In situ passive sampling of sediments in the Lower Duwamish Waterway Superfund site: Replicability, comparison with *ex situ* measurements, and use of data

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ABSTRACT

Superfund sites with sediments contaminated by hydrophobic organic compounds (HOCs) can be difficult to characterize because of the complex nature of sorption to sediments. Porewater concentrations, which are often used to model transport of HOCs from the sediment bed into overlying water, benthic organisms, and the larger food web, are traditionally estimated using sediment concentrations and sorption coefficients estimated using equilibrium partitioning (EqP) theory. However, researchers have begun using polymeric samplers to determine porewater concentrations since this method does not require knowledge of the sediment's sorption properties.

In this work, polyethylene passive samplers were deployed into sediments in the field (*in situ* passive samplers) and mixed with sediments in the laboratory (*ex situ* active sampling) that were contaminated with polychlorinated biphenyls (PCBs). The results show that porewater concentrations based on *in situ* and *ex situ* sampling generally agreed within a factor of two, but *in situ* concentrations were consistently lower than *ex situ* porewater concentrations. Imprecision arising from *in situ* passive sampling procedures does not explain this bias suggesting that field processes like bioirrigation may cause the differences observed between *in situ* and *ex situ* polymeric samplers.

CAPSULE ABSTRACT

Porewater concentrations of PCBs found using *in situ* passive PE sampling were lower than those found using *ex situ* active PE sampling, which is likely due to natural processes like bioirrigation.

INTRODUCTION

Historical production and use of hydrophobic organic compounds (HOCs) has led to the contamination of numerous aquatic ecosystems, and particularly their sediments, throughout the world. Even though production of many common HOCs has been reduced or even eliminated, the accumulated contaminants are still present in the sediments, and significant research efforts are ongoing to understand food web exposures, potential toxicities, and the effectiveness of remediation designs (Bridges and Gustavson, 2014; Ghosh et al., 2014; Kupryianchyk et al., 2015; Lydy et al., 2014; Nadeau and Skaggs Jr, 2007; Patmont et al., 2015).

Researchers have previously found that some environmental fate processes and toxic effects depend on the freely-dissolved porewater concentrations of HOCs and not their total sediment concentrations (Hawthorne et al., 2007; Kraaij et al., 2003; Lydy et al., 2014). In order to estimate the freely-dissolved porewater concentrations from the measured sediment concentrations, models based on the equilibrium partitioning (EqP) of chemicals between the organic carbon in the sediment and the water phase have been used (Di Toro et al., 1991). Unfortunately, these models often perform poorly for many HOCs because of the widely-varying sorption behaviors of carbonaceous phases in sediments (Apell and Gschwend, 2014; Fernandez et al., 2009b; Friedman and Lohmann, 2014; Kraaij et al., 2003).

Despite this difficulty, remedial investigations of HOC-contaminated sediments often still use EqP modeling to estimate exposures, and consequently risk, to aquatic organisms and humans (AECOM, 2012). This calculated risk is then used to inform remedial decisions and designs. This strategy was used for the remedial investigation for the Lower Duwamish Waterway (LDW) in Seattle, WA, which is managed under the U.S. Environmental Protection Agency's Superfund program, and is expected to have a remediation cost of US$342 million (AECOM, 2012; United States Environmental Protection Agency, 2014).

As an alternative to EqP modeling, researchers have been investigating the use of polymeric materials as environmental samplers (Arthur and Pawliszyn, 1990). These polymeric samplers absorb HOCs in proportion to the compounds' polymer-water partition coefficients ($K_{\text{P-W}}$) and the freely-dissolved water concentration; therefore, freely-dissolved concentrations can be deduced from the measured polymer concentrations. Because of their relative ease of use, this sampling method has been applied to answer a variety of research questions regarding the fate and effects of HOCs such as predicting bioaccumulation into organisms and quantifying the flux to/from environmental compartments (Arp et al., 2011; Fernandez and Gschwend, 2015; Fernandez et al., 2014; Mäenpää et al., 2015; Morgan and Lohmann, 2010; Muijs and Jonker, 2011). In some of these research areas, measurements of *in situ* freely-dissolved porewater concentrations are highly beneficial or even necessary to draw accurate conclusions and make informed decisions.

However, the use of polymeric samplers used passively in sediment beds has been limited. One reason for this is that passive polymeric samplers deployed in sediment beds will not come close to equilibrium during typical deployment times (e.g., 1-3 months) for many of HOCs of interest (Apell et al., 2015). If isotopically-labeled performance reference compounds (PRCs) are impregnated in the passive sampler before deployment, then the measured rate of dissipation of the PRCs can be used to adjust the sampler concentrations to their corresponding equilibrium concentrations using previously published models (Apell and Gschwend, 2014; Fernandez et al., 2009a; Lampert et al., 2015; Tcaciuc et al., 2015).

