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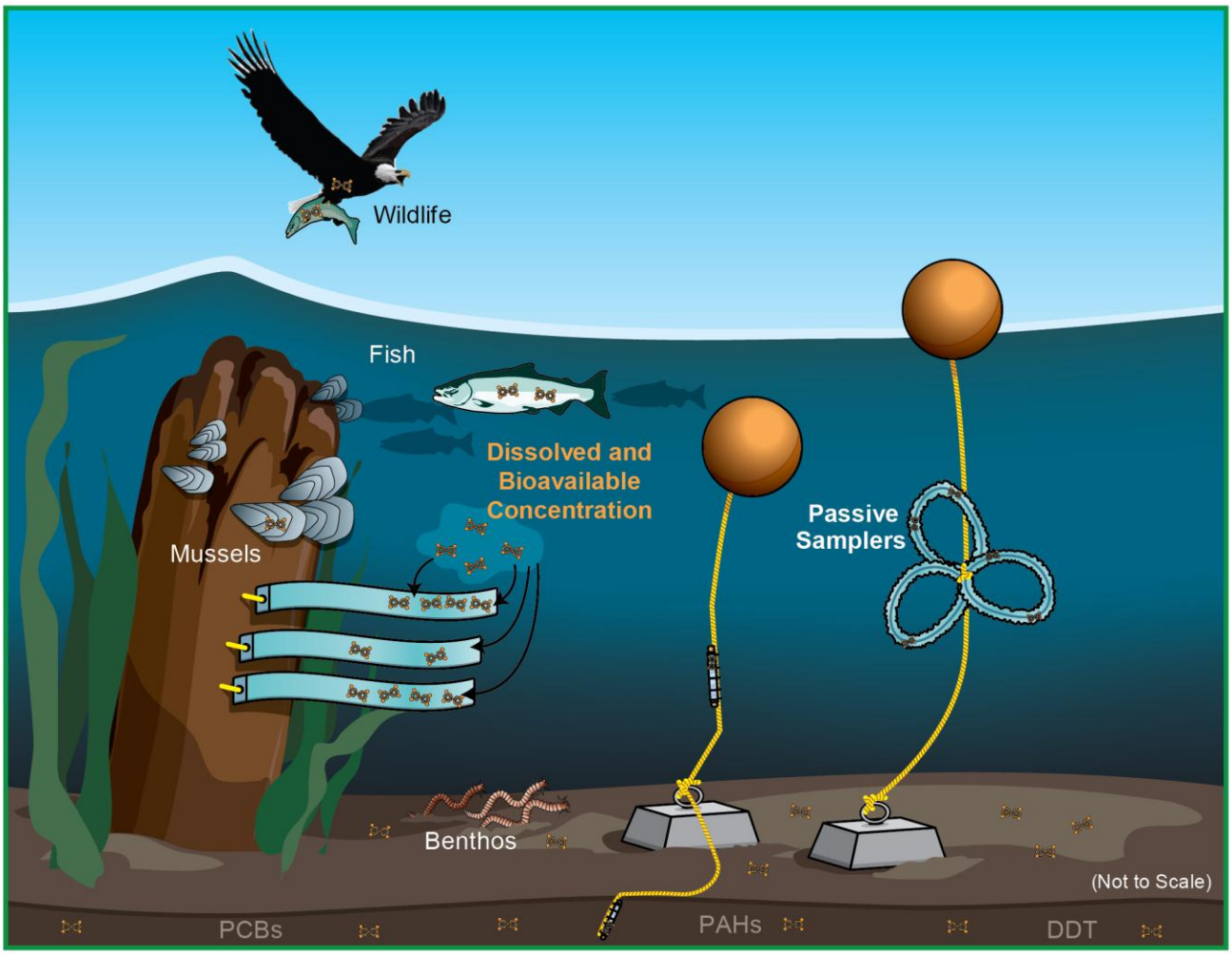
Agency

Office of Superfund Remediation and Technology Innovation
and
Office of Research and Development

Sediment Assessment and Monitoring Sheet (SAMS) # 3

Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites



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1. Introduction

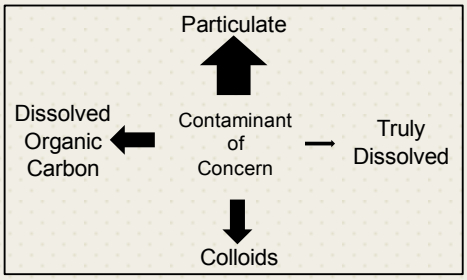
The objective of this Sediment Assessment and Monitoring Sheet (SAMS) is to provide introductory information on the use of passive samplers at Superfund sediment sites contaminated with hydrophobic organic contaminants. The concept of passive sampling in the environment was first developed in the 1980s, and samplers started to be deployed in the field for research purposes in the 1990s. Since then, passive samplers have been used for monitoring contaminant concentrations in the water column, soil and sediment interstitial waters, and air at sites around the world. Their use in sediments to date has been primarily for research, however. As discussed below, passive samplers are useful new tools for assessing contaminant exposures and evaluating the potential for adverse environmental effects at Superfund sites. After reading this SAMS, users will have a fundamental understanding of some common passive samplers and their potential applications at Superfund sites.

This SAMS discusses passive samplers that can be used in both water column and sediment deployments, and in some cases both simultaneously. These passive samplers use polyethylene (PE), polyoxymethylene (POM), and solid phase micro-extraction (SPME) materials. Another type of passive sampler called semi-permeable membrane devices (SPMDs) have been used primarily in the water column as surrogates for biota such as fish, but will not be discussed here in any depth. When deployed together, passive samplers placed in the water column and in the sediment can provide information about contaminant gradients between the sediment and the water. For example, when an engineered cap is used as part of a site cleanup, passive samplers can be used as a monitoring tool to evaluate the contaminant flux from the underlying contaminated sediment, into the cap layers and into the overlying water. Passive samplers collect information about the dissolved concentrations of contaminants. The dissolved concentration is a useful measure of the amount of contaminant that is bioavailable to aquatic organisms. Passive samplers do not provide information about the concentrations of contaminants associated with bedded, suspended or colloidal particles in aquatic systems and therefore do not address directly the transport of contaminants associated with such particles. The focus of this document is on a subset of those contaminants of concern (COC) often found at Superfund sites that, chemically speaking, are known as the hydrophobic or nonionic organic chemicals. These include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dioxins and furans (PCDD/Fs) and chlorinated pesticides such as DDT. These chemicals are particularly persistent in the environment and bioaccumulate in aquatic organisms, often drive the risks as Superfund sediment sites, and are the focus of this SAMS. Metal COC such as cadmium, copper, lead, mercury and zinc are not discussed. There is a growing scientific literature on using other types of passive samplers to monitor metals, but the field is not as established, and that work is beyond the scope of this SAMS. This document briefly discusses the use of passive samplers but does not provide specific protocols on deployment and recovery, nor does it describe the chemical analysis procedures for passive samplers (it is not a U.S. Environmental Protection Agency [EPA] standard method or operating procedure). However, with the increasing use of passive samplers at sites around the United States and the world, these types of specialized protocols and procedures are likely to be available in the near future.

2. Why Use Passive Samplers? The Advantages

At Superfund sites, there often is the need to know the concentrations of hydrophobic organic contaminants in the water column and sediment interstitial water, and to understand the relationship between these levels and the total levels in the sediment (i.e., bulk sediment chemistry). Depending on the contaminant, there may be several ways to measure these concentrations. The typical analytical methods are gas chromatography with mass spectroscopy (GC/MS) or electron capture detection (GC/ECD) for most of the contaminants considered in this SAMS. These methods measure the quantity of these contaminants in a selected matrix like water or sediment. However, before the analysis can be performed, it is necessary to collect the sample matrix and extract the contaminants from that matrix. For the last 40 years, these hydrophobic contaminants have been extracted from a volume of water or mass of sediment using organic solvents. This conventional approach has several disadvantages. First, for water samples, even at the most contaminated sites, contaminant concentrations are frequently so low that they are not detectable with the GC/MS or GC/ECD unless very large volumes of water (e.g., tens to thousands of liters) are extracted. Furthermore, even when contaminants can be detected, the results are often affected by sample artifacts like the presence of very small sediment particles, colloids and dissolved organic carbon (DOC), and thus the measured concentrations do not represent the truly dissolved and bioavailable concentrations. These additional environmental phases (defined in Table 1 and discussed in *Information Box #1*) can result in overestimations of the dissolved concentrations in the water column and interstitial water. Second, for sediments, solvent extraction removes nearly all of the contaminants from the sediment, including that portion tightly bound or sequestered in the sediment matrix. While this type of information is useful for quantifying the total mass of

Information Box 1 *Environmental phases* are often used to divide the aquatic environment into separate components, each with its own unique characteristics. Understanding environmental phases and where a contaminant resides in these phases can assist in establishing whether the contaminants will be in a form resulting in exposure to aquatic organisms, wildlife and humans. Principal environmental phases important to contaminated sediment sites are defined in Table 1. Definitions are generally based on the particle size or chemical qualities (e.g., sorption strength of carbon types) of the substances making-up the phase. Hydrophobic organic chemicals partition between these environmental phases. In general, the majority of these contaminants will be associated with the particulate phase and are not typically readily bioavailable to result in an exposure. A portion of these contaminants will also associate with the colloidal and dissolved organic carbon (DOC) phases, where they are also not readily bioavailable. Often the least amount of contaminants will be in the truly dissolved phase, but this is the phase where they are the most readily bioavailable for exposure and uptake by organisms.



