RPM Guide

Integrating Passive Sampling Methods into Management of Contaminated Sediment Sites: A Guide for Department of Defense Remedial Project Managers

ESTCP Project ER-201216

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List of Acronyms

COC	Chemicals of Concern
CSM	Conceptual Site Model
DDT	dichlorodiphenyltrichloroethane
DGT	Diffusive Gradient
DOD	Department of Defense
DQOs	Data Quality Objectives
EMNR	Enhanced Monitored Natural Recovery
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FS	Feasibility Study
g	Gram
ITRC	Interstate Technology and Regulatory Council
kg	Kilogram
mg	Milligram
MNR	Monitored Natural Recovery
PAH	Polyaromatic hydrocarbons
PCB	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
PE	Polyethylene
POM	Polyoxymethylene
PRC	Performance Reference Compound
PSM	
QA	Quality Assurance
QAPP	Quality Assurance Assessment Program
RI	Remedial Investigation
RPM	Remedial Project Manager
SAM	Sediment Assessment and Management
SERDP	Strategic Environmental Research and Development Program
SPAWAR	Space and Naval Warfare System Command
SPMD	Solid-phase membrane device
SPME	Solid-phase microextraction
SWAC	Surface-weighted Area Concentration
USEPA	U.S. Environmental Protection Agency
µm	Micrometer

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1.0 OVERVIEW

This document provides guidance to Department of Defense Remedial Project Managers (DOD RPMs) on integrating passive sampling methods into the management of contaminated sediment sites. The focus is on the passive sampling devices that are most commonly used to measure non-polar organic chemicals such as polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs). These include various fibers, probes, and sheets made from polyethylene (PE), polyoxymethylene (POM), and polydimethylsiloxane (PDMS). Passive samplers, such as diffusive gradient in thin films (DGT) are also available for metals, but the use of these samplers is less widespread at present, and these samplers are not discussed in this document. However, DGT samplers are discussed in a companion document, *Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual* (Strategic Environmental Research and Development Program/ Environmental Security Technology Certification Program/Environmental Protection Agency [SERDP/ESTCP/EPA] 2016), which provides technical details and standard operating procedures (SOPs) for organic and inorganic samplers.

As described in the acknowledgements section, this document reflects input from a large number of individuals with experience on the technical and regulatory aspects of using passive samplers. Most importantly, the document has been crafted to consider suggestions and address questions and concerns raised by DOD RPMs regarding the use of passive samplers. Two critical suggestions made by DOD RPMs and echoed by others guided the structure and content of this document:

- The document must show where and how passive samplers provide value, especially because many sites are well into the investigation, feasibility study, and remediation process.
- The document should be short and to the point: Does this work? Under what situations is it useful? Where has it been applied? This structure is more helpful for a DOD RPM than step-by-step guidance.

Passive Samplers

A passive sampler is a device that can be placed into sediments or surface water, in the field or laboratory, to extract chemicals from the water phase within the sediment matrix. The amount of chemical accumulated by the sampler can be used to calculate the amount that is freely dissolved in the water phase of the sediment. This amount correlates strongly to the freely dissolved concentration that is relevant to exposure of biota. As described further in the document, information on the amounts of chemical present in the water phase is especially important for evaluating chemical fate and exposure, for guiding remedy selection, and for evaluating the efficacy of remedial actions.

1.1 INTENDED AUDIENCE

This document has been prepared for DOD RPMs, to provide them with insight on the use and application of passive samplers at contaminated sediment sites. Specifically, the document provides insight regarding the premise that risk associated with certain groups of compounds - and management of that risk - are governed by the bioavailable fraction; and that passive samplers provide better and more reliable

information on that fraction than can be obtained from conventional bulk chemical analytical methods. The Environmental Protection Agency (EPA) and state RPMs may also find this information useful. This is not a detailed guidance document; technical information on the use of passive samplers can be found in SERDP/ESTCP/EPA (2016), USEPA (2012a,b), and Greenberg et al. (2014). Instead, this document helps DOD RPMs answer the following questions:

- What do passive samplers measure?
- What value do passive sampling measurements provide?
- For which chemicals are passive sampling measurements most useful?
- Can passive samplers be used at any stage of the remedial investigation, feasibility study, or remediation process?
- Can passive samplers be useful if data for remedial investigations have been collected using other methods?
- How important are Data Quality Objectives (DQOs) and the quality assurance (QA) process for incorporating passive sampling into your program?
- What do I need to know about sample collection and processing?
- What do I need to know about working with congeners for PCBs, dioxins/furans, and individual compounds for mixtures of PAHs?
- Are there commercial laboratories that can do this work?
- Does this work require specialized expertise?

This document reflects information provided in the literature, as well as insights gained through conversations with RPMs within the DOD and the U.S. Environmental Protection Agency (USEPA), and with scientists who specialize in the use of passive samplers. A set of case studies is provided at the end of the document as examples of applications within a management context.

2.0 WHAT ARE PASSIVE SAMPLERS?

The passive samplers described in this document refer to materials and devices used to measure the quantities of freely dissolved hydrophobic chemicals in water. As discussed in more detail later in this document, the real value of these measurements is that the freely dissolved forms of the chemicals within the sediment matrix are what matter with respect to exposure and risk to biota. Such exposures can result in direct effects on these animals or in bioaccumulation into food webs that lead to wildlife and people.

Please refer to the following images to get a more concrete feel for what passive samplers are and how they are typically deployed. Photographs were obtained from Upal Ghosh, Phil Gschwend, Danny Reible, Sean Sheldrake, Tom Parkerton, and Tim Thompson.

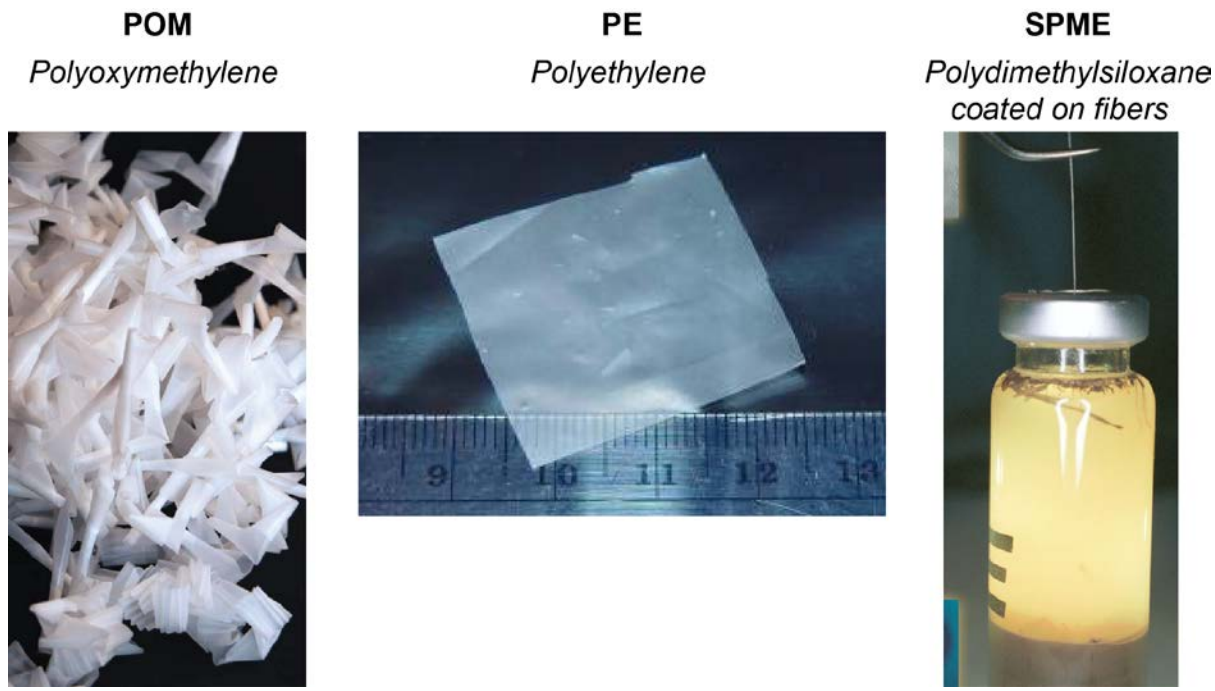
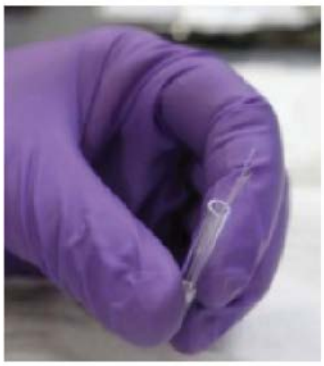


Image 1. Passive Sampling Materials

Passive samplers for non-polar organic chemicals such as PCBs, chlorinated pesticides, and PAHs are made from various plastic materials that sorb the chemicals from water.

Devices that expose flat sheets of absorptive materials (POM or PE)

A probe within which there is a thin fiber



SPME fiber
(thin glass rod coated
with PDMS)

Image 2. Devices to House Passive Sampling Materials for Sampling in Sediment

The POM, PE, or PDMS materials are placed on or within various devices that provide spatial configuration and help protect the integrity of the materials so that they can be placed into the sediment.

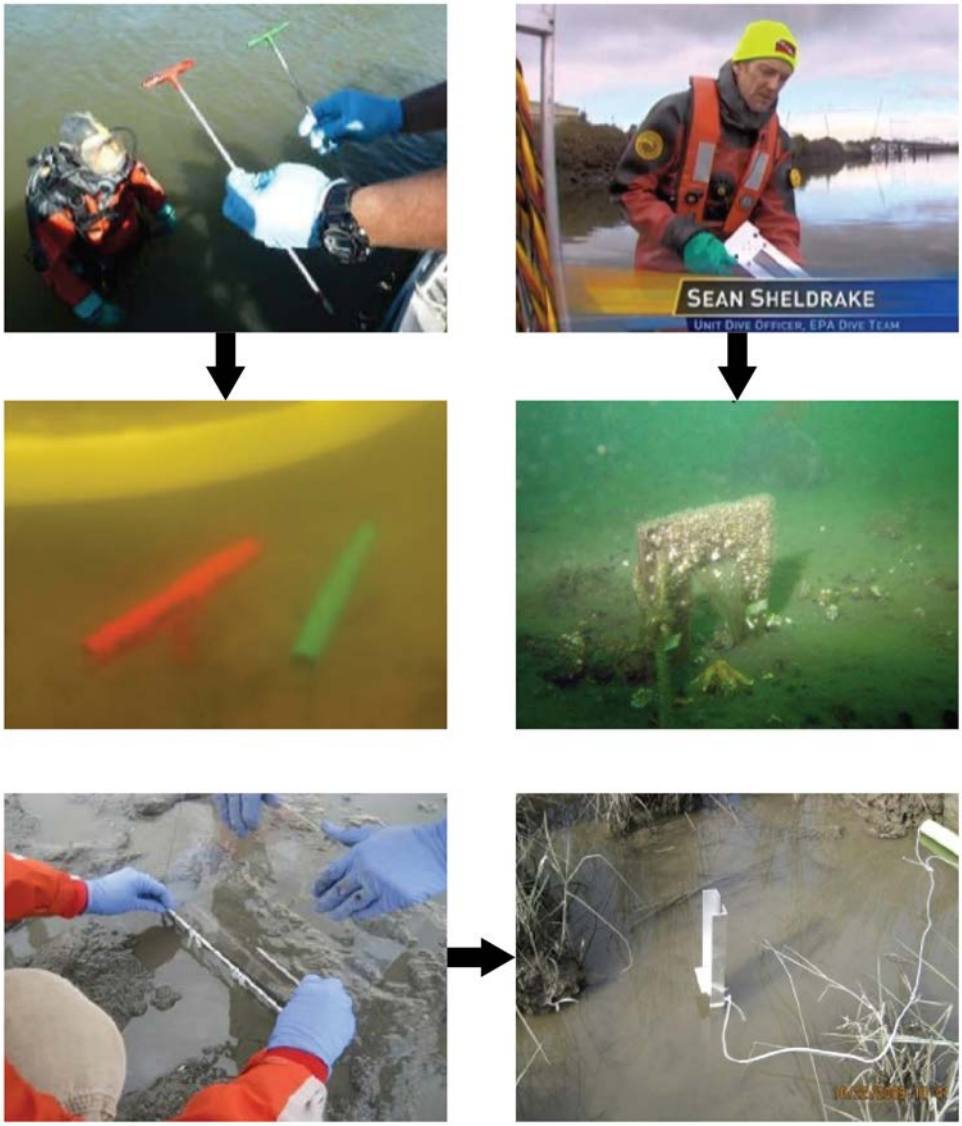


Image 3. Passive Samplers Deployed in the Field

Deployments may involve placing devices in the field for specified periods of time (referred to as *in situ* sampling).

Image 4. Passive Samplers Deployed in the Field from Boat

Most open-water deployments in deeper water have involved divers. Gear is being developed for achieving deployments using devices that will carry the samplers to the sediments and subsequently insert them into the sediments.

Image 5. Passive Sampler Retrieved from Lake Sediment

This is what a sediment bed/water PE sampler might look like after deployment in lake sediment. The clear, lower PE portion was in the sediment, while the fouled upper portion was in the bottom water. The fouled water-column portion is then cleaned in a laboratory and used for analysis of the water-column exposure. The portion that had been in the sediment can be cut into strips and analyzed for the vertical chemical profile of the sediment porewater.

Image 6. POM Passive Sampler in the Laboratory

This is an example of an *ex situ* setup of a passive sampler; here, an intact core taken from a wetland system contaminated with PCBs has been set up in the laboratory. POM strips have been inserted vertically into the core. These will sorb PCBs and provide a vertical profile of the chemicals present. *Ex situ* setups may also include probes and other devices.

Image 7. *Ex situ* SPME Passive Sampler Setup

The setup starts with 250-m spools of glass fiber with two coating thicknesses (10 and 100 µm [micrometer]) of PDMS; these are purchased. Disposable fibers (shown) are then cut to 4-cm lengths. The vial on the left contains about 5–7 g of sediment from the field (contents are chemically killed to stop biological activity). The fibers are then placed in the sediment and tumbled at room temperature to facilitate mixing and allow for chemical equilibrium to be reached. The fibers are removed for subsequent analysis.

2.1 WHAT DO PASSIVE SAMPLERS MEASURE?

Understanding the influence of contaminants on an aquatic system involves understanding exposure concentrations in surface waters, sediment, and biota. These surface water concentrations can be influenced by sediments, as well as by inputs from outside the system. Passive samplers, whether deployed in surface water or sediment, provide a means of measuring the freely dissolved concentrations of target contaminants in the water phase.[1] The freely dissolved concentrations are also commonly referred to as the bioavailable concentrations. Passive samplers measure chemical concentrations in surface water and/or sediment porewater over the duration of their deployment.

