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Passive Sampler C_{free} Measurements at Superfund Sites

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Application of Passive Sampling for Measuring Dissolved Concentrations (C_{free}) of Organic Contaminants in the Water Column at Three Marine Superfund Sites

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Abstract

Historically, acquiring the freely dissolved concentration (C_{free}) of HOCs has been challenging. In recent years, passive sampling has been demonstrated to be an effective tool for determining C_{free} in the water column and in sediment interstitial waters. Currently, there is an effort underway encouraging remedial project managers (RPMs) at contaminated sites to use passive sampling to collect C_{free} data in order to improve site assessments. The objective of this investigation was to evaluate the use of passive sampling for measuring water column C_{free} for several HOCs at three U.S. EPA Superfund sites. Sites investigated included New Bedford Harbor, Palos Verdes Shelf and Naval Station Newport and the passive samplers evaluated were polyethylene (PE), polydimethylsiloxane (PDMS) coated solid phase microextraction (SPME) fibers, semi-permeable membrane devices (SPMD), and polyoxymethylene (POM). In general, the different passive samplers demonstrated good agreement with C_{free} values varying by a factor of two to three. Further, at New Bedford Harbor, where conventional water sample concentrations were also measured (i.e., grab samples), passive sampler-based C_{free} agreed within a factor of two. These findings suggest that all of the samplers were experiencing and measuring similar C_{free} during their respective deployments. Also, at New Bedford Harbor, a strong log-linear, correlative and predictive relationship was found between PE passive sampler accumulation and (lipid-normalized blue mussel bioaccumulation of PCBs ($r^2 = 0.92$; $p <<< 0.05$). This evaluation demonstrates the utility of passive sampling for generating scientifically accurate water column C_{free} which is critical for making informed environmental management decisions at contaminated sediment sites.

Key Words: Passive sampling, Superfund, Bioavailability, C_{free}, Polyethylene (PE), Polyoxymethylene (POM), Solid phase microextraction (SPME), Semi-permeable membrane devices (SPMD)

Introduction

Studies over the last few decades have demonstrated that many aquatic organisms including fish and wildlife are exposed to anthropogenic contaminants present in the water column that originate from contaminated sediments [1, 2]. Consequently, to accurately and holistically assess exposures at contaminated sediment sites, including U.S. EPA Superfund sites, it is critical to measure the water column concentrations directly. The exposure of aquatic organisms to hydrophobic organic chemicals (HOCs) like polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenylethers (PBDEs), polychlorinated dibenzo-p-dioxins and dibenzofurans, and chlorinated pesticides in the water column is most strongly correlated to the freely dissolved concentration (C_{free}) while uptake from environmental sorptive phases like colloids or suspended particles is often limited [3, 4]. Consequently, C_{free} is considered a strong surrogate measurement for the bioavailable concentrations of many HOCs. However, measuring the C_{free} in the water column in the field remains technically challenging because of the relatively low concentrations of contaminants, potential for contamination from the sorptive phases, and losses to collection gear. Several recently developed passive sampling methods selectively measure C_{free} for HOCs [5] including polyethylene and triolein-based semipermeable membrane devices (SPMDs) [6, 7], polydimethylsiloxane (PDMS)-based solid phase microextraction (SPME) [8-10] polyoxymethylene (POM) [11-13], and polyethylene (PE) [14-21].

All of these passive sampling methods use essentially the same approach for sampling C_{free}. In this approach, contaminants partition between C_{free} (ng/L) in the aqueous phase and some form of passive sampling absorptive carbon based polymer or liquid phase (C_{PS}) (ng/L):

$$C_{free} \leftrightarrow C_{PS} \qquad [1]$$

Under equilibrium conditions, the relationship between the passive sampler phase and dissolved phase can be expressed as a passive sampler-dissolved phase partition coefficient ($K_{PS\text{-}free}$) (L/L) and used to estimate the C_{free} concentration of a given contaminant:

$$C_{free} = \frac{C_{PS}}{K_{PS-free}} \qquad [2]$$

If equilibrium conditions cannot be assumed or demonstrated, Equation 2 can be adjusted to estimate equilibrium concentrations using performance reference compounds (PRCs) similar in physicochemical behavior to the target contaminants [17, 22]. The PRCs are introduced to the passive sampler before deployment in the environment and partition into the aqueous phase at a rate comparable to the partitioning of the target contaminants into the polymer. In principle, with these techniques, only the C_{free} contaminants partition into the passive sampler. Therefore, uptake of contaminants into the passive sampler reflects the bioavailable concentration and can be compared to bioaccumulation by water column and sediment deployed biomonitoring organisms (e.g., blue mussels, polychaetes) and/or used to estimate HOC C_{free} exposed to organisms using Equation 2 [12, 16, 23-25]. This type of exposure information is very important for understanding the direct exposure to water column organisms (e.g., fish) and serving as input information for modelling bioaccumulation and assessing risk to human and ecological health higher in the food chain (e.g., avians, wildlife). Therefore, to successfully predict exposures to water column organisms and model higher level impacts it is critical to insure that measurements of C_{free} are as accurate and scientifically-robust as possible.

In recent years, the use of passive sampling for measuring C_{free} at U.S. EPA Superfund sites has been encouraged as a scientifically-robust tool for assessing exposure (e.g., [26-28]) and, in a limited number of cases, remedial project managers (RPMs) at Superfund sites have applied passive sampling (e.g., [18, 19, 29]). To this end, the current investigation evaluates the application of passive samplers at three U.S. EPA Superfund sites for measuring water column C_{free} of target contaminants including PCBs, PAHs and PBDEs. The Superfund sites investigated included New Bedford Harbor (NBH) (New Bedford, MA, USA), the Naval Station Newport (NSN) (Newport, RI, USA), and Palos Verdes Shelf (PVS) (Los Angeles, CA, USA). Risk at each of these sites is driven by concerns with human consumption of contaminated seafood as well as adverse ecological effects due to exposure to dissolved concentrations of bioavailable contaminants (i.e., C_{free}). In general, studies were designed to compare the performance of different types of passive samplers (e.g., SPME, PE, POM, SPMD) to one another, and in some cases, to biomonitoring organisms (e.g., blue mussels *Mytilus edulis*) under field conditions. These studies also had regulatory objectives which included establishing baseline water column C_{free} of target contaminants at the sites (e.g., NBH, NSN) and evaluating the feasibility of using passive samplers at a deep water Superfund site (PVS). At the NBH Superfund site, water column samples were also collected and extracted using conventional techniques (i.e., grab sample with liquid-liquid extraction with organic solvents) and solid phase extraction (SPE) for comparison to passive sampling-based findings. Results of this work are intended to encourage RPMs at contaminated sediment sites to use passive sampling as an additional tool for making informed environmental management decisions.