The image above shows the partitioning of a hydrophobic COC between the principal environmental phases, with the thickness of the arrows indicating the relative degree to which a contaminant associates with a given phase (based on Schwarzenbach and others (2003)).

contaminant present in the sediments, it does not tell us anything about what fraction of the contaminants are bioaccessible or bioavailable to environmental receptors and thus responsible for exposure and potential risks to human health and environment (see *Information Box #2*). In addition, conventional extractions use large volumes of organic solvents that are both expensive and environmentally harmful. By comparison, passive samplers require much smaller volumes of solvent.

Table 1. Definitions of principal environmental phases in the aquatic environment.

Environmental Phases in Water	Definition
Black carbon (BC)	A form of carbon produced by the burning of biomass and fossil fuels that can accumulate in sediments. This form of carbon has a very large affinity for hydrophobic COC and can substantially reduce bioaccessibility and bioavailability. Depending on the type of sediment, the BC generally constitutes 0.05 to 1.0 percent of the sediment mass.
Colloidal	Very small particles that do not settle as a result of gravity (larger than 10 nanometer [nm] to less than 10 micrometer [µm]) when present in the water column and in sediment interstitial water. When associated with colloids, COC bioavailability is substantially reduced.
Dissolved	Contaminants existing in a dissolved form in the water column and interstitial waters, a highly bioavailable form of most organic COC.
Dissolved organic carbon (DOC)	Organic matter, smaller in size than colloids, that is chemically dissolved in water. As in the case with colloids, when associated with dissolved organic carbon, the bioavailability of COC is substantially reduced.
Interstitial or pore water	In the sediment bed, water present between particulates; it contains colloidal, dissolved organic carbon and the truly dissolved phase of COC.
Particulate	Large sediment particles (larger than 10 µm) containing organic and black forms of carbon that settle fairly quickly via gravity when resuspended.
Particulate organic carbon (POC) or sedimentary organic carbon (SOC)	Organic carbon associated with sediment particles and formed by the natural degradation of biomass (such as plants and animals). Depending on the type of sediment, the POC can constitute 0.5 to 10 percent of the sediment mass. Many COC are sequestered by POC, which reduces their bioaccessibility and bioavailability. The affinity of this form of carbon for COC is substantially less than their affinity to black carbon. When analyzed by scientific instrumentation, POC is also known as total organic carbon (TOC) and the fraction organic carbon (f_{OC}).

Passive samplers represent an alternative approach for collecting and extracting some key organic COC and have many advantages over the conventional approaches. For example, passive samplers can be deployed directly in the environment and concentrate COC *in situ*. This concentrating process increases the sensitivity of the GC/MS or GC/ECD used to analyze the sampler because there is more contaminant present in the final extract. Other advantages are that passive samplers can be deployed for several days at a time (up to several months) and provide a time-averaged representation of COC concentrations at the sampling stations. In contrast, conventional water samples provide a "snap shot" of conditions at one, often brief, moment in time that may not be representative of average or real concentrations to which receptors are exposed. Finally, while the actual cost of a chemical analysis by GC/MS or GC/ECD for a passive sampler is similar to a conventional sample, passive samplers themselves can be inexpensive. Therefore, the cost of the passive sampler deployment generally is $100 to $200 less than conventional sampling, and the loss of a passive sampler during a deployment as a result of bad weather or boat traffic is not a large financial loss.

Information Box 2 *Bioaccessibility and bioavailability* are terms that describe the likelihood that a contaminant will be exposed to an organism. Actual definitions vary, but a general definition of bioaccessibility is the amount of a chemical that is in a form that an organism can access from an environmental phase. If that contaminant is able to interact within an organism (for example, it can be accumulated by a fish's lipids), the contaminant is considered bioavailable. As noted in *Information Box 1*, contaminants may be associated with several environmental phases in water and not all are equally bioaccessible or bioavailable. For example, contaminants associated with the black carbon in a sediment are considered almost completely non-bioaccessible and therefore not likely to be bioavailable. In contrast, contaminants truly dissolved in the water are considered very bioaccessible and therefore likely to be bioavailable and taken up by an organism. It is critical to note that contaminants truly dissolved in the water are not the only bioavailable contaminants in an environmental system. Other phases can contribute bioavailable contaminants; however, the dissolved water concentration is often a good surrogate for the bioavailable concentration in a given environmental system. Passive samplers collect contaminants only from the bioaccessible form and thus are good estimators of what is bioavailable. See Reichenberg and Mayer (2006) for more discussion.

As an example of comparative expenses, Table 2 presents the costs of analyzing several types of samples for the 20 PCB congeners measured by the National Oceanic and Atmospheric Administration (NOAA) as part of its National Status and Trends Program. Built into these estimates is the assumption that 10 to 20 water samples are being extracted by conventional methods or passively sampled then analyzed by GC/MS.

Table 2 shows that total costs for the analysis of the PE, POM and SPME passive samplers range from $310 to $425, with most of the cost associated with the chemical analysis; materials costs range from only $5 to $50. It is worth noting again that once a conventional sample has been reduced to the chemical extract and injected into the GC/MS or GC/ECD for analysis, the costs are identical regardless of the type of sampler. The overall costs vary depending on material expenses and any preparation related to the sample. The labor associated with extracting contaminants from 5 liters of water also adds costs compared with extracting a few grams of sampler, or milligrams of sampler, in

the case of the SPME. Finally, the analysis of the PE, POM and SPME samplers is still relatively new to many commercial analytical laboratories. The cost of analysis is likely to decrease as these types of samplers continue to be used more often and the procedures become more familiar.

Table 2. Comparison of costs for analyzing different types of samples for 20 National Oceanic and Atmospheric Administration (NOAA) PCBs.

Type of Sample	Materials (samplers & deployment equipment) ($)	Chemical Analysis ($)	Total ($)
Water (5 L by conventional method)	<5	525	530
Polyethylene (PE)	~5	375	380
Polyoxymethylene (POM)	~50	375	425
Solid Phase Micro-extraction (SPME)	~35	275	310

Note: Costs provided courtesy of an independent laboratory. Cost values in dollars are reported per sample.

3. What Passive Samplers Tell Us

Passive samplers can provide a more scientifically sound and cost effective way to measure or predict the concentration of hydrophobic contaminants in the dissolved phase. Furthermore, data from passive samplers can result in more accurate as well as more biologically relevant measurements than conventional sampling methods. For example, current sampling methods typically define the dissolved phase as the amount of a contaminant that passes through a 0.4-micron (μm) filter. This operational definition, however, does not have a real biological basis.

Figure 1 is a conceptual diagram showing how actual water column concentrations of a COC at a site might vary over time (shown as a blue line). We do not currently have the technology to accurately measure the actual dissolved concentration represented in Figure 1 in a fashion that is free of artifacts. Conventional methods, which involve collecting a sample of water at one point in time only provide a "snap shot" of the COC concentration. However, such a measurement can be valuable, especially when information is needed quickly or a chemical is acutely toxic but it can also be biased by the artifacts discussed above (e.g., presence of DOC and colloids). Furthermore, these measurements can be affected by short-term temporal events (such as storms) that either result in an elevated or a reduced dissolved concentration that does not accurately reflect long-term average concentrations at the site.

Knowing the long-term average concentrations is critical when we want to understand what local organisms are being exposed to over longer time periods. Because passive samplers monitor water column or interstitial water concentrations over time, they provide a more representative "time-integrated" measurement that better reflects the average exposures experienced by local organisms. In Figure 1, the red line reflects the passive sampler-based water column concentration of a COC showing the time-integrated measurement of dissolved concentrations.