How is passive sampling different from what is currently done? First, in the case of surface water, conventional methods involve the collection of large volumes of water in order to make accurate measurements of dissolved contaminant concentrations, and to achieve low detection levels for trace chemical concentrations. Those measurements reflect chemical concentrations present in that specific volume of water. Therefore, a grab sample of water provides only a snapshot of what is present in the water at a particular location and time. Because water is continually flowing past a location, dissolved chemical concentrations in the water can vary by the minute, hour, or day, and at longer time scales. Passive samplers accomplish two things with respect to measuring chemicals in water: (1) they serve as the extracting material that concentrates the chemicals

Notes on Using Passive Samplers

The value of using passive samplers is situation specific. They are most useful for providing insights into the mobility and biological availability of chemicals. This information can be used to support investigations, select remedial alternatives through pilot studies, and monitor remediation.

The state of the practice for passive samplers is that they are most useful for sites where hydrophobic chemicals such as PCBs, pesticides, and PAHs are of concern.

Careful development and implementation of data quality objectives (DQOs) is important for sampling design and analyses. Expertise in deployment and retrieval is recommended, because nuances in technique can influence data quality.

Practitioners and commercial laboratories are building expertise on the deployment and analysis of these samplers. However, it is sensible to obtain guidance from individuals with expertise in this area.

Passive samplers increase the options and opportunities for RPMs to make decisions with greater confidence, because they provide data on the bioavailable component of the chemicals that may not be available from measurements of bulk chemical concentrations. This information makes it possible to consider remedies that target this specific bioavailable component.

[1] The term "measurement" is used here to refer to the overall process by which passive samplers are used to eventually yield a concentration of a chemical in water. That procedure has several well-defined steps, as is the case with many types of measurements. The sampler itself does not yield a value, digital or otherwise, but is the starting point for obtaining the eventual estimated concentration. Details on these measurements are provided in a companion document, *Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual* (SERDP/ESTCP/EPA 2016).

relative to their concentrations in water, and (2) they integrate water concentrations over time, providing a better estimate of the central tendency of concentrations at a location than can be gained from a single whole-water sample. Deployment durations and the passive sampler design (material, size, surface area, thickness, etc.) can be adjusted to establish a deployment period that corresponds to the exposure scenario of interest; that is, passive samplers can be designed to be deployed for hours, days, or longer. The passive sampler measurement integrates the chemical concentration at a particular location with the duration of deployment. This information is more useful than whole-water concentrations at specific time points for estimating exposure. This is especially true in complex, dynamic systems such as an estuary with a moving tidal wedge and fluctuating groundwater input through the bedded sediments. Passive samplers also avoid other complications associated with bulk-water collection, including the need to filter the water samples and to consider an appropriate filter size, whether to analyze the water as filtered or unfiltered, how to account for sorption onto sample media, and how water chemistry changes if composite samples are collected over time.

Data obtained from passive samplers can complement bulk-sample data, in that passive samplers enable the measurement of freely dissolved chemicals, which is the exposure metric of primary concern with respect to biological uptake and effects on biota. This measure reflects overall organism exposure as it relates to compartments other than the water itself, because the water concentrations are related to the concentrations in these other exposure compartments. There are, of course, physical and biological differences between a passive sampler and an organism. Passive samplers do not ingest sediment or eat other animals, and they do not actively move through the sediment. Those types of activities could change the exposure regime, although as noted, the measurement of one compartment provides information on the others. Work is underway to explore the extent to which movement might be important, and passive samplers are being developed that incorporate small movements. An advantage of these types of “bioturbating” passive samplers is that they minimize the influence of the sampler on the concentrations of freely dissolved chemicals at the interface of the sampler and the water. In other words, the movement replenishes the water.

Bulk contaminant sediment measurements are important for understanding what is present and how chemicals move with sediment transport, but that measurement alone does not reveal the amount of freely dissolved chemicals that biota experience and that is the source of risk. Contaminants in sediments can be bound differently at different sites depending on the site-specific geochemistry. For hydrophobic pollutants such as PCBs and PAHs, association with sediment black carbon forms can greatly attenuate the exposure to biological receptors (NRC 2003). For example, PAHs associated with weathered coal by-products have been demonstrated to be strongly bound and, when present in sediments even at a high concentration of 3000 mg/kg, exhibit reduced water-phase concentration and toxicity to invertebrates (Kreitinger et al. 2007). Bulk contaminant sediment measurements do not reveal the differences across sediments that control biological exposure and partitioning between sediment and water. It has always been necessary to estimate biological exposure either indirectly by using various algorithms (such as equilibrium partitioning coefficients) or by various extraction tests (USEPA 2003a,b). Passive samplers offer an alternative approach to directly measure freely dissolved chemical concentrations in the sediment environment, which in turn, allows the investigator to calculate site-specific partitioning constants and true exposure to biota. This approach then allows the investigator to incorporate the effect of site geochemistry on the true biological availability of the contaminant in sediments. Practitioners

familiar with the various analytical approaches also express the view that there is less uncertainty in measurements of freely dissolved concentrations made using passive samplers, as compared to estimating these concentrations indirectly from other methods.

2.2 WHAT VALUE DO PASSIVE SAMPLING MEASUREMENTS PROVIDE?

The value of passive sampling is different from the cost associated with making a measurement. Those costs could be more or less than the costs of collecting, extracting, and analyzing for chemicals using more traditional methods. The value of information relates to how it serves to reduce uncertainty in decision making, provides better insight into the efficacy of remedial alternatives, and possibly supports decisions that are less expensive in terms of economic and ecological costs. For example, because passive samplers provide insight into the biological availability of chemicals, they provide a more precise and reliable means of quantifying risk, and in turn, provide a more reliable means for delineating remedial areas where reductions in risk can best be achieved.

Experience

The use of porewater measurements, including those provided by passive samplers, reduces the uncertainty in estimating the potential for bioaccumulation into biota and the derivation of biota sediment accumulation factors (BSAFs).
Victor Magar, ENVIRON

Passive samplers support the evaluation of a broader range of remedial options than was possible previously, and a greater choice has implications for overall project costs. Passive sampling devices can be used to support pilot studies and remedial actions that involve capping, enhanced natural recovery, *in situ* treatment, and monitored natural recovery. These *in situ* remedial actions involve leaving chemically affected sediment in place. Because passive sampler results are more closely linked to the presence of freely dissolved chemicals and associated risk, compared to bulk sediment sampling, passive samplers can be used to monitor *in-situ* remedial actions that are designed to reduce the amount of freely dissolved chemicals while leaving sediment in place. Also, passive samplers can be used to evaluate the efficacy of remedial actions that involve dredging.

Insight

Passive samplers often provide additional lines of evidence that can support decision making. Measurements made with these samplers can help explain other results and increase confidence in conceptual site models.

2.3 FOR WHICH CHEMICALS ARE PASSIVE SAMPLING MEASUREMENTS MOST USEFUL?

Sediments at DOD sites can be contaminated with a variety of chemicals based on the history of each site. Common classes of chemicals found in sediments include metals, synthetic organic chemicals and hydrocarbons, and munitions. While passive samplers could conceivably be developed for all classes of chemicals, this guide focuses on the use of these samplers for hydrophobic organic chemicals that are considered persistent and bioaccumulative. Some of these bioaccumulative chemicals can be transferred through the food web, resulting in exposures to

people and wildlife that feed on fish and invertebrates, while others can affect wildlife through direct contact or ingestion; regardless, both effects are influenced by and generally proportional to the bioavailability of chemicals in the water phase.

Types of chemicals for which passive samplers are currently most useful include PAHs, PCBs, dioxins, dibenzofurans, and chlorinated pesticides such as dichlorodiphenyltrichloroethane (DDT) and chlordane. PAHs and PCBs are examples of chemicals that are often sources of concern for human health and ecological risks at contaminated sediment sites. These are the types of chemicals for which passive samplers can be used to provide measures of exposure to the freely dissolved chemicals during all phases of sediment management. PAHs are risk drivers primarily because of the potential for adverse effects on benthic invertebrates and sediment-associated fish. PAHs can bioaccumulate to toxic levels in the tissues of invertebrate animals that live on or in the sediments. Because of this particular type of exposure and associated toxic effects, USEPA has developed guidance for evaluating exposure and effects (USEPA 2003a, 2012a,b). Those guidance documents emphasize that the toxicity of PAHs in sediments is more closely related to the concentration of freely dissolved chemical in porewater, which reflects the bioavailable "activity" of the chemical in sediment, than to the concentration in bulk sediment. That is exactly the type of information that passive samplers can provide. Note, however, that the finding that exposure is most closely related to concentrations of bioavailable contaminants in porewater does not imply that exposure is solely from porewater. Rather, the amount of freely dissolved chemicals in porewater reflects partitioning among all phases of the environment, including tissues of benthic organisms.

PCBs are risk drivers for sediments primarily because of potential exposures to humans and wildlife that eat fish and shellfish in which these chemicals bioaccumulate. The exposure pathways begin with PCBs present in the sediment and porewater, as well as chemicals present in the overlying water. Passive samplers can provide insight on how best to reduce exposure of biota to chemicals. Geochemical mechanisms that increase partition constants (reduce porewater concentrations) also reduce exposure from direct ingestion of sediment. These pieces of information can be used together with measures of chemicals in fish tissue to build site-specific food-web models that are properly calibrated to the system.

2.4 CAN PASSIVE SAMPLERS BE USED AT ANY STAGE OF THE REMEDIAL INVESTIGATION, FEASIBILITY STUDY, OR REMEDIATION PROCESS?

The short answer is "Yes." Passive samplers can be used at any stage of the remedial investigation (RI), feasibility study (FS), remediation, or long-term monitoring processes. As with all sampling methods, the value of using passive samplers will depend on the questions posed and the utility of the method to answer those questions. The following information is based on discussions with regulatory personnel at the USEPA, Navy, and other practitioners. An overview of potential uses of passive samplers for risk management that includes present as well as future considerations is provided in Greenburg et al. (2014). Here, we provide DOD RPMs with insight into using passive samplers at various stages of the RI/FS process under the current regulatory environment. Case studies are provided in the Appendix.

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3.0 GUIDANCE FOR ASSESSING AND MANAGING CONTAMINATED SEDIMENTS

To be of value, passive sampling methods must be integrated into existing approaches. This is already occurring at many sites, but it is helpful to identify a few approaches and frameworks that are useful for the RI/FS process. USEPA (2005) set out a framework for managing contaminated-sediment sites that recognized the various alternatives that might be employed and the conditions under which they best apply. The *Implementation Guide for Assessing and Managing Contaminated Sediment at Navy Facilities* (Space and Naval Warfare System Command [SPAWAR] Systems Center and Battelle 2005) describes elements that are common to most sediment evaluation and remediation programs for DOD sites. Although approaches may vary among regions, the outline provided in Figure 1 is an example of an approach that is relevant to most DOD sites. This approach is supported by a variety of guidance documents identified in Table 1.

Over the past decade, numerous advances were made in measuring exposure concentrations using passive samplers, understanding chemical bioavailability as an aspect of exposure, and remediating sediments through technologies other than excavation and/or dredging. The Interstate Technology and Regulatory Council (ITRC) recently published guidance that summarizes the range of possibilities for use of passive samplers (ITRC 2011, 2014). USEPA also issued guidelines on the use of passive samplers for monitoring organic contaminants at Superfund sites. The guidance developed by ITRC and the guidelines issued by USEPA are consistent with USEPA and DOD principles for site remediation; they also provide a useful platform for considering whether and how to integrate passive sampling methods into site investigation and remediation. Aspects of these documents are highlighted in the following sections.

3.1 REMEDIAL INVESTIGATION

The measurements obtained using passive samplers can be used within remedial investigations to evaluate contaminant sources, chemical transport processes, and exposures to contaminants in water, and for parameterizing food-web models involving wildlife, fish, and humans. With regard to the latter, data generated using passive samplers offer an advantage over the traditional parameterization of food-web models based on bulk chemical measurements and apparent empirical bioaccumulation relationships (e.g., biota-sediment accumulation factors) that may not accurately reflect site-specific mechanistic relationships.

Data obtained from passive samplers can be used to refine conceptual site models (CSMs). These are a standard element of most remedial investigations that is used to provide a blueprint for consideration of important exposure pathways that may be the focus of risk assessment and remediation. The sediment CSM is shown in Figure 2 and provides an example of the use of passive samplers to enhance understanding of various routes of exposure in a sediment CSM.

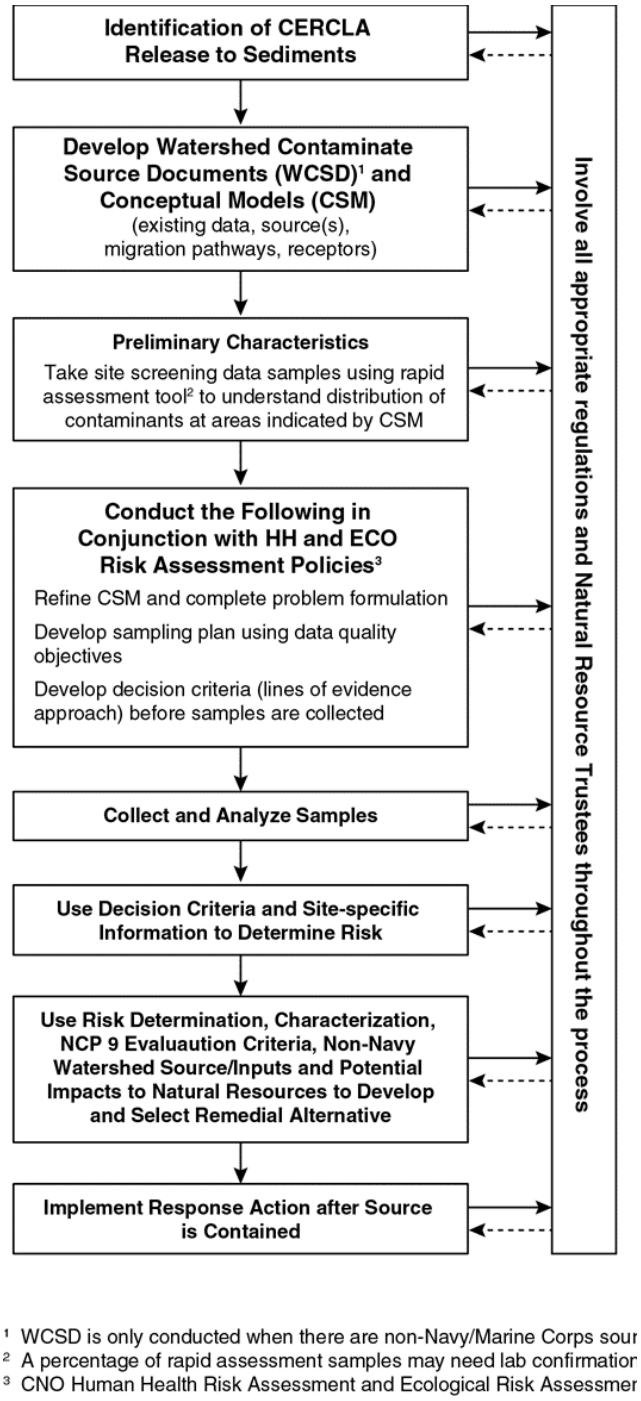

Figure 1. Navy IR Sediments Framework (SPAWAR Systems Center and Battelle 2005)

Passive samplers could be used in almost all stages of the framework.

