PSM-derived C_{free} in calibration of bioaccumulation models at contaminated sediment sites is discussed further by Greenberg et al. (this issue).

ASSESSING AND PREDICTING SEDIMENT TOXICITY TO BENTHIC ORGANISMS

The traditional dose metric used for toxicity assessment is the total sediment concentration, which is determined by exhaustive extraction techniques. The relevance of C_{free} as a preferred dose metric for predicting benthic organism toxicity has been confirmed not only in laboratory-spiked sediments but also in field-contaminated sediments (Lydy et al. this issue). The most straightforward way in which passive samplers can be used in

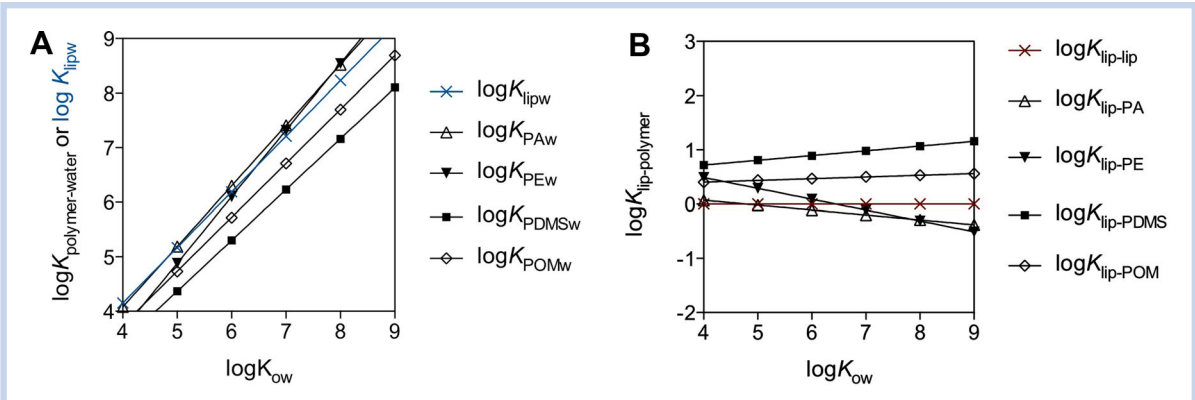

Figure 2. A. Polymer-water partition coefficients (log $K_{polymer-water}$) for common polymers used as passive samplers as a function of K_{OW} for PAHs ($K_{PDMSw} = 0.93$ log $K_{OW} + 0.17$, average value for different PDMS types (Smedes et al. 2009), $K_{LDPEw} = 1.22$ log $K_{OW} - 1.22$ (Lohmann 2012), $K_{POMw} = 0.99$ log $K_{OW} + 0.12$ (Hawthorne et al. 2011), $K_{Paw} = 1.11$ log K_{OW} - 0.37 (Lohmann 2012). B. Estimated lipid-polymer partition coefficient (calculated using the $K_{OW} - K_{lipw}$ QSAR of (Endo et al. 2011) and the QSARs in Figure 2A (log $K_{lip-polymer} =$ log $K_{lipw} -$ log $K_{polymer-water}$).

sediment toxicity assessment is via deployment in conjunction with actual sediment toxicity test exposures. In this way, polymer concentrations are used as an exposure metric, thereby allowing direct calibration with empirical effect data. This strategy has been applied for both single compounds as well as complex mixtures (Parkerton et al. 2000; Leslie et al. 2004; Ding et al. 2012).

A second application of passive samplers is to predict sediment toxicity to benthic species by using internal body residues that correspond to adverse effects, i.e., internal effect concentrations (IEC) (McCarty and Mackay 1993; Escher and Hermens 2004; Escher et al. 2011). Given an IEC, for a toxicity test species and effect endpoint, a polymer-based effect concentration can be derived:

$$EC_p = IEC[K_{pw}/BCF]. \quad (6)$$

Based on this framework, the target lipid model (TLM) uses water-based effects data to derive the target lipid-normalized IEC ($IEC_{target\ lipid}$) (Di Toro and McGrath 2000). Given an $IEC_{target\ lipid}$ estimate for a given benthic organism, a polymer effect concentration EC_p can be deduced:

$$EC_p = IEC_{target\ lipid}[K_{pw}/K_{target\ lipid-water}]. \quad (7)$$

The translation of the $IEC_{target\ lipid}$ to an EC_p thus depends on the relative partition affinity of chemicals between the polymer and the target lipid.