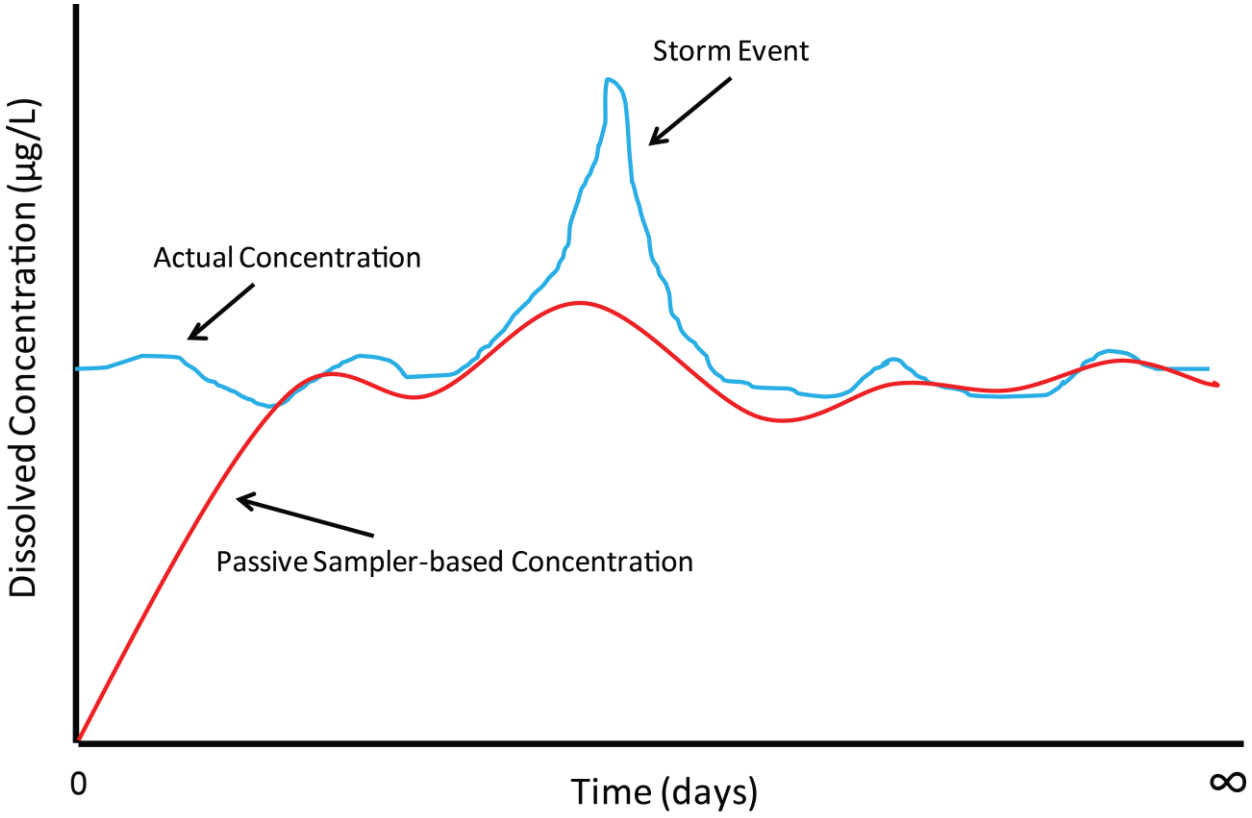


Figure 1. Conceptual diagram of the dissolved water column concentration of a hydrophobic contaminant shown as the actual concentration (blue line) and the passive sampler-based concentration (red line).

Passive samplers provide two basic types of information:

(1) Concentration of COC in the passive sampler. This type of information is obtained by analyzing the solvent extract collected from the sampler. This information is useful because there is growing evidence that a good correlation exists between the concentration of COC accumulated by passive samplers and the concentration bioaccumulated by aquatic organisms, especially those closely associated with sediment (e.g., benthic invertebrates). For example, in a limited number of studies, bioaccumulation by organisms used in biomonitoring and sediment assessments, like benthic worms,

showed good agreement with the concentration accumulated by passive samplers (i.e., a linear relationship) (Vinturella and others 2004, Friedman and others 2009, Gschwend and others 2011). This agreement suggests that, under appropriate conditions, passive samplers could be used as surrogates for these animals.

(2) Concentration of COC dissolved in the aqueous phase around the passive sampler. The dissolved concentration of COC in the water column or interstitial waters is the most bioavailable concentration and therefore the quantity needed to better understand the true exposure conditions at the site. This concentration is calculated based on the concentration of COC in the sampler (data from [1] above) and a simple mathematic relationship discussed in Section 8. In practice, this concentration can be compared with water quality standards or criteria, risk-based values, or background levels to assess the impact of potentially high concentrations in the water column and sediment interstitial waters.

4. Types of Passive Samplers

This SAMS discusses the three most commonly used types of passive samplers. These are:

- Polyethylene (PE)
- Polyoxymethylene (POM)
- Solid Phase Micro-extraction (SPME)

Passive samplers are essentially pieces of plastic, or more specifically, organic polymer. Their composition is discussed in more detail in the next section. As pieces of plastic, they are fairly simple objects. Figure 2 provides photographs of the three passive samplers. As shown in Figure 2, the PE and POM passive samplers are simply pieces of plastic sheeting that range from about 15 µm to 100 µm in thickness and can be easily cut with scissors to be as large or small as needed. The PE plastic drop cloth available from hardware stores is frequently used as passive sampler material. The POM passive sampler uses a more specialized type of polymer, but it also can be purchased in large sheets. The SPME passive sampler is, as Figure 3 illustrates, actually fiber-optic cable. The inner fiber core consists of glass that does not readily absorb hydrophobic contaminants but the insulating polymer, polydimethylsiloxane (PDMS), coating the glass core is an absorptive material effective for passive sampling. The PDMS coating can be purchased in a variety of thicknesses from about 10 to 100 µm. The coated fibers can be various lengths but can be fragile, so shorter lengths of 1 to 20 centimeters are commonly used; however, lengths up to one meter have been deployed in the environment.

Figure 2. Photographs of selected passive samplers.

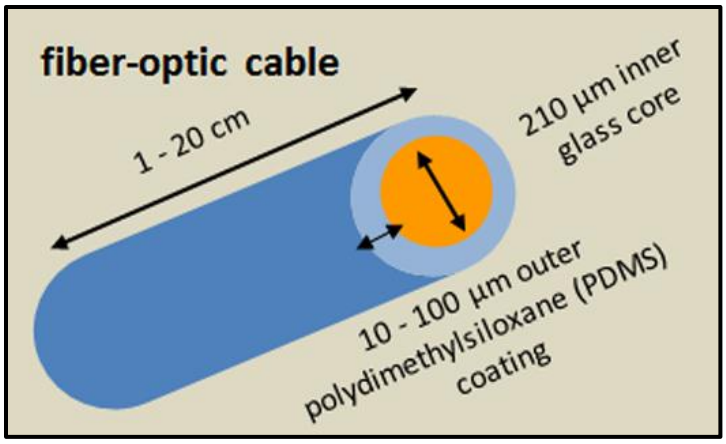


Figure 3. Close-up view of SPME fiber.

As noted earlier, a fourth sampler called a SPMD was one of the first environmental passive samplers developed and it has been applied extensively in water column deployments for decades (Huckins and others 1993, 2006). However, SPMDs have not been used very frequently in sediments although they have been applied to examine sediment-water interface processes (Schubauer-Berigan and others 2012). Because of their infrequent use in sediments, SPMDs will not be discussed any further in this SAMS.

5. Some Theory on How Passive Samplers Work

As noted earlier, commonly found COC, like PCBs, DDTs, and high molecular weight PAHs are hydrophobic. That is, they have little affinity for water. Passive sampling takes advantage of the hydrophobicity of COC to collect and concentrate these contaminants by deploying material in the system being assessed or monitored that is also hydrophobic. Hydrophobic contaminants follow the old organic chemistry adage "like dissolves like"; that is, if a hydrophobic material is placed into water under the right conditions, hydrophobic contaminants will dissolve into the other environmental phases, including a passive sampler, rather than remain dissolved in the water.

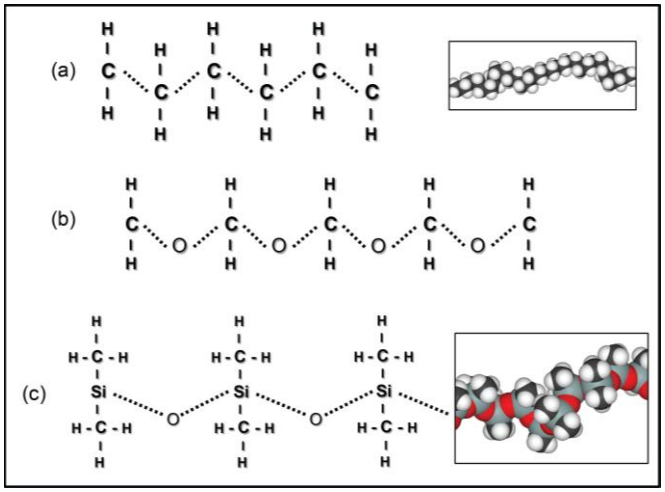


Figure 4. Basic polymer structure of (a) polyethylene, (b) polyoxymethylene and (c) polydimethylsiloxane. C is carbon, H is hydrogen, O is oxygen and Si is silicon. Three dimensional views of polyethylene and polydimethylsiloxane are also shown (from Wikipedia).

Information Box 3 *Equilibrium* is a physicochemical term that describes, for this SAMS, the apparent lack of transfer of contaminants from one environmental phase to another. Specifically, equilibrium is established when the change in the amount of COC transferring from one phase to another, on average, is equivalent to zero. Though it can be an abstract concept, equilibrium simply indicates that we do not expect any significant change over time in the concentration of a COC in any phase we may want to measure. By knowing the system is at equilibrium and the concentration of COC is no longer changing in any phase, we can be confident that any inferences we make about concentrations within the system will be accurate and will not change significantly. A clear way to visualize equilibrium for COC concentrations is to plot concentration versus time. Once the concentration in the sampler is no longer changing with time, we can conclude that equilibrium has been achieved. See Schwarzenbach and others (2003) for more discussion.