Table 1. Guidance Documents Relied Upon to Investigate and Manage Contaminated Sediments at Navy Sites (SPAWAR Systems Center and Battelle 2005)

Guidance Document	URL
Navy Policy on Sediment Site Investigation and Response Action (CNO 2002)	http://enviro.nfesc.navy.mil/erb/erb_a/regs_and_policy/don_policy_sediment.pdf
Navy Policy for Conducting Ecological Risk Assessments (CNO 1999)	http://enviro.nfesc.navy.mil/erb/erb_a/regs_and_policy/cno-era-policy.pdf
Navy Guidance for Ecological Risk Assessment	http://web.ead.anl.gov/ecorisk/
Navy Policy for Conducting Human Health Risk Assessments (CNO 2001)	http://enviro.nfesc.navy.mil/erb/erb_a/regs_and_policy/HRA policy.pdf
Navy Guidance for Human Health Risk Assessment	http://www-nehc.med.navy.mil/hhra/
Navy Interim Final Policy on the Use of Background Chemical Levels (CNO 2000)	http://enviro.nfesc.navy.mil/erb/erb_a/regs_and_policy/don-background-pol.pdf
EPA General Superfund Web Site	http://www.epa.gov/oerrpage/superfund/index.htm http://www.epa.gov/oerrpage/superfund/whatissf/sfproces/ (index of Superfund document chapters)
EPA Guidance for Human Health and Ecological Risk Assessments (USEPA 1989, 1998)	http://www.epa.gov/superfund/programs/risk/tooltrad.htm#gp
EPA Guidance for Conducting the RI/FS under CERCLA (USEPA 1988)	http://www.epa.gov/oerrpage/superfund/whatissf/sfproces/rifs.htm
Principles for Managing Contaminated Sediment Risks at Hazardous Waste Sites (USEPA OSWER Directive 9285.6-08, February 12, 2002)	http://www.epa.gov/superfund/resources/remedy/pdf/92-85608.pdf

Chief of Naval Operations (CNO)
Office of Solid Waste and Emergency Response (OSWER)

While data collected with passive samplers can be used to support site risk assessments, experience with using passive samplers as the basis for expressing clean-up target levels is currently limited, as is experience among regulators for defining clean-up actions in terms of concentrations determined via passive samplers. Instead, regulators prefer to see clean-up levels expressed in terms of contaminant concentrations in the bulk sediment. The current hesitation to use passive sampling measurements directly is largely due to lack of familiarity with and confidence in the information, and greater familiarity with measurements based directly on concentrations in sediment or surface water. To overcome this obstacle, some sites have combined passive sampler data and bulk sediment data, along with organic carbon data, to establish a relationship between porewater concentrations and bulk sediment concentrations. If and when such a relationship is developed with a reasonable degree of confidence, passive samplers can be used to more accurately characterize risk, while bulk sediment concentrations can be used to delineate sediment management areas for remediation. This approach can be costly, because the amount of sampling and analysis increases, and it requires an understanding of the composition of chemical constituents in sediment, geochemical conditions, and the types of organic carbon that influence partitioning behavior between sediment organic matter and porewater.

Experience: United Heckathorn

To understand and characterize recontamination by DDT, passive samplers are being used to measure sediment porewater concentrations, as well as water concentrations immediately above the sediments. This project emphasized the DQO process and how data quality can be impacted by planning and execution of good deployment and retrieval techniques (or lack thereof), because the use of passive samplers is relatively new. For example, ensuring adequate *in situ* time for samples ensures higher likelihood of equilibrium being reached, for performance reference compounds to better enhance data quality. Further information is on the website. *Rachelle Thompson, USEPA RPM; Alan Humphrey USEPA, Environmental Response Team Dive Unit (QA and deployment expertise)*

3.2 SELECTION AND IMPLEMENTATION OF REMEDIAL ALTERNATIVES

A number of activities occur during a feasibility study for which passive samplers can provide useful information. In particular, if the feasibility study uses pilot studies to evaluate the efficacy of capping, enhanced natural recovery, or *in situ* treatment, passive samplers can be used to monitor the performance of these technologies at the scale of the pilot study. It is important to realize that because pilot studies usually involve a small portion of the contaminated area, methods that examine exposures within the area of the pilot study can be especially useful for evaluating the relative performance of these alternatives. Passive sampling can also be a key environmental baseline gauge to pair with fish tissue levels, as a point of reference for comparison once remediation is complete.

The ITRC (2014) guidance document on remediation of contaminated sediments offers an approach that explicitly includes the full range of remedial alternatives, from monitored natural recovery through dredging (Figure 3). The investigations and evaluations of these alternatives depend primarily on their relative efficacy for reducing exposure. This requires understanding how contaminants in sediments influence water concentrations within the sediments, in the overlying

water, and in biota. Passive samplers provide one method by which these freely dissolved water concentrations can be measured. The ITRC (2014) identifies passive samplers for use in site characterization, evaluation of groundwater-to-surface-water pathways, and monitoring of treatment efficacy in pilot studies and following implementation of remedial alternatives.

The ITRC (2014) guidance is new but appears to be consistent with emerging DOD policy. A recent Department of the Navy policy memorandum (U.S. Navy 2012) stressed the use of green and sustainable methods during the remediation process. The document stressed application during the site characterization, remedy evaluation and selection, construction, and long-term management phases. Reducing the remedial footprint is a goal of the policy.

The ITRC flow chart (Figure 2) is used to illustrate where passive samplers could be used to answer specific questions.

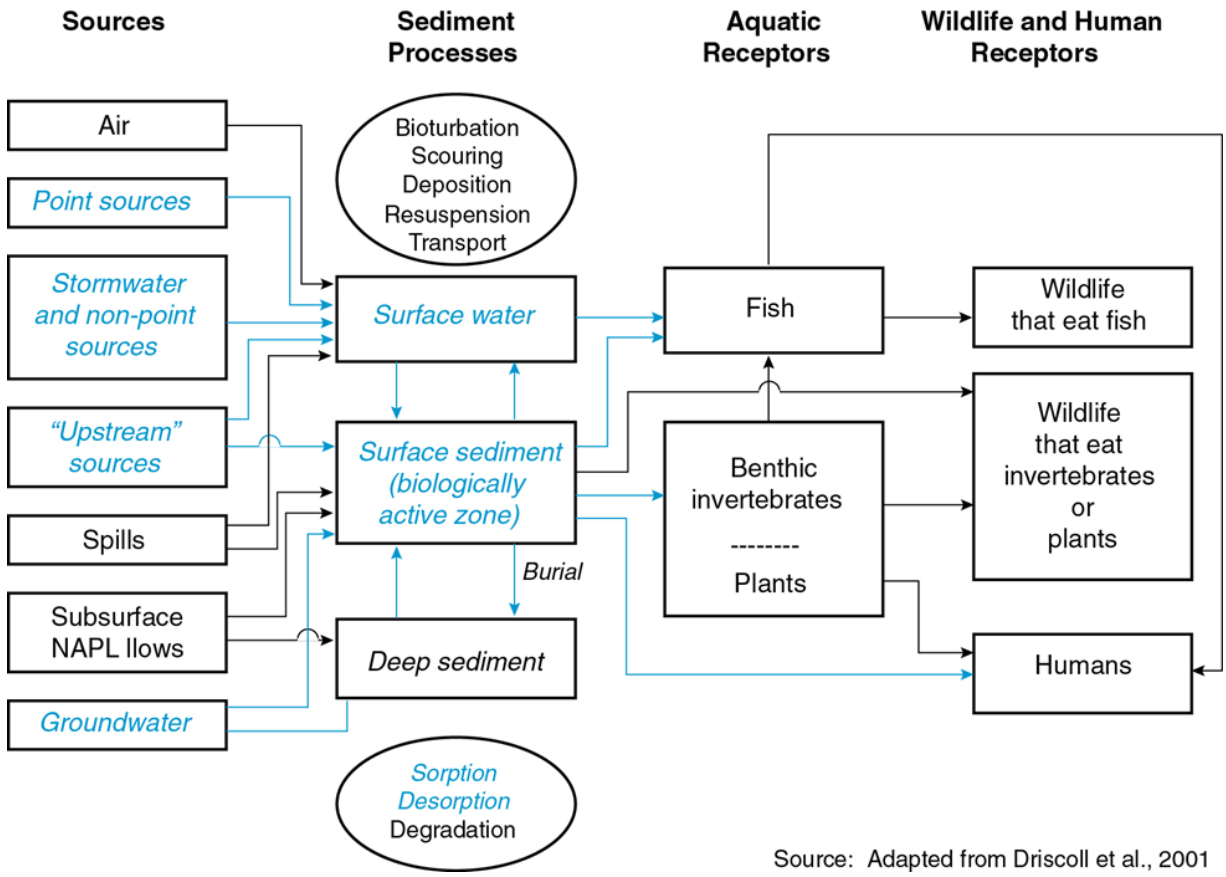

Figure 2. Conceptual Model of Most Common Sources, Compartments, and Processes Related to Contaminants in Sediments Text

Arrows and text highlighted in blue are conditions for which passive samplers can provide useful information.

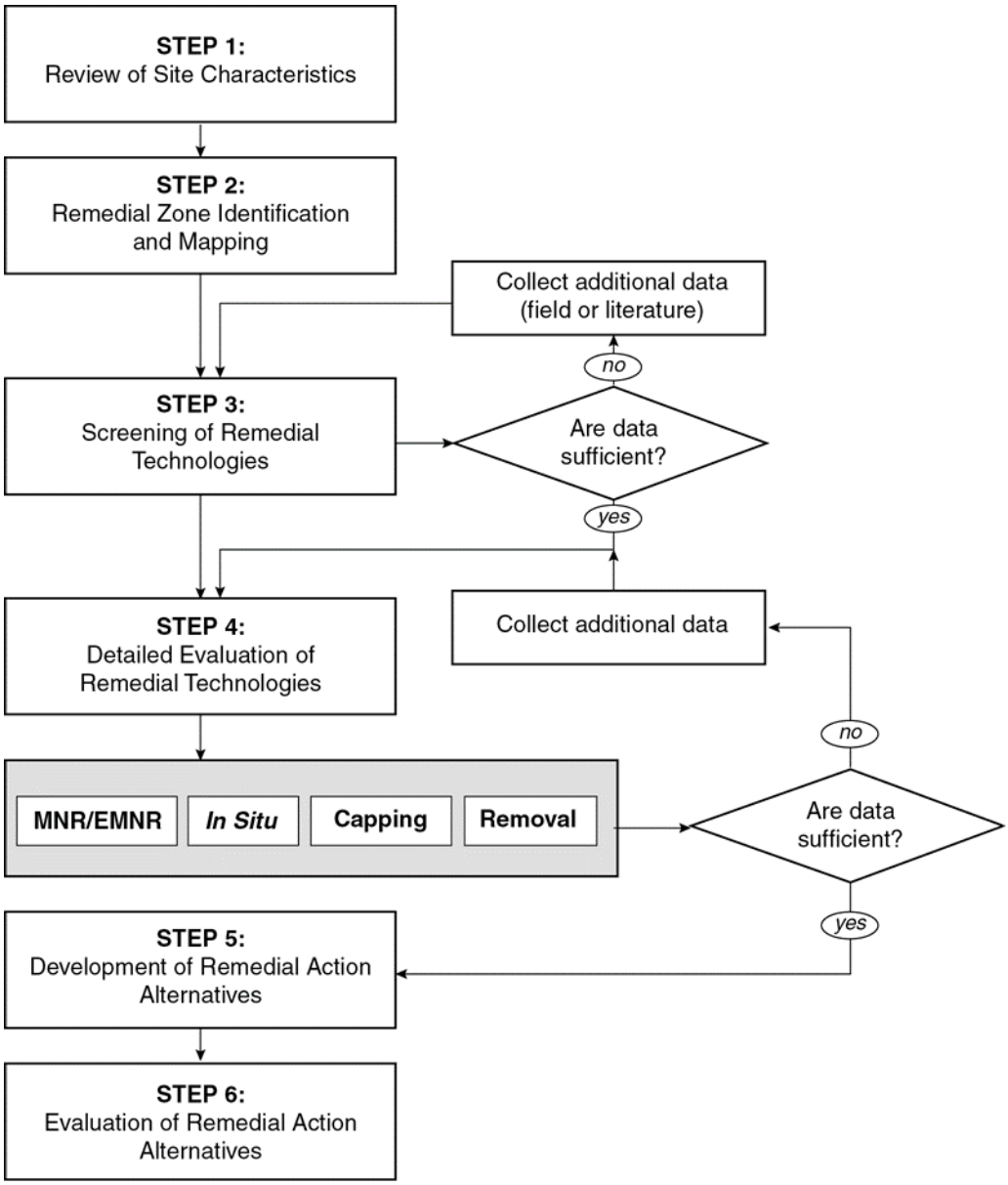

Figure 3. Decision Matrix Flow Chart for Selecting among Remedial Alternatives (ITRC 2014)

The flow chart includes several remedial technologies for which passive sampling methods would be particularly valuable.