Materials and Methods

Study Designs

New Bedford Harbor Superfund Site To assess baseline water column concentrations of total PCB C_{free}, two deployments were performed. Passive samplers were deployed at NBH2 and NBH4 which are two long-term U.S. EPA monitoring locations (Table 1) (Supplemental Data Figure S1). In each deployment, passive samplers were deployed in four temporal intervals: days 0-7, days 0-14, days 0-21 and days 0-28 or 29 one meter above the sediment bed. Water samples were also collected one meter above the sediment bed at the time of passive sampler recovery. In the first study (fall), triplicate PE attached by stainless wire to the mooring lines were deployed from 10 October 2007 to 7 November 2007 for a total of 28 days. For comparative purposes, bagged blue mussels (M. *edulis*), also suspended one meter above the bottom, were exposed for 33 days at stations NBH2 and NBH4 from 19 October 2007 to 21 November 2007. In the second deployment (winter), at each station, SPMD, SPME and PE were deployed on triplicate moorings. On day 0 at each station, a total of 12 SPMD and SPME (in cannisters), and wire-attached PE passive samplers were deployed on individual moorings (Supplemental Data Figure S2a). The monitoring period extended from 19 November 2007 through 18 December 2007 for a total of 29 days. Three SPMD and SPME containing canisters and three PE polymer strips were recovered from the moorings on each of the four following time periods: 7, 14, 21, and 29 days after deployment. As in the fall deployment, water samples were also collected on a weekly basis.

Palos Verdes Shelf Superfund Site For this investigation, three to five month deployments were performed at seven stations at depths ranging from 19 to 65 m (Table 1) (Supplemental Data Figure S1) with PCBs as the target contaminant. To assess the effectiveness of passive sampling at this deep water site, individual PE samplers were deployed, fastened using stainless steel wire, to United States Geological Survey (USGS) acoustic Doppler current profilers resting on the sediment surface (Supplemental Data Figure S2b). Samplers were attached 1.2 to 5.2 m above the sediment surface often with multiple samplers on a given profiler (Table 1).

Naval Station Newport Superfund At this site, one deployment was performed at four stations with PCBs, PAHs and PBDEs as the target contaminants (Table 1) (Supplemental Data Figure S1). Two types of passive samplers, PE and POM, were deployed for 21 days in extended minnow traps (Supplemental Data Figure S2c) to assess baseline C_{free} in the water column prior to initiation of remediation of portions of the site. All samplers were deployed one meter above the sediment surface. Additional information about each site is provided in the Supplemental Data section.

Passive Sampler Design, Deployment and Recovery

For NBH deployments, SPMDs were composed of 91.4 cm long, 2.5 cm wide, lay flat, hollow low-density polyethylene ribbons (70-95 µm thick) containing 1 mL pure (99%), high-molecular weight lipid glyceryl trioleate (triolein) (Sigma-Aldrich, St Louis, MO, USA) in a thin film. Prior to deployment, a PRC mixture containing chlorinated biphenyl (CB) 38 and CB50 was prepared in hexane at Battelle (Duxbury, MA, USA) and shipped to Environmental Sampling Technologies, Inc. (EST) (St. Josephs, MO, USA). At EST, SPMD polyethylene tubing was triple washed with optima grade hexane, injected with PRC-loaded triolein, and heat sealed. Triolein had been amended with the PRC mixture for a final concentration of approximately 25 ng/mL triolein each of CB38 and CB50. SPMDs were loaded onto stainless steel deployment rigs (“spiders”), packed in air-tight, pre-cleaned aluminum containers, and shipped to Battelle (Duxbury, MA, USA). Packages containing the SPMD deployment spiders were stored at -4ºC until the day of deployment. Spiders consisted of a stainless steel plate equipped with a central hole and several Teflon or stainless steel posts. Canisters were deployed in triplicate per deployment period and were constructed from stainless steel containing ports for ample movement and circulation of the water column through the device.

For NBH deployments, disposable SPMEs consisted of 2.5 cm long pieces of optical fiber with a 210 µm silica core and a 10 µm polydimethylsiloxane (PDMS) coating (equivalent to 0.000173 mL PDMS) (Fiberguide, Stirling, NJ, USA). Prior to deployment, fibers and protective stainless steel pouches (3 cm x 4 cm) were soaked in analytical grade methanol for at least 10 minutes, dried at ambient temperatures, and wrapped in aluminum foil. Samplers were then placed in storage containers (e.g., solvent-rinsed glass jars) and shipped to the site. Each SPME replicate consisted of 15 or 30 fibers (total of 0.0026 or 0.0052 mL PDMS) per pouch affixed to the top of the SPMD spider inside a canister using stainless steel wire and nylon zip ties. There were three replicate SPMEs deployed at each station per deployment period. Upon recovery, SPMD cannisters and SPME pouches were kept on ice, returned to the laboratory, and stored at -4ºC until extraction and chemical analysis.

All PE and POM samplers were pre-cleaned by soaking in acetone or hexane for 24 h and then in dichloromethane (DCM) for 24 h. For NBH deployments, PEs were prepared from 51 µm thick, 30.5 cm long and 7.62 cm wide polyethylene film (1.19 mL PE) (Carlisle Plastics Inc., Minneapolis, MN, USA). Polyethylene was deployed in triplicate approximately one meter above the sediment surface for each exposure interval using an anchor and flotation buoys. Prior to deployment, these PEs were amended with PRCs in 80:20 methanol and deionized water solution including 2,5-dibromobiphenyl (PBB), 2,2',5,5'-PBB, and 2,2',4,5,6-PBB at approximately 21 ng/mL, 14 ng/mL, and 9.0 ng/mL PE, respectively, using methods described by Booij et al. [22]. In addition, for a subset of NBH deployments, two thicknesses (i.e., 25 and 51 µm) (0.58 mL versus 1.19 mL PE) of PE were evaluated for assessing equilibrium. For the Palos Verdes Shelf deployments, 50 cm long and 10 cm wide polyethylene PE strips (51 µm thick) (2.55 mL) (Carlisle Plastics Inc., Minneapolis, MN, USA) were fastened using stainless steel wire to the USGS acoustic Doppler current profilers. Prior to the deployments, as with the NBH deployments, the same three PBBs and concentrations were used as PRCs. For Naval Station Newport deployments, low-density PE (25 µm thickness; Covalence Plastics, Minneapolis, MN, USA) and POM (75 µm; CS Hyde Company, Milwaukee, IL, USA) were prepared in 15 cm x 40 cm (1.5 mL PE) and 6 cm x 40 cm (1.8 mL POM) films, respectively. Prior to deployments, PE and POM were amended with stable carbon PRCs including ^{13}C-CB28, ^{13}C-CB52 and ^{13}C-CB138 in 80:20 methanol:water solutions for at least 21 days on an orbital shaker using the methods described in Perron et al. [20]. Films of PE and POM were attached to stainless steel wire (diameter = 0.081 cm; Malin Company, Cleveland, OH, USA) fastened inside galvanized extended minnow traps (diameter = 22 cm, length = 76.2 cm) (Tackle Factory, Fillmore, NY, USA). Inside each trap, three strips of PE and POM were arranged to maximize their surface area. Samplers were deployed using an anchor and flotation buoys on a shore-fastened mooring line. Upon recovery, all PE and POM films were immediately wrapped in pre-cleaned metallic foil or placed in pre-cleaned glass jars, stored on ice or ice packs, and transferred to the laboratory for storage at -4ºC in the dark until extraction and analysis.

