NAVFAC
Naval Facilities Engineering Command
EXWC Engineering & Expeditionary Warfare Center

ENVIRONMENTAL RESTORATION

Passive Sampling for Contaminated Sediment Sites

Introduction

Passive sampling is a group of data collection methods based on spontaneous transfer of the analyte from the sampled medium to the passive sampler material due to the difference in chemical potentials (Górecki and Namiesnik, 2002). Passive sampler materials are selected to preconcentrate the analytes (meaning that the analytes accumulate in the passive samplers at concentrations much higher than those in the sampled water). Through this process, passive sampling can achieve improved detection limits compared to traditional water sampling methods. Passive samplers have been used to measure aqueous concentrations of a wide variety of chemicals, most notably hydrophobic organic contaminants (HOCs) including polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), dioxins, dibenzofurans, and pesticides, as well as transition metals such as cadmium, copper, nickel, lead, and zinc.

Passive sampling eliminates the need for transporting large sample volumes back to the laboratory and/or the use of difficult porewater extraction procedures. Another major advantage of passive sampling is that it allows separation of the colloid and dissolved organic carbon-bound contaminants form their truly dissolved form (C_{free}), which has been shown to correlate well with bioavailability (Mayer et al., 2014). Additionally, passive samplers are more suitable for long-term monitoring applications as they offer time-integrated results over the period of exposure, as opposed to traditional water or sediment grab sampling methods which only measure conditions at a specific point in time. Therefore, passive sampling has the potential to provide more representative data to support sediment site management decisions.

The primary limitation of the passive sampling approach is that the dissolved concentrations are not directly measured. Instead, certain calculation steps must be conducted to convert the concentration of the analyte in the passive sampler (typically expressed in mass of analyte per mass or surface area of the passive sampler) into water concentration (in mass of analyte per liter) at the sampled site. Therefore, the accuracy of the obtained results depends on the availability of high quality data on the analyte uptake by the passive sampler.

Passive samplers can be used as monitoring tools for contaminated sites, as well as in remedial investigations and feasibility studies (Menzie et al., 2016). Recently, a U.S. Environmental Protection Agency (EPA) guidance document was released advising on laboratory and field procedures for passive samplers (U.S. EPA/SERDP/ESTCP, 2017). The use of C_{free}, including values obtained from passive samplers, has also been employed in remedial goal design (U.S. EPA, 2017). Passive sampling may also be useful for forensic investigations where the improved detection limits can support PAH fingerprinting from different sources (Benotti et al., 2018).

This fact sheet provides an overview of the types of passive samplers available, along with preparation and deployment considerations. Key data analysis steps are highlighted related to extraction and analysis and the interpretation of results related to the calculation of water concentrations, mass transfer models, quality assurance/quality control (QA/QC), and bioaccumulation prediction.

This fact sheet can serve as an introduction for Remedial Project Managers (RPMs) to sediment passive sampling concepts, while in-depth resources on the use and implementation of passive sampling are provided for more information. A key resource for those who wish to further explore this subject is the guide titled, Integrating Passive Sampling Methods into Management of Contaminated Sediment Sites: A Guide for Department of Defense Remedial Project Managers (Menzie et al., 2016).

Distribution Statement A: Approved for public release; distribution is unlimited.

September 2018

Types of Passive Samplers

Many types of passive samplers have been developed in the last three decades (Górecki and Namiesnik, 2002; Vrana et al., 2005). The most commonly used types of passive samplers, including polyethylene devices (PEDs), polyoxymethylene (POM), polydimethylsiloxane (PDMS)-coated solid-phase microextraction (SPME), polar organic chemical integrative samplers (POCIS), and diffusive gradient in thin film (DGT®), are described below.[1]

Polyethylene Devices (PEDs)

PEDs consist of thin (typically 25-50 µm) low-density polyethylene sheets (Figure 1), which due to their hydrophobic properties passively accumulate HOCs such as PCBs, PAHs, dioxins and furans, or chlorinated pesticides (Adams et al., 2007; Lohamann and Muir, 2010). PED sampling is an equilibrium regimen sampling process, where dissolved water concentration (C_d) of the analyte can be calculated using the concentration of the analyte in the PEDs and the appropriate polymer-water partition coefficient. PEDs have been used both in situ (deployed in the field) and ex situ (laboratory exposures) and are suitable for analytes with a log octanol-water partition coefficient (log K_{ow}) of 3 or more (Vrana et al., 2005). The polyethylene sheets themselves are very inexpensive and durable, meaning that framed PEDs can be inserted into most softer sediment beds without the addition of protective membranes or a metal mesh. The PED material can be easily cut to any size or shape depending on the sampling needs. For example, if low environmental concentrations of the analytes are expected, larger sheets can be used to increase the mass of the analyte for analysis. The major disadvantage of PEDs is that they display relatively slow equilibration. More hydrophobic analytes will not reach equilibrium during the typical one- or two-month exposures, necessitating use of performance reference compounds (PRCs) which serve as exposure standards. If isotopically-labeled PRCs are used, their purchase can add significantly to the cost of PED preparation.