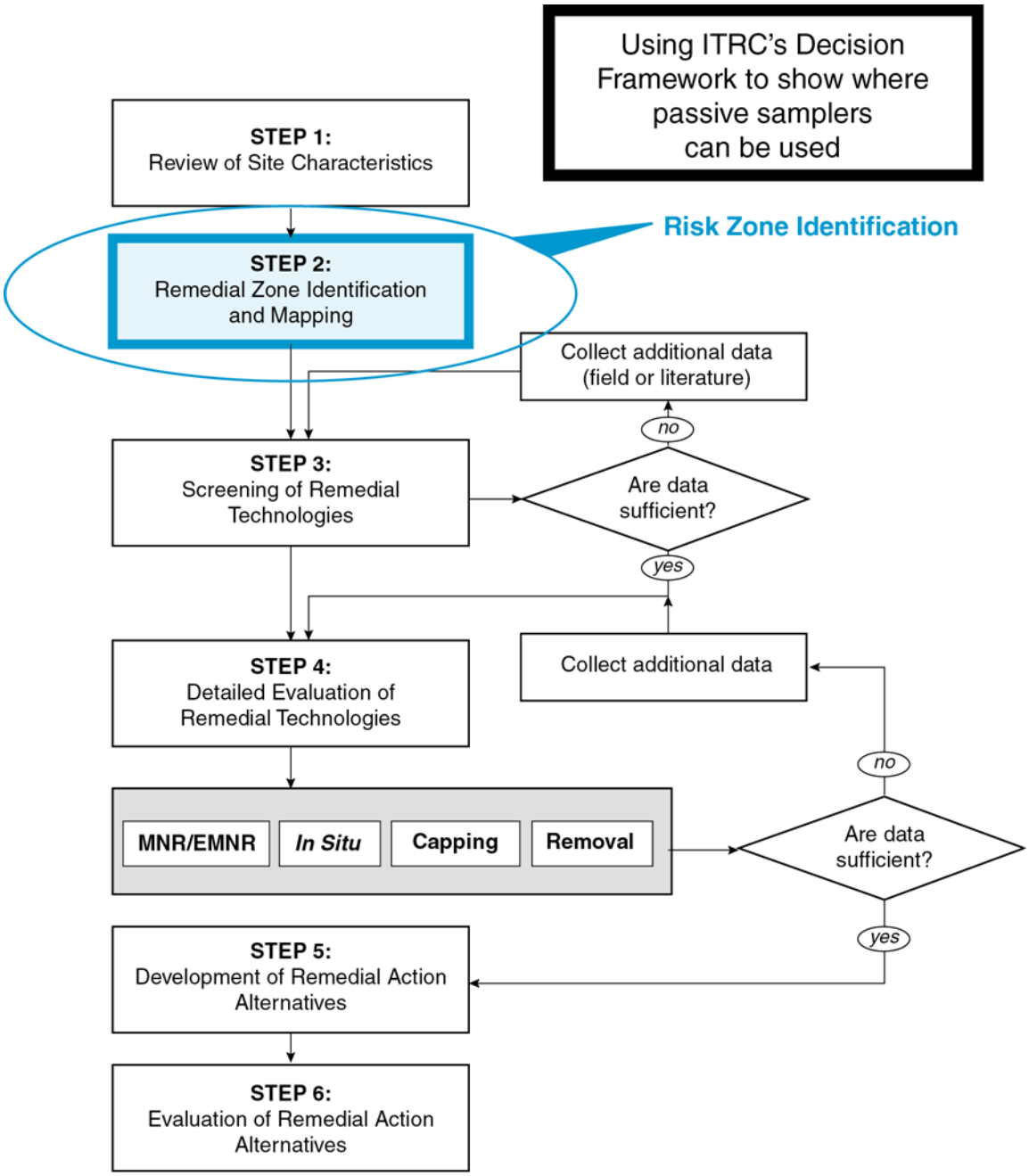

Figure 4. ITRC Decision Framework

Early in the assessment process, passive samplers can be used to help delineate risk zones that reflect various magnitudes of exposure associated with the amounts of freely dissolved contaminants present in sediments. These can be defined in various ways depending on state and federal jurisdictions but, in general, refer to a gradient from negligible to high levels of exposure that may warrant different types of remedial strategies.

3.2.1 Risk Zone Delineation

The delineation of risk zones is a critical part of characterizing the scale and magnitude of exposure associated with chemicals in sediments. An example of a risk-zone map (Figure 5) is shown below for a site on a river.

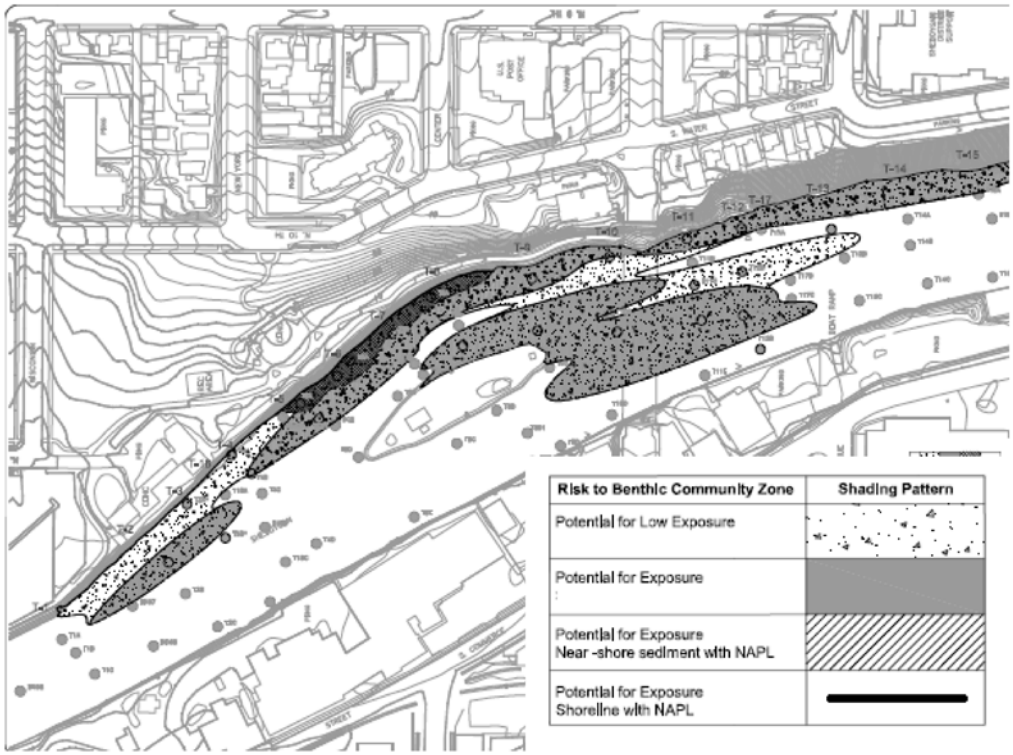

Figure 5. Map of Risk Zones

The terminology for such zones can vary depending on the regulatory program and agreements among parties on how to communicate about exposure and risk.

The primary concept behind establishing risk zones is to delineate areas and sediment volumes that represent different degrees of exposure and other characteristics that bear on the selection of remedial actions. Therefore, rather than having a black-and-white determination (risk vs. no risk), the delineation of a gradient of risk zones provides better insight into which remedial measures are most appropriate for different portions of the site. The map can be developed using a variety of methods. However, passive sampler measurements of freely dissolved chemicals of concern (COCs) can be used to help delineate these various exposure zones. Maps of risk zones serve as input to evaluating remedial alternatives. An example of a remedial alternative based on the map of risk zones is shown in Figure 6.

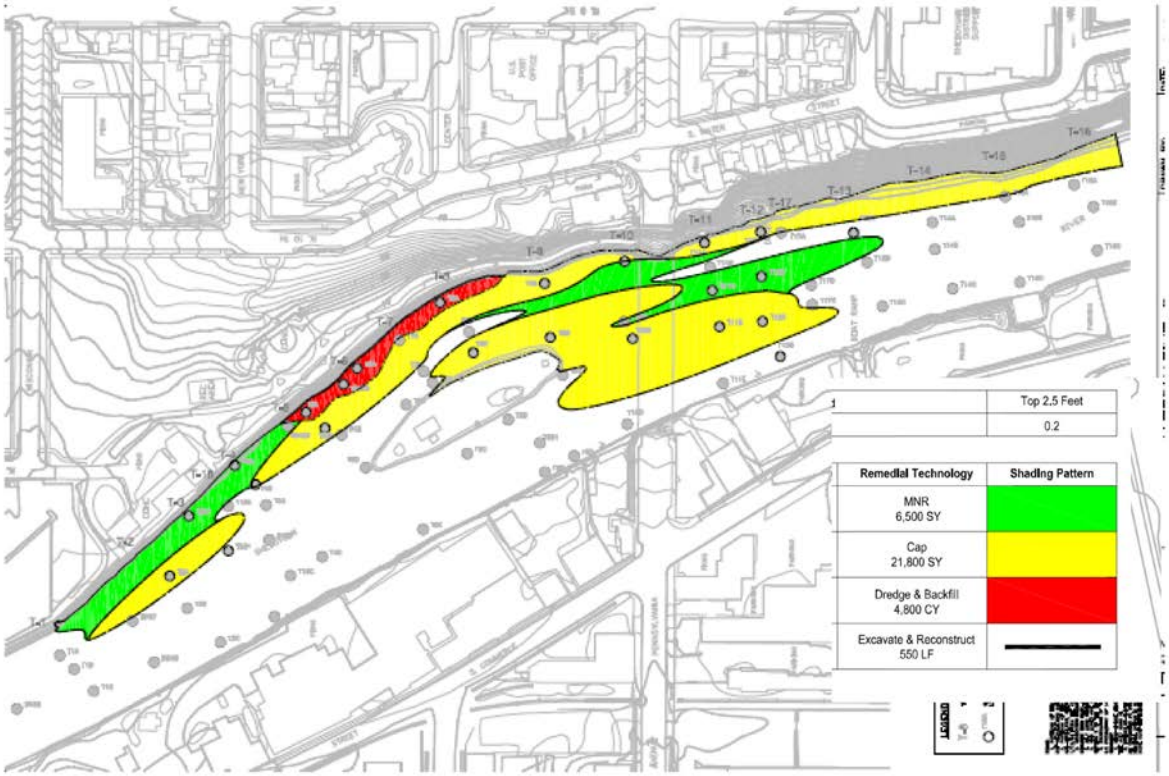

Figure 6. An Example of a Remedial Alternative Developed from a Map of Risk Zones
Passive samplers can be used to obtain the data needed to develop such maps and can be used along with other site data to determine which alternatives are most appropriate for particular zones.

3.2.2 Monitoring Remedy Efficacy

After decisions have made about the selection of remedial alternatives, consideration needs to be given to monitoring the efficacy of that remediation. Passive samplers can be useful for this purpose. Consider, for example, monitoring the effectiveness of a cap, as illustrated in the ITRC flowchart (Figure 7).

Passive samplers are already being used to monitor capping efficacy for both freshwater (e.g., Great Lakes and rivers) and marine coastal environments. One of the more common methods is to insert probes containing passive samplers down through the capping material (Figure 8). These probes are designed to provide a vertical profile of the freely dissolved chemical of concern beneath, within, and above the cap.

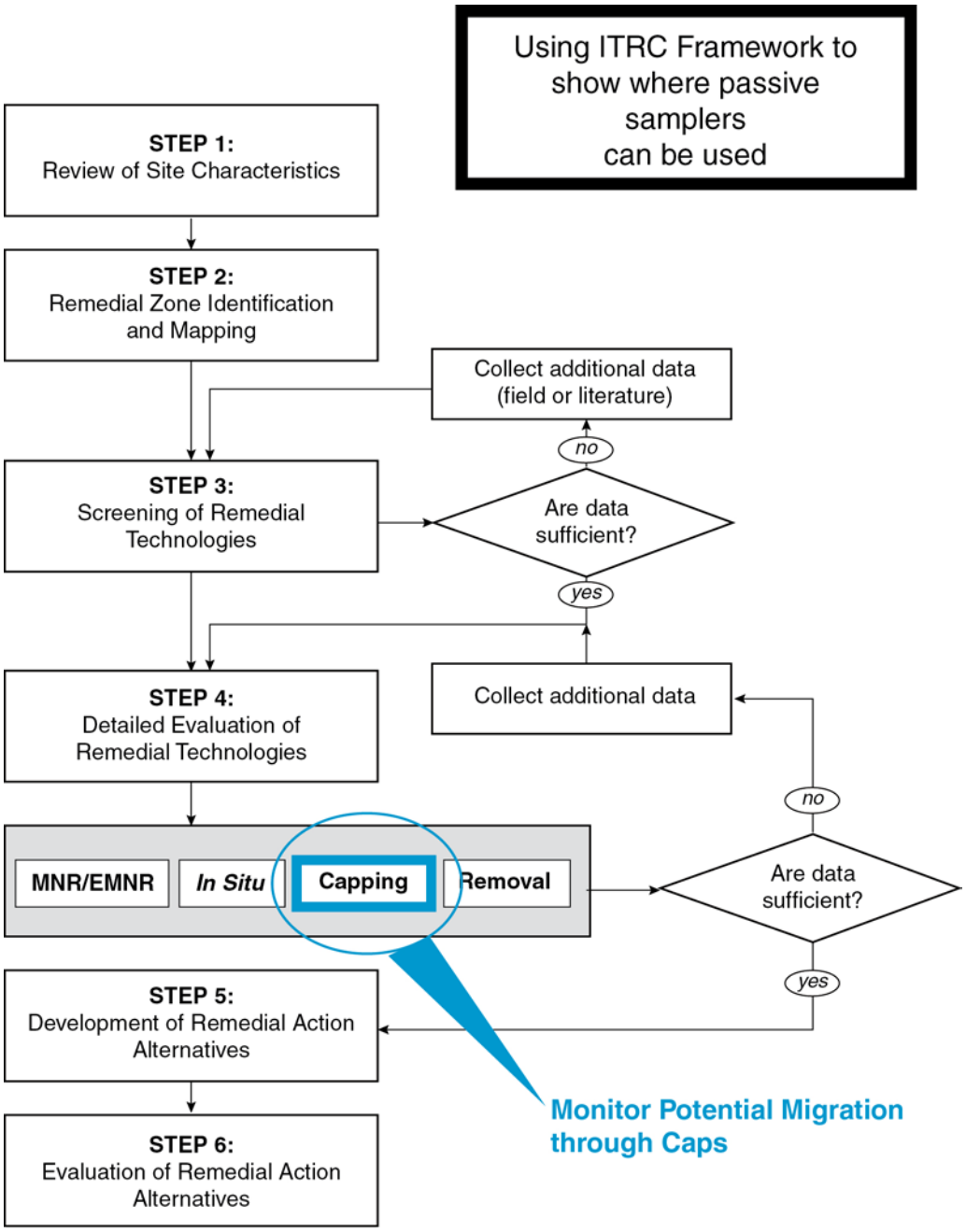

Figure 7. Illustration of where in the Remedial Planning Process Passive Samplers would be Considered for Monitoring the Efficacy of Capping

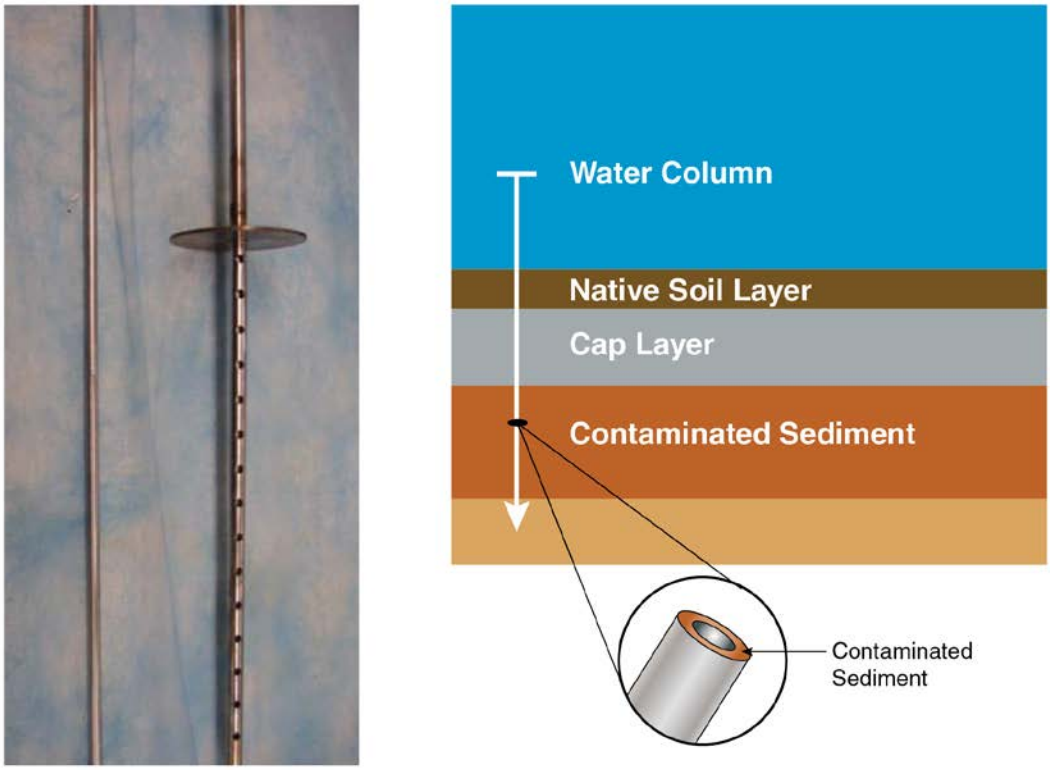

Figure 8. Passive Sampling Probe Used to Monitor Conditions Within and Below a Cap
The passive sampler is located within the device, and the ports along the side of the device allow porewater within the sediment to come into contact with the passive sampler material. Hydrophobic organic chemicals such as PCBs and PAHs that are dissolved in that water are sorbed by the passive sampler. Analyses of discrete lengths (pieces) of the passive sampler provide information on whether contaminants are migrating up into the cap from below. Pictures are courtesy of Danny Reible.