Water Sample Collections

At the NBH stations, discrete water samples (one liter) were collected in triplicate on a weekly basis, following the retrieval/deployment of passive samplers during the fall and winter deployments. Because of logistic issues, samples were not collected on Day 14 (3/12/07) in the winter deployment. Water samples were collected using a 12-volt Teflon diaphragm pump, a length of tygon tubing to reach the sampling depth (i.e., 1 m above the bottom) of the passive sampling devices, and stored in clean glass containers. Following sample collection, the pump and tubing were purged twice with DI water and one rinsate blank was collected. Samples were placed on ice for transport to the laboratory. Once at the laboratory, water samples were filtered through solvent-rinsed glass fiber filters (1 µm effective pore size) within 24 hours of collection. As described in the Supplemental Data, water samples were analyzed and reported in two ways: as “total” (i.e., dissolved and colloidal) and “C_{18}-based”. The C_{18}-based technique is an alternative approach for measuring C_{free}. For discussion, these two measurements of PCB concentrations will be referred to jointly as “aqueous” PCB measurements. Prior to extraction and chemical analysis, the samples were stored at 4°C.

Mussel Deployments

For the fall NBH deployment, blue mussels (*M. edulis*) collected from clean sites in coastal Sandwich (MA, USA) were selected by size (approximately 5-7 cm) and placed in mesh plastic bags (approximately 25 mussels per bag). Deployments consisted of three to four replicate bags exposed at each station positioned one meter above the bottom. After the 33 day exposure, mussels were recovered, returned to the laboratory in coolers on ice, frozen at -4 ºC, and stored in the dark until chemical analysis.

Chemical Analyses

Passive samplers, tissues, and water samples were analyzed using gas chromatography/mass spectroscopy (GC/MS) for selected PCBs, PAHs and PBDEs. Total PCBs was defined as the sum of measured PCB congeners at each Superfund site: total PCB at New Bedford Harbor, Palos Verdes Shelf and Naval Station Newport was the sum of 18, 29 and 26 congeners, respectively (Supplemental Data). Water samples from the NBH deployments were also analyzed for dissolved organic carbon. Preparation, extraction and instrumental analysis is described in the Supplemental Data section.

Calculation of Passive Sampler-based Dissolved Concentrations (C_{free})

When assuming equilibrium conditions, C_{free} was calculated using Equation 2. For non-equilibrium conditions, C_{free} based on PE and POM deployments were calculated using PRC with the following equation:

$$C_{free} = \frac{C_{PS}}{(1 - e^{-k_e t}) * K_{PS-free}} \qquad [3]$$

where, k_e is the PRC transfer coefficient (1/day) and t (day) the duration of the deployment:

$$k_e = \frac{\ln \frac{C_{PRC_i}}{C_{PRC_f}}}{t} \qquad [4]$$

and C_{PRCi} and C_{PRCf} are the initial and final concentrations (ng/g) in the polymer, respectively, of the PRCs during the deployment. PRC % equilibration (i.e., k_e * 100) values were regressed against PRC K_{OW}s to develop correlative relationships for estimating % equilibration values for target contaminants. If target contaminant % equilibration values were less than 10%, the C_{free} were not calculated because of insufficient evidence of equilibration of those compounds between the polymer and environmental phases. Sources of partition coefficients for each type of polymer used in this study are provided in the Supplemental Data.

For calculating C_{free} based on mussel bioaccumulation of PCBs, the lipid-water partition coefficient ($K_{lipid\text{-}free}$) was derived for each PCB congener using the log $K_{lipid\text{-}free}$ to log K_{OW} linear free energy relationship (LFER) reported by Schwarzenbach et al. [30] (i.e., log $K_{lipid\text{-}free}$ = 0.91*log K_{OW} + 0.5). The C_{free} based on mussel lipid concentrations was calculated based on Equation 7:

$$C_{free} = \frac{C_{lipid}}{K_{lipid-free}} \qquad [5]$$

where, C_{lipid} is the lipid-normalized PCB concentration measured in the mussel tissues [5].

Statistical Analyses

Unless otherwise noted, the mean and one standard deviation of three replicates are reported for passive sampler, water sample, DOC and mussel data. Statistical comparisons were performed using analysis of variance (ANOVA) followed by protected least significant difference (LSD) multiple comparison tests (SAS Institute, Cary, NC, USA) if more than two treatments were being analyzed. Differences between treatments were considered as statistically significant using an alpha (α) set at ≤ 0.05.

Results and Discussion

Comparison of C_{free} Measurements

New Bedford Harbor During the fall deployments, total PCB C_{free} ranged from 25 ng/L to 360 ng/L for NBH4 and NBH2, respectively, based on PE measurements (Figure 1a). Aqueous measurements of total PCB concentrations, based on the total water extractions and C_{18}-based measurements, ranged from 21 to 120 ng/L at the same stations with total water extractions and C_{18}-based measurements found to be similar (i.e., 5 to 18%). Further, PE-based C_{free} at NBH4 were relatively similar to the aqueous measurements; that is, within 20% while PE C_{free} were three time larger than aqueous concentration at NBH2. Finally, mussel-based estimates of C_{free}, based on Equation 5, at NBH2 were also fairly similar to PE-based C_{free}, 400 ng/L versus 360 ng/L, while at station NBH4 mussels-based C_{free}, 58 ng/L, was about two times greater than PE-based C_{free} (i.e., 25 ng/L). At NBH2, statistical analysis found mussel and PE C_{free} were not significant different; similarly, water and C_{18}-based C_{free} values were also not significantly different from one another. However, mussel C_{free} was significantly greater than C_{free} from the other three treatments at NBH4. A more detailed comparison of mussel bioaccumulation and PE accumulation of PCBs will be discussed later.

In the winter deployments, passive sampler-based total PCB C_{free} ranged from 76 to 170 ng/L and 7.7 to 31 ng/L at stations NBH2 and NBH4, respectively (Figure 1b). For comparison, aqueous measurements of total PCBs ranged 53 to 97 ng/L and 16 to 30 ng/L at NBH2 and NBH4, respectively. Within the passive sampler-based measurements of C_{free}, PE generated the largest C_{free} values compared to SPME and SPMD. For example, at NBH2, PE-based C_{free} was 170 ng/L while SPME and SPMD C_{free} values were 110 ng/L and 76 ng/L, respectively. At NBH4, PE-based C_{free} values were 31 ng/L and SPME and SPMD C_{free} values were 18 ng/L and 7.7 ng/L, respectively. Statistical analysis of the winter deployment data was more complicated to interpret than the fall deployment. At NBH2, C_{free} for PE was significantly different from all other treatments while C_{free} based on SPME and total water were not different, total water and SPMD C_{free} were also not different, and, finally, SPMD and C_{18}-based C_{free} were not different. The NBH4 C_{free} were not different for PE and total water, SPME and C_{18}-based, and SPMD and C_{18}-based.

Despite the range of C_{free} values, all of the passive sampler-based concentrations were generally within about a factor of two to three of one another suggesting they were "experiencing" (i.e., exposed to) and measuring similar truly dissolved concentrations of PCBs in the ambient water column of the two stations in New Bedford Harbor during their respective deployments. This finding is encouraging and suggests the samplers will provide comparable C_{free} data for PCBs even though they are deployed and analyzed in different ways using various designs and gear, partition coefficients, and assumption regarding equilibrium status. For example, as discussed above, for the SPME, equilibrium was assumed for the winter deployment while the PE data were adjusted for non-equilibrium conditions based on the PRC concentrations using Equation 5. With the exception of CB206 and CB209, which had less than 10% equilibrium and their C_{free} are not reported, the degree of PE non-equilibration by congener ranged from 20 to 96% resulting in a relatively minor difference in the unadjusted and equilibrium adjusted C_{free} for total PCBs after the 29 day winter deployment (i.e., adjusting for non-equilibrium conditions based on the PRCs increased total PCB C_{free} by only 4% to 8%).