In passive sampling, the hydrophobic material is an organic polymer that is fundamentally similar in hydrophobicity to many hydrophobic contaminants. Figure 4 illustrates the molecular structure of these polymers. In the actual polymer, these structures would be repeated millions of times to form large, layered sheets of material. As shown in Figure 5, when a sheet of this material is placed in water with contaminants, such as PCBs, present in the dissolved phase, the PCBs will partition into the polymer, moving out the water and dissolving into the polymer (Figure 5a). Over time, the PCBs will accumulate in the sampler (Figure 5b) until the change in the PCB concentration in the passive sampler no longer is increasing (Figure 5c). Note that if concentrations of PCBs decline in the water, PCB concentrations in the passive sampler may also decrease. Once these changes in PCB concentrations in the passive sampler are no longer

significant, the PCBs are considered to be at equilibrium between the passive sampler and the various environmental phases, most importantly the dissolved phase in the water (see *Information Box #3*). Once a sampler has achieved equilibrium, it can be retrieved, and analyzed for COC to acquire the information samplers provide, as discussed in Section 3.

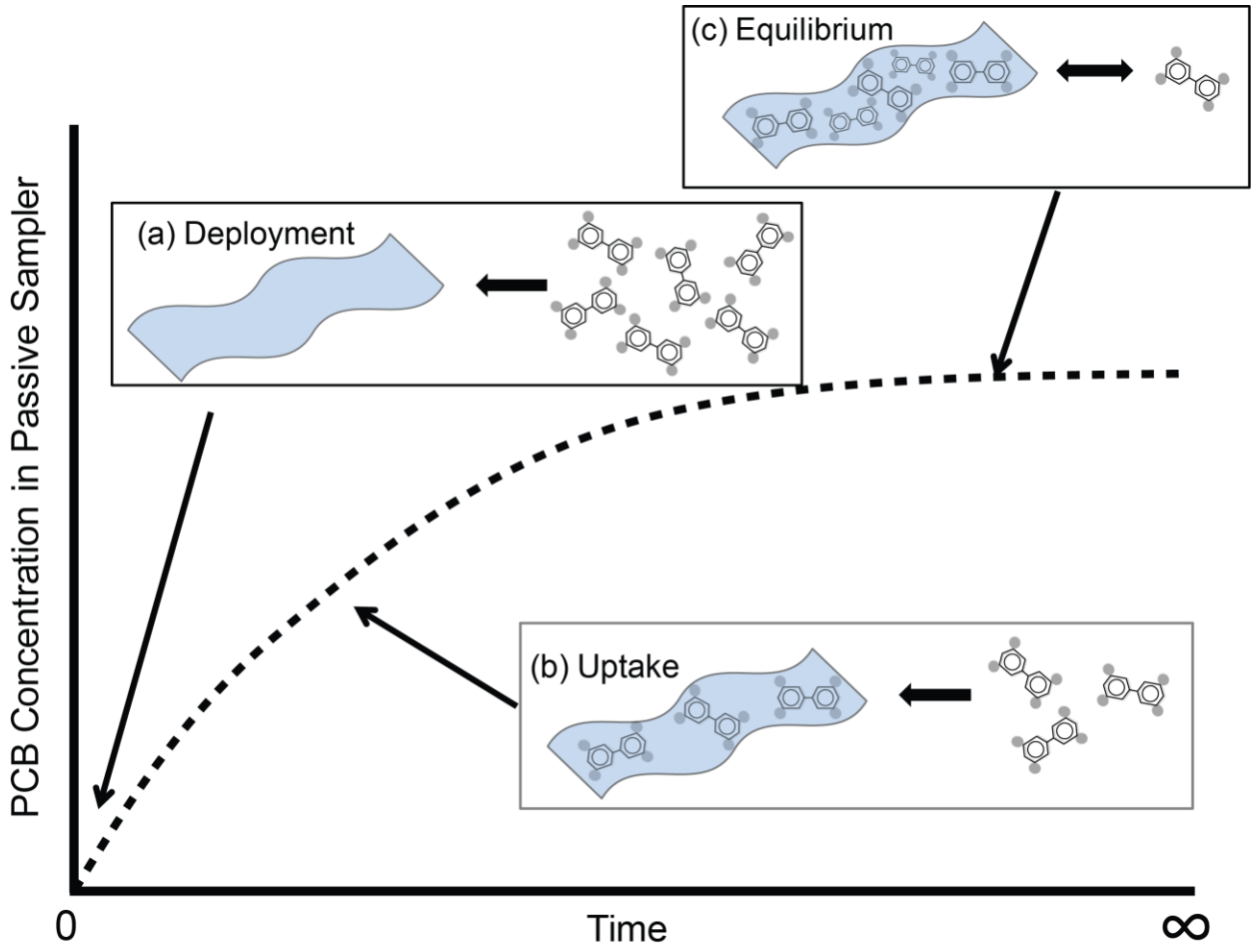


Figure 5. Conceptual schematic of PCB ( ) uptake by a passive sampler ( ) from (a) initial deployment, (b) through uptake, and (c) achieving equilibrium. The number of PCB molecules is not intended to be quantitative but rather demonstrate relative changes in the concentrations of PCBs over the deployment period.

6. Preparing, Deploying, Recovering, and Storing Passive Samplers

This section provides an overview of the steps involved in preparing, deploying, recovering, and storing recovered passive samplers. As previously noted, more specific guidance is being developed by others and should be available soon. Before deployment, it is critical to ensure samplers are not contaminated with any COC. As shown in Figure 5a, the assumption is that the samplers are free of any contamination at the time of deployment. Generally, preparation of the samplers involves soaking them in organic solvent for several hours to days before deployment, followed by soaking or rinsing with clean water. After they have been cleaned, it is also critical to reduce the potential for recontamination from laboratory, air, car or truck, boat and dock surfaces, or other sources. After the cleaning and rinsing, the samplers are often wrapped in aluminum foil, placed inside a plastic bag, and frozen (-4ºC) until they are ready for deployment. Different types of samplers require different kinds of deployments. PE and POM can be deployed in the water column on stainless steel wire loops that maximizes the sampler surface area exposed to the water (and dissolved contaminants) (Figure 6a). They can also be deployed in enclosures like fish traps to reduce the potential for sampler loss and protect them from being torn by currents, severe weather, or boat traffic, or eaten by aquatic organisms (Figure 6b). In general, stainless steel wire can be used to attach the passive samplers to anchor lines and to the inside of fish traps during deployments. These types of passive samplers are often deployed in 0.5 to 1.0 meter-long strips that are about 10 to 15 centimeters wide.

SPME samplers can be fragile, especially those fibers with a very thin coat of PDMS (such as 10 µm) and need to be deployed in some form of protective container. These containers can include stainless steel or copper mesh envelopes or tubing (see Figure 7). Often, several SPME fibers 2 to 20 centimeters long will be placed inside the mesh to increase the amount of polymer, which enhances the sensitivity of later chemical analysis. However, pieces of SPME fiber up to a meter long have been deployed in stainless steel tubes (Figure 7d). Sediment deployments require less polymer because COC concentrations in sediment are usually much higher than are observed in the water column. Therefore, the concentrations that accumulate in the sampler reach levels that are analytically detectable with less need for large amounts of polymer. For instance, a piece of PE or POM one to three centimeters square can easily be inserted into sediment without any special protection or equipment (Figure 7a). For example, using a large pair of forceps, PE was inserted into sediments during a standard bioaccumulation study (Friedman and others 2009). For field deployments, PE and POM have been placed in sediments *in situ* with metal frames that maintain the surface area of the polymer (Figure 7b) (Fernandez and others 2009). Furthermore, when passive samplers are in these metal frames, interstitial water and surface water concentrations can be measured simultaneously to assess the gradient of contaminants between the sediment bed and the water column. To avoid damaging the PDMS-coated fibers, copper tubing and other types of tubing and casings (such as stainless steel and copper mesh) have been used to deploy SPME in sediments (Figure 7c) (Maruya and others 2009, D. Reible, personal communication). Other variations on these types of *in situ* deployments in sediments of passive samplers are described by Booij and others (2003), Tomaszewski and Luthy (2008), Janssen and others (2011), Oen and others (2011) and Burton and others (2012).

Passive samplers can easily be deployed in the field with limited costs using inexpensive equipment. Figure 8 illustrates a number of deployment strategies for passive samplers in the water column and sediment at a contaminated site. As noted above, passive samplers can be deployed in the water column using fish traps (Figure 8a), stainless steel wire loops (Figure 8b), and copper tubes (Figure 8c). Figure 8d shows passive samplers deployed in sediments using metal frames with PE or POM polymers and a copper tube and stainless steel rod containing SPME fibers. In some waterbody locations it may be better not to use buoys at the surface, but below the surface to prevent tampering and disruption by wave action. The Office of Superfund Remediation and Technology Innovation (OSRTI) Environmental Response Team's Dive Team as well as Region 10's Dive Team have extensive experience deploying and retrieving passive samplers in sediments and can be a valuable, cost-effective resource to use when considering the application of passive samplers at sediment sites. More information on the dive teams can be found at:
www.ert.org/mainContent.asp?section=Dive&subsection=About and
yosemite.epa.gov/R10/OEA.NSF/investigations/dive+team+videos.

After the deployment period (often 28 days), the samplers are recovered and wiped clean with laboratory tissues to remove site water and sediments and any biological growth. If the samplers still retain a film of residual sediment or biological growth, they should be rinsed with clean water for about a minute or wiped with a damp laboratory tissue to remove as much remaining material as possible without damaging the samplers. Once samplers are cleaned, they are wrapped in clean aluminum foil, stored in an ice-filled or artificial ice-filled cooler, and returned to the laboratory as soon as possible, and then stored at -4ºC until chemical analyses are initiated.