Passive samplers can also be used to monitor changes in exposure resulting from monitored natural recovery (MNR), enhanced monitored natural recovery (EMNR), and *in situ* treatment, as indicated in the ITRC flowchart. In all these cases, the relevant exposure metric is the freely dissolved contaminant in the sediments and/or in the water column. Passive samplers can be inserted into the sediment to help measure the distribution of these contaminants from above the sediment-water interface down into the sediment (Figure 9). These vertical profiles can be evaluated over time to determine the changes in exposure.

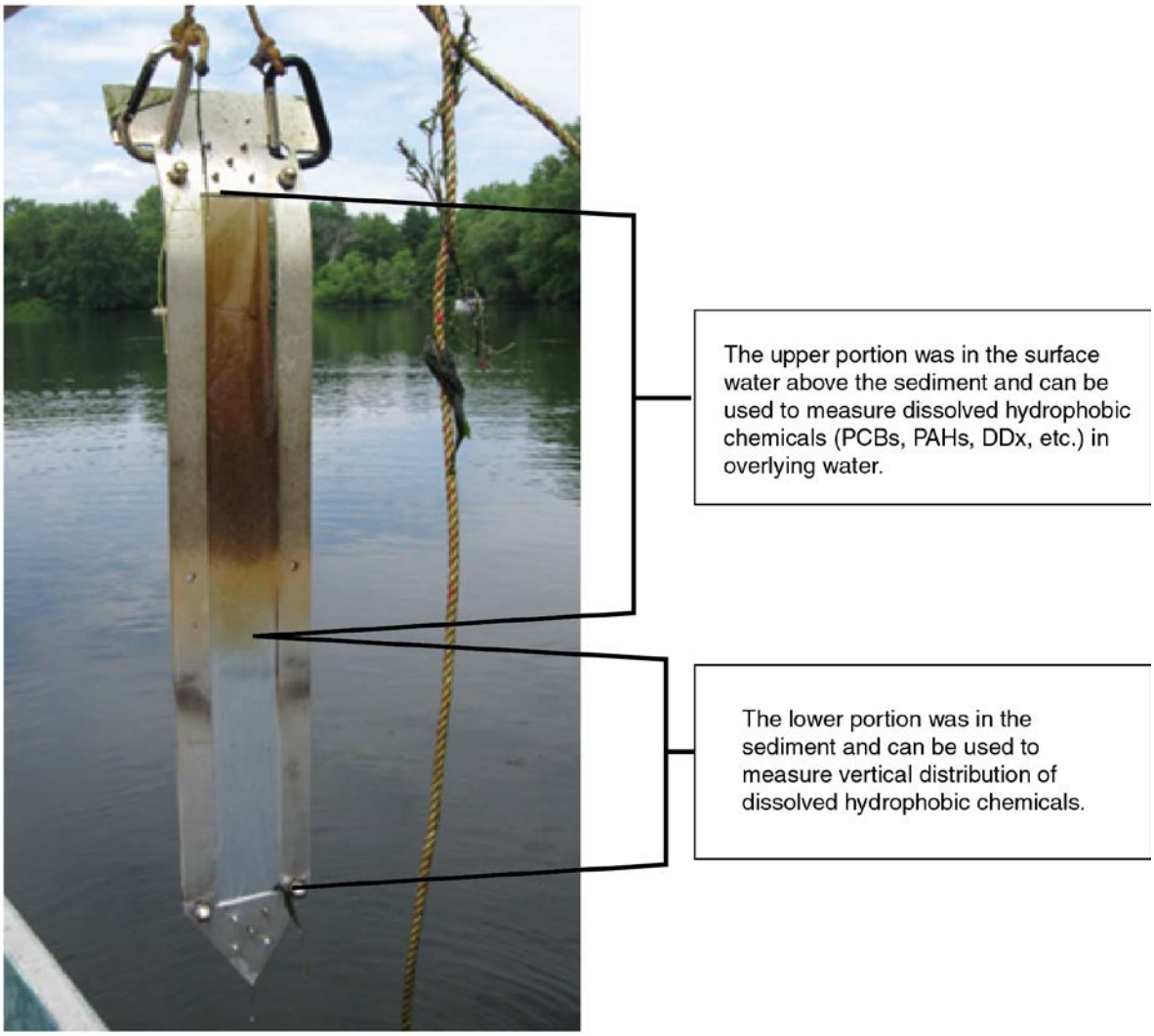

Figure 9. Passive Sampler Retrieved from a Deployment in the Sediment

Discriminating between freely dissolved chemicals in sediments and bulk chemicals in sediments is especially important for evaluating the efficacy of *in situ* treatments that act to bind or degrade the freely dissolved chemicals. Measures of the freely dissolved chemicals are essential for evaluating the efficacy of these methods, and passive samplers can meet that need. Results from a location receiving *in situ* treatment of PCBs by activated carbon are shown in Figure 10 as an example of using a passive sampler to evaluate efficacy.

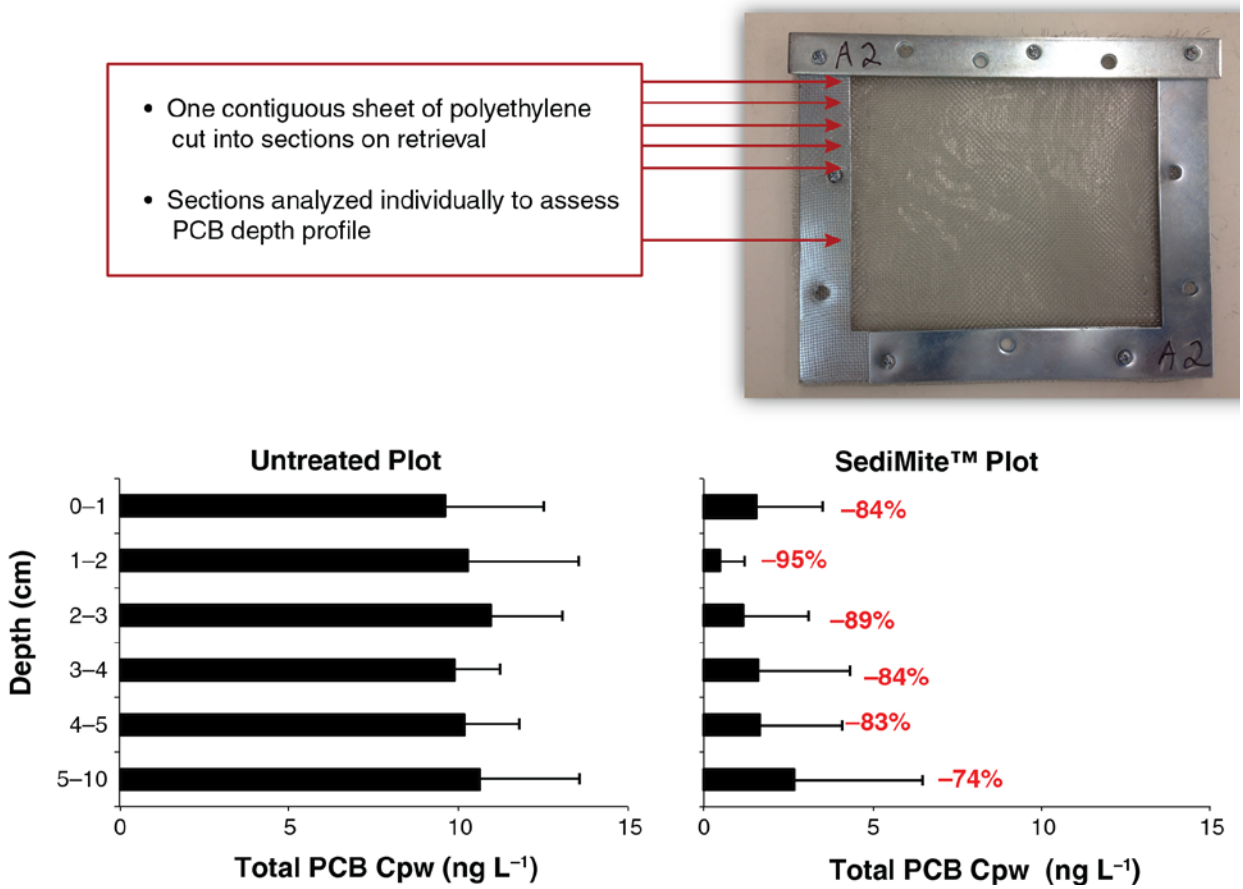

Figure 10. Results from a Study of *in situ* Treatment of PCBs by Activated Carbon

Passive samplers were inserted vertically into the sediment in treated and untreated plots. The vertical distributions of PCBs in sediment porewater can be determined by analyzing vertical sections of the passive sampler. The results serve as a basis for comparing the exposure levels in the treated plot to those in the untreated plot, and this is one basis for judging efficacy. Photo and graphics are from Sanders et al. (2015).

USEPA developed a Superfund Remedial Program Review Action Plan (USEPA 2013) that stresses measures to increase the effectiveness of remedial actions and increase efficiencies in program management. The remedial process actions include discussions on adaptive management, site assessment, remedial design and action, and design and construction phases. New policies, innovative tools, and efficient, cost-effective solutions are constant issues for DOD RPMs to evaluate as they manage their sites.

Complex challenges occur during the remedial process for contaminated-sediment sites. These challenges are discussed in key federal government documents, such as the USEPA contaminated sediment remediation guidance (USEPA 2005) and the U.S. Navy guidance for assessing and managing contaminated sediments at naval facilities (U.S. Navy 2005). For sediment sites, site characterization, exposure pathways, bioavailability of contaminants, monitoring of COCs, remedy selection, and effectiveness of remedial actions are of particular concern due to physical shifts in the sediment and subsequent distribution of COCs, sediment chemistry influencing COC bioavailability, bioaccumulation of COCs, and sensitive analytical methods to measure hydrophobic chemicals in the overlying water column. Once the remedy has been implemented and source control ensured, long-term monitoring will assess the effectiveness of the remedy. The increased emphasis on green remediation methods often involves *in situ* methods or monitored natural recovery as part of a step-wise remediation process. To address these issues, USEPA and U.S. Navy have published technical documents and guidance documents to provide further details on the technical area and procedures to address a given topic. USEPA has published sediment assessment and management documents (SAMs) to address focused topics such as using fish-tissue data and passive samplers to produce data for use in models to assess remedy effectiveness (USEPA 2008, 2009, 2012a).

Experience: Pilot Studies

Passive samplers made from POM have been used successfully in the field and/or with cores taken to the laboratory to monitor efficacy of *in-situ* remediation of PCBs with activated carbon delivered via SediMite at Fort Eustis (VA), Aberdeen Proving Ground (MD), and Berrys Creek (NJ). *Upal Ghosh, Sediment Solutions and UMBC*

Passive samplers are an innovative method to provide DOD RPMs and their technical advisors with data for sensitive targeted hydrophobic chemicals, to support decision making. USEPA (USEPA 2012a) published a guidance document on the use of passive samplers in monitoring contaminants at Superfund sites. The document stresses that passive samplers enable measurement of freely dissolved hydrophobic chemicals (e.g., PCBs) in the water column and in sediment porewater. The USEPA document provides information on the selection of PSMs, quality control and analytical methods, and application of data to management decisions.

In the field of passive sampling during and after remediation, some applications are ready for federal SOPs, some have been used at specific sites (but are still in development), and some are still active research topics. Table 2 reflects the state of the practice in the use of passive samplers in the remediation process; the information contained in the table is gleaned from discussions with DOD and EPA RPMs and USEPA scientists, and the recent special series publications on PSMs (Parkerton and Maruya 2014; Greenberg et al. 2014; Ghosh et al. 2014). As can be seen, the samplers are currently being used for assessment and monitoring. While it is conceivable that passive samplers may be used to help support the derivation and application of “clean-up levels,” experience in using them for that purpose is currently more limited.

Table 2. Passive Sampler Application in Each Step of the Contaminated Sediment Remediation Process*

Remediation Process	PSM Ready for SOPs to guide DOD RPMs	PSM Used in case studies, site specific projects	Current Research Area	Barriers
Preliminary Assessment/ investigation		Source identification		
RI/FS				
Site Characterization	Source identification/ Prioritization; nature and extent of COCs	Source identification; concentration gradients and phase distributions	Spatial and temporal distribution, forensic interpretations of PSM for source attribution	
Risk Assessment				
- Exposure	Groundwater-Surface Water sources, Contaminated Sediments as a source to overlying water Transport (i.e., direction of flux, gradients)	Correlate with pore water; Correlate to SW; calibrating site-specific models,	Correlate with pore water to macrobenthos, fish tissue; bioavailability	Communication to DOD RPMs and stakeholders regarding use of the data for Remedial Objectives
- Effects	Benthic organism bioaccumulation PAH narcosis toxicity to benthic invertebrates	Sed Toxicity Tiers Tier 1 ESBs Tier 2 PSMs Tier 3 Toxicity Testing	Use of exposed PSs for dosing in toxicity testing	Characterizing the mixtures of contaminants (targeted and unknown) and impact on toxicity
- Risk Characterization	Weight of Evidence	Weight of Evidence		Fish tissue is the standard; linkage to criteria used by DOD RPM; comm. Success stories
Early action	Monitoring of the efficacy of early action			Have been used to evaluate recontamination
Treatability studies	Monitoring of treatability studies		Comparison of alternative PS methods in parallel to standard approaches	

Remediation Process	PSM Ready for SOPs to guide DOD RPMs	PSM Used in case studies, site specific projects	Current Research Area	Barriers
Development of alternative technologies			Reactive cap performance	
Analysis of alternatives	Monitoring of treatments			
Green remediation	Monitor effectiveness on in-situ treatments, e.g. capping and MNR	Monitor effectiveness on in-situ treatments, e.g. capping and MNR		
Remedy selection				
Record of Decision	Long term monitoring for remedy performance	Confirmation sampling of remedy performance and source control		
Remedy Implementation			Assist to delineate sediment contamination, risk of remedy (pulse of contaminants during remedy)	Communication with RPMs on how data can be used to specifically calibrate cap, dredge/cap design.
Long Term Oversight & Monitoring	Remedy effectiveness: cap integrity, MNR; Source control	Remedy effectiveness: cap integrity, MNR; Source control, new source discovery	Determine spatial and temporal coverages to characterize performance, restoration metrics	

*Greenberg et al. 2014; Ghosh et al. 2014; M. Mills, personal communication, May 2014

3.3 CAN PASSIVE SAMPLERS BE USEFUL IF DATA FOR REMEDIAL INVESTIGATIONS HAVE BEEN COLLECTED USING OTHER METHODS?

The answer to this question is yes. However, to combine all the data, it may be necessary to develop relationships among data sets. Remedial investigations have been under way or completed at many DOD sites. Where PCBs have been contaminants of concern, the investigations have often involved analyses of PCBs as Aroclors®, the product name for PCBs. However, nearly always, passive sampling requires analysis to be performed at the congener level. For such sites, a DOD

Experience

The East Eagle Harbor cap and monitored natural recovery areas are good examples of passive sampling applications conducted after the remedies have been decided and implemented. The areas were monitored to evaluate contaminant influx either from the covered NAPLs at that former creosote site, or whether the PAHs were coming from offsite sources. *Timothy Thompson, Science and Engineering for the Environment, Danny Reible, Texas Tech University, Region 10 Dive Unit (Sean Sheldrake)*

RPM who has acquired a data set based on one type of analytical procedure would be justifiably concerned about changing or incorporating different analytical methods because of the concern about incompatible data sets. This section of the report provides DOD RPMs with some insights into the value of using passive samplers and measuring congeners at later stages in the RI\FS process, even though earlier data were obtained using Aroclor analysis.