The following example is provided to illustrate potential application of this concept for assessing narcotic potency or baseline toxicity of contaminated sediments. Sediment toxicity tests with *Hyalella azteca* were performed on 192 sediment samples from 12 manufactured-gas plant sites and compared to the freely dissolved concentrations of the "EPA-34" PAHs using the USEPA hydrocarbon narcosis model (McDonough et al. 2010). Using measured porewater concentrations obtained, these investigators reported a 94% specificity in predicting mortality, and yielded an $IEC_{target\ lipid}$ of 31 μmol/g lipid from the 192 field samples, which was in good agreement with the estimate of 25 to 39 μmol/g lipid obtained in toxicity tests with this same species using fluoranthene (Schuler et al. 2006).

In a related study (Manning 2006), ex situ passive sampling with 10 μm coated PDMS fibers was applied to a subset of the 33 sediment samples discussed above. The amount of nonpolar organic compounds including PAHs that partitioned to PDMS fibers was then quantified using thermal desorption coupled with flame ionization detection (FID). The area under the curve of the FID chromatograms was translated into molar concentration estimates using 2,6-dimethylnaphthalene as an external standard. Subsequent application of the target lipid model to *H. azteca* water-only survival data have been compiled to derive an $IEC_{target\ lipid}$ for this species of 32 μmol/g lipid (McGrath and Di Toro 2009).

Substituting the $IEC_{target\ lipid}$ for *H. azteca* and using the polymer and target lipid–water partition coefficients in Equation 7 from Smedes et al. (2009) and McGrath et al. (2009), respectively, toxicity is predicted when C_P exceeds an EC_p value of 16 $mmol/L_{PDMS}$. Observed 28 d survival is plotted as a function of C_P for this data set in Figure 3 and shows that observed toxicity is consistent with theory within a factor of 2 because no mortality was observed at $C_P < 8\ mmol/L_{PDMS}$ (=16/2) and significant or complete mortality was shown at $C_P > 32\ mmol/L_{PDMS}$ (=16 × 2) in 10 of 11 samples. A key advantage of this approach is that the additive effects of HOC mixtures present in the sediment can be simply assessed without the need for a detailed evaluation of the exact nature of the mixture components.

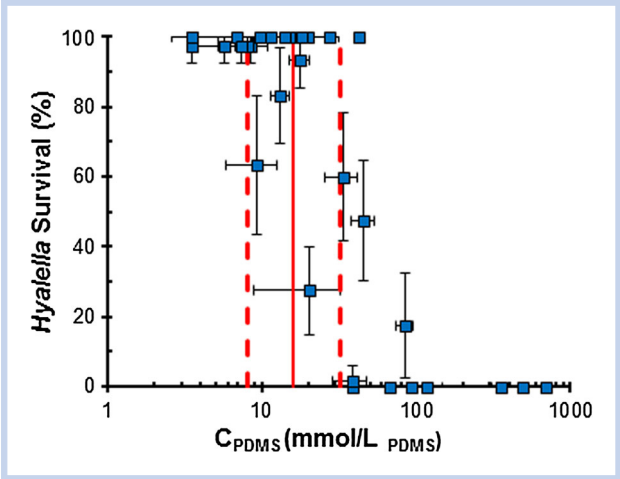

Figure 3. 28-d Hyalella survival as a function of PDMS fiber concentrations of hydrophobic organic contaminants determined in ex-situ sediment analyses using GC/FID analysis. The solid red line represents the predicted PDMS effect concentration obtained using equation (7). The dashed red lines illustrate a factor of two range of uncertainty from the theoretical estimate derived using the target lipid model.

Chemical activity (a) has recently been suggested as an exposure parameter for HOCs, because it drives partitioning into organisms and target membranes, and because baseline toxicity has been observed within a rather narrow chemical activity range of 0.01 to 0.1 (Reichenberg and Mayer 2006; Mackay et al. 2011). The chemical activity of individual chemicals can be added to determine the sum of a ($\sum a$), which provides a surrogate measure of narcotic potency for mixtures (Engraff et al. 2011; Smith et al. 2013). Sediment toxicity can then be assessed by comparing $\sum a$ to the range of a known to produce baseline toxicity (Witt et al. 2009; Smith et al. 2013).