Passive samplers can also be used in *ex-situ* conditions. In this approach, contaminated sediment is collected in the field and returned to the laboratory. Passive samplers are then added to the sediment during laboratory bioaccumulation and partitioning studies (Mayer and others 2000, Booij and others 2003, Vinturella and others 2004, Friedman and others 2009, Gschwend and others 2011, Hawthorne and others 2005, 2009, Lampert and others 2011, Lu and others 2011) to measure the COC concentrations. This *ex-situ* strategy has the advantage of being able to control, under laboratory conditions, many of the environmental variables, such as temperature, that are uncontrollable in the field. This type of deployment is also often less expensive than in *situ* deployments. However, the *ex situ* approach departs from the natural conditions that reflect reality at contaminated sites.

Passive samplers can be deployed in both freshwater and saltwater systems. The fundamental processes affecting the uptake of COC by the PE, POM or SPME are essentially the same regardless of the salinity of the water except for one difference. The presence of the salt dissolved in seawater will make the COC accumulate into the organic polymer more readily than in freshwater. For example, a COC at a given dissolved concentration in seawater will accumulate to a greater degree in a passive sampler deployed in seawater than the same COC at the same dissolved concentration in freshwater. However, the most substantial difference between freshwater and saltwater systems when passive sampling is probably the adverse effects to the deployment gear. In saltwater systems, the potential for corrosion of any metal is obviously much greater than in freshwater systems. The forthcoming guidance on deploying and recovering passive samplers will discuss considerations for using passive samplers in saltwater systems.

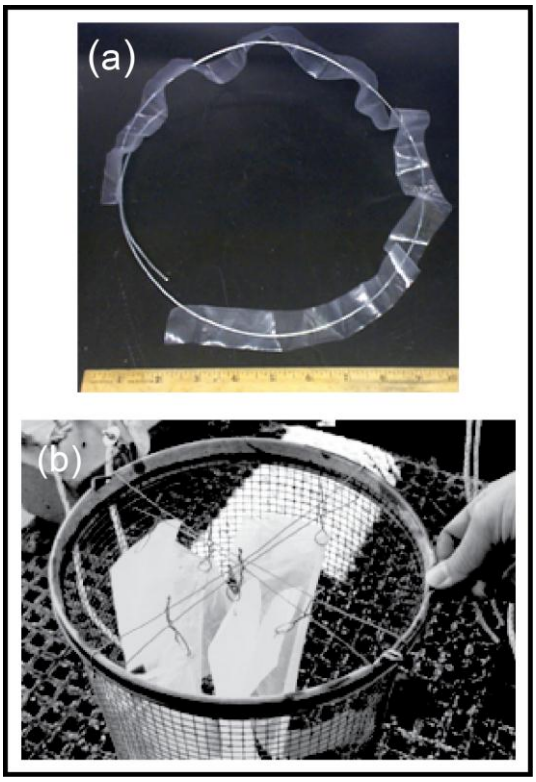


Figure 6. Passive samplers designed for water column deployments: (a) long strip of polyethylene on a stainless steel wire loop, and (b) polyethylene and polyoxymethylene strips fastened to the interior of a fish trap.

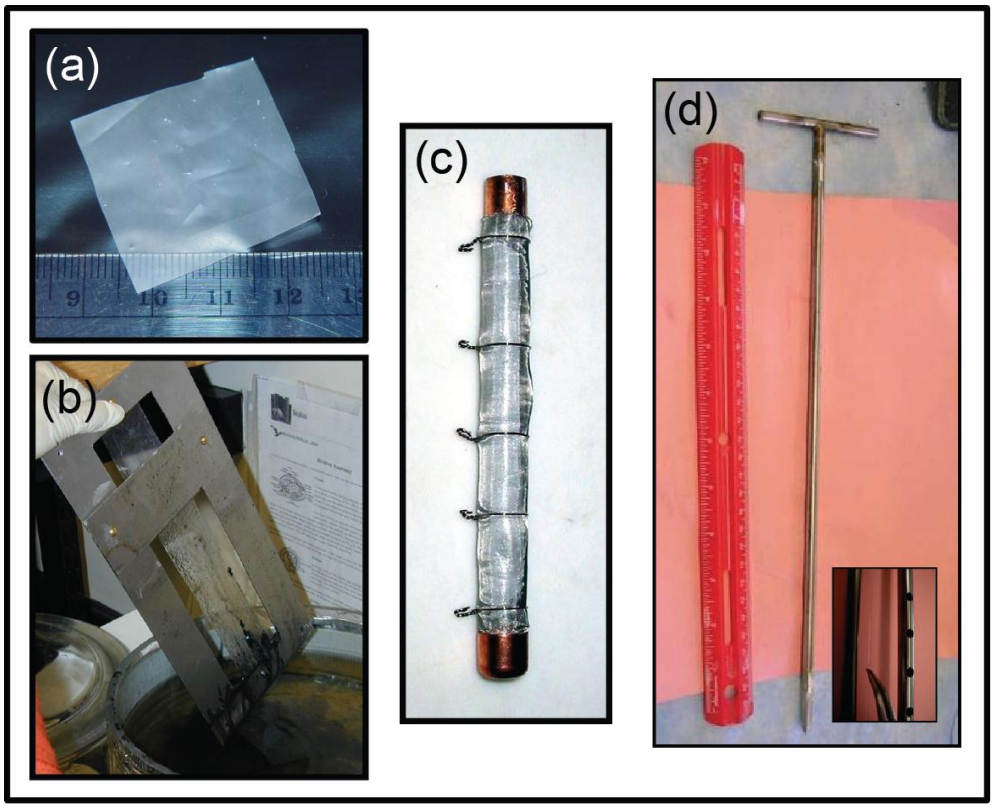


Figure 7. Passive samplers designed for whole sediment deployments: (a) small piece of polyethylene, (b) polyethylene arrayed in a metal frame, (c) copper tubing holding SPME fibers, and (d) stainless steel tubing containing SPME fibers.

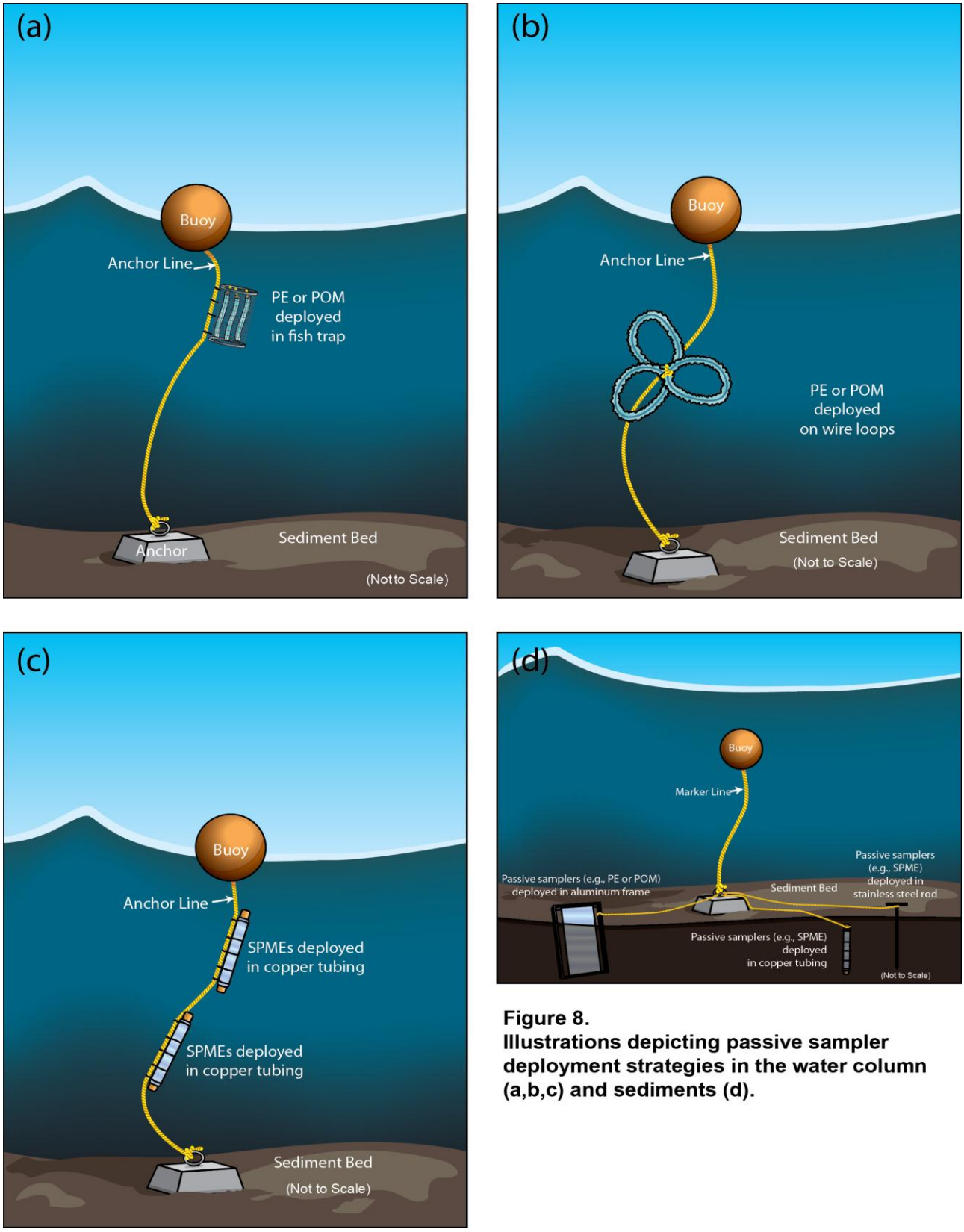


Figure 8.
Illustrations depicting passive sampler deployment strategies in the water column (a,b,c) and sediments (d).