As discussed earlier, passive samplers can be employed for a variety of purposes at contaminated-sediment sites. For a site where the data are compiled as Aroclors, the decision to use passive samplers and congeners is usually driven by a desire to obtain greater insight into a particular process or exposure. The passive sampler data can stand alone and focus on particular questions, or they can be integrated with other site data as described below.

At sites where bulk sediments have been used to characterize sediments, questions may remain about sources, food-web transfers of chemicals, bioavailability, and the efficacy of alternative remedial solutions. Some of those questions can be answered more effectively by using passive samplers instead of or in addition to the traditional methods used to that point in the remedial investigation.

Another good example of where passive samplers might provide insights later in the RI/FS process is in evaluating the relative effectiveness of remedial alternatives. A common example of this application involves the use of passive samplers to evaluate the efficacy of MNR, EMNR, capping, and *in situ* remediation. For these alternatives, the primary interest is in comparing relative reductions in freely dissolved hydrophobic chemicals within the sediments over space and time. Passive samplers can provide the type of time-integrated and spatial coverage that may be especially useful for addressing those questions. This is particularly relevant to remediation methods that do not change the bulk chemistry concentration but do affect chemical bioavailability. The use of activated carbon, for example, has been shown to reduce bioavailability by one to two orders of magnitude, while having a negligible impact on bulk sediment concentrations. This is because activated carbon relies on increasing the black-carbon content in surface sediments, but it does not rely on substantially decreasing the bulk sediment chemical concentration. MNR is another *in situ* method that relies on natural processes to reduce surface sediment exposures over time—in the case of MNR, a reduction in bioavailability is a better metric of success than a reduction in bulk sediment concentrations, although the two processes are likely to be well correlated.

Perhaps one of the more challenging applications for passive samplers involves monitoring the efficacy of a completed remediation project. This stage of work occurs near the end of the process but is one of the most beneficial applications of passive samplers, even when earlier RI/FS work involved other methods. In particular, beyond the mass reduction in surface-weighted area concentrations (SWACs) that are part of most sediment remediation projects, there may be interest in evaluating how well the remediation has reduced exposure to fish and other ecological and human receptors. While measuring tissue levels in fish may be the most apparent approach for judging the efficacy of remediation, fish monitoring programs can be challenging in some circumstances. For example, fish often swim around and move in and out of areas of exposure, and there may be times when fish are simply unavailable in adequate numbers or sizes to perform monitoring that yields samples of comparable quality. Fish also may require years to depurate (i.e., release) chemicals from their bodies, whereas passive samplers can measure changes in real time. In such cases, a passive sampler can provide insight into the relative reduction in exposure that occurs as a result of the remediation. The devices can be deployed over various areas and at all times of the year. This provides a very useful and consistent way of judging changes in exposure with time and space. Monitoring media and biota could still be part of such a program, but interpretation of efficacy would be greatly informed by inclusion of a standard method that integrates exposure over time and space (i.e., a passive sampler).

Experience: Great Lakes

At sites in the Great Lakes, passive samplers have been used for source identification and tracking. This work has involved placing passive samplers in the water column, sediments, and in piezometers. They provide data that can be used to determine whether chemicals are migrating through caps, and information on recontamination from uncontrolled sources. *Marc Mills, USEPA*

In summary, passive samplers and associated analytical methods can complement a remediation program that has been historically carried out using a different analytical program. Passive samplers can provide the DOD RPM with important insights into the selection of remedial measures beyond what would be possible with sole reliance on bulk chemistry data generated with traditional methods. That insight pertains to the premise that risk and risk management for certain groups of compounds is governed by the bioavailable fraction, and that passive samplers provide better and more reliable information on that fraction than can be obtained from conventional bulk chemical analytical methods. As described later, building simple empirical relationships among different types of data sets is straightforward.

3.4 HOW IMPORTANT ARE DATA QUALITY OBJECTIVES AND THE QUALITY ASSURANCE PROCESS FOR INCORPORATING PASSIVE SAMPLING INTO YOUR PROGRAM?

Data quality objectives (DQOs) are critical to the success of any remedial program involving contaminated sediment. Because the use of passive samplers is relatively new, it is especially important that DQOs be developed that account for the many aspects related to the design, implementation, and analysis of passive sampling methods. Several documents are already

available that can guide the DQO process. USEPA published an overview document that provides users with the conceptual framework for why and how to use passive samplers (USEPA 2012a). SERDP/ESTCP/EPA (201X) has prepared a user's manual that incorporates a number of SOPs for use with passive samplers. Also, technical papers have recently been published that convey the findings of the Society of Environmental Toxicology and Chemistry (SETAC) Pellston Conference on passive sampling November 2012 in Costa Mesa, California, USA. Collectively, these publications provide useful starting points for developing DQOs and preparing a quality assurance plan. DQOs, as they relate to the analytical methods, are described in SERDP/ESCTP/EPA (201X).

Experience: DQOs

RPMs from USEPA were interviewed as part of developing this guidance. The overwhelming recommendation was that the use of passive samplers needs to be supported by a clear DQO process.

There are several considerations particular to the use of passive samplers, and these should be captured within the DQO process. The first, of course, relates to understanding the purpose of using passive samplers for a particular project. The purpose(s) can be captured in a series of questions. Examples include:

- What are the sources of exposure to fish and other water-column organisms?
- What is the relationship between porewater exposure levels of the chemical(s) of interest and biological effects or risk?
- Which passive sampling methods can be used to measure porewater concentrations before and after remediation?
- What is the effectiveness of a remedy for reducing porewater and surface-water exposures?

USEPA established guidance for the DQO process (USEPA 2006). The DQO process can also be guided by existing DQO documents prepared for sites at which passive sampling devices have been used.

Because of the importance of the DQO process for the successful conduct of sampling with passive samplers, it is recommended that an expert review the quality assurance assessment program (QAPP) documents and work plans and the DOD RPM, and that contracting staff understand these documents.

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4.0 WHAT DO I NEED TO KNOW ABOUT SAMPLE COLLECTION AND PROCESSING?

There are two major things to be aware of with respect to sample collection and processing. The first concerns the design of the collection process, and the second concerns the subject of *in situ* versus *ex situ* samples.

4.1 DESIGNING A SAMPLING PROGRAM

Designing a sampling program with passive samplers is no different from sampling design using more familiar techniques. The various types of passive samplers described by SERDP/ESTCP/ EPA (201X) include devices with different shapes and dimensions, ranging from probes to larger flat sheets. The physical features of the sampling devices influence the degree to which they characterize the local environmental regime into which they are placed. The narrow probe is inserted into the sediment, where it responds to chemicals that are present in the immediate area around the probe. The flat sheet, however, can respond to a larger area over the two dimensions of the sheet. The hardness of the substrate can drastically affect the ability to place a membrane at a target depth. Consideration should also be given to probe length relative to placement time with respect to stability (e.g., 1-ft probes are often displaced in Region 10 dive experience, so 3-ft probes are used and sectioned as needed).

Questions regarding sample size, variability, and the power of analysis are no different conceptually from any other sampling program. However, it should not be presumed that a design used in the past for bulk sediment sampling can simply be recast as a passive sampling program. Key questions related to sampling design with passive samplers are as follows:

1. At what temporal and spatial scale is information needed?
2. How do passive samplers need to be deployed to provide representative information at the desired temporal and spatial scale?
3. For passive samplers inserted into sediment, what are the appropriate depth intervals to address questions of exposure and/or fate?

The length of time that the passive sampler needs to remain in contact with the sediment will depend, in part, on the chemicals being evaluated. Some will partition to the sampler more quickly than others. Performance reference compounds (PRCs) can aid in assessing the rate of partitioning between the water and the sampler. Typically, samplers can be placed in sediments for weeks to months, to allow for a steady state to be established. If the purpose of the sampling is to track changes over time, a program would include a series of sampling deployments at the desired time steps (e.g., bi-annually, annually, every five years, etc.).

The sampling strategies that can be employed to balance costs and data adequacy are the same as those used for other applications. The main distinction between a passive sampler and bulk sample collection is the area or volume of the sample that is captured or included in the sample. This is not an issue when conditions in sediments are homogeneous, but this is rarely the case. Therefore, thought needs to be given to how to best deal with scales of spatial variability. This can be accomplished by first obtaining a limited number of samples to gain insight into spatial variability and then designing a more robust sampling approach based on the variability seen in the initial

samples. While this two-step approach is the most statistically sound way to proceed, site investigations often proceed absent such site-specific information, because the value is often unclear to DOD RPMs, and instead, the sampling strategy is based largely on professional judgment. In such cases, data on site conditions are used to determine how and where to deploy samples. Some steps can be taken to ensure that small-scale variability is dealt with appropriately. The two major ways this is accomplished are as follows:

1. **If averages are the desired statistics (e.g., for SWACs or exposures to fish, wildlife, or humans):** Use composite samples to represent areas of interest, and take sufficient numbers of composites in the area to provide an estimate of variance for the composite; this approach is attractive when there is an area of interest for management, and the statistic of interest is the average concentration for that area. The number of samples needed to form a composite depends on the size of the area being represented. As a practical rule of thumb, five composite samples (each a composite of a number of discrete individual samples) would typically provide the basis for estimating the average concentration in an area of interest. Note, there are various statistical procedures for determining these aspects of sampling design. Averages can also be derived from numerous individual discrete samples.

Insight

It is essential that the questions be well defined and understood when deciding about the use of either *in-situ* and/or *ex-situ* passive samplers. Based on Region 10 and MIT experience, use of PRCs is critical to evaluate how groundwater flux is impacting the degree to which equilibrium is reached. *Danny Reible, Texas Tech University*

2. **If point samples are desired (e.g., for evaluation of effects on benthos, to capture outliers, or to monitor for cap performance):** Collect discrete measurements using a randomized distribution within the area of interest; the sample size could be informed by previous information, or it may be possible to identify locations where exposures are suspected to be highest and can be included within the sampling effort to yield information that is knowingly biased high.

Experience: Health and Safety Considerations

For deeper waters, many passive sampling programs involve divers. That brings with it all the safety considerations that must be taken into account for a diving program. In addition, because work is often being conducted at contaminated sites, health and safety procedures that ensure protection from exposure to contaminants must also be incorporated into the effort.

4.2 USING *IN SITU* AND *EX SITU* APPROACHES

In situ (in the field) and *ex situ* (in the laboratory) deployments of passive samplers offer advantages and disadvantages, depending on the purpose. Key considerations that may favor one method over another include the following:

- Derivation of an equilibrium concentration for exposure

- Conducting bench-scale studies of treatments
- Determining actual field conditions
- Evaluating performance of implemented remedial actions
- Cost

An additional consideration is the degree of control over sample conditions desired by the analyst, as well as logistics. It is generally easier to take cores from the field and set them up in a laboratory than it is to deploy samplers into the field and recover them after a period of equilibration. In general, *ex situ* measurements made to determine the exposures of contaminants to biota and water will generally either be equivalent to or will overestimate the amount of sediment-related exposure that occurs in the field. Overestimates can occur when sediment conditions in the field may not be in equilibrium with porewater or surface water. This can happen, for example, when groundwater fluxes through the sediments at such a rate that the contaminants in the sediments are not in equilibrium because of the flushing groundwater; tidal pumping can exert a similar effect. Individuals with knowledge of these types of problems offered the following solutions:

- Conduct a limited number of both *ex situ* and *in situ* measurements
- Use information available from hydrogeological studies and sediment studies to identify areas where non-equilibrium conditions might exist and *in situ* methods might be useful to evaluate exposures
- Research regional conditions that might be influencing the larger hydrogeology within the water body.

To evaluate the performance of in-place remedial alternatives, it is often desirable and necessary to use *in situ* measurements. This is particularly true for the performance evaluation of capping and treatment remedies. The integrity of caps and the potential that contaminants are migrating through the cap are site-specific conditions that are difficult to replicate and represent in the laboratory. For capping alternatives, it is fairly common to use *in situ* passive samplers to evaluate whether contaminants are migrating through the cap. *In situ* methods are often used to evaluate the efficacy of treatment alternatives, as well as alternatives that have involved the removal of sediments through wet dredging or excavation. Nevertheless, there are some circumstances where these conditions can be evaluated using *ex situ* methods. For example, in the case of sediment treatment alternatives, it is possible to take cores from the treated area and evaluate them in the laboratory to determine the degree to which exposures in surface sediments have been reduced. That approach is appropriate for situations where there is not a strong movement of contaminants from beneath the treated area up through the treated area. The *ex situ* approach for evaluating treatment efficacy has been used on several sites already, and at the very least, it provides a basis for comparison between treated and untreated sediments.

The success of an *in situ* passive sampling program depends in large part on the success of deployment and retrieval of the samples. Experienced dive teams have been used at a number of sites. The advantage of using divers is the higher assurance of control over placement of the samplers. Placement involves achieving the proper aspect and depth into the sediment. However, diver-facilitated deployments and retrievals take time and have health and safety issues that must be addressed. Therefore, work is proceeding on deployment systems that are not diver dependent.

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5.0 WHAT DO I NEED TO KNOW ABOUT WORKING WITH PCB CONGENERS AND INDIVIDUAL COMPOUNDS IN PAH MIXTURES?