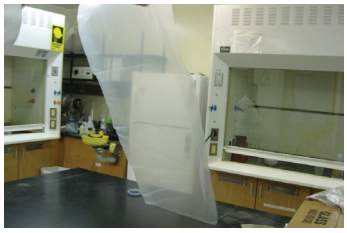


Figure 1. Low-Density Polyethylene Sheet Used for PED Preparation (Courtesy of Battelle)

Polyoxymethylene (POM)

POM material is inexpensive and commercially available in several forms, including small beads and thin sheets (e.g., 76-µm thick sheets) (Figure 2). The sheets are similar in appearance to PED, but are more rigid and have a smoother surface, which decreases the chances of significant biofouling and facilitates easier removal of attached particulates. POM samplers have been used most commonly in ex situ (laboratory) exposures; for in situ (field) deployments, metal mesh is often used to protect the polymer which tends to tear and crack, particularly when thin sheets of POM are used (U.S. EPA/SERDP/ESTCP, 2017). The results achieved with POM are highly reproducible and consistent with PED results. However, due to low diffusivity of HOCs in POM, the uptake kinetics are slower compared to PEDs and custom fabrication of commercially available sheets to make them thinner may be necessary to improve equilibration (Cornelissen et al., 2008). Another disadvantage of the POM sampler is that the analyte uptake mechanisms are still not well understood (Oen et al., 2011; Arp et al., 2015).

Figure 2. POM Film (Courtesy of U.S. EPA/ SERDP/ESTCP, 2017)

Polydimethylsiloxane (PDMS)-Coated Solid-Phase Microextraction (SPME)

SPMEs consist of a silica fiber covered with a PDMS coating that serves as the adsorbent for hydrophobic contaminants (Figure 3). The fiber is inexpensive and commercially available. SPMEs are suitable for compounds with log K_{ow} values from 3 to 7 (Vrana et al., 2005). The main advantages of SPME fibers are fast equilibration and their use in measuring vertical concentration profiles with minimal sediment disturbance. Additionally, the PDMS coating equilibrates faster with the porewater compared to PEDs and POM due to high diffusivities of HOCs in PDMS (Rusina et al., 2007; U.S. EPA/SERDP/ESTCP, 2017). Typically, exposures on the order of days are sufficient to reach equilibrium; however, 30 days may be required for more hydrophobic compounds. Due to the relatively small size of the coating layer, the preconcentration factors achieved by SPMEs are smaller compared to PEDs and POM. The fibers are easy to clean, but fragile enough to require a protective casing for deployment.

[1] The earliest passive samplers, semipermeable membrane devices (SPMDs), have been used since the early 1990s. They consist of a low-density polyethylene tubing filled with triolein which accumulates hydrophobic contaminants. Their popularity has decreased with the discovery of single-phase polymeric materials that show similar affinity for hydrophobic contaminants and offer faster equilibration, easier data modeling, and are not subject to loss in the field due to accidental lipid escape. Therefore, SPMDs will not be discussed in more detail in this document. See Alvarez (2010) for more information.

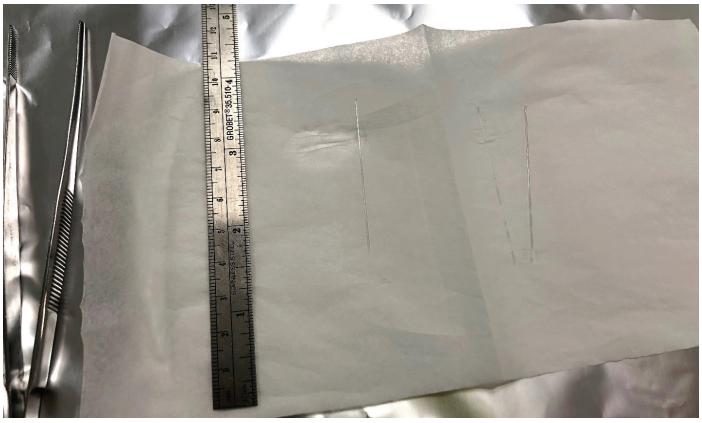


Figure 3. PDMS-Coated SPME Fibers (Courtesy of Battelle)

Other types of silicone passive samplers have also been developed, including silicone-coated glass jars (Schmidt et al., 2017) and silicone strips (Rusina et al., 2010; Smedes and Booij, 2012). In general, the advantage of silicone rubber-based passive samplers is faster equilibration compared to PEDs or POM, but it comes at a cost of lower durability and lower preconcentration factors (Rusina et al., 2007).