In general, SPMD data would also be adjusted for non-equilibrium conditions based on PRC recovery. As discussed, the PRCs selected for the SPMD in the winter deployment were CB38 and CB50, two congeners not usually found in the commercial Aroclor mixtures known to contaminate NBH. Unfortunately, following deployments, analysis of the SPMD extracts detected concentrations of both congeners at levels close to (NBH4) or exceeding (NBH2) their original amendment concentrations. These results indicate both CB38 and CB50 were present unexpectedly in the NBH water column or matrix interference with similar molecular weights were present. In either case, the PRC data were not viable and equilibrium of the SPMD data was assumed for calculation of the C_{free}. This demonstrates a weakness in using non-Aroclor PCB congeners as PRCs for target PCBs, especially at very contaminated sites, like Superfund sites, where there may be unexpected sources of rare congeners. For the PE, which used brominated biphenyls as PRCs, there was no evidence of a background presence of these compounds in the NBH water column.

As noted in the Introduction, the value of conventionally-collected total PCBs water concentrations is debatable because of the artifacts that can plague such samples. However, they do serve as a potentially useful point of comparison to passive sampler inferred C_{free}. Similarities in water concentrations of total PCBs, based on total water extraction or C_{18} solid phase extraction, and passive sampler C_{free} varied by station and deployment. For example, in the fall deployment at NBH4, PE C_{free} and aqueous measurements were similar ranging from 21 to 25 ng/L (Figure 1a). Similarly, in the winter deployment at NBH4, PE C_{free} were fairly comparable to water concentrations with passive sampler C_{free} values ranging from 7.7 to 31 ng/L and aqueous concentrations ranging from 16 to 30 ng/L (Figure 1b). In contrast, at NBH2 in the winter deployment, passive sampler C_{free} values ranged more widely 76 to 170 ng/L while aqueous concentrations were 53 to 97 ng/L. As discussed above, the SPMD data was not adjusted for non-equilibrium and may represent under-estimations of C_{free} (76 ng/L) resulting in the coincidental similarity to the lower trending water concentrations.

Palos Verdes Shelf Concentrations of total PCB C_{free} across this site ranged from 45 to 430 pg/L (Figure 2). Stations closer to shore (PVS1 and PVS2) had the lowest total PCB C_{free} (45 to 86 pg/L) at the site. Stations PVS3, PVS4 and PVS5, all in the vicinity of the LACSD outfalls, demonstrated the highest C_{free} with values ranging from 220 to 430 pg/L. In addition to the general distribution of C_{free} in the water column, the data in Figure 2 indicate, as expected, that PCBs are originating from the sediments of the site and diffusing from the interstitial water into the water column over time. For example, at all stations where PE samplers were deployed at multiple depths on the current profilers, except PVS6, total PCB C_{free} were observed to increase when approaching the sediment. A second observation is the spatial distribution of total PCB C_{free}. The dominant oceanic current along this section of the Pacific Ocean coastline is the California Current which follows the California coast 200 to 300 Km off-shore with a depth of 300 meters moving in a southeastern direction [31]. However, in the area of the California coast where the Palos Verdes Shelf Superfund site is located (i.e., the Southern California Bight), the Southern California Countercurrent forms the Southern California Eddy deflecting water in a direction counter to the California Current; that is, in a northwestern direction [32]. As a consequence, the concentration of water column PCBs and other contaminants associated with sedimentary sources at the site increase in a northwestern direction from the LACSD outfalls. For example, the C_{free} at stations PVS3 and PVS4 reflect these higher values (250 to 430 pg/L) while stations PVS6 and PVS7 (directly to the southeast of the outfalls) show lower C_{free} (90 to 180 pg/L). Using passive sampling, Fernandez et al. [18] observed similar depth and spatial distribution trends for DDTs and PCBs in the water column at the Palos Verdes Shelf site.

A principal goal of this investigation was to evaluate the deployment of passive samplers in deep water without using elaborate deployment gear. As can be seen in Supplemental Data Figure S2b, for this deployment, PE samplers were simply attached to the current profilers with stainless steel wire. Of the 21 samplers deployed, all were recovered successfully (although three were lost or compromised after recovery) demonstrating the versatility and robustness of the PE and simple deployment system. In another study examining water column concentrations using PE and SPME passive samplers deployed at 11 stations at the PVS Superfund site, Fernandez et al. [18] lost several samplers in the middle and upper water column where the current is the strongest. The losses were attributed to fatigue of the aluminum wire used to secure the samplers to the deployment gear. In the same study, the SPME attached to the gear by stainless steel hose clamps were successfully recovered [18] as were SPME samplers Zeng et al. [33] deployed, also using stainless steel hose clamps, in another study in the Southern California Bight.

Naval Station Newport Baseline C_{free} was determined for three categories of target contaminants of regulatory concern including high molecular weight (MW) PAHs, B[a]P and total PCBs (Figure 3), Additionally, total PAHs and total PBDEs were investigated (Supplemental Data Figure S3). High MW PAHs C_{free} ranged from 8.9 to 16 ng/L and 3.2 to 6.0 ng/L based on PE and POM, respectively, demonstrating an approximate factor of two difference in C_{free} between polymers. Using PE, B[a]P, a component of the high MW PAHs, C_{free} values ranged from 100 to 780 pg/L compared to POM-based C_{free} values which ranged from 100 to 220 pg/L. The B[a]P C_{free} values showed at most a factor of three difference between polymers (e.g., NSN2). Total PCB C_{free} ranged from 110 to 170 pg/L based on PE while C_{free} using POM were much lower, ranging across the site from 5.8 to 11 pg/L. Total PCB C_{free} were the lowest at this Superfund site as compared to the other two Superfund sites in this investigation. Total PAH and PBDE C_{free} ranged from 25 to 48 ng/L and 130 to 230 pg/L, respectively, for the PE-based measures. These values are very similar to the POM-based measures of C_{free} across the site: 16 to 40 ng/L for total PAHs and 160 to 170 pg/L for total PBDEs (Supplemental Data Figure S3). Differences in total PCB C_{free} between the PE- and POM-based estimates are the largest we found across this entire investigation. Analysis of POM for PCB congeners found much lower accumulation than in the PE: POM C_{free} were, on average, only 6% of PE C_{free}. In addition, POM accumulated a smaller diversity of PAH molecules compared to PE. Further, PRC data for the POM was problematic when used for adjusting any of the target contaminants for non-equilibrium conditions. Consequently, for POM, C_{free} was calculated using Equation 2 which assumes the target contaminants have attained equilibrium with the polymer. In this case, it is uncertain if that assumption is accurate. It is unclear what caused the problems when working with POM and PRCs in this investigation but the loss of PRCs from the polymer was not found to be linearly correlated with contaminant molecular weight or K_{OW}. In a previous deployment, Perron et al. [19] also reported difficulties working with PRCs and POM when trying to calculate C_{free} for PCBs. In general, as shown in New Bedford Harbor, C_{free} based on different samplers were relatively similar lending weight to the conclusion that the samplers "experienced" and measured similar C_{free} in the water column. Supplemental Data Table S1 shows the results of statistical analyses comparing C_{free} by passive sampler type and station. Specific trends from the analysis include total PCB C_{free} values, as well as high molecular weight PAH C_{free} values, based on PE and POM were always statistically different. Further, PE- and POM-based total PAHs C_{free} values were never significantly different. In between these extremes, significant differences in PE and POM C_{free} values occurred at 50% of the stations for B[a]P and total PBDEs