7. Selecting Passive Samplers

Of the three types of passive samplers discussed in this document, each has its own advantages and disadvantages, and, to a certain extent, each has its own following of practitioners. Table 3 lists some of the more relevant characteristics of each type of sampler when considering which one to use. Because they are similar in form (polymer sheets), PE and POM demonstrate several common advantages. Both PE and POM are relatively inexpensive, rugged, easy to work with (can be cut into pieces with scissors for deployment), simple to deploy, deployable in large masses, which increases analytical sensitivity, and are enjoying increased use in the scientific and regulatory communities. In addition, both PE and POM are effective for water column and sediment deployments. However, PE and POM have some differences and disadvantages. PE is very flexible and can fold in on itself, making it difficult to clean, especially after deployment. Conversely, the rigid structure of POM reduces folding, which makes it easier to clean, but also renders it prone to ripping away from the wire during the deployment (whereas PE will stretch well before ripping). In contrast to PE and POM, SPME are believed to achieve equilibrium faster than the other two polymers, which can be a significant advantage. In addition, SPME, once secured in the protective tubing or casing, are easily deployed, recovered and cleaned, in part because of their compact size. Furthermore, SPME has wide usage around the world. However, SPME fibers can be fragile as compared with PE or POM, which affects ease of handling. It is also difficult to deploy large masses of SPME, which reduces analytical sensitivity compared with PE or POM. For this reason, SPME can be better suited for deployment in sediments rather than the water column.

8. Analyzing Passive Sampler Data

Regardless of the type of passive sampler selected for use, analysis of passive sampler data can be handled in the series of steps described below. As noted in Section 3, passive samplers provide two types of information:

(1) *Measured* concentration of COC in the passive sampler
(2) *Predicted* concentration of COC dissolved around the passive sampler

These types of information can be expressed in several different ways. Examples of the common concentration units for passive sampler data are shown in Table 4. In general, the laboratory analyzing the passive samplers will provide data on the amount of contaminant in the passive samplers ([1] above). Using these data, the following steps can be followed to translate the measured concentrations in the passive sampler into dissolved concentrations around the passive samplers:

(1) Convert units to micrograms per gram (µg/g):

If the units reported by the laboratory are microgram (µg) COC/milliliter (mL) sampler, convert the units to µg COC/g sampler by dividing by the density of the passive sampler. Commonly reported densities for PE are 0.92 g/mL, for POM are 1.4 g/mL, and for PDMS are 0.97 g/mL.

(2) Calculate the dissolved COC concentration:

Using the concentration of COC in the passive sampler in µg COC/g sampler, the dissolved concentration (in the water column or interstitial water around the passive sampler) is calculated using Equation 1:

$$COC_D = \frac{COC_{PS}}{K_{PS-D}} * 1000 \qquad [1]$$

where COC_D is the dissolved concentration (µg COC/L) of a given COC in the surrounding water, COC_{PS} is the concentration of the COC in the passive sampler (µg COC/g sampler) from Step 1, and K_{PS-D} is the passive sampler-dissolved phase partition coefficient (in liters per kilogram [L/Kg]). A multiplier of 1,000 is included to address the change in units (1,000 g/Kg). Values for a limited number of K_{PS-D} are available in the scientific literature. For example, U.S. EPA (2012) provides a set of provisional K_{PS-D} for a range of hydrophobic contaminants and passive samplers (PE [K_{PE-D}], POM [K_{POM-D}], SPME [K_{SPME-D} or K_{PDMS-D}]). In addition, K_{PS-D} can be calculated based on the contaminant's K_{OW} (see Appendix A). Fortunately, K_{OW} is a fairly common contaminant characteristic available in the scientific literature (see for example Mackay and others 1992a, b, U.S. EPA 2003, 2008, 2012).

(3) Example Calculation:

Table 5 reports the results of an analysis of PE samplers deployed in the water column for 30 days. The chemical analyses were for several PAHs, including phenanthrene, benzo[a]pyrene and benzo[ghi]perylene, the pesticides endrin, toxaphene, DDT, DDE and DDD, and three PCB congeners (28, 52, 118). The concentrations of the contaminants accumulated by the passive sampler ranged from 0.07 to 12.5 micrograms per milliliter (µg/mL) PE and 0.08 to 13.6 when converted to µg/g PE. Using Equation A1 from Appendix A, log K_{PE-D} values were calculated with log K_{OW} from the scientific literature. Using Equation 1 above, the dissolved concentrations of contaminants were calculated to range from 0.00002 to 0.841 micrograms per liter (µg/L) or ppb. Multiplying these concentrations by 1,000 converts them to 0.02 to 841 nanograms per liter (ng/L) water or parts per trillion (ppt) (Table 4).

Some general trends can be observed from these example calculations. First, the concentrations of contaminants accumulating in the passive sampler tend to be higher when the contaminants have lower log K_{PE-D} values. The concentrations are higher because the lower K_{PE-D} chemicals tend to be more water soluble than higher K_{PE-D} chemicals. Consequently, the lower K_{OW} chemicals can dissolve into water more readily than the higher K_{OW} chemicals. Higher concentrations in the water column result in higher concentrations in the sampler. While the higher K_{OW} chemicals have a greater affinity for passive sampler polymers (e.g., PE, PDMS or POM) as compared with the low K_{OW} chemicals, this does not result in elevated concentrations of high K_{OW} chemicals in the passive sampler (Table 5) because these chemicals must first dissolve into the aqueous phase and then partition into the polymer. Because of their low solubilities in water, the high K_{OW} contaminants do not dissolve very readily and therefore do not accumulate to high concentrations in the samplers. The same sort of example calculations could be performed on contaminants measured in sediment interstitial water.

Table 3. Advantages and disadvantages of different types of passive samplers.

Passive Sampler	Advantages	Disadvantages
Polyethylene	● Inexpensive polymer ● Robust and rugged ● Easy to work with ● Simple to deploy and recover ● Not limited by sample mass (greater analytical sensitivity) ● Will stretch during deployment before it rips ● Increasing use globally ● Good for both water column and sediment deployments	● Slower equilibration than SPME ● Folds on itself, making cleaning difficult
Polyoxymethylene	● Inexpensive polymer ● Robust and rugged ● Easy to work with ● Simple to deploy and recover ● Not limited by sample mass (greater analytical sensitivity) ● Cleans easily ● Increasing use globally ● Good for both water column and sediment deployments	● Slower equilibration than SPME ● Can rip easily compared with PE
Solid Phase Micro-extraction	● Inexpensive polymer fibers ● Rapid equilibrium ● Widely used globally ● Once protected, simple to deploy and recover ● Clean easily ● Good for sediment deployments	● Fragile – need to protect during deployment ● Relatively difficult to handle ● Limited polymer mass (less analytical sensitivity) ● Poor for water column deployments because of the limited polymer mass

Table 4. Type of data and units provided by passive samplers.

Type of Data	Units
(1) Concentration of COC in the passive sampler	µg COC/mL sampler (ppm[1]) µg COC/g sampler (ppm)
(2) Concentration of COC dissolved around the passive sampler	µg COC/mL water (ppm) µg COC/L water (ppb[2]) mg COC/L water (ppm) ng COC/L water (ppt[3]) pg COC/L water (ppq[4])

[1] parts per million, [2] parts per billion, [3] parts per trillion, [4] parts per quadrillion

Table 5. Example calculation of dissolved concentrations of selected contaminants of concern (COC) based on concentrations measured in a polyethylene passive sampler.

COC	Measured Concentration in Sampler		Log K_{OW} (L/Kg)	Log K_{PE-D} (L/Kg PE)[b]	Calculated Dissolved Concentration (COC_D) (ng/L)[c]
	(COC_{PS}) (µg/mL)	(COC_{PS}) (µg/g)[a]			
Phenanthrene	12.5	13.6	4.57	4.21	841
Benzo[a]pyrene	3.45	3.75	6.11	5.83	5.60
Benzo[ghi]perylene	0.75	0.81	6.51	6.25	0.46
Endrin	10.3	11.2	5.06	4.72	212
Toxaphene	8.95	9.73	5.50	5.19	63.5
PCB 28	4.98	5.41	5.67	5.36	23.4
PCB 52	0.78	0.85	5.84	5.54	2.44
PCB 118	0.08	0.08	6.74	6.49	0.03
p,p' DDT	0.43	0.47	6.53	6.27	0.25
p,p' DDE	0.07	0.08	6.76	6.51	0.02
p,p' DDD	0.54	0.59	6.10	5.82	0.90

[a] COC_{PS} * mL/0.92 g

[b] Log K_{PE-D} = -0.59 + 1.05*Log K_{OW}

[c] Equation 1 * 1,000 to report as ng/L

9. Brief Case Study

The Palos Verdes Shelf Superfund site is located in more than 50 meters of water off the coast of Los Angeles (Figure 9). The site has been contaminated by historic discharges from four effluent pipes from the Los Angeles County Sanitation Districts since 1937. As a result, the sediments along the shelf are contaminated with PCBs and DDTs, and the area was designated a Superfund site in 1989. Ingestion of contaminated fish by humans and wildlife are the risk drivers (U.S. EPA 2009).