An example demonstrating the use of chemical activity in sediment assessment is provided by Witt et al. (2009). In this study, disposable PDMS-coated fibers were used to determine chemical activity of PAHs at different depths in sediment cores. The measured chemical activity was then compared to the range corresponding to baseline toxicity (Figure 4A). The authors concluded that despite elevated total PAH concentrations in these sediments, PAH bioavailability was limited because the estimated $\sum a$ was well below baseline toxicity levels. The charts in Figure 4B and C demonstrate the distribution of freely dissolved concentrations and chemical activity for different PAHs. Although phenanthrene dominates the freely dissolved concentration, it only moderately contributes to the overall exposure when expressed as chemical activity. In contrast, benzo[a]pyrene, which contributes 1.1% to C_{free} has the same contribution to exposure as phenanthrene when evaluated in terms of chemical activity.

ENVIRONMENTAL QUALITY BENCHMARKS BASED ON PSMs

As an alternative to C_{free} determinations, a logical future extension of PSMs in environmental risk assessments and management decisions is through the development of sediment quality criteria that are expressed directly in terms of polymer

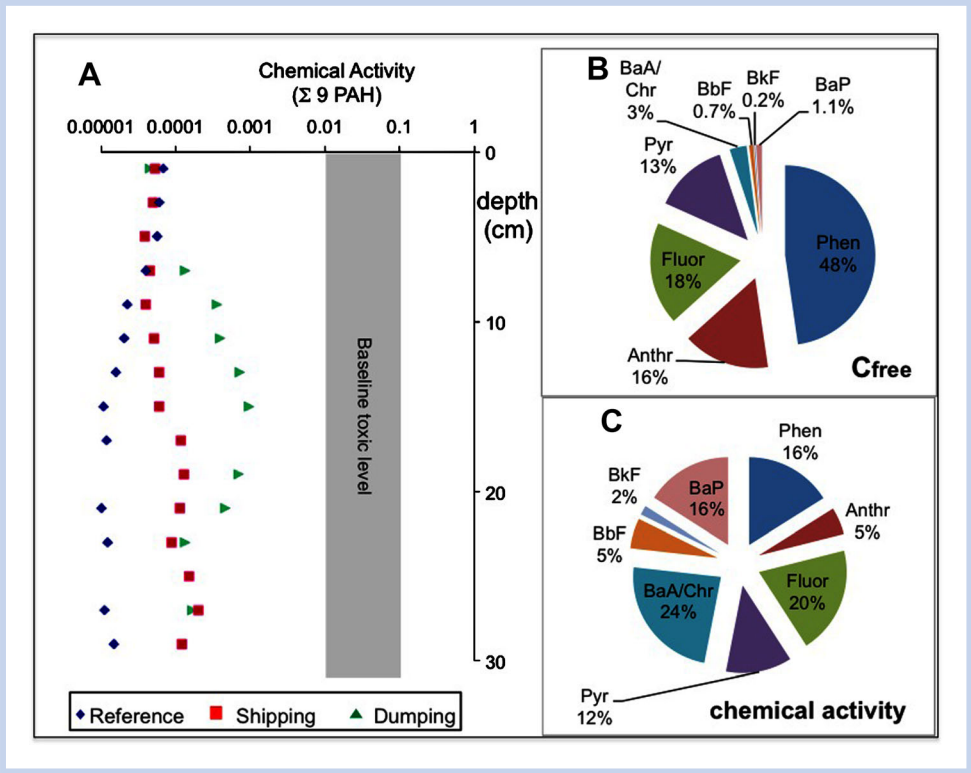

Figure 4. A. Comparison of chemical activities in field sediments at selected depth intervals at 3 sampling sites. Chemical activities were obtained by summing 9 individual PAHs. The grey zone indicates the region where lethality caused by baseline toxicity is expected. B. Contribution of the 9 PAHs to C_{free} at Dumping site. C. Contribution to the chemical activity at the Dumping site. Figure adapted with permission from Witt G et al. (2009). © (2009) Elsevier.

