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Passive Sampling in Contaminated Sediment Assessment: Building Consensus to Improve Decision Making

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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.

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ABSTRACT

Contaminated sediments pose an ongoing, pervasive, global challenge to environmental managers, because sediments can reflect a legacy of pollution that can impair the beneficial uses of water bodies. A formidable challenge in assessing the risks of contaminated sediments has been the elucidation and measurement of contaminant bioavailability, expressed as the freely dissolved concentration (C_{free}) in interstitial water, which serves as a surrogate measure of the substances' chemical activity. Recent advances in passive sampling methods (PSMs) enable C_{free} of sediment-associated contaminants to be quantified at trace levels, thereby overcoming current limitations of predictive models. As a result, PSMs afford the opportunity for a paradigm shift from traditional practice that can effectively reduce uncertainty in risk assessment and bolster confidence in the science used to support management of contaminated sediments. This paper provides a brief overview of the 5 subsequent papers in this series that review literature on PSM use in sediments for both organic and metal(loid) contaminants, outline the technical rationale for using PSMs as a preferred basis for risk assessment over conventional chemical analyses, describe practical considerations for and uncertainties associated with laboratory and field deployment of PSMs, discuss management application of PSMs, including illustrative case studies in which PSMs have been used in decision making, and highlight future research and communication needs. *Integr Environ Assess Manag* 2014;10:163–166. © 2013 SETAC

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BACKGROUND TO THE SPECIAL SERIES

Chemical properties often dictate the distribution of many contaminants that enter the aquatic and marine environment to sediments. Sediment-associated contaminants may directly impact benthic life as well as pose deleterious indirect effects on other organisms, including humans, via bioaccumulation and subsequent transfer through the food web. As emission controls have improved, particularly in developed countries, the legacy of contaminants that remain in sediments poses concern because of impairment of beneficial water body uses, such as fishable, navigable, and swimmable. Experience has shown that remediation is often difficult, costly, time consuming, and disruptive to the local environment and community. Furthermore, the ultimate objective of reducing risk to humans and the environment has met with limited success (NRC 2007). Recognizing the need to improve progress in addressing this challenge, a growing consensus has arisen that a transformation in practice is needed that better addresses key uncertainties and promotes a focus on achieving true risk reduction, where warranted, through use of an appropriate combination of assessment and remedial technologies (Bridges et al. 2012).

A key uncertainty in assessing the risks of contaminated sediments as well as predicting the efficacy of potential remedial actions has been the inability to quantify contaminant bioavailability (Ehlers and Luthy 2003). The traditional analytical measure of sediment chemistry based on total concentration (C_{total}) has proved to be a poor predictor of contaminant bioavailability. To address the bioavailability issue, equilibrium partitioning models were developed to predict freely dissolved concentrations in sediment porewater, or C_{free}, for both hydrophobic organic compounds (HOCs) and selected metal(loid)s. This approach was convenient because bioavailability was accounted for by simple normalization of C_{total} to the dominant sediment binding phase. Thus, organic carbon normalization was applied to HOCs, and acid volatile

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sulfide normalization was used for some metals (Wenning et al. 2005). However, application of such normalization procedures to field sediments that contained a variety of heterogeneous binding phases has often not yielded accurate predictions of C_{free}, thereby introducing large uncertainties in decision making (Cornelissen et al. 2005). Whereas more advanced models for describing partitioning of organics in field sediments have been developed, results indicated orders of magnitude of uncertainty (Arp et al. 2009). The ability to estimate C_{free} from C_{total} is further complicated for metal(loids) because of complexation with inorganic and organic ligands (Di Toro et al. 2005). Moreover, direct determination of C_{free} using conventional methods (e.g., isolation and solvent extraction of sediment interstitial water samples) is difficult, time consuming, and costly, usually requiring large sample volumes and postcollection manipulation to achieve the desired degree of detectability. Therefore, practical methods that reduce the uncertainty in quantifying C_{free} are a critical need for improving risk assessment and long-term management of contaminated sediments (Thompson et al. 2012).