Polar Organic Chemical Integrative Samplers (POCIS)

POCIS samplers (Figure 4) consist of a sorbent layer sandwiched between two layers of a hydrophilic polyethersulfone membrane which is biofouling resistant. The sorbent can be adjusted based on the analyte of interest. POCIS are used to measure more hydrophilic compounds than the abovementioned samplers (log K_{ow} values <3 [Vrana et al., 2005; Alvarez, 2010]) such as phosphorous pesticides, pharmaceuticals, and personal care products. POCIS are also useful for a number of military-relevant emerging contaminants of concern (e.g., per- and polyfluoroalkyl substances [PFAS], 2,4,6-trinitrotoluene [TNT], and 1,3,5-trinitro-1,3,5-triazinane [RDX]) (Kaserzon et al., 2012; Belden et al., 2015; Rosen et al., 2018). The use of POCIS for munitions constituents (MC) has been demonstrated through Space and Naval Warfare Systems Command (SPAWAR) research efforts (ESTCP ER-201433). Unlike equilibrium-based passive samplers, POCIS are kinetic regimen passive samplers, meaning that the analyte uptake is directly proportional to time of deployment and knowledge of sampling rates for each analyte is required to obtain quantitative data. It should be noted the majority of the published sampling rate data were obtained through laboratory calibrations which can vary significantly from field exposures, and the applicability of exposure standards (PRCs) is not sufficiently understood, increasing uncertainty of the obtained results. POCIS can be prepared in house or purchased from commercial sources for approximately $65 per POCIS, not counting the cost of reusable hardware.

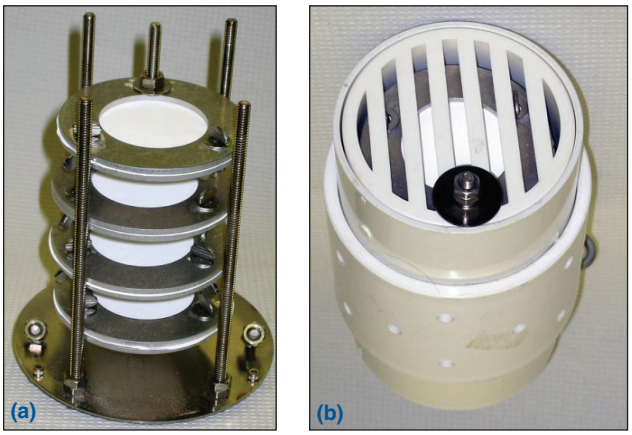


Figure 4. POCIS Apparatus with Four Sampling Discs in a Stainless Steel Canister. (a) Without (left) and (b) With Protective Cover (right) (Courtesy of U.S. Geological Survey) https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf

Diffusive Gradient in Thin Films (DGTs)

Initially proposed by Davison and Zhang (1994), DGTs are still the most common passive sampler method for trace metals. They consist of a binding gel (e.g., Chelex-impregnated polyacrylamide), covered by a diffusive gel (typically 0.8 to 1.0 mm-thick polyacrylamide consisting of ~95% water), and finally a hydrophilic membrane filter which ensures only dissolved chemicals interact with the gel (Figure 5). The binding gel shows high affinity towards the sampled analytes and provides a "sink" which is extracted and analyzed at the end of the deployment period. Like POCIS, DGTs are kinetic regimen samplers and the analyte uptake is directly proportional to time of deployment. The typical assembly for sediments is usually less than 25 cm long and 4 cm wide. Because DGTs provide rapid uptake, deployment times of 6 to 72 hours are most common

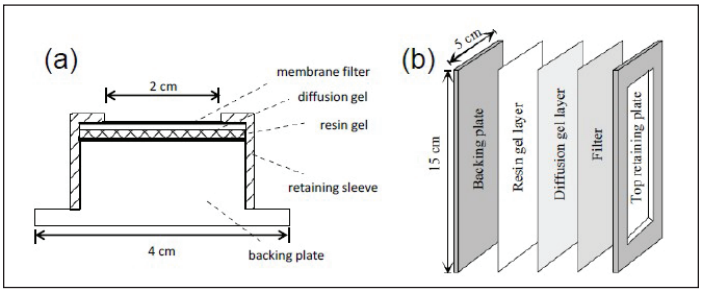


Figure 5. DGT Schematics: (a) Cross-Section of a Disk-Type Commercial DGT and (b) DGT Probe Components (Courtesy of DGT Research Limited)

(Peijnenburg et al., 2014). Advantages of using DGTs when compared to traditional water sampling include elimination of saltwater interferences and reduction of contamination risk. Additionally, high affinity of the binding gel towards the sampled metals offers a preconcentration factor of about 300 and improves the detection limits compared to traditional water sampling (Zhang and Davison, 1995). The drawback of this type of sampler is that they are relatively difficult to prepare. However, commercially available, ready to use probes can be purchased for approximately $100 a probe. Other types of metal passive samplers and more sophisticated methods for two-dimensional metal measurements using DGT and diffusion equilibrium in thin films (DET) are summarized by Peijnenburg et al. (2014) and Santner et al. (2015).

Preparation and Deployment

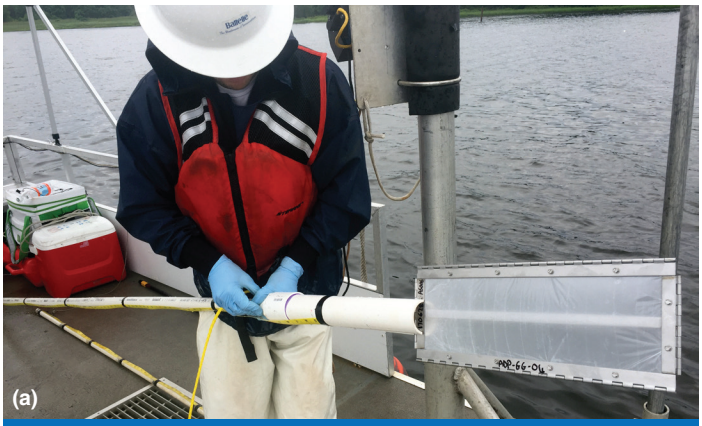
A variety of methods are used to prepare and deploy passive samplers as described below.