Passive Sampler Equilibrium at the New Bedford Harbor Superfund Site

Deployments performed at the New Bedford Harbor Superfund site offer a unique opportunity to assess passive sampler equilibrium status. This is because several different types of samplers were deployed over multiple time periods. As discussed above, for the SPMDs and SPMEs equilibrium was assumed while for PE, PRCs were used to adjust C_{free} for non-equilibrium conditions. It should be noted that for the SPMDs, because of the polymers thickness on two sides (i.e., tube configuration), this assumption is suspect and the reported concentrations may represent underestimates. Beyond assuming equilibrium or using PRCs, other empirical approaches for assessing the equilibrium status of the passive sampler can be used. One is to perform a temporal series analysis, collecting passive samplers over time to assess when target contaminant concentrations no longer show statistically significant changes in the passive sampler polymer. As discussed above, a time series analysis was performed with PE, SPME and SPMD in the winter deployments at New Bedford Harbor. Figure 4 shows the concentrations of total PCBs over the 29 day deployment at seven day intervals for each sampler. In general, all three samplers showed similar trajectories for total PCB uptake. For example, by Day 29, concentrations of total PCBs ranged from 29,000 to 39,000 ng/mL polymer and 3,200 to 7,500 ng/mL polymer at stations NBH2 and NBH4, respectively. Statistical analysis indicated the SPMD samplers were continuing to accumulate PCBs at NBH2 after 21 days but had achieved equilibrium after Day 21 at NBH4 (i.e., no statistically significant difference between polymer and triolein concentrations on days 21 and 29) (Figure 4a). In contrast, after 14 days at

NBH2, the SPME samplers were at equilibrium while at NBH4 days 21 and 29 were significantly different and equilibration had not been achieved (Figure 4b). Finally, analysis of the winter PE samplers suggests equilibrium was achieved after 14 and 21 days at NBH2 and NBH4, respectively (Figure 4c). This finding agrees with the relatively small PRC-based correction (< 10%) applied to the winter PE to adjust for non-equilibrium conditions discussed above. A similar analysis is provided in the Supplemental Data section for selected PCB congeners (Supplemental Data Figures S4, S5).

For a seasonal comparison, Figure 4d shows the accumulation of total PCBs by the PE in the fall deployment indicating equilibrium by days 21 and 14 at NBH2 and NBH4, respectively. At NBH4, the final deployment period (day 28) was similar to the final concentration in the winter deployment (day 29): 7,700 ng/mL PE versus 7,500 ng/mL PE. However, at NBH2 and unlike NBH4, concentrations of total PCBs were much higher in the fall relative to the winter deployment: 84,000 ng/mL PE versus 39,000 ng/mL PE. Interestingly, the total water and C_{18}-based measures of total PCBs indicated that during the fall deployment, NBH2 and NBH4 concentrations were often also elevated compared to the winter deployment (Figure 5a, b).

One other approach for assessing equilibrium status, is to measure the concentration of target contaminants in polymers of different thicknesses. The premise for this approach is that as target contaminants accumulate they will partition homogeneously within the polymer. Therefore, when expressed on a mass or volume basis, for two different polymer thicknesses, equal concentrations would indicate equilibrium. This type of analysis was performed with two PE thicknesses (i.e., 25 µm and 51µm) in both fall and winter deployments at NBH2 and NBH4. At both stations, in the winter, after 29 days there were no statistical differences between thicknesses, suggesting the PE was at equilibrium (Figure 6a, b). Conversely, at both NBH2 and NBH4, in the fall, after 28 days, the two thicknesses were statistically different suggesting equilibrium had not yet been achieved (Figure 6a, b). As noted previously, relatively higher total water concentrations of PCBs in the fall deployment were observed during some of the collections (Figure 5).

Comparing Passive Sampler Uptake and Mussel Bioaccumulation

Thus far, the focus of this study has been on examining contaminant C_{free} (i.e., PCBs, PAHs, PBDEs) in the water column at three Superfund sites and assessing equilibrium based on the concentration of PCBs in the polymer at the New Bedford Harbor Superfund site. However, another very valuable type of information that passive samplers can provide is an estimate of concentrations of target contaminants that organisms are likely to bioaccumulate. Currently, biomonitoring organisms, like marine polychaetes and mussels, and freshwater and marine fish, are used to determine the amount of bioavailable contaminants in the water column and interstitial waters of Superfund sites [34]. This information has been used for several purposes including assessing the effectiveness of remediation and performance of long-term monitoring [34, 35]. However, there are limitations to using organisms for measuring bioavailable concentrations. These include field conditions (e.g., high or low water temperatures, low dissolved oxygen, ice formation) adversely affecting biomonitoring organisms, seasonal unavailability of biomonitoring organisms, and logistical challenges and financial costs associated with deploying living organisms [36]. The concept of using passive samplers as surrogates for biomonitoring organisms when such limitations are an issue has a great deal of appeal. Scientific data comparing biomonitoring organisms and passive samplers continues to be collected in order to evaluate this approach [12, 16, 23-25, 37]. In the current study, mussels were deployed during the fall passive sampler deployment at New Bedford Harbor and provide an opportunity to compare mussel bioaccumulation with passive sampler accumulation of PCBs at two stations.

Mean concentrations of total PCBs in deployed mussels at NBH2 and NBH4 were 350,000 ng/g lipid and 64,000 ng/g lipid, respectively. By comparison, total PCB PE concentrations adjusted for non-equilibrium conditions were 110,000 ng/g PE and 9,300 ng/g PE for samplers at NBH2 and NBH4, respectively. This difference results in a mussel bioaccumulation to PE accumulation ratio of 3.2 and 6.9 for NBH2 and NBH4, respectively. Hofelt and Shea [37], in their study in NBH, reported total PCB ratios for mussel bioaccumulation to SPMD accumulation ranging from about 1.2 to 4.8. Based on Equation 7, these tissue concentrations expressed, on a mussel lipid basis, are equivalent to mussel-based C_{free} of 404,000 pg/L and 58,000 pg/L at NBH2 and NBH4, respectively. These values compare relatively well to polyethylene-based C_{free} of 360,000 pg/L and 25,000 pg/L at NBH2 and NBH4, respectively. However, to more directly compare mussel bioaccumulation to passive sampler accumulation, Figure 7 shows mussel and PE concentrations of individual PCB congeners at NBH2 and NBH4. There were a total of 27 congeners that had matching accumulation data for both mussels and PE. If mussels and polyethylene accumulated PCB molecules identically, the data points in Figure 7 would fall on the 1:1 line. Instead, a mean offset of approximately 8.6 is observed indicating, that in general, the mussels accumulated PCBs about nine times more than the PE. In addition, the offset suggests a concentration dependency on the amount of PCB congeners in the overlying water. In other words, at NBH4, where C_{free} is relatively low (Figure 1a), the offset ranges from a factor of 2.9 to 22 and at NBH2, where C_{free} is relatively high (Figure 1b), the offset range is a factor of 1.5 to 15. Despite the offset, summary statistics demonstrate a strong correlative log-linear relationship between mussel bioaccumulation and PE accumulation:

$$\text{Log PCB bioaccumulation (ng/g lipid)} = 0.74 * \text{Log PCB accumulation (ng/g PE)} + 1.62$$

$$(r^2 = 0.92;\ n = 27;\ p <<< 0.05)$$

Further, the log-linear correlation indicates the relationship between bioaccumulation and PE accumulation is highly significant with p values much less than 0.05 (Figure 7). In a similar comparison of PCB passive sampler accumulation versus bioaccumulation, using the marine polychaete *Nereis virens* exposed to New Bedford Harbor sediment, Friedman et al. [24] also reported a strong linear relationship ($r^2 = 0.88$; n = 48). In addition, Gschwend et al. [16], using PCB-contaminated sediments from the Hunter's Point Naval Station in San Francisco Bay (CA, USA), exposed to the marine polychaete *Neanthes arenaceodentata*, under two exposure regimes (i.e., mixed and passive), reported linear relationships: $r^2 = 0.64$ (n= 7) and $r^2 = 0.59$ (n = 7), respectively. Interestingly, in the Gschwend et al. [16] comparison of polychaete bioaccumulation to passive sampler accumulation, they also included PDMS-coated SPME fibers and POM. In all four cases, they found an off-set between the 1:1 line between bioaccumulation and accumulation similar in behavior (i.e., linear and favoring bioaccumulation) and scale (i.e., an order of magnitude) to the one described in the current study. They attributed the off-set to the preferential partitioning of PCBs to lipid as compared to the polymers.

This representative selection of measures demonstrates that PE accumulation is correlated and potentially predictive of organism bioaccumulation, which in turn, suggests PE could be considered as a surrogate for biomonitoring organisms (at least at the New Bedford Harbor Superfund site with PCBs). In their evaluation of the relationship between SPMD accumulation and bioaccumulation from a review of nine studies (including Hofelt and Shea [37]), Booij et al. [38] recommended using passive sampling (in this case SPMDs) for new biomonitoring programs because of the associated advantages relative to the disadvantages of using biomonitoring organisms. These advantages include: $K_{lipid\text{-}free}$ show greater variability than $K_{PS\text{-}free}$; determining equilibrium status is more difficult with organisms compared to passive samplers; and the need to use different organisms (to accommodate different habitats) limits the standardization of methods across broad geographic areas, whereas one type of passive sampler can be applied everywhere. For existing monitoring studies, Booij et al. [38] acknowledged that switching from biomonitoring organisms to passive samplers is problematic because of the potential loss in data consistency. However, they suggest the performance of multiple comparative studies on a site-specific basis to develop conversion factors between historic bioaccumulation and new passive sampler accumulation data. Similarly, the concept of the systematic global deployment of aquatic passive samplers for monitoring purposes has recently been proposed in the literature [39, 40]. Despite the off-set observed in this dataset and others (e.g., [16]), there is growing evidence that passive sampler accumulation of PCBs is linearly correlated with organismal bioaccumulation suggesting these are predictive relationships that could be useful in instances when the deployment of biomonitoring organisms is not viable.

Comparison of Passive Sampler-based C_{free} to Other Studies

Of the three Superfund sites investigated, New Bedford Harbor has been the most frequently studied using passive samplers. For example, several studies have used passive samplers to examine the distribution and bioavailability of contaminants in NBH sediments. Specifically, Vinturella et al. [23], Friedman et al. [24] and Lu et al. [25] evaluated PE and SPME as surrogates for measuring the bioaccumulation of PCBs and PAHs by a benthic polychaete (*Neries virens*) and an oligochaete (*Ilyodrilus templetoni*). Other than the current study, only Hofelt and Shea [37] have used passive sampling to estimate the C_{free} of PCBs in the New Bedford Harbor water column. They performed 30 day SPMD deployments at five stations inside and outside of the harbor and detected several organochlorine pesticides and PCBs. Total PCB C_{free} based on SPMDs ranged from 1,400 to 17,000 pg/L (Table 2). By comparison, total PCB C_{free} in the current study was about an order of magnitude greater: 25,000 to 359,000 pg/L based on PE; 18,000 to 107,000 pg/L based on SPME; 8,000 to 76,000 pg/L based on SPMD. While the studies were performed about ten years apart they analyzed for the same PCB congeners to determine total PCBs. Consequently, it is not clear why such large differences in total PCB C_{free} exist between the investigations.

Three previous studies used passive sampling to investigate the C_{free} of total PCBs and DDTs at the Palos Verdes Shelf Superfund site. Zeng et al. [33] applied SPME to estimate the C_{free} of total DDTs two meters above the sediment surface in 30 day deployments resulting in 4,900 pg/L at a station close to the current investigation's stations (Table 2). In one of two studies at PVS, Fernandez et al. [18] deployed PE and SPME samplers at three depths in the water column at 11 stations. For samplers five meters above the sediment, C_{free} for total DDTs ranged from 260 to 1,100 pg/L using SPME and 750 to 2,600 pg/L for PE. The differences in the heights of the samplers above the sediments (5 m versus 2 m) may explain the lower C_{free} values in the present study when compared to Zeng et al. [33] measurements. For total PCBs at PVS, the current study found C_{free} ranged from 45 to 430 pg/L while Fernandez et al. [18] reported 90 to 320 pg/L for PE samplers deployed 5 meters above the sediment surface. In a second study, Fernandez et al. [19] measured C_{free} of 230 to 460 pg/L and 130 to 450 pg/L with PE and POM, respectively, located about 20 cm above the sediment surface. For total PCBs, all of these C_{free} values from the different studies are relatively similar despite using different types of passive samplers over a ten year period of time; for example, high C_{free} values ranged from 320 to 460 pg/L. Further, any substantial differences can be explained by the depth the samplers were deployed (i.e., higher in the water column resulted in lower target contaminant concentrations) indicating the sediments serve as the primary source of target contaminants at PVS. In addition, Fernandez et al. [19] found total DDT C_{free} in the water column ranging from 26,000 to 32,000 pg/L and 7,800 to 16,000 pg/L using PE and POM, respectively, in samplers deployed about 20 cm above the sediment surface. In the same study, SPME deployed approximately one meter above the sediments measured C_{free} of 1,700 to 4,000 pg/L. Finally, in both Fernandez et al. [18, 19], SPME were deployed to monitor for total PCB C_{free} but unlike the total DDTs, no PCBs were detected analytically. In contrast, both PE and POM were able to detect total PCB C_{free} in the water column at PVS. This difference in the sampler's performance most likely reflects the greater mass of PE and POM that can be deployed compared to SPME. While SPME achieves equilibrium more rapidly than POM or PE, the smaller mass of PDMS that is generally deployed is sometimes unable to accumulate sufficient target contaminant for detection by analytical instrumentation. However, other configurations of PDMS can be deployed [e.g., 41] and attain greater detection sensitivity than afforded by SPME.