This research, which was a supplemental effort in the site investigation of the Lower Duwamish Waterway Superfund site, compares the polychlorinated biphenyl (PCB) porewater concentrations obtained using *in situ* passive sampling with those from *ex situ* active sampling. The effort adds to the literature supporting the use of PRCs for *in situ* passive sampling of sediment aimed at determining porewater concentrations (Fernandez and Gschwend, 2015; Fernandez et al., 2014; Janssen et al., 2011; Liu et al., 2013a; Liu et al., 2013b; Oen et al., 2011; Thomas et al., 2014; Tomaszewski and Luthy, 2008). We also assess the precision of the *in situ* passive sampling method, allowing use of the data to determine if the *in situ* and *ex situ* concentrations are statistically different from each other. Lastly, the porewater concentrations determined using sediment concentrations normalized by sorptive equilibrium coefficients are evaluated against the porewater concentrations determined using *ex situ* active and *in situ* passive sampling. This comparison adds to the growing literature suggesting (a) sediment concentration-based calculations do not yield accurate porewater concentration estimates, and (b) porewaters may not be in sorptive equilibrium with the surface sediments in which biota are active.

MATERIALS AND METHODS

Materials

Low-density polyethylene (PE, Film-Gard), with a sheet thickness of 25 μm (1 mil), was used as a polymeric sampler. The PE sheet was cut into strips of 5×65 cm and cleaned by soaking twice in dichloromethane and twice in methanol. Each soaking was for 24 h. The PE was then placed into an 80:20 (v/v) methanol:water solution spiked with performance reference compounds (PRCs, ^{13}C-labeled congeners 28, 47, 54, 97, 111, 153, and 178) for > 1 week (Booij et al., 2002). PRC concentrations were chosen to mimic the expected concentrations that would be accumulated from the environment. The PE strips were then soaked in deionized water for 24 h twice to remove residual methanol. PE strips were stored in deionized water until use.

All solvents used were UltraResi-Analyzed (Avantor, Phillipsburg, NJ). All glassware was combusted at 450°C for 18 h. All samples were stored in amber glassware.

In Situ (Field Deployment) PE Samplers

PE strips were mounted into aluminum frames with cut out windows of 5×50 cm. At that time, subsamples were collected from the PE strips and stored in amber vials filled with dichloromethane in order to quantify initial PRC concentrations. The PE samplers were wrapped tightly in aluminum foil to minimize losses to air and were then placed in a cooler at ambient temperature for shipping and deployment.

On November 14-15, 2012, samplers were deployed by the Region 10 Environmental Protection Agency (EPA) dive team into the sediments of the Lower Duwamish Waterway (LDW) in Seattle, WA. Five sites, which were spread over 3 mi of the 5 mile-long site, were chosen along the river with duplicate samplers deployed about 1 m apart at each site (Figure S1 and Table S1).

On January 15, 2013, all 10 samplers were retrieved by the Region 10 EPA dive team. The samplers were taken to the nearby Analytical Resources Inc. Laboratory (Tukwila, WA) for processing by the authors. The PE strips were wiped with a lint-free tissue and cut into 10 cm segments starting at the sediment-water interface. The interface was identified by discoloration on the PE and aluminum frame (U.S. EPA, 2012).

The 10 cm segments were stored in 40 mL amber glass vials with two drops of deionized water to ensure 100% relative humidity in the vial for shipment back to MIT. Upon arrival at MIT, the water was removed, the PE was spiked with surrogate standards (listed in the SI), and dichloromethane was added to the vial to submerge the PE. PE segments were extracted three times sequentially by shaking on a rotary shaker table for at least 24, 12, and 3 h with dichloromethane to ensure complete extraction, and extracts were combined in a glass round-bottom flask. The extract was concentrated using a Rotavapor-R (BÜCHI, Switzerland), operated with a 40°C water bath and less than 15 in Hg vacuum, to a volume of $\approx$1 mL and quantitatively transferred to a 4 mL vial. The extract was then further concentrated under a stream of ultra-high purity N_2 at room temperature. The extracts were solvent exchanged into hexane, quantitatively transferred to small volume inserts in autosampler vials, and spiked with internal standards (listed in SI) before analysis.

Ex Situ (Laboratory) PE Samplers

During deployment of the PE samplers, sediment cores from a depth of 0-10 cm were taken by the divers near the samplers. The sediments were immediately scooped out from the uppermost 10 cm of the cores, placed in an amber glass jar, and stirred to homogenize. At the laboratory, wet sediments were placed in 250 mL glass round-bottom flasks with pieces of PE loaded with PRCs (>70 g dw sediment, 20 mg PE), and deionized water (≈100 mL) was added to minimize headspace. The sediment slurry was tumbled end over end for 2 mo at room temperature. PE pieces were removed from the sediment, rinsed quickly with deionized water, and wiped with a lint-free tissue. The PE was then added to amber vials, spiked with surrogate standards, and dichloromethane was introduced. The PE extracts were processed following the same procedure as for *in situ* PE described above. The absence of PRCs in the PE after 2 mo supported that the PE had reached equilibrium with the sediment and demonstrated the large sorptive capacity of the sediment in each test as compared to the PE.