PED, POM, and SPME Preparation and Deployment

Laboratory preparation of PED,[2] POM, and SPME samplers is very similar. The commercially available material is first cut to the appropriate size and pre-cleaned with a solvent. The samplers can then be spiked with PRCs, which are used to determine the state of equilibration. As an alternative to PRC use, samplers of varying thickness can be deployed side by side, or one thickness of sampler can be analyzed until constant concentration is achieved.

For water deployments, PEDs and POM can be simply suspended in the water column using a buoy or otherwise anchored above the sediment-water interface. For sediment deployments, PEDs and POMs are typically mounted in stainless-steel frames, which can be inserted entirely into the sediment to measure porewater. The samplers can also be partially exposed above the sediment-water interface for coupled measurement of porewater and overlying water (Figure 6). PEDs and POM can also be deployed into a piezometer (or a groundwater monitoring well) for investigation of groundwater contamination. In addition, PEDs and POM can be used for ex situ sampling conducted in the laboratory via sediment slurry method on a field-obtained sediment sample (Apell and Gschwend, 2016).

Due to their fragile nature and small size, SPME fibers must be enclosed in a stainless-steel tubing (Figure 7) or copper mesh pocket prior to deployment. The advantage of SPMEs is that they can be used to measure vertical concentration profiles with minimal disturbance of the sediment surface. For that purpose, a long SPME fiber is placed in a perforated stainless-steel piezometer (e.g., 60 cm-long) that protects the fiber and allows easy insertion into sediment. Post-deployment, the fiber is cut into smaller sections that are extracted separately to create a concentration depth profile (Lampert et al., 2013). Time-series measurements can be useful in post-capping monitoring of contaminated sediments and contamination movement tracing.



Example of the apparatus that can be used to deploy PEDs in water depths up to ~20 feet (depending on the substrate). The apparatus is equipped with a hold and release system that allows the PED to be pushed into the sediment to a desired depth and then to retract the pole while leaving the PED in place. The PED is then marked with a float attached to the line.

PED deployed in a shallow water. The frame size is 40 x 15 cm. The lower half of the PED is inserted into the sediment and measures the porewater concentrations, while the top half is exposed to the surface water.

PED retrieved from the sediment following 34-day exposure. Significant biofouling visible in the top half of the PED which was exposed to the surface water; no biofouling present in the porewater portion (bottom half) allows easy identification of the sediment-water interface.

Figure 6. PED Deployment: (a) Example of Apparatus, (b) PED Deployed in Shallow Water, and (c) Retrieved PED Sampler (Courtesy of Battelle)

[2] A series of standard operating procedures (SOPs) on PED preparation, deployment, and analysis were released as part of ESTCP project ER-200915 (Gschwend et al., 2012a; 2012b; 2012c; 2014).

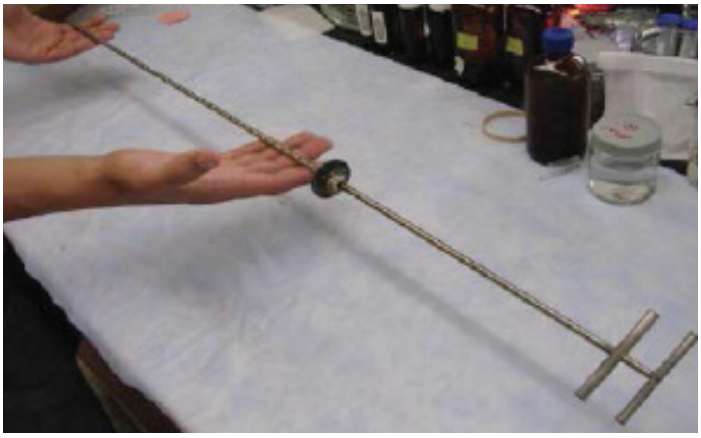


Figure 7. SPME Enclosed in a Metal Probe for Insertion into the Sediment (Courtesy of Menzie et al., 2016)

POCIS Preparation and Deployment

For deployment, one or more POCIS are usually mounted in a disc-shaped metal frame, which is then enclosed in a metal or plastic protective canister that prevents damage while allowing unrestricted water exchange. The canisters are then deployed in the water column by attaching to floats and/or anchors (Figure 8). Post-deployment, the sorbent is extracted and analyzed, and the results are converted into the water concentrations using sampling rates that are either experimentally determined in the laboratory during POCIS calibration or found in the literature (Alvarez, 2010; Morin et al., 2012; Rosen et al., 2017).