Recent analytical advances in passive sampling methods (PSMs) have led to their growing use in global environmental monitoring of air and water (Betts 2009; Lohmann and Muir 2010), as well as in soils and sediments (ter Laak et al. 2006; Maruya et al. 2012; Gouliarmou and Mayer 2012). PSMs can be broadly defined as techniques that rely on the partitioning of contaminants from the sampled media (e.g., sediment) to a reference sampler phase, typically a polymer, to concentrate the analyte of interest. PSMs have been used to investigate bioavailability in contaminated soils and sediments using 2 conceptual approaches (Reichenberg and Mayer 2006). One approach is based on the concentration or fraction of C_{total} that can be rapidly desorbed using a sorbent that serves as an infinite sink (e.g., Tenax beads or XAD resin). Such depletive methods aim to quantify the bioaccessibility of the particle-bound contaminant. A recent application of this approach is provided by Mackenbach et al. (2012). A second approach relies on the thermodynamic concept of chemical activity that is directly related to C_{free} in contaminated sediments. A recent study describes how both approaches can be combined (Smedes et al. 2013).

Despite significant advances in the development and application of PSMs, practical incorporation of these tools in contaminated sediment management decisions has been limited. Primary barriers to broader acceptance and use include not understanding the technical basis underpinning PSMs over traditional analytical methods; confusion regarding the plethora of different methods and formats that are increasingly reported in the literature; lack of consensus technical guidance for PSM selection and use to provide accurate C_{free} data; uncertainty associated with PSM-derived estimates of C_{free}, and how well such estimates compare with actual in situ porewater values and predict bioaccumulation and toxicity; standardization and incorporation in regulatory decision-making contexts; and limited experience in use and analysis of PSMs by commercial laboratories.

To promote understanding of PSMs and provide consensus recommendations for use in contaminated sediment management decisions, a Society of Environmental Toxicology and Chemistry (SETAC) workshop was held that covered PSM application to HOCs and metals, including metalloids and other inorganic contaminants of concern. Consensus was reached by workshop participants to focus on chemical–activity based PSM approaches given acceptance of C_{free} in current regulatory paradigms and advantages of directly linking activity measurements to key processes (Mackay et al. 2011) as discussed in the following sections. Further information regarding this workshop can be found in Parkerton et al. (2013).

PREVIEW OF THE SPECIAL SERIES

The papers in this special issue serve as the deliverables from this workshop. In the first paper, Lydy et al. (this issue) introduce the science by cataloging numerous published papers and reports on PSMs that targeted HOCs, focusing on studies that have been developed (or adapted) for the assessment of contaminated sediments. In summarizing the current state of the science, these investigators were tasked to identify those PSMs that were "ready for use." This was not an easy undertaking, because sampler materials and configurations that constitute PSMs are diverse. However, Lydy et al. (this issue) focus on PSMs that share a common ability to estimate C_{free} or relate to parameters and endpoints for HOCs that are most relevant to managers.

This journey through the literature leads to an understanding of the 2 basic modes of operation for PSMs (equilibrium vs. kinetic), and which methods performed well in laboratory ("ex situ") versus field ("in situ") applications. Finally, these investigators were tasked to identify studies that focused on issues of quality assurance/quality control, such as those in which PSM standardization, comparison, or interlaboratory comparison were addressed. A key comparative study showed that the uncertainty in estimating C_{free} in interstitial water is reduced to within a factor of 10 using different PSMs, compared with the orders of magnitude uncertainty in concentrations obtained using equilibrium partitioning assumptions. The outcomes described serve as the basis for advancing PSMs for HOCs, as described in subsequent papers in this series.

Although comparatively less work is currently available for inorganic sediment contaminants, the workshop steering committee recognized that PSMs offer the potential for cost-efficient and accurate in situ characterization of C_{free} for trace metals and metalloids (Peijnenburg et al. this issue). Like HOCs, multiple passive sampler configurations have shown promise for estimating low-level, time-integrated trends in C_{free} for some divalent metals (e.g., Cu, Ni, Pb). Moreover, PSMs for these divalent metals have been applied in laboratory exposures and field deployments to characterize fine-scale spatial gradients, to gain insights with regard to dissolved metal speciation, and to capture episodic events and cyclic changes that may be missed by grab or "snapshot" sampling approaches. However, because of the complexity associated with metal speciation in sediment environments, the metal species represented by C_{free} measured using different PSMs tend to be less well defined or uniform than for HOCs. Furthermore, the recognized role of dietary exposure to labile metal forms in the digestive tract of sediment-dwelling organisms further complicates PSM use in quantifying metal bioavailability (Luoma and Rainbow 2005; Baumann and Fisher 2011). To address these complexities, Peijnenburg et al. (this issue) delve into the need for stronger linkages between PSM measurements and relevant biological endpoints for metals, through controlled laboratory experimentation and in situ characterizations, as well as integration with the development and application of models (e.g., the biotic ligand model).