concentrations (Figure 5). For sediments, this could be achieved by translating existing, causality-based sediment quality guidelines (SQGs) into polymer quality benchmarks (PQBs).

$$\mathrm{PQB} = \frac{K_{\mathrm{pw}}}{K_{\mathrm{oc}}} \times \mathrm{SQG}. \quad (8)$$

In the cases where no SQGs are available or for assessments including water exposures, a water quality guideline (WQG) could be used (Eqn. 9), provided that it is protective of benthic species (Di Toro and McGrath 2000). Polymer quality benchmarks for various chemicals, for which water quality guidelines are available, can be derived by multiplying the WQG for the chemical by K_{pw}:

$$\mathrm{PQB} = K_{\mathrm{pw}} \times \mathrm{WQG}. \quad (9)$$

As in the case of Equation 7 involving internal effect concentrations, conversion of sediment or water quality guidelines to polymer-based quality benchmarks using Equations 8 and 9 allows the risk to the benthos to be assessed by directly measuring polymer concentrations of target contaminants in passive samplers deployed in sediments. An advantage of using PQBs is that polymer concentrations are much easier to measure. A further advantage is that these values can be extended to passive sampling measurements in other compartments (e.g., surface and groundwaters, storm water, whole effluents, and process waters).

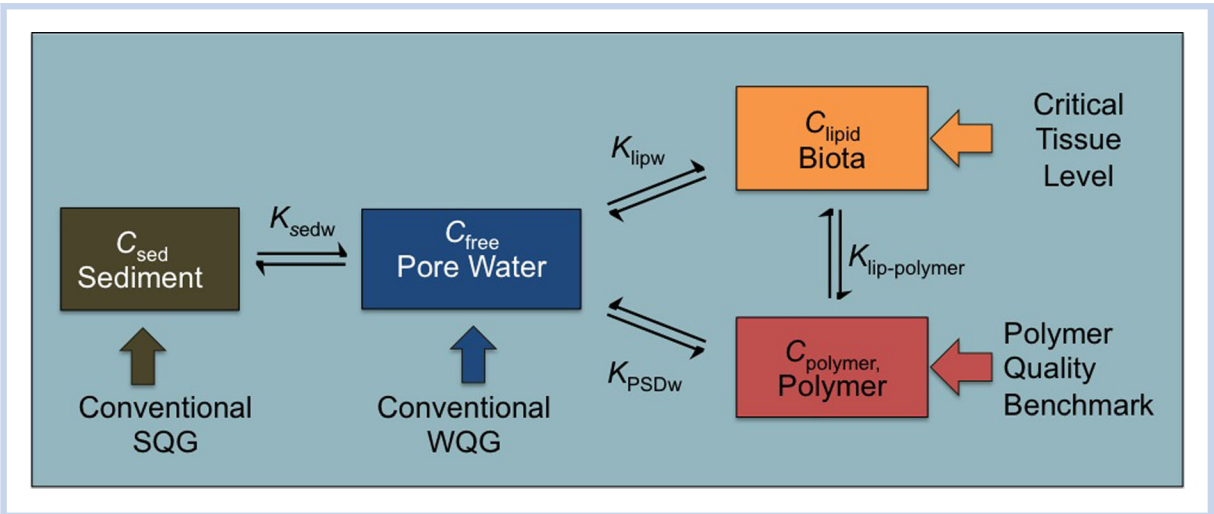

Figure 5. Setting Environmental Quality Benchmarks with PSMs. K_{lipw} refers to the target-lipid to water partition coefficient, and K_{PSDw} refers to the polymer-water partition coefficient.