Figure 8. POCIS Deployment: (a) Placement of a POCIS Canister Adjacent to a Munition and (b) Preparing POCIS Samplers for Laboratory Analysis Following Recovery from Field (Courtesy of Rosen et al., 2017)

DGT Preparation and Deployment

Preparation of DGT probes starts with casting the diffusive and binding gels. The probe is then created by overlying the binding gel with the diffusive gel and a protective membrane, and then securing the whole assembly in a holder (Zhang and Davison, 1995). Alternatively, ready to use DGT probes can be purchased. The most common holder is a rectangular backing plate that provides rigidity needed to insert the probe into the sediment and a front plate with an exposure window (Figure 9). Two DGT assemblies can be also attached to the opposite faces of the same backing plate to create a twin DGT probe (Zhang et al., 2002). The probe is deoxygenated before deployment by immersing in anoxic water (water bubbled with nitrogen or other inert gas). After retrieval, the binding gel is usually sliced into smaller depth intervals (typically 3 mm or more) to obtain vertical profiles or into squares to prepare two-dimensional distribution maps (Tankere-Muller et al., 2007). Each section is then extracted and analyzed using standard analytical methods.

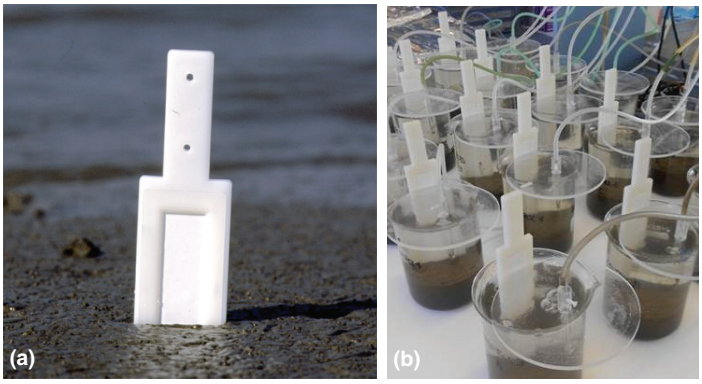


Figure 9. DGT Probe Deployed: (a) In Situ in Intertidal Sediment (Courtesy of DGT Research Limited) and (b) Ex Situ in Oxygen-Controlled Setting (Courtesy of Commonwealth Scientific and Industrial Research Organisation)

Sampling Plan Considerations

Passive sampling offers time-integrated results, therefore minimizing effects of temporal changes compared to grab samples. While surface waters are typically well-mixed and lateral variability is generally minimal, the high heterogeneity of sediments must be considered when preparing a sampling plan for sediment porewater. Field duplicate samplers can be deployed at a subset of locations to help characterize data reproducibility; however, collection of just one or two field duplicates may not be sufficient to properly assess site-wide reproducibility. Depending on site conditions, deployment of additional samplers could be considered to account for the potential loss of samplers due to vessel activity, vandalism, or other disturbances. Deployment and retrieval of the passive samplers can be conducted on foot (in shallow water/intertidal areas), from a boat (e.g., using a push pole or a frame lowered by a pulley system), or by using divers. Location of the passive sampler is typically marked with a buoy or by cording the sampler to the shoreline. Retrieval of such passive samplers is as easy as pulling on the line

connecting the passive sampler with the buoy or the shore. Sometimes remote release devices are used; they can release a small submerged float at a desired time, which makes the passive sampler safer in high boat traffic areas or areas prone to vandalism as there is no visible buoy/line on the water surface.

Passive Sampling Data Analysis

Extraction and Analysis

After retrieval, passive samplers are visually inspected and photographed. Preparation of passive samplers for extraction starts with cleaning any attached particulates and/or biofouling or discarding the protective membrane. The passive sampler can then be extracted as a whole or sectioned into smaller pieces. Some examples of sampler sectioning may include separating the sampler at the sediment-water interface (e.g., PEDs used to calculate flux of dissolved contaminant based on the concentration gradient between porewater and surface water), cutting the porewater section into smaller depth intervals to obtain vertical profiles (typically for DGTs and SPMEs), or cutting the porewater section into small squares to create a two-dimensional solute concentration map (DGTs).

Extraction and analysis procedures vary somewhat between laboratories but generally follow the standard operating procedures (SOPs) for solid matrices. Sections of passive samplers are extracted using appropriate organic solvents or solvent mixtures such as hexane, dichloromethane or methanol (PED, POM, SPME/PDMS, and POCIS) or inorganic acids (DGT). The extract is often treated much like the extract from a sediment or soil extraction and subjected to appropriate cleanup steps, particularly for PEDs, which are more difficult to clean than SPMEs or POM. Standard analytical methods are then used to analyze the extracts[3] and PRCs (if used) are treated as any other analyte. Results of the analysis are usually reported in mass of analyte per sampler or mass of analyte per gram of sampler, and certain calculation steps are required to estimate the water concentrations in the sampled water as described below.

Calculation of the Water Concentrations – PED, POM, and SPME

For equilibrium regimen passive samplers (PED, POM, SPME), dissolved concentrations of the analytes (C_d) are calculated based on the concentration in the passive sampler (CPS) using the following equation:

$$C_d = \frac{C_{PS}}{K_{PW}\ DEQ}$$

where K_{PW} is the polymer-water partition coefficient and DEQ is the degree of equilibration.