A dialogue group of eight individuals participated in discussions on this topic. A summary is distilled in the text box Insights Regarding Analysis of Congeners and Aroclors. The question "What do we analyze?" is important for any site at which PCBs and PAHs are COCs. The question often arises for PCBs because of three different analytical methods: congeners (e.g., by USEPA Method 1668a), homologues (e.g., by USEPA 680), and Aroclors (e.g., by SW-846 Method 8082). Aroclor analyses have historically been used most commonly, because most laboratories performing organic chemical analyses in sediments had that capability. Aroclor data were judged adequate for most site management purposes, and analyzing for Aroclors was less expensive than measuring congeners. Over the past decade, the relative merits of the two methods have been discussed extensively, and the group convened for this discussion generally agreed that, while Aroclor data are useful and provide a cost-effective means of guiding remediation, there are situations for which congener analyses provide a higher value of information for particular purposes. For example, congeners are more informative for identification of sources via forensic methods and for fate-and-transport studies.

Insights Regarding Analysis of Congeners and Aroclors

1. Either congeners or Aroclors can be used for site management decisions.
2. Congener data provide more detail that can be useful for the following: (a) forensic analyses, (b) source identification, (c) parameterizing food webs, (d) fate-and-transport studies, and (e) employing risk assessment methods that require toxicological information in the form of congeners.
3. Passive samplers for PCBs and PAHs generally require the analysis of congeners and the inclusion of performance reference compounds (PRCs).
4. Management decisions for PCBs in sediments are usually stated in terms of total PCBs. Estimates of total PCBs in sediments based on weathered Aroclors are expected to be within a factor of three of estimates derived from total congeners. The uncertainty is likely small compared to other sources of uncertainty in analysis of exposures and risks.
5. Site-specific empirical relationships can be developed, as needed, that relate Aroclor-based data with congener-based data to address questions that benefit from integrating both types of data. Empirical relationships can also be developed between sources in sediments, exposures, and clean-up levels.

The primary technical issue associated with relying on Aroclor analyses for environmental samples is that the chemical composition of the Aroclor mixture can change as a result of environmental fate processes. The result is that the Aroclor signal can become more difficult to recognize, which introduces uncertainties into fate and exposure estimates for the chemicals. Further, as the composition of the PCB mixture changes over time, quantification of total PCBs based on presumed Aroclor patterns can differ from actual totals. Members of the dialogue group report that estimated PCB totals based on recent analyses of weathered Aroclors in bulk sediments may differ

from actual totals by a factor of two to three.[2] The uncertainty in Aroclor-based estimates of total PCBs is not especially large, considering all the other uncertainties within a remedial investigation, and such uncertainties can be managed in a variety of ways. For example, if the assessment is based on relative levels of PCBs (for source and exposure terms and eventual clean-up levels), empirical relationships developed on a site-specific basis can be used to support management decisions.

The choice of analytical method for PCBs and PAHs is also influenced by the characteristics of the available toxicity data used to assess risks. A considerable body of toxicity data has been developed for Aroclors. Thus, it is historically common and appropriate to align exposure information derived from Aroclor analyses with Aroclor-related effects information. Data based on congeners are also being collected to determine any toxicological effects. In particular, a risk framework has been introduced for humans and wildlife species that involves assessing exposures to dioxin-like PCB congeners and estimating risks associated with this group of PCBs based on the toxicity of TCDD. This dioxin-based approach essentially involves transforming the PCBs into their dioxin equivalents based on relative potencies and then assuming effects and risks associated with dioxin. While some consensus has been reached around this approach, there is also considerable debate about its reliability and the uncertainties associated with derived toxicity values. For PAHs, analytical approaches based on analysis of 34 parent and alkylated compounds have become most common.

Although Aroclor-based approaches remain in use and can serve to inform management decisions, congener-based methods are increasingly being used. Note that if passive samplers are employed, it is best to use congener-based approaches. At sites where both Aroclor and congener-based methods have been employed, it is possible to develop site-specific empirical relationships among the data sets, so that both data sets can be used to inform risk-management decisions and monitoring.

The debate surrounding the value of alternative methods for PCB analysis has been a source of consternation and confusion for DOD RPMs. This section does not settle that debate but sheds light on reasons why one analytical method might be selected over another. In addition, we provide insights from practitioners and regulators regarding how to use data to inform management decisions at sediment sites. Because congeners are typically measured when passive samplers are used, these insights provide guidance on the use of passive samplers for informing site management decisions.

5.1 CHOOSING WHICH CONGENERS TO MEASURE

If a decision has been made to measure congeners, a common question is, “Which congeners should be measured?” This question arises because various subsets of congeners have been used

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[2] Both under- and overestimates have been reported. One analyst reported that natural dechlorination in sediments had greatly shifted the congener distribution to a few dominant dechlorination products, which resulted in the total Aroclor method underestimating by a factor of 3 the actual total based on the sum of congeners. Another reported they found just the opposite: the Total Aroclor method overestimated the total summed congeners. Under- and over estimates have been reported for other sites as well.

for different purposes. The consensus from the professional discourse is that if a congener approach is being used, it makes sense to analyze the suite of congeners that are germane to the questions being asked; a more complete list of congeners increases the overall utility of the data.[3] While shorter lists of congeners can answer specific questions, more comprehensive lists can be used to estimate total PCBs, support forensic analyses (by way of “fingerprints”), help assess fate and transport, parameterize models, and evaluate health and ecological risks. Cost will often be a consideration, but planning is essential to determine the appropriate suite of congeners to include in the analyses. Based on feedback, cost is not usually a major impediment relative to the value of information. However, there may be specific circumstances where the cost may justify an alternative approach along the lines articulated in the footnote. For PAHs, it is recommended that DOD RPMs quantify the 34 PAHs that USEPA currently considers "Total PAHs" for sediment investigations; this includes parent PAH compounds and their alkylated derivatives.

For a mixture of PCBs in any matrix (including passive samplers), most of the individual congeners can be measured without too much difficulty. Also, the individual congeners in any one medium (e.g., passive sampler) can be translated to associated media (e.g., porewater) if equilibrium is assumed and known partition coefficients are applied. A possible exception may be black carbon sorption coefficients. By measuring total congeners, the congeners measured or estimated in the environmental matrix of interest (e.g., fish) can be summed to give total PCBs present in that matrix. This provides useful detail and eliminates the uncertainty that may be associated with analysis of Aroclors or with subsets of congeners.

Experts on PCB forensics and source evaluations favor the analysis of total congeners. Indicators of PCB products can be found throughout the range of PCB congeners. For example, PCB 11, a low-chlorinated PCB congener, appears inadvertently in manufacturing of yellow dyes and can be discharged in a paper recycler’s effluent. At the other end of the range is deca-chlorinated biphenyl, which is also indicative of certain type of sources. Most Aroclors have various mixtures of congeners with various degrees of chlorination.

Depending on the information available and the regulatory program, human health risk assessors may use Aroclor and/or congener data. If congener data are being used, two metrics are commonly derived. The first is for the dioxin-like compounds as a group, and the second is for total PCBs. Also, there is considerable research under way on the effects of non-dioxin-like PCBs. Feedback from the regulatory community suggests that the use of congener data is the future direction for human health risk assessment. However, a contentious issue with this approach is that the cancer assessment portion is tied to dioxin and all the technical concerns that are related to that. It might

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[3] There are some variations of thought. For example, there was a recommendation to analyze a subset of PCB congeners. The NOAA 28 includes dioxin-like PCB congeners and those prevalent in Aroclors. This would not allow detection of non-Aroclor PCBs such as PCB 11 and other dye-related PCBs or dechlorination products or patterns. Another recommendation is that, because total PCBs can be reasonably estimated from a subset of congeners (e.g., NOAA 18), measurements of this subset can be used to support decisions.

therefore be wise to develop a translation between congener composition and the Aroclors for which current cancer potency factors were developed.[4]

Total PCBs are typically used for mapping extent or delineating clean-up boundaries. If a mix of data on congeners and Aroclors is part of the assessment and remedial planning, then a bridge (i.e., an empirical relationship) is needed between the two types of analytes. While traditional mapping has been done in terms of total bulk levels of PCBs in sediments, it is also possible to use passive samplers to map the spatial distribution of the porewater concentrations. Placing a map of chemical activity (commonly referred to as the freely dissolved concentration, or C_{free}) based on measurements of total congeners adjacent to a map of bulk sediment concentrations could provide important insights into the selection and possible efficacy of remedial alternatives.

5.2 UNDERSTANDING HOW TO HANDLE DETECTION LEVELS AND NON-DETECTS

The expert discourse revealed different approaches to handling non-detected values depending on the purpose of the data application. It should be noted that detection levels achieved with passive samplers are generally lower than those obtained by other methods. Individuals involved in the evaluation of sources and fate and transport report non-detect data but tend to work with the data for detected values and treat non-detects as zero. This is consistent with the goal of examining patterns. On the other hand, risk assessors tend to guard against underestimating exposures by treating non-detects in one of several ways:

- If the congener or Aroclor is not observed to be present based on a reasonably sized set of data, then it is presumed to be absent and is treated as a zero.
- If the congener or Aroclor is present in a particular medium, then non-detects are presumed to be present at some level; that level is estimated in one of two ways and included in the exposure assessment:
    - A specific fraction of the detection limit (DL) is used, such as half the DL
    - A statistical procedure is used to estimate the non-detected concentrations based on the nature and characteristics of the mixture[5]
- Sensitivity analyses are commonly used to determine whether inclusion or exclusion of non-detects makes much of a difference to the exposure estimates.

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[4] Research has been proposed to evaluate PCB-related effects that may exist beyond those associated with dioxin-like effects (i.e., via mechanisms other than the ArH receptor). To the extent that there are such effects, analysis of total congeners is warranted.

[5] While statistical methods can be useful and use uncertainties introduced by choosing a fraction of a DL, it is easy to get hung up on the methods and underlying assumptions and whether they are appropriate. It is much easier to either specify a fraction of the DL or set the non-detects to zero (ND=0) than it is to argue for statistics. This makes the conduct of sensitivity analysis the most practical recommendation at most sites. A method has been developed that automatically calculates dioxin TEQs using ND = 0, ½ DL, and DL, and using the Kaplan-Meier method to handle non-detects. The results and some basic sensitivity analysis results are plotted in an Excel table side by side. All the user has to do is import the laboratory report to the spreadsheet. A similar approach could be developed for PCBs.

5.3 STRATEGIES WHEN WORKING WITH DATA SETS FROM DIFFERENT SAMPLING AND ANALYTICAL METHODS

At sites where different methods have been used, there may be a need to develop strategies for integrating information. Site-specific empirical relationships could be developed from a subset of sampled sites to establish the relationships among different measurement types. Remedy decisions could be based on total PCBs expressed as the sum of the homologues. Also, rather than relying solely on a concentration of total PCBs in bulk sediment, porewater measures could be used as a performance objective for remediation. The combination of bulk and porewater remedial performance metrics could support the range of remedial alternatives, including those that are more directly associated with MNR, capping, and *in situ* remediation.

Experience

Developing site-specific empirical relationships may be an important integration strategy. For example, the Lower Duwamish Work Group (LDWG 2010) RI looked at congeners and Aroclors and found site-specific relationships there.

LDWG assumed that one can estimate the organic-carbon normalized sorption coefficient, K_{oc}, of the total PCBs by using an average of PCB congener sorption properties. Moreover, the weighting for this average was done using the relative concentrations of PCB congeners detected in benthic invertebrate tissues (LDWG 2010), rather than the relative concentrations in the sediments themselves. *John Wakeman, USACE*

5.4 DEALING WITH CO-ELUTING COMPOUNDS

Co-elution refers to compounds coming out at the same time or being seen at the same locus in the analysis and can introduce uncertainty for such chemicals and for the quantification of risk. Co-elution can be especially important to recognize when at least one of the co-eluted compounds is particularly toxic. For example, PCB 126 co-elutes with PCB 185 and is one of the more toxic PCB congeners. Because the chemical co-elutes, there is uncertainty about whether or not it is present, and the concentrations at which it is present when a PCB126/185 peak appears in the analysis. Comprehensive two-dimensional gas chromatography holds promise for resolving co-eluting compounds, but note that co-elution may still occur with this method. Co-eluting peaks can possibly be resolved by using de-convolution software; however, this is not currently a standard procedure.

5.5 WORKING WITH PERFORMANCE REFERENCE COMPOUNDS

The rates of diffusion of hydrophobic organic chemicals into passive samplers vary among the chemicals, largely in relationship to the size and partitioning behavior of the molecules. Smaller molecules tend to come into equilibrium with the surrounding environment faster than larger molecules. As a result, passive samplers that have been placed in the field for a few to several weeks will contain organic compounds in various stages of approaching equilibrium with the environment. Performance reference compounds (PRCs) are used to correct for this variable degree of equilibration. These are a suite of deuterated compounds of varying molecular weight and partitioning behavior, and the passive samplers are prepared with known amounts of these

PRCs. The basic concept is that the rate of effusion out of the passive sampler is equivalent to the rate of diffusion into the sampler. Thus, by measuring the amounts of PRCs at the beginning and end of the sampler's field deployment, an estimate can be made of the PRCs percent lost from the samplers and the equivalent percent gained of chemicals in the environment. The details of this method and the algorithms used to translate from the PRC data to estimates of environmental concentrations are provided in SERDP/ESTCP/EPA (2014).

The important points for managers to recognize with respect to use of PRCs are that: (1) this part of the method is needed when passive samplers are being placed in the field (*in-situ* measurements) and/or when exposure times are not long enough to achieve equilibrium between the passive samplers and the environment for the compounds being investigated; (2) the accuracy of the measurements depends on how well and when the PRCs are measured before or after deployment (ideally, the measurements of deuterated compounds are made immediately before deployment and shortly after the passive samplers are recovered); (3) in general, three to five samples from each batch should be analyzed prior to placement of the passive samplers in the field; (4) if passive samplers have been stored for an extended period after the introduction of PRCs, the analyses of PRCs should be made at the beginning of the deployment; (5) *in situ* placement of passive samplers is most appropriate for aqueous and sediment environments that are covered by water or remain moist, as in the case of fine-grained sediment or intertidal mud—if the intertidal sediments are coarse grained and heated by the sun, there could be some loss of PRCs, and such losses would bias high any estimate of concentrations; in such cases, it may be best to conduct *ex-situ* measurements and model the influences of tidal influence or groundwater flux.

5.6 ARE THERE COMMERCIAL LABORATORIES THAT CAN DO THIS WORK?

A number of commercial laboratories are building experience with testing passive samplers. Examples are provided in Table 3, along with brief descriptions provided by the laboratories regarding their capabilities. Because capabilities are continually being developed, we recommend that laboratories be re-consulted when a passive sampling program is being contemplated. However, the list gives DOD RPMs a starting place and also indicates that the capability and capacity for obtaining analyses at commercial laboratories is growing.