In 2007, EPA decided to use passive samplers to measure the dissolved concentrations of PCBs in the water column above the contaminated sediments (Burgess and others 2011). The conceptual model for the site suggests contaminants in the sediments enter the water column and are bioavailable to site fish. Because of the depth of the water column at much of the site and the low dissolved contaminant concentrations, the use of conventional water sampling methods was not viable. Polyethylene passive samplers were therefore deployed at seven stations (Figure 9) a few meters above the sediment surface and allowed to equilibrate for approximately 4 months. Using the approach discussed in Section 8, dissolved concentrations of PCBs in the water column were calculated. Figure 10 reports the concentrations of total dissolved PCBs at the seven stations. There were not any problems detecting the contaminants in the passive samplers because the PE samplers accumulated and concentrated the PCBs over the 4-month equilibration period. As expected, the concentrations of PCBs in the passive samplers reflected the concentrations of contaminants in the sediments; that is, if sediments were highly contaminated, then the water column concentrations were also contaminated. For example, stations B3A, B3B and B5 are located above the most contaminated sediments and demonstrated the highest concentrations in the passive samplers (Figure 10). Furthermore, from a regulatory perspective, the dissolved concentrations could be used to compare with water quality standards. In this case, the calculated dissolved concentrations for total PCBs were contrasted with the ambient water quality criteria (AWQC) based on aquatic life and human health. The dissolved concentrations ranged from 100 to 800 picograms/liter (pg/L) or parts per quadrillion. The aquatic life AWQC for total PCBs is 30,000 pg/L and was clearly not exceeded at any station. However, the human health AWQC based on fish consumption is only 64 pg/L and every station exceeded that criterion value. The planned remediation of the Palos Verdes Shelf Superfund site should reduce these concentrations in the water column. As a result of the successful use of passive samplers here, they will also be used to evaluate the effects of site remediation on the water column concentrations of PCBs and DDTs during and after remediation (capping the most heavily

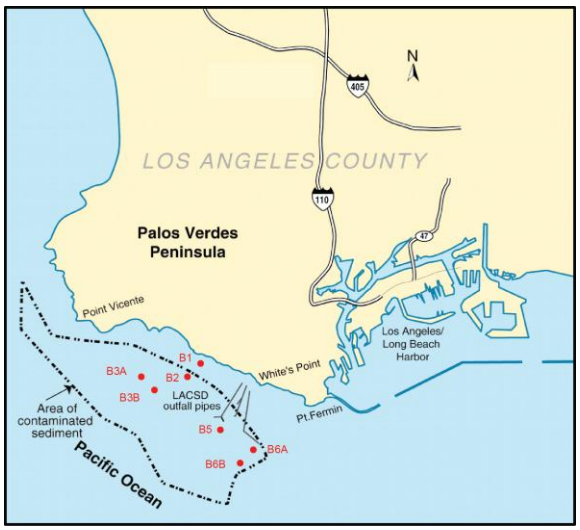


Figure 9. Locations of passive sampler deployment stations at the Palos Verdes Shelf Superfund site.

contaminated areas). While this brief case study focused on water column concentrations, similar analysis of sediment interstitial water concentrations of contaminants is also viable.

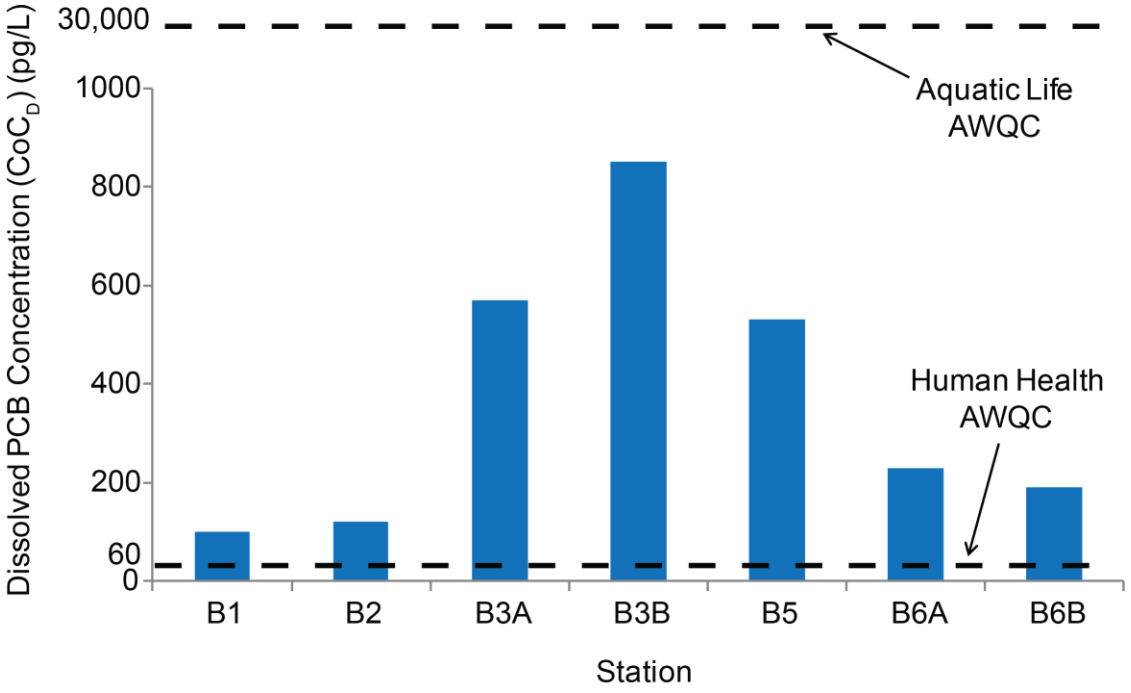


Figure 10. Concentrations of dissolved total PCBs in the water column at the Palos Verdes Shelf Superfund site passive sampler deployment stations.

10. Remaining Scientific Challenges in Using Passive Samplers

A great deal of confidence exists in the utility of passive sampling at Superfund sites. As noted, passive samplers provide information about the concentrations of contaminants in the samplers that can be used to more accurately predict the bioavailable concentrations in the surrounding water column or interstitial waters. However, a few outstanding scientific challenges exist that may limit their wide spread acceptance and use. First, it is critical to determine when a contaminant has achieved equilibrium between the dissolved phase and the sampler and any other environmental phases present. Currently, there are approaches available to decide when equilibrium has been reached, but there exists the need to better understand how and when equilibrium occurs and to have alternative options for evaluating concentration data when equilibrium does not occur. *Information Box #4* explains some of the available approaches for obtaining equilibrium information.

A second scientific challenge deals with interpreting the meaning of contaminant accumulation by passive samplers. As noted, some studies have suggested that passive samplers accumulate COC in ways similar to benthic organisms (Vinturella and others 2004, Friedman and others 2009, Gschwend and others 2011). In theory, this suggestion makes a great deal of sense because the lipid in organisms, where COC accumulate, is chemically similar in partitioning behavior to the polymers used

for passive samplers, and many benthic invertebrates receive their exposures from contaminants dissolved in the interstitial water. Additional laboratory and field research is needed to better understand the relationship between passive sampler accumulation and organism bioaccumulation. This research could result in a statistically robust but simple linear model that predicts organism bioaccumulation based on knowing how much COC accumulated in a passive sampler (COC_{PS}). Furthermore, risk at Superfund sediment sites is often driven by adverse effects to human health by the consumption of contaminated fish and shellfish. At this point, using passive samplers to predict concentrations of COC in pelagic fish is especially challenging because of the potential for trophic transfer and exposure to sources of COC other than from the site sediments. In other words, while there is evidence passive samplers can serve as surrogates for benthic organisms, more research is needed before a similar statement can be made about pelagic fish. However, it is feasible that passive sampler-based dissolved concentrations could be input into a bioaccumulation model (Gobas 1993, Gobas and Arnot 2010) to predict concentrations in edible fish tissue.

Finally, there is a need to develop a standard set of passive sampler-dissolved phase partition coefficients (K_{PS-D}) for a range of passive samplers and COC. As discussed, this partition coefficient is used in Equation 1 to estimate the dissolved concentration of COC. These partition coefficients are available in the scientific literature and can also be calculated based on K_{OW}. This need is not so much a scientific challenge as a task to compile scientifically-sound values that can be used universally and consistently by the entire passive sampling community.