Availability of good quality polymer-water partition coefficients is an important factor for processing the passive sampler data. While large amounts of experimentally derived partitioning data for PCBs and PAHs exist, for some pesticides or dioxins relatively little data have been published to date. For these compounds, empirically determined relationships between the polymer-water partition coefficients and the molecular properties of the analyte such as K_{ow}, molecular size or molar volume are often used to predict the partitioning of the compounds (DiFilippo and Eganhouse, 2010; Arp et al., 2015; Lohmann, 2011; U.S. EPA, 2012a).

The DEQ can be calculated based on the loss of PRCs during the deployment. DEQ is equal to the mass of PRC lost during the deployment divided by the initial mass of PRC in the sampler. When almost all of the PRC is dissipated during the deployment, DEQ approaches 1 and it can be dropped from the equation. The kinetics of the compound's equilibration with the sampler is generally slower for more hydrophobic (higher K_{ow}) compounds. For example, while anthracene (log K_{ow} = 4.45) often approaches equilibrium within about one month of exposure, more hydrophobic compounds with log K_{ow} values above 6 almost never approach equilibrium during the typical one- or two-month exposures. For that reason, it is important to select a suite of PRCs that cover the range of hydrophobicities of the analytes of interest.

PRC Mass Transfer Models

Several approaches have been used to model the PRC data. The first order model (Adams et al., 2007) assumes simple first order kinetics and is appropriate to surface water due to the boundary conditions assumptions. In that approach, DEQ is calculated for each PRC and used for a group of analytes with most similar properties (e.g., if five PRCs were used,

[3] Please refer to Table 7-1 in U.S. EPA/SERDP/ESTCP (2017) for the list of U.S. EPA methods used for passive sampler extracts depending on the analyte type.

analytes would be divided into five groups based on their K_{ow} values and the DEQ from one PRC would be applied to calculate water concentration of each analyte in the group). The advantage of the model is that it is easy to set up in a regular spreadsheet. The diffusion model (Fernandez et al., 2009) is based on different boundary condition assumptions and is applicable to porewater passive samplers. This model interpolates the DEQs based on the recoveries of all the PRCs, rather than assigning a single PRC to a specific group of analytes. While the model is significantly more complicated, a convenient online calculator is available through the Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) website (https://www.serdp-estcp.org/Tools-and-Training/Tools/PRC-Correction-Calculator). The primary limitation of the diffusion model is that the PRCs with fractional equilibrations below 0.1 or above 0.9 should be excluded from modeling. Another popular model is the sampling rate model (Rusina et al., 2010; Booij and Smedes, 2010). This model is applicable to both surface water and porewater, and like the diffusion model, it allows interpolation of DEQs for each analyte based on all of the PRC data (regardless of their fractional equilibration). This model was made available as a spreadsheet by its authors.

Calculation of the Water Concentrations – POCIS and DGT

For the kinetic samplers, including POCIS and DGT, the dissolved concentration of the analytes in the water phase can be calculated as (Alvarez, 2010):

$$C_d = \frac{N}{R_s \; t}$$

where N is the amount of analyte accumulated in the passive sampler, Rs is the sampling rate, and t is the time of exposure. For POCIS, the sampling rates are determined from experimental data during the calibration process; when conducting calibration is not feasible, published literature data can be used.

For DGTs, known diffusion coefficients (D) of the analytes through the diffusive gel of a thickness Δg and the area A can be used to calculate the sampling rate, so the above equation takes the form of (Zhang and Davison, 1995):

$$C_d = \frac{N \Delta g}{D \; A \; t}$$

Quality Assurance/Quality Control (QA/QC)

As mentioned before, SOPs regarding PED extraction and analysis differ somewhat between laboratories, but generally are a modified version of SOPs for solids. The modifications may regard preparation steps (e.g., removal of biofouling from passive samplers) and sorbent weight or volume determination for reporting purposes. To our knowledge, currently there are no laboratory accreditations specific to passive samplers, so they fall under the category of solids.

Typical QA/QC measures used when sampling with passive samplers include:

- PRCs – PRCs constitute "exposure standards" for passive sampling. They are compounds similar to analytes, but not present in the sampled medium and are added to the passive sampler during laboratory preparation. They are assumed to be released at the same rate that the analytes are being accumulated in the passive sampler. Initial concentration of PRCs in passive samplers should be measured by extracting one or more samplers from each spiking batch, as between-batch variability can be significant. Preferably, a few passive samplers from each batch would be analyzed to determine the within-batch variability.
- Trip blanks – A passive sampler that is delivered to the field during sampling and recovery activities and exposed to the air for a similar length of time as it takes to deploy/recover a passive sampler in the sediment. If PRCs are used, the trip blank will contain the PRCs as well. The role of the trip blank is to measure potential loss or PRCs during storage and transport and potential contamination with other compounds during field activities.
- Storage time and conditions tend to vary laboratory to laboratory, but generally post-deployment passive samplers are stored frozen to avoid loss of analyte due to volatilization or microbial degradation.
- Surrogate internal standards (SIS) – SIS are used to measure the efficiency of the sampler extraction. They consist of compounds not present in the sample and not used as a PRC (typically an isotopically labeled compound) and are added just prior to extraction.
- Post-extraction, the typical set of QA/QC applies (instrument calibration, second-source standard check, continuing calibration verification, method blank, laboratory control sample, etc.).