Finally, no previous studies using passive samplers have investigated C_{free} in the water column at the Naval Station Newport Superfund site. However, Perron et al. [20, 21] reported C_{free} total PCBs, total PAHs and total PBDEs of 38 to 120 pg/L, 32 to 91 ng/L and 40 to 91 pg/L, respectively, using PE and POM passive samplers for a station in Newport Harbor about 5.5 kilometer south of the Superfund site (Table 2). In general, these concentrations compare relatively well with C_{free} reported in the present study where total PCBs, total PAHs and total PBDEs based on PE were 110 to 170 pg/L, 26 to 40 ng/L and 160 to 230 pg/L, respectively, and based on POM were 5.8 to 11 pg/L, 16 to 40 ng/L and 160 to 170 pg/L, respectively. The decades of industrial maritime activity and the resulting sediment contamination at NSN make the higher total PCB C_{free} there compared to Newport Harbor unsurprising. Further, Newport Harbor is an active commercial and recreation harbor, therefore elevated total PAH C_{free} from boat engines and related sources is not unexpected. However, what is of interest are the elevated C_{free} for total PBDEs at NSN. These chemicals are used as flame retardants in some consumer products and are undergoing scrutiny in the United States and Europe because of concerns with mammalian toxicity. The levels at NSN were up to three times higher than those seen in Newport Harbor (and anywhere else in Narragansett Bay [21]) suggesting there may be an unknown source in the NSN that requires further investigation.

Summary

In general, the different passive samplers demonstrated good agreement in C_{free} with values varying by a factor of two to three. This level of agreement was clearly demonstrated at the Palos Verdes Superfund site where C_{free} determined by different passive samplers over several years and deployments varied by less than a factor of two. Further, in most instances where conventional water samples were collected (i.e., grabs) and compared to passive sampler C_{free} values (i.e., New Bedford Harbor), values were also within a factor of two of aqueous measurements. Also, in most cases in New Bedford Harbor, total PCBs were approaching equilibrium in the samplers after nearly 30 days of deployment. These findings suggest all of the samplers were experiencing and measuring the same C_{free} during their respective deployments and that the RPM's selection of which passive samplers to use at their site can be based on variable like costs, availability and logistics rather than which passive sampler is more scientifically accurate. More importantly, passive sampling will enable the RPM to determine both the spatial and temporal trends of target contaminants, key factors for successfully remediating a contaminated site. At New Bedford Harbor, a strong log-linear, correlative and predictive relationship was found between passive sampler accumulation and mussel bioaccumulation. Finally, all of the Superfund site investigations discussed here, except for the SPMD deployments, used unsophisticated deployment gear and passive samplers. This evaluation demonstrates the practical utility of passive sampling for generating scientifically accurate water column C_{free} which is critical for making informed environmental management decisions at contaminated sediment sites.

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References

1. National Research Council. 2001. *A Risk-Management Strategy for PCB-Contaminated Sediments*. National Academy Press, Washington, DC, USA.

2. National Research Council. 2003. *Bioavailability of Contaminants in Soils and Sediments*. National Academy Press, Washington, DC, USA.

3. Di Toro DM, CS Zarba, DJ Hansen, WJ Berry, RC Swartz, CE Cowan, SP Pavlou, HE Allen, NA Thomas, PR Paquin. 1991. Technical basis for the equilibrium partitioning method for establishing sediment quality criteria. *Environ Toxicol Chem* 11:1541-1583.

4. Burgess RM, DR Mount, WJ Berry, DM Di Toro. 2013. Mechanistic sediment quality guidelines based on contaminant bioavailability: equilibrium partitioning sediment benchmarks. *Environ Toxicol Chem* 32:102-114.

5. Mayer P, TF Parkerton, RG Adams, JG Cargill, J Gan, T Gouin, PM Gschwend, SB Hawthorne, P Helm, G Witt, J You, BI Escher. 2014. Passive sampling methods for contaminated sediments: scientific rationale supporting use of freely dissolved concentrations. *Integr Environ Assess Manag* 10:197-209.

6. Huckins JN, GK Manuweera, JD Petty, D Mackay, JA Lebo. 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ Sci Technol* 27:2489-2496.

7. Booij K, R van Bommel, HM van Aken, H van Haren, G-T A Brummer, H Ridderinkhof. 2014. Passive sampling of nonpolar contaminants at three deep-ocean sites. *Environ Pollut* 195:101108.

8. Hawthorne SB, CB Grabanski, DJ Miller, JP Kreitinger. 2005. Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K_{DOC} values. *Environ Sci Techno.* 39:2795-2803.

9. Maruya KA, EY Zeng, D Tsukada, SM Bay. 2009. A passive sampler based on solid-phase microextraction for quantifying hydrophobic organic contaminants in sediment pore water. *Environ Toxicol Chem* 28:733–740.

10. Witt G, S-C Lang, D Ullmann, G Schaffrath, D Schulz-Bull, P Mayer. 2013. Passive equilibrium sampler for in situ measurements of freely dissolved concentrations of hydrophobic organic chemicals in sediments. *Environ Sci Technol* 47:7830–7839.

11. Jonker MTO, AA Koelmans. 2001. Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. *Environ Sci Technol* 35:3742–3748.

12. Oen AMP, EML Janssen, G Cornelissen, GD Breedveld, E Eek, RG Luthy, 2011. *In situ* measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environ Sci Technol* 45, 4053–4059.

13. Beckingham B, U Ghosh. 2013. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* 91:1401-1407.

14. Lohmann R, Burgess RM, Cantwell, MG, Ryba SA, MacFarlane JK, Gschwend PM. 2004. Dependency of polychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in *Mya arenaria* on both water column and sediment bed chemical activities. *Environ Toxicol Chem* 23: 2551-2562.

15. Adams RG, R Lohmann, LA Fernandez, JK MacFarlane, PM Gschwend. 2007. Polyethylene devices: passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. *Environ Sci Technol* 41:1317-1323.

16. Gschwend PM, JK MacFarlane, DD Reible, X Lu, SB Hawthorne, DV Nakles, T Thompson. 2011. Comparison of polymeric samplers for accurately assessing PCBs in pore waters. *Environ Toxicol Chem* 30:1288-1296.

17. Fernandez LA, JK MacFarlane, AP Tcaciuc, PM Gschwend. 2009. Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals. *Environ Sci Technol* 43:8888-8894.

18. Fernandez L, W Lao, K Maruya, C White, RM Burgess. 2012. Passive sampling to measure baseline dissolved persistent organic pollutant concentrations in the water column of the Palos Verdes Shelf Superfund site. *Environ Sci Technol* 46:11937−11947.

19. Fernandez LA, W Lao, K Maruya, RM Burgess. 2014. Calculating the diffusive flux of persistent organic pollutants between sediments and the water column on the Palos Verdes Shelf Superfund Site using polymeric passive samplers. *Environ Sci Technol* 48:3925-3934.

20. Perron, MM, RM Burgess, EM Suuberg, Cantwell MG, KG Pennell. 2013. Performance of passive samplers for monitoring estuarine water column concentrations 1. Contaminants of concern. *Environ Toxicol Chem*. 32:2182-2189.

21. Perron, MM, RM Burgess, EM Suuberg, Cantwell MG, KG Pennell. 2013. Performance of passive samplers for monitoring estuarine water column concentrations 2. emerging contaminants. *Environ Toxicol Chem*. 32:2190-2196.