5.7 DOES THIS WORK REQUIRE SPECIALIZED EXPERTISE?

Passive samplers have been used for a number of years, but only recently have they seen use within regulatory programs. As a result, contractors are less familiar with the use of passive samplers than traditional methods, although EPA divers in Region 10 and ERT have a wealth of experience available to assist in the planning and execution of this sampling technique. There will be a period of learning, as with any new technology, during which contractors, regulatory personnel, and DOD RPMs become more familiar with passive sampling devices and knowledgeable about their use. As such, the progression of using and building knowledge about passive samplers will proceed as it has for past technologies, such as groundwater monitoring wells, field screening methods, and vapor intrusion measurements. Until the level of familiarity is adequate for fairly routine applications of passive samplers, it is wise for programs that incorporate passive sampling methods to include individuals with relevant expertise. That expertise can be found among a number of research institutions, and is also present within USEPA's Office of Research and Development, regional offices of the Agency, and in the U.S. Army Corps of Engineers environmental research

lab. In some cases, it may make sense to bring an individual with the requisite expertise into the program as a participant. In other cases where the knowledge base has been built, it may be appropriate to have experts serve in a reviewing capacity. There are at least four stages where expertise is valuable: (1) planning and design, (2) field sampling, (3) lab analyses, and (4) interpretation. The most important stage at which experts can be useful is the planning stage.

Table 3. Commercial Laboratories that have Reported Experience with Preparation and/or Analysis of Passive Samplers

Laboratory	Contact	Reported Experience / Capability
ALS	Jeff Christian (jeff.christian@alsglobal.com)	Prepares PE passive samplers with PRCs. Does not mount PE strips or deploy samplers in the field. Extracts and performs chemical analyses on passive samplers. Reports results to client in mass/mass. Currently testing the use of PRCs loaded onto PDMS coated Solid-phase microextraction (SPME) fibers.
Alpha	Jim Occhialini (jocchialini@alphalab.com)	Prepares PE passive samplers with client-specified PRCs. Capable of working with solid phase membrane device (SPMD) as a passive sampler. Extracts and performs chemical analyses on passive sampling material. Reports results to client in mass/mass.
AXYS	Georgina Brooks (gbrooks@axys.com) and Richard Grace (rgrace@axys.com)	Prepares SPMD and SPME passive samplers with PRCs for organics only. Extracts and performs chemical analyses on passive samplers. Reports results to client as pg or ng per sample.
PACE	Mary Christie (mary.christie@pacelabs.com)	Does not provide passive samplers. Has analyzed SPMD samples after they have undergone dialysis.
Test America	Patricia McIsaac (patrica.macisaac@testamericainc.com)	Capable of performing chemical analyses on PE and PDMS-coated fiber passive sampling materials. Client must specify the type of and have the ability to acquire passive sampling material, identify appropriate compounds of concern, provide requirements to spike the material with PRCs, understand the length of deployment, and understand how the data is reported. Reports results to client in mass/mass.

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7.0 REFERENCES

SERDP/ESTCP/U.S. EPA. 201x (In prep.). Laboratory, field, and analytical procedures for using passive sampling in the evaluation of contaminated sediments: User's manual. EPA-600-R-xx-xxx. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

Ghosh U, Kane Driscoll S, Burgess R, Gobas FAPC, Maruya K, Jonker M, Gala W, Choi Y, Beegan C, Apitz S. 2014. Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration and implementation. Integrated Environmental Assessment and Management 10:210–223.

Greenberg MS, Chapman PM, Allan IJ, Anderson KA, Apitz SE, Beegan C, Bridges TS,Brown SS, Cargill JG IV, McCulloch MC, et al. 2014. Passive sampling methods for contaminated sediments: Risk assessment and management. Integrated Environmental Assessment and Management 10:224–236.

ITRC. 2011. Incorporating bioavailability. Considerations into the evaluation of contaminated sediment sites. CS-1. Interstate Technology & Regulatory Council, Contaminated Sediments Team, Washington, DC. www.itrcweb.org .

ITRC. 2014. Contaminated sediments remediation: Remedy selection for contaminated sediments (CS-2). Interstate Technology & Regulatory Council, Contaminated Sediments Team, Washington, DC. http://itrcqweb.org/contseds_remedy-selection.

Kreitinger JP, Neuhauser EF, Doherty FG, Hawthorne SB. 2007. Greatly reduced bioavailability and toxicity of polycyclic aromatic hydrocarbons to *hyalella azteca* in sediments from manufactured gas plant sites. Environmental Toxicology and Chemistry 26(6):1146–1157.

National Research Council (NRC). 2003. Bioavailability of contaminants in soils and sediments. Processes, tools and applications. Committee on Bioavailability of Contaminants in soils and sediments. National Research Council. National Academies Press.

Parkerton TF, Maruya KA. 2014. Passive sampling in contaminated sediment assessment: Building consensus to improve decision making. Integrated Environmental Assessment and Management 10(2):163–166.

Sanders JP, Andrade NA, Ghosh U, Menzie CA, Amos B, Brown SS, Gilmour CC, Henry B. 2015. Bioavailability reduction of PCBs with in situ sorbent amendments in a tidal phragmites marsh. Battelle International Conference on Remediation and Management of Contaminated Sediments — New Orleans, January 2015.

SPAWAR Systems Center (SSC) and Battelle. 2005. Implementation guide for assessing and managing contaminated sediment at Navy facilities. NFESC User's Guide UG-2053-ENV.

U.S. EPA. 1989. Risk Assessment Guidance for Superfund. EPA 540/1-89/002. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC.

U.S. EPA. 1998. Guidelines for ecological risk assessment. Risk Assessment Forum (8061-D), EPA/630/R-95/002F. Fed Reg 63(93):26846–26924. U.S. Environmental Protection Agency, Washington, DC

U.S. EPA. 2003a. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures. EPA-600-R-02-013. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

USEPA. 2003b. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metals mixtures (cadmium, copper, lead, nickel, silver and zinc). EPA-600-R-02-011 (draft). U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

U.S. EPA. 2005. Contaminated sediment remediation guidance for hazardous waste sites. EPA-540-R-05-012. OSWER 9355.0-85 December 2005. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. http://www.epa.gov/superfund/-resources/sediment/guidance.htm.

U.S. EPA. 2006. Guidance on systematic planning using the data quality objectives process. EPA QA/G-4. EPA/240/B-06/001. U.S. Environmental Protection Agency, Office of Envir4onmental Information, Washington, DC.

U.S. EPA. 2008. Sediment assessment and monitoring sheet (SAMS) #1. Using fish tissue data to monitor remedy effectiveness. OSWER Directive 9200.1-77D. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation and Office of Research and Development, Washington, DC.

U.S. EPA. 2009. Sediment assessment and monitoring sheet (SAMS) #2. Understanding the use of models in predicting the effectiveness of proposed remedial actions at Superfund sediment sites. OSWER Directive 9200.1-96FS. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation and Office of Research and Development, Washington, DC.

U.S. EPA. 2012a. Sediment assessment and monitoring sheet (SAMS) #3: Guidelines for using passive samplers to monitor organic contaminants at Superfund sediment sites. OSWER Directive 9200.1-110 FS. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation and Office of Research and Development, Washington, DC.

U.S. EPA. 2012b. Equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Procedures for the determination of the freely dissolved interstitial water concentrations of nonionic organics. EPA-600-R-02-012. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

U.S. EPA. 2013. Superfund remedial program review action plan. U.S. Environmental Protection Agency, Washington, DC. http://www.epa.gov/superfund/cleanup/pdfs/Final_SPR_Action_Plan-11_26_2013_(2).pdf.

APPENDIX A. THREE CASE STUDIES FOR WHICH PASSIVE SAMPLERS WERE USED TO GUIDE WATER QUALITY AND SEDIMENT MANAGEMENT DECISIONS

Types of information generated using passive samplers include assessments of:

- Contaminant sources and fate (Case 1)
- Health and environmental risks (Case 2)
- Remedy effectiveness (Case 3)

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CASE STUDY 1: UNITED HECKATHORN SUPERFUND SITE, RICHMOND, CALIFORNIA

How passive samplers were used

Deployed in surface water and sediment to help develop an understanding of chemical sources and fate

Citation(s)

United Heckathorn Superfund Site, Richmond, California, DDT Fate and Transport. Final May 2014. Prepared for: CH2M HILL under contract to EPA Region 9 Prepared by: Sea Engineering, Inc. 200 Washington Street, Suite 101 Santa Cruz, CA 95060 Study http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/3dc283e6c5d6056f88257426007417a2/d9263fb3f9c7358e88257d18005d365d/$FILE/Final_Heckathorn_DDT_FateAndTransport.pdf

Draft Focused Feasibility Study United Heckathorn Superfund Site Richmond Contra Costa Country, California USEPA Contract No. EP-S9-08-04 USEPA Work Assignment No. 025-RIFS-09R3 CH2M HILL Project NO. 385441 Prepared for U.S. Environmental Protection Agency Region 9 75 Hawthorne Street San Francisco, California 94105 Prepared by CH2M HILL 155 Grand Avenue Suite 800 Oakland, CA 94612 February 2015. http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/3dc283e6c5d6056f88257426007417a2/8a7f7ade7f70c89188257df60066d69c/$FILE/Draft_FFS_Feb_2015_withoutAppCandD_v2.pdf

Narrative

Passive samplers constructed of polyethylene were used in 2009, 2012, and 2013 to evaluate sources of dissolved-phase DDT within the Lauritzen Channel. The passive samplers enabled direct assessment of the dissolved phase, which was considered particularly important to assess bioaccumulation of the chemicals into biota. The 2012 and 2013 studies were used to evaluate the diffusive flux of DDT from the sediment bed to the overlying water column and to infer dissolved DDT concentrations in porewater and surface water. The results of the investigation were used to inform the 2015 Draft Focused Feasibility Study. The passive sampling results provided the following insights: (1) a potential important additional input of total DDT was occurring somewhere mid-channel or farther south during the 2013 study, which cannot be explained by in-channel sediment resuspension; (2) mussels were accumulating DDT from both the seawater and resuspended solids in the water column, suggesting that resuspension from the sediment bed is a potential source; (3) there is ongoing diffusion of DDT from the sediment. When combined with other information for the site, the passive sampling results are consistent with a conclusion that the embankment adjacent to the former plant site is a source of the additional DDT. The previous removal actions along the embankment did not address sediment below about 0 ft. mean lower low water (MLLW), or embankment soils with total DDT concentrations below 100 mg/kg. Thus, the passive sampler study supported the premise that historical contamination in un-remediated areas continued to be a source to the adjacent waters.

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CASE STUDY 2: LOS ANGELES AND LONG BEACH HARBOR TMDL DEVELOPMENT

How passive samplers were used

Used to evaluate exposure concentrations for use in screening for human health and ecological risks

Citation

Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters Toxic Pollutants Total Maximum Daily Loads. Prepared by California Regional Water Quality Board Los Angeles Region and U.S. Environmental Protection Agency Region 9, May 5, 2011. http://www.waterboards.ca.gov/losangeles/board_decisions/basin_plan_amendments/technical_documents/66_New/11_0630/03%20Final%20Staff%20Report%2006%2030%2011.pdf

Narrative

The development of total daily maximum loads (TMDLs) is a part of the water quality regulatory programs implemented under the Clean Water Act. These are similar in some ways to contaminated sediment sites, in that ***concentration-based target levels*** are established for water and/or sediments, and calculations are made to determine the input loads that must be achieved over some time horizon to meet those targets. Passive samplers are being used to assess existing exposure concentrations for harbors and rivers, and that information is being used to inform the TMDL process. In the case of Long Beach and Los Angeles Harbors, solid-phase microextraction (SPME) was used to reach the following key findings: "SCCWRP has utilized special analytical techniques to obtain measurements of priority organics in the water column at various sites along the Southern California Bight. Special, highly sensitive, SPME devices were deployed into the water column for sufficient time periods as to yield actual ambient results for DDT and PCBs with extremely low detection levels (sub-ng/L). The initial research efforts measured dissolved phase DDE (metabolite form of parent DDT compound) throughout the Bight (Zeng et al. 2005). Results from four stations within Inner and Outer Harbor waters show elevated levels of DDE in comparison to CTR human health numeric criteria. Total PCB measurements also exceed the California Toxics Rule human health numeric criteria at these stations. Concentrations of DDE and total PCBs were higher at surface (2 m sub-surface) than those measured in water overlying (2 m above) contaminated sediments."

The case study points to the fact that passive samplers are increasingly being used to support regulatory determinations. With respect to the TMDLs that are being developed for these harbors and elsewhere, the determinations of chemical concentrations in water are being used to judge exposures to people, as well as ecological receptors. This is beyond what is currently being done at contaminated sediment sites. However, the fact that this is occurring in another regulatory program indicates that the foundation for using passive samplers to evaluate risks is already being laid.

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CASE STUDY 3: CHATTANOOGA CREEK AT TENNESSEE PRODUCTS SUPERFUND SITE

How passive samplers were used

Performance monitoring for the sediment cap.

Citation(s)

Five-Year Review Report First Five-Year Review Report for Tennessee Products Superfund Site EPA ill # TND071516959 Chattanooga Hamilton County, Tennessee September 2011 Prepared By: TDEC-DoR. 540 McCallie Ave, Suite 550 Chattanooga, Tennessee 37402 For: United States Environmental Protection Agency Region 4 Atlanta, Georgia. http://www.epa.gov/superfund/sites/fiveyear/f2011040004115.pdf

Narrative

The ROD for this site involved placement of an AquaBlok® cap over PAH-contaminated sediment. While required performance monitoring was limited to visual observations, funds were made available from USEPA ORD to use passive samplers to monitor the potential migration of PAHs into and through the cap. That information was incorporated into the Five-Year Review (FYR), a document that assesses overall performance. Passive sampling involved the use of solid-phase microextraction (SPME) monitoring samplers. Data from the 2009 and 2010 monitoring events were included in the FYR. The SPME samplers consisted of polydimethylsiloxane fibers enclosed in perforated stainless-steel tubes (1 to 3 ft long), which were inserted into the creek bed and allowed to equilibrate for a minimum of 14 days. As noted in the FYR, "The very low surface water and sediment porewater concentrations [of PAH compounds] observed (e.g. in the parts per trillion range) indicates that the remedy is protective." It also states, "The preliminary conclusion of the sampling to date is that the Chattanooga Creek remedy is effectively maintaining surface water concentrations below relevant surface water criteria. In addition, little change over the past 12 months has been noted in concentrations of PAHs in sediments or cap material suggesting that no significant migration of contaminants is occurring up through cap material."

The FYR included the following statement on performance:

> Question A: Is the remedy functioning as intended by the decision documents? Yes. Two years of SPME monitoring of the AquaBlok® cap indicate the barrier is effectively isolating any residual NAPL source material remaining in the subsurface. Porewater concentrations in the upper layers of the cap are very low (e.g. in the parts per trillion range) and do not exceed chronic surface water quality criteria. It is important to note that comparisons of porewater concentrations to surface water quality criteria [are] very conservative in that substantial dilution would be expected between porewater and surface water. Moreover, there is little change between the 2009 and 2010 PAH concentrations in the cap material suggesting that no significant migration of contaminants is occurring up through the AquaBlok® barrier.

There are several other case studies that involve using passive samplers as described above to monitor cap performance. These have been used in both marine and freshwater systems.