Information Box 4 *Performance Reference Compounds (PRCs)* As discussed in this document, passive samplers accumulate COC until equilibration has been achieved between the various environmental phases. However, determining when equilibrium has been achieved is challenging. One approach is to deploy the samplers for an extended period of time (e.g., 28 days) and assume the samplers are at equilibrium. Conversely, another approach is to collect subsamples of the passive samplers over time and plot the concentration of contaminants (COC_{PS}) versus time and empirically identify when equilibrium is reached. Both of these approaches are viable but have disadvantages. The first approach requires an assumption that will often be wrong for the higher molecular weight, more hydrophobic COC that require more than 28 days to achieve equilibrium. The second approach is expensive and may not always be logistically feasible. A third approach developed by Huckins and others (2002) is to add chemicals (PRCs) to the passive samplers at the start of the deployment. These PRCs are selected to behave like the target COC except that, as the passive sampler absorbs target COC, the sampler is also releasing PRCs at similar rates. Because the PRCs are selected to behave like the target COC, by knowing how much PRC was present at the start of the deployment and how much remains at the end (which are both easily measured), and using some algebra, the equilibrium status of each COC can be calculated. For example, based on PRC data, a specific PCB congener is found to be 89 percent equilibrated after 28 days. By adjusting the measured PCB congener concentration upward by 11 percent, the actual concentration at equilibrium is predicted. The advantages and disadvantages of PRCs are currently being assessed.

11. U.S. EPA Contacts Working with Passive Samplers

Table 6 provides a list of U.S. EPA contacts working with passive samplers. These personnel may be contacted to provide technical assistance and site-specific advice on the use of passive samplers at sites around the United States.

12. Summary

Passive samplers are site assessment and monitoring tools that can provide faster, cheaper, and more scientifically-sound information about the dissolved water column and interstitial water concentrations of hydrophobic organic COC at Superfund sites. Often passive samplers are more effective at determining accurately the bioavailable concentrations of COC than the application of conventional sampling techniques. This passive sampler-based information can be used to better understand contaminant concentrations that result in real exposures and risks at Superfund sites. However, passive samplers do not provide information about the concentrations of COC associated with bedded, suspended or colloidal particles in aquatic systems and therefore do not address the transport of contaminants associated with such particles. The technology for using passive sampling to evaluate exposures to metals is still under development and was not discussed in this document. Because of the many advantages over conventional sampling, passive sampling is likely to have an increasingly important role in the future of environmental sampling as more guidance and standard operating procedures become available. Furthermore, the availability of contract laboratories with the capability to deploy passive samplers and analyze them after deployment is also increasing as passive sampling becomes more routine.

Table 6. List of U.S. EPA contacts working with passive samplers.

Name	Passive Sampler Application	Office and Location	e-mail
Robert Burgess	Water column and sediments deployments: Performance of different passive samplers; Use of performance reference compounds; Relationship to organism bioaccumulation	ORD/NHEERL/ AED-Narragansett, RI	burgess.robert@epa.gov

Name	Passive Sampler Application	Office and Location	e-mail
Lawrence Burkhard	Sediment deployment: Relationship to organism bioaccumulation	ORD/NHEERL/MED-Duluth, MN	burkhard.lawrence@epa.gov
Mark Cantwell	Water column deployments in riverine systems: COC and emerging contaminants	ORD/NHEERL/ AED-Narragansett, RI	cantwell.mark@epa.gov
Bruce Duncan	Use of passive samplers at Superfund sites	Region 10 – Seattle, WA	duncan.bruce@epa.gov
Marc Greenberg	Use of passive sampler information for decision making	OSWER/OSRTI/ ERT-Edison, NJ	greenberg.marc@epa.gov
Judy Huang	RPM for Palos Verdes Shelf site deploying passive samplers	Region 9 – San Francisco, CA	huang.judy@epa.gov
Matthew Lambert	Sediment deployments: Evaluate contaminant partitioning and bioavailability; Passive sampler use in baseline and remedy effectiveness monitoring	OSWER/OSRTI Washington, DC	lambert.matthew@epa.gov
Marc Mills	Water column and sediment deployments: Source tracking and identification; Relationship to organism bioaccumulation; Emerging contaminants	ORD/NRMRL/ LRPCD-Cincinnati, OH	mills.marc@epa.gov

Joseph Schubauer-Berigan	Water column deployments: Restoration and risk management evaluations and applications; Comparison of different passive samplers	ORD/NRMRL/ LRPCD-Cincinnati, OH	schubauer-berigan.joseph@epa.gov
Sean Sheldrake	Diving Officer; Passive sampler deployment techniques and diver related QA/QC issues	Region 10 - Seattle, WA	sheldrake.sean@epa.gov
Rachelle Thompson	RPM for United Heckathorn site deploying passive samplers	Region 9 – San Francisco, CA	thompson.rachelle@epa.gov

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Questions regarding this document should be forwarded to Robert Burgess (burgess.robert@epa.gov) or Stephen Ells (ells.steve@epa.gov). This is U.S. EPA ORD/NHEERL Atlantic Ecology Division contribution number AED-11-097.

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Appendix A. Provisional passive sampler – dissolved phase partition coefficients (K_{PS-D}) (L/Kg) for selected hydrophobic contaminants.

Class	Contaminants	Log K_{PE} [a]	Log K_{POM} [b]	Log K_{SPME} [c]
PAHs	Naphthalene	2.93	2.79	2.86
	C1-naphthalenes	3.40	3.24	3.22
	Acenaphthylene	2.79	2.66	2.75
	Acenaphthene	3.62	3.45	3.40
	C2-naphthalenes	3.93	3.74	3.64
	Fluorene	3.83	3.65	3.56
	C3-naphthalenes	4.45	4.25	4.05
	Anthracene	4.17	3.98	3.83
	Phenanthrene	4.21	4.02	3.86
	C1-fluorenes	4.37	4.17	3.99
	C4-naphthalenes	4.98	4.75	4.47
	C1-phenanthrene/anthracenes	4.70	4.49	4.25
	C2-fluorenes	4.87	4.65	4.39
	Pyrene	4.58	4.37	4.16
	Fluoranthene	4.75	4.53	4.29
	C2-Phenanthrene/anthracenes	5.14	4.91	4.60
	C3-fluorenes	5.40	5.16	4.80
	C1-pyrene/fluoranthenes	4.96	4.74	4.46
	C3-phenanthrene/anthracenes	5.63	5.38	4.98
	Benz(a)anthracene	5.37	5.13	4.78
	Chrysene	5.41	5.17	4.81
	C4-Phenanthrenes/anthracenes	6.05	5.78	5.32
	C1-Benzanthracene/chrysenes	5.86	5.60	5.17
	Benzo(a)pyrene	5.83	5.57	5.14
	Perylene	5.85	5.60	5.16
	Benzo(e)pyrene	5.85	5.60	5.16
	Benzo(b)fluoranthene	5.99	5.73	5.27
	Benzo(k)fluoranthene	6.02	5.75	5.29
	C2-benzanthracene/chrysenes	6.16	5.89	5.41
	Benzo(ghi)perylene	6.25	5.97	5.47
	C3-benzanthracene/chrysenes	6.70	6.41	5.83
	Indeno(1,2,3-cd)pyrene	6.47	6.19	5.65
	Dibenz(a,h)anthracene	6.46	6.18	5.64
	C4-benzanthracene/chrysenes	7.14	6.83	6.18

Class	Contaminants	Log K_{PE} [a]	Log K_{POM} [b]	Log K_{SPME} [c]
Other Chemicals	Benzene	1.65	1.55	1.84
	Delta-BHC	3.38	3.22	3.21
	Gamma-BHC, Lindane	3.33	3.17	3.17
	Biphenyl	3.57	3.40	3.36
	4-Bromophenyl phenyl ether	4.66	4.45	4.22
	Butyl benzyl phthalate	4.49	4.29	4.09
	Chlorobenzene	2.41	2.29	2.44
	Diazinon	3.30	3.14	3.14
	Dibenzofuran	3.68	3.51	3.45
	1,2-Dichlorobenzene	3.01	2.86	2.92
	1,3-Dichlorobenzene	3.01	2.86	2.92
	1,4-Dichlorobenzene	3.00	2.85	2.91
	Di-n-butyl phthalate	4.25	4.06	3.90
	Dieldrin	5.05	4.82	4.53
	Diethyl phthalate	2.04	1.93	2.15
	Endosulfan mixed isomers	3.72	3.54	3.47
	Alpha-Endosulfan	3.43	3.27	3.25
	Beta-Endosulfan	4.16	3.97	3.82
	Endrin	4.72	4.51	4.27
	Ethylbenzene	2.71	2.57	2.68
	Hexachloroethane	3.61	3.44	3.39
	Malathion	2.44	2.32	2.47
	Methoxychlor	4.74	4.53	4.29
	Pentachlorobenzene	4.93	4.71	4.44
	1,1,2,2-Tetrachloroethane	1.92	1.81	2.05
	Tetrachloroethene	2.21	2.10	2.29
	Tetrachloromethane	2.28	2.16	2.34
	Toluene	2.30	2.18	2.35
	Toxaphene	5.19	4.96	4.64
	Tribromomethane (Bromoform)	1.88	1.77	2.02
	1,2,4-Trichlorobenzene	3.62	3.45	3.40
	1, 1, 1-Trichloroethane	2.01	1.90	2.13
	Trichloroethene	2.26	2.14	2.32
	m-Xylene	2.77	2.63	2.73

[a] $\text{Log } K_{PE-D} = -0.59 + 1.05 \text{ Log } K_{OW}$ (Equation A1) (Lohmann and Muir 2010)
[b] $\text{Log } K_{POM-D} = -0.60 + 1.01 \text{ Log } K_{OW}$ (Equation A2) (Endo and others 2011)
[c] $\text{Log } K_{SPME-D} = 0.07 + 0.83 \text{ Log } K_{OW}$ (Equation A3) (DiFilippo and Eganhouse 2010)