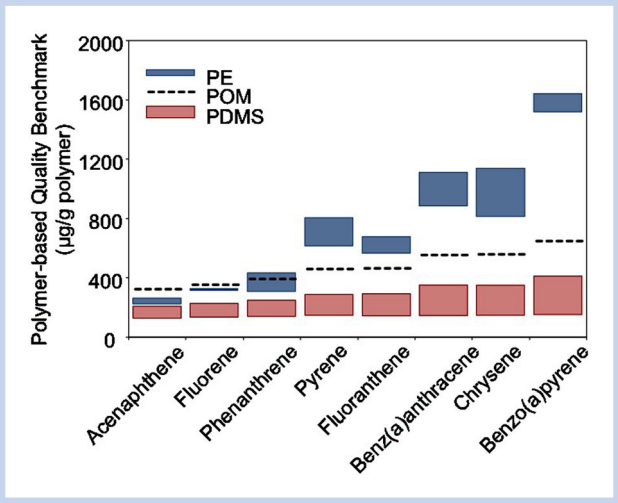

Figure 6. Polymer-specific sediment quality benchmarks (PQBs) for benthic toxicity assessments of PAHs. Values are based on narcosis Secondary Chronic Values (SCVs) in Burgess et al. (2013). SCVs (in mg/L) were converted to polymer-based values using equation (10) and empirical $K_{polymer\text{-}water}$ relations for each polymer: log K_{PDMSw} - log K_{OW} relations listed in (Smedes et al. 2009), log K_{LDPEw} - log K_{OW} equation (1) and best fit log K_{LDPEw} values in (Lohmann 2012), and the K_{POMw} - log K_{OW} relation from Hawthorne et al. (2011).

Further development, standardization, and validation are required before PQBs can be implemented. However, the following example illustrates this approach by calculating PQBs (µg/g polymer) based on narcosis secondary chronic values (narcosis SCVs; listed in Burgess et al. [2013]) for polycyclic aromatic hydrocarbons (PAHs) (Figure 6). Measured polymer concentrations from PAH-contaminated sites can be directly compared to the PQBs to determine if C_{free} concentrations of PAHs are sufficient to pose toxicity concerns to benthic organisms. This is an analogous approach to the use of EqP sediment benchmarks (ESBs), which attempts to account for bioavailability of the contaminant using organic carbon normalization (Burgess et al. 2013). However, the advantage of using a polymer rather than sediment organic carbon as the reference phase for quality criteria is that the polymer phase is homogeneous, well-defined, and constant. As a result, partitioning from sediment to the polymer will be much less variable than organic carbon in field sediments, which is heterogeneous in nature.

Measured and predicted (based on empirical relations) K_{pw} values are subject to uncertainties that need to be characterized and considered in the derivation of generic PQB values. K_{pw} values have been shown to vary for a type of polymer when determined by several researchers, e.g., polyethylene (Lohmann 2012) and for the same polymer type but different formats and products, e.g., PDMS (Smedes et al. 2009). This variability is illustrated in Figure 6 for the minimum and maximum K_{pw} values determined from the relations of Smedes et al. (2009), and the range between best fit and log K_{ow} predicted values from Lohmann (2012). The individual PQBs vary by less than a factor of 3 within the polymer groups. Given the variability associated with derivations of guideline values, and the uncertainty factors noted in the calculations of ESBs (Burgess et al. 2013), the potential error in PQB seems manageable for use in risk assessment. The uncertainty of PQBs can be further reduced when applying the K_{pw} values for the actual polymer material that is used for the passive sampling rather than a generic value. Another strategy to derive PQBs would be to calibrate the polymer directly to the toxicity endpoints of interest in dedicated toxicity tests where exposure either is measured by equilibrium partitioning into the polymer (Xu et al. 2007; Ding et al. 2012) or controlled by passive dosing from this polymer (Smith et al. 2010; Engraff et al. 2011).

PASSIVE SAMPLING METHODS DIRECTED AT READILY DESORBING FRACTIONS AND BIOACCESSIBILITY

Although it is generally agreed that spontaneous processes such as diffusion and (passive) uptake by small invertebrates are governed by chemical activities, and hence tightly related to C_{free}, some depletive processes, such as digestive uptake and biodegradation, are also closely related to the readily desorbing contaminant fraction. The readily desorbing fraction often represents the contaminant pool that is accessible to organisms over a relevant time scale (Reichenberg and Mayer 2006). It was decided at the workshop to mainly focus on equilibrium sampling directed at C_{free}, and methods directed at readily desorbing contaminant fractions are thus only briefly mentioned.