Relating Passive Sampler Results to Bioaccumulation

It has long been known that sorption of contaminants to sediment particles (particularly organic matter) significantly decreases the contaminant bioavailability and therefore C_{free} is a much better predictor of risk than total sediment concentration (Di Toro et al., 1991; U.S. EPA, 2012b). However, determination of C_{free} can be complicated by challenges associated with expression of porewater and/or separation of the colloid- and dissolved organic carbon-bound fractions. Passive sampling overcomes these difficulties and offers a more accurate method for measuring C_{free} in porewater, surface water, and groundwater. Determination of the C_{free} offers significant improvement in bioaccumulation prediction compared to bulk sediment and provides an alternative to costly and time-consuming bioassays. Strong relationships between C_{free} and bioaccumulation have been observed through many studies (e.g., Vinturella et al., 2004; Friedman et al., 2009; Joyce et al., 2016; Paulik et al., 2016). The ability of the passive sampler to accurately predict bioaccumulation is complicated and depends on the choice of passive sampler material, analyte of interest, and a number of organism-related differences, including trophic level, species-specific differences in bioaccumulation potential, organism's living and feeding habits, size, sex, and age (Muijs and Jonker, 2012; Schäfer et al., 2015; Bridges et al., 2017). However, the consensus is growing that using C_{free} allows improved assessment and management of contaminated sediments (Mayer et al., 2014; U.S. EPA, 2017).

Case Study

Introduction

New Bedford Harbor, Massachusetts is an 18,000-acre urban estuary with sediment highly contaminated with PCBs. The main historical source of the contamination is located within the inner harbor (see Figure 10), which is separated from the outer harbor by a hurricane barrier. Risk evaluations conducted in the outer harbor (referred to as Operable Unit 3 [OU3]) showed that the PCB concentrations measured in biota were inconsistent with the sediment PCB concentrations used to predict bioaccumulation. A passive sampler study was conducted to: 1) collect water column data to support further risk assessment; and 2) collect porewater PCB concentration data and calculate diffusive PCB exchange between porewater and overlying water in order to investigate the current PCB sources to the local biota.

Methods

PEDs were deployed at five nearshore stations within OU3 and at one reference station (see Figure 10). Three PRC-spiked PEDs in metal frames (40 x 15 cm) were deployed at each station by inserting them into the sediment half-way, which allowed simultaneous sampling of the porewater and overlying water. The PEDs were retrieved following a 28-day exposure period. Whole water samples were also collected at deployment and recovery of the PEDs.

At the laboratory, PEDs were sectioned at the sediment-water interface line. The surface water sections from the triplicate PEDs at each station were combined and extracted together, as were the porewater sections (except station HB1 where two PEDs were combined as a parent sample and the third PED was used as a field duplicate). The extracts were analyzed for 139 PCB congeners, representing 95% or more of the total PCBs in the environment, along with the added PRCs the laboratory. PRC data were used to correct the results for lack of equilibration using the first order model. Paired porewater-surface water concentration data from half-buried PEDs were used to calculate the flux of PCB following Fick's first law of diffusion. The results are shown in Figure 10.

Results

Use of PEDs which preconcentrate hydrophobic analytes allowed measurement of PCB concentrations even at the stations where whole water analysis results were non-detect. Additionally, because the PED results are time-integrated, short-term variability due to environmental factors such as tidal water exchange or precipitation is removed. As shown in Figure 10, the flux calculations revealed strong downward (from overlying water to sediment) flux of PCBs at the hurricane barrier (station HB1) suggesting that the dissolved PCBs are being transported out of the inner harbor through surface water. Surface water PCB data proved more consistent with the biota body burdens compared to the initially attempted bulk-sediment predictions and led to refinement of the risk evaluation.

Other interesting case studies with the use of passive sampling at contaminated sediment sites can be found in Menzie et al. (2016), U.S. EPA/SERDP/ESTCP (2017), and Benotti et al. (2018).

Future Research Directions

Passive samplers have been widely recognized as a reliable tool by researchers for several decades. The use of passive samplers has also been generally encouraged by regulators in the U.S. (Booij et al., 2017). Growing regulatory acceptance of passive samplers is exhibited by the passive sampler guidance documents released in recent years by EPA and ESTCP, providing comprehensive information on the laboratory, field, and analytical aspects of passive sampling, as well as the development of remediation goals based on porewater data (U.S. EPA, 2012a and 2012b; Gschwend et al., 2012a, 2012b, 2012c and 2014; Menzie et al., 2016; U.S. EPA, 2017; U.S. EPA/SERDP/ESTCP, 2017). An interlaboratory ESTCP study (ER-201735) is also being conducted to optimize SOPs for PED and SPME samplers, and to confirm comparability of the data between participating laboratories. Meanwhile, the suite of passive sampler-water partitioning coefficients for different groups of compounds is expanding by continued collection of new data, allowing application of the passive sampling techniques to a wider range of chemicals, including emerging contaminants. The relationship between bioavailability and passive sampler-measured C_{free}, and the comparison of the in situ (field) versus ex situ (laboratory) passive sampling results are also the subject of continued investigations. New passive sampling capabilities are being developed as well, including vibration-enhanced sampling for faster equilibration (Jalalizadeh and Ghosh, 2016); passive samplers for munitions compounds (e.g., Warren et al., 2018; Rosen et al. 2018); diverless deployments in deep water (Fernandez et al., 2014), and high-resolution passive sampling (ER-201734).