Articulating a consensus view of the technical basis for using chemical activity–based PSMs is a prerequisite for broader regulatory acceptance. In the third paper in this series, Mayer et al. (this issue) explain that C_{free} for HOCs is directly related to chemical activity, which drives processes including diffusive uptake into benthic organisms and exchange with overlying water or surface–groundwater interfaces. The PSMs that measure C_{free} are thus a more relevant exposure metric than $C_{total.}$ These authors also explain that for successful application of PSMs, 2 critical conditions must be met: 1) attainment of equilibrium (or near-equilibrium) should be achieved, or a means for correcting for non-equilibrium conditions is required; and, 2) PSMs should not by virtue of introduction into the sample appreciably alter the chemical activity of the contaminant, that is, cause local depletion that reduces C_{free}. In cases in which long deployment times to achieve equilibrium are impractical, correction using the release rate of performance reference compounds that are incorporated into the PSM before deployment is discussed. These authors identify key sources of uncertainty in PSM estimates of C_{free} and highlight that overall uncertainty is thought to increase from ex situ, equilibrium, to in-situ, non-equilibrium sampling conditions.

A key impediment to widespread use and thus acceptance of PSMs for assessment of contaminated sediments is the current lack of consensus on practical applications and implementation within the community of PSM developers, (potential) users, and decision makers. For example, some investigators will advocate that PSMs should only be used ex situ, that is, under controlled laboratory conditions, whereas others emphasize the utility and in some cases, criticality, of obtaining information on *in situ* conditions. In the fourth paper in this series, Ghosh et al. (this issue) provide practical guidance on the selection, calibration, testing, and application of PSMs that target C_{free} for sediment-associated HOCs. Their work covers the broad range of passive sampler materials and configurations used in laboratory-based ex situ and field-based in situ sampling approaches described previously in Lydy et al. (this issue) and begins by describing key, overarching principles that serve as a starting point for interested audiences. This is followed by delineation of calibration principles and steps that are critical to generating high-quality measurements of C_{free}, including newly developed or adapted quality assurance/quality control guidelines that are specific to PSMs. Different sources of potential error that contribute to the uncertainty in PSM-derived estimates of C_{free} are also reviewed.

In the last paper, Greenberg et al. (this issue) detail how PSMs can be used to characterize key endpoints included in conceptual site models that are widely used in weight-of-evidence–based decision frameworks. A variety of practical applications for site characterization, remediation, and risk management are discussed. Several examples in which PSMs have been adopted in past and current projects or programs to improve decision making over the status quo are highlighted. Currently, applications in management contexts are best suited for HOCs, where PSM data can reduce uncertainty in site investigation and management. Future applications of PSMs include assessment of biogeochemical processes, mixtures, emerging contaminants, and direct measurement of alternative matrices including biota. Communication across sectors, disciplines, and geographies, led by the scientists and managers at the forefront of PSM development and use, is needed to increase confidence among stakeholders and encourage consistent application by practitioners.

Although PSMs have progressed to the point where practical application is now clearly feasible, work remains to improve quality, enhance availability, and expand use for more effective, comprehensive contaminated sediment management:

1. Better standardize PSMs, including
   a. refinement of the process for selecting or estimating calibration parameters (e.g., K values), including those applicable for in-situ applications
   b. development of reference materials for quality control
   c. round-robin exercises to characterize interlaboratory and intralaboratory precision
   d. additional guidance on performance reference compound use
2. Further characterize and communicate sources of uncertainty for ex situ and in situ applications
3. Expand list of analytes targeted by PSMs
4. Engage key sectors (academia, industry, regulatory, and resource management) to effect
   a. broader availability of PSM expertise and services
   b. practitioner exchanges on lessons learned
5. Solidify linkages between PSM measurements and
   a. endpoints of management interest (uptake, bioaccumulation, toxicity, flux)
   b. model calibration, prediction, and refinement
6. Promote a better understanding of metal speciation and bioavailability using PSMs

In summary, PSMs afford a unique opportunity for improving the current state of the science used in assessment and management of contaminated sediments. The aim of the accompanying workshop papers in this series is to further contribute the technical basis and practical guidance needed to routinely use PSMs for this purpose.

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