Passive sampling methods can be applied to measure the rapidly desorbing fraction or bioaccessible contaminant pool. For example, Tenax beads have been used for the continuous adsorption of contaminants as they desorb from the sediment matrix (Cornelissen et al. 2001), whereas more recently silicone has been applied as sorptive sink within bioaccessibility extraction methods (Gouliarmou and Mayer 2012). The fundamental distinction between PSMs that target readily desorbing fraction and C_{free} measurements is the capacity of the sorbent relative to the sediment sample (Cui et al. 2013). The capacity of the sorbent should be negligibly small when aiming at measurements of C_{free} (negligible depletion), whereas the capacity of the sorbent should be dominating when targeting bioaccessibility (full depletion) (Reichenberg and Mayer 2006; Smedes et al. 2013). Smedes et al. (2013) have recently developed a passive sampling approach with varying polymer to sediment mass ratios that range from negligible to full depletion conditions, which allows the simultaneous measurement of C_{free} and readily desorbing fraction. In terms of application within a regulatory context, readily desorbing fractions might facilitate bioavailability to be taken into account even when the regulatory threshold is expressed on a C_{total} basis: exceeding a threshold limit might be acceptable if the (readily) desorbing fraction is well below this limit. The use of bioacessibility measurements based on depletive PSMs may also be instructive for evaluating the potential for different sediment remedial strategies (i.e., in situ adsorbents, bioremediation) if C_{free} concentrations are shown to pose a concern.

NEEDS FOR IMPROVED INTEGRATION AND ACCEPTANCE OF PASSIVE SAMPLING IN ENVIRONMENTAL MANAGEMENT OF CONTAMINATED SEDIMENTS

To date, passive sampling methods have largely been applied in support of research activities (e.g., bioavailability studies, monitoring the effectiveness of remediation strategies), but have not gained widespread acceptance by the regulatory community for decision making. To gain wider recognition and use, candidate PSMs must be amenable to validation, and must be transferable to a larger community of practitioners.

As is the case for many emerging technologies, different PSMs have been reported without consensus or comprehensive guidance for application. Nonspecific or multiple terms used to describe these methods such as "bioavailable fraction" lead to confusion, as does the fact that PSMs rely on equilibrium partitioning rather than on exhaustive extractions that are the basis of traditional, standardized methods. The following 5 issues were identified as crucial for further development, application, and implementation of passive sediment sampling methods:

1. Most PSM methods have until now been applied to only a limited number of target compounds. Regulatory applications generally require more comprehensive target compound lists.
2. The polymers and materials used for PSM construction need to be readily available to the research and commercial services communities.
3. For equilibrium sampling methods, C_{free} is calculated as the ratio of C_p and K_p. A key source of error will often be related to K_{pw}. Consequently, this parameter needs to be determined with high accuracy, and its dependency on environmental conditions (e.g., temperature) must be understood.
4. If equilibrium cannot be reached during deployment, as it is often the case for in situ passive sampling, there will be an additional error associated with the disequilibrium correction, which adds complexity and deserves special attention to better characterize potential errors.
5. Quality assurance and control (QA/QC) strategies are well developed for instrumental analysis. Equally important is the adoption of robust QA/QC strategies for the passive sampling process as well as subsequent calculations. Thus, more attention on validity criteria is needed including confirmation of true equilibrium and negligible depletion criteria and the accuracy (or at least consistency) of the applied K_{pw} values.

Research over the last decades has demonstrated the usefulness of PSMs for sediment analysis. Presently, PSMs are increasingly being used to investigate the environmental fate, bioaccumulation, and toxicity of HOCs in sediments. The wide range of passive sampling formats and methods have been a driver for advancement of this field. In the future, it will be crucial to continue further development, while at the same time striving for consensus among the science, management and practitioners on the appropriate use of PSMs in supporting contaminated sediment management. Such consensus guidance will foster consistent PSM data sets and could eventually be memorialized and accepted as standard methods (e.g., by international organizations such as ISO and OECD).

In summary, there is growing consensus that C_{free} of HOCs: 1) can be measured by PSMs, 2) can provide an improved basis for mechanistic understanding that is needed for fate and transport modeling, 3) can facilitate linking exposure to bioaccumulation and toxicity, and 4) would enable improved assessment and management of contaminated sediments.

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