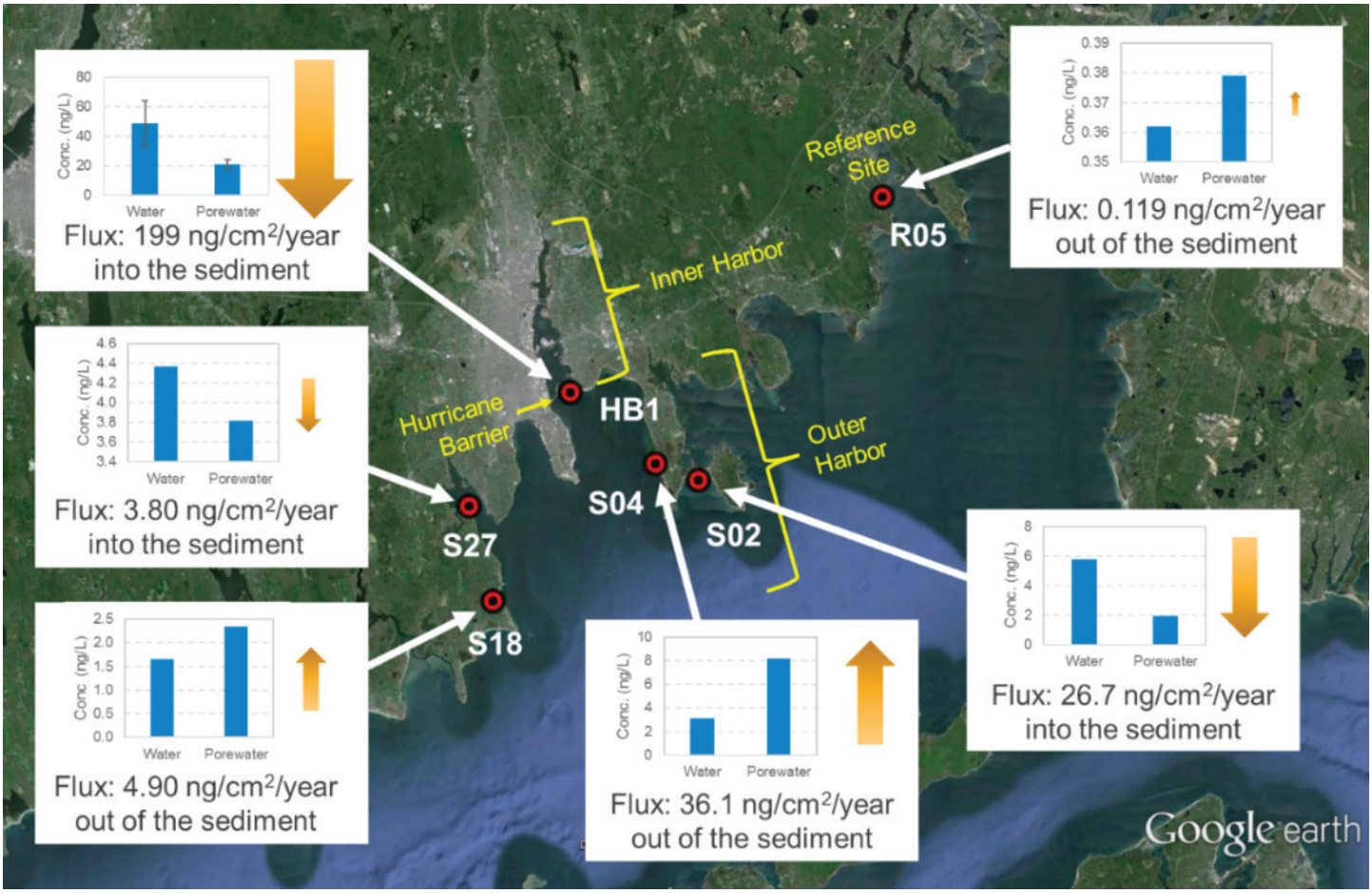


Figure 10. PED Deployment Sites at New Bedford Harbor Operable Unit 3 (Note: The size and orientation of the orange arrows visualizes the magnitude and direction of the flux at each station. Courtesy of Battelle as prepared for the U.S. Army Corps of Engineers (USACE). 2015. Draft Final Technical Memorandum, New Bedford Harbor OU3 Passive Sampler Study. Contract Number W912WJ-12-D-0004. August).

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ESTS N39430-16-D-1802