22. Booij K, F Smedes, EM van Weerlee. 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* 46:1157-1161.

23. Vinturella AE, RM Burgess, BA Coull, KM Thompson, JP Shine. 2004. The use of passive samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polychaetes. *Environ Sci Technol* 38:1154-1160.

24. Friedman CL, RM Burgess, MG Cantwell, KT Ho, R Lohmann. 2009. Comparing polychaete bioaccumulation and passive sampler uptake to assess the effects of sediment resuspension on PCB bioavailability. *Environ Sci Technol* 43:2865-2870.

25. Lu X, B Drake, A Skwarski A, D Reible. 2011. Predicting bioavailability of PAHs and PCBs with pore water concentrations measured by disposable solid-phase micro-extraction fibers. *Environ Toxicol Chem* 30:1109–1116.

26. United States Environmental Protection Agency. 2012a. *Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Procedures for the Determination of the Freely Dissolved Interstitial Water Concentrations of Nonionic Organics*. EPA-600-R-02-012. Office of Research and Development. Washington, DC, USA.

27. United States Environmental Protection Agency. 2012b. *Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites*. Sediment Assessment and Monitoring Sheet #3. Office of Research and Development/Office of Superfund Remediation and Technology Innovation, Washington, DC, USA.

28. Greenberg MS, PM Chapman, IJ Allan, KA Anderson, SE Apitz, C Beegan, TS Bridges, SS Brown, JG Cargill IV, MC McCulloch, CA Menzie, JP Shine, TF Parkerton. 2014. Passive sampling methods for contaminated sediments: risk assessment and management. *Integr Environ Assess Manag* 10:224-236.

29. Schubauer-Berigan JP, Foote EA, Magar VS. 2012. Using SPMDs to assess natural recovery of PCB-contaminated sediments in Lake Hartwell, SC: I. A field test of new in-situ deployment methods. *Soil Sed Contam* 21:82–100.

30. Schwarzenbach RP, PM Gcshwend, DM Imboden. 2003. *Environmental Organic Chemistry*. John Wiley and Sons, Inc., Hoboken, NJ, USA.

31. Lynn RJ, JJ Simpson. 1987. The California Current system: the seasonal variability of its physical characteristics. *J Geophys Res* 92:12947-12966.

32. Di Lorenzo E. 2003. Seasonal dynamics of the surface circulation in the Southern California Current system. *Deep-Sea Res II* 50: 2371-2388.

33. Zeng E, D Tsukada, DW Diehl. 2004. Development of a solid-phase microextraction-based method for sampling of persistent chlorinated hydrocarbons in an urbanized coastal environment. *Environ Sci Technol* 38: 5737-5743

34. United States Environmental Protection Agency. 2005. *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites*. EPA-540-R-05-012. Office of Solid Waste and Emergency Response. Washington, DC, USA.

35. Nelson WG, BJ Bergen. 2012. The New Bedford Harbor Superfund site long-term monitoring program (1993–2009). *Environ Monit Assess*. 184: 7531-7550.

36. Lohmann R, Booij K. Smedes F, Vrana, B. 2012. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environ Sci Pollut Res* 19:1885-1895.

37. Hofelt CS, D Shea. 1997. Accumulation of organochlorine pesicides and PCBs by semipermeable membrane devices and *Mytilus edulis* in New Bedford Harbor. *Environ Sci Technol* 31:154-159.

38. Booij K, F Smedes, EM van Weerlee, PJC Honkoop. 2006. Environmental monitoring of hydrophobic organic contaminants: the case of mussels versus semipermeable membrane devices. *Environ Sci Technol* 40:3893-3900.

39. Lohmann R, D Muir. 2010. Global aquatic passive sampling (AQUA-GAPS): using passive samplers to monitor POPs in the waters of the world. *Environ Sci Technol* 44:860-864.

40. Allan IJ, C Harman. 2011. Global aquatic passive sampling: maximizing available resources using a novel exposure procedure. *Environ Sci Technol* 45:6233-6234.

41. Maenpaa K, MT Leppanen, F Reichenberg, K Figueiredo, P Mayer. 2011. Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment: comparison of two approaches to determine equilibrium partitioning concentrations in lipids. *Environ Sci Technol* 45:1014-1047.

Table Legends

Table 1. Superfund sites, sampling stations deployment locations, water depths, and sample types (e.g., polyethylene (PE), solid phase microextraction (SPME), polyoxymethylene (POM), semi-permeable membrane devices SPMDs).

Table 2. Comparison of C_{free} concentrations for several organic contaminants in the water column of the Superfund sites investigated in this study. Available C_{free} ranges observed in other studies using passive sampling are also presented.

Figure Legends

Figure 1. Total PCB C_{free} measured in the water column of the New Bedford Harbor Superfund site (New Bedford, MA, USA) during (a) the fall deployments of polyethylene (PE), mussels, and collection of total and C_{18}-based grab water samples and (b) the winter deployments of polyethylene (PE), solid phase microextraction (SPME), semi-permeable membrane devices (SPMDs), and collection of total and C_{18}-based grab water samples. Total PCB is equivalent to the sum of measured PCB congeners.

Figure 2. Total PCB C_{free} measured in the water column of the Palos Verdes Shelf Superfund site (CA, USA) during polyethylene (PE) deployments. Total PCB is equivalent to the sum of measured PCB congeners.

Figure 3. High molecular weight PAH (a), benzo[a]pyrene (b), and total PCB (c) C_{free} measured in the water column of the Naval Station Newport Superfund site (Newport, RI, USA) during the polyethylene (PE) and polyoxymethylene (POM) deployments. High molecular weight PAH was equivalent to the sum of pyrene, fluoranthene, chrysene, benzo[a]pyrene, benz[a]anthracene and dibenz[a,h]anthracene. Total PCB is equivalent to the sum of measured PCB congeners. Note: concentrations of benzo[a]pyrene and total PCBs are in pg/L and high molecular weight PAH concentrations are in ng/L.

Figure 4. Total PCBs accumulated by (a) SPMD, (b) SPME, and (c) PE during the winter deployment, and (d) PE during the fall deployment over multiple sampling periods at the New Bedford Harbor Superfund site. Statistically significant differences ($\alpha = 0.05$) between sampler concentrations for the last deployment period (day 28 or 29) and previous deployment periods are indicated by *. Total PCB is equivalent to the sum of measured PCB congeners.

Figure 5. Total PCBs based on total water and C_{18}-based measurements during fall and winter sampling periods at stations (a) NBH2 and (b) NBH4 of the New Bedford Harbor Superfund site. Total PCB is equivalent to the sum of measured PCB congeners.

Figure 6. Total PCBs in polyethylene (PE) passive samplers of different thicknesses (e.g., 25 µm and 51 µm) at (a) NBH2 and (b) NBH4 in the fall and winter deployments. Significant statistical differences ($\alpha = 0.05$) between thicknesses at a given station and season are indicated by *. Total PCB is equivalent to the sum of measured PCB congeners.

Figure 7. Concentration of PCB congeners accumulated by polyethylene (PE) passive samplers versus bioaccumulated by blue mussels (*Mytilus edulis*) during the fall deployment at the New Bedford Harbor Superfund site. Open and full circles represent stations NBH2 and NBH4, respectively. Polyethylene concentrations have been adjusted for equilibrium conditions.