Sediment Samples

Subsamples of sediment from the cores were dried at 55°C. The dried sediments were ground with a mortar and pestle. Approximately 4 g of dried sediment were spiked with the surrogate standard and extracted with an Accelerated Solvent Extractor (ASE 200) using 90:10 dichloromethane:methanol. The ASE was operated with 5 cycles at 100°C and 1,000 psi. This method was verified using the NIST standard reference material 1941a. ASE extracts were concentrated under a stream of ultra-high purity N_2 and quantitatively transferred to chromatography columns containing 5 g of fully-activated silica (100-200 mesh) and activated copper. The extract was eluted with 100 mL of 90:10 (v/v) hexane:dichloromethane, concentrated under a N_2 stream, and quantitatively transferred to a 2 mL autosampler vial. The extracts were then spiked with the internal standard.

Organic/Black Carbon Measurements

Organic carbon (OC) and black carbon (BC) samples were measured on an Elementar Vario El III (Mt. Laurel, NJ) operated at an oven temperature of 950°C. Samples of 10-20 mg of dried, ground sediment were weighed out in silver capsules. Samples for black carbon measurement were combusted at 375°for 24 h. All samples were acidified with 300 μL of 50% sulfurous acid and dried before carbon analysis (Gustafsson and Gschwend, 1997).

Total organic carbon contents were 2.07-2.89% (w/w). Black carbon content measurements were 0.15-0.23% (w/w), which is equal to 7-9% of the organic carbon content. Averages and standard deviations can be found in Table S2.

Instrumental Analysis

Extracts were analyzed on a Hewlett-Packard 6890 gas chromatograph and JEOL GCmate mass spectrometer (GC/MS). Samples were injected using splitless injection on an Agilent 60 m DB-5MS column. During each series of GC/MS runs, a four-point calibration curve was used and standards, run throughout the day, made up approximately half of the samples run each day. Additionally, at least two procedural blanks were run each day. Both procedural blanks (reflecting laboratory processing contamination) and field blanks (reflecting transport and sampler handling contamination) had non-detectable levels of PCBs.

Surrogate standards were isotopically-labeled PCBs with 3-8 chlorines, and the recoveries for 30 PE samples were 65±7%, 82±5%, 96±6%, 97±6%, 98±5%, and 96±6% for the tri- through octa-chlorobiphenyl surrogate standards, respectively (sediment recoveries are in Table S3). Measurements of PCB congeners were corrected using the surrogates of the same or closest chlorination level. Additionally, the surrogate standards can be used to quantify the expected variation from analytical measurements and sample processing in the laboratory. The method precision, expressed as relative standard deviation of the surrogate results, for the 30 samples ranged from ±5% (heptachlorobiphenyl) to ±11% (trichlorobiphenyl).

Data Analysis

To adjust the measured concentrations of native PCB congeners to their equilibrium concentrations, the extent to equilibrium was modeled for all the PCB congeners using the measured losses of the PRCs (Gschwend et al., 2014). It should be noted that the initial PRC concentrations were measured for each PE sampler and used to calculate PRC losses for that sampler using $(C_0 - C_t)/C_0$ where C_0 is the initial PRC concentration and C_t is the PRC concentration in the PE after retrieval. Therefore, the calculations of PRC losses were independent between duplicates. As expected, smaller PRCs (e.g., congeners 28, 54, and 47) were found to be lost to much greater extents (average 51%, 69%, and 34%, respectively) than larger PRCs (e.g., 97, 111, 153, and 178 averaged losses of 26%, 15%, 13%, and 5%, respectively). Only PRC data with losses greater than 10% were employed in the mass transfer modeling using the 1-D diffusion model of a chemical in an unmixed sediment bed being absorbed into a finite sheet of polymer (Apell and Gschwend, 2014; Fernandez et al., 2009a). The measured PRC losses and modeled fractions equilibrium (f_{eq}) can be found in SI Tables S4-S8 and S21-S26.

For each site, 35 congeners or co-eluting congener groups were quantified. These congeners represented approximately 85% of the PCB mass measured in the sediments. A list of the congeners can be found in the SI with the dominant congener listed first (based on Aroclor composition information (Schulz et al., 1989) and co-eluting congeners expected to be minor listed in parenthesis. For data analysis, the chemical properties (e.g., K_{PEW}) of the dominant congeners were used (Table S9).

RESULTS AND DISCUSSION

Reproducibility of Passive Sampler Measurements

To the authors' knowledge, there are currently no estimates of measurement precision for *in situ* sediment polyethylene passive samplers available in the literature. Although this work only deployed two PE samplers at each station, 15 sets of duplicate samples (derived from analyzing three depths for each pair of samplers) can be pooled to provide a measure of sampler precision using equation 1 (Hyslop and White, 2009; Taylor, 1987):

$$RSD\ (\sigma, \%) = \sqrt{\frac{1}{2n}\sum_{i=1}^{n}\left[\left(\frac{C_{iA} - C_{iB}}{\bar{C}_i}\right)^2\right]} \times 100\% \qquad (1)$$

This calculation includes the variability that is introduced during sampler preparation, deployment, analysis, and data processing using surrogate recoveries and equilibrium corrections. In equation 1, C_{iA} and C_{iB} are the concentrations (ng/g_{PE}) in the duplicate samplers (A and B) for a given congener *i* and *n* is the number of duplicate sampler pairs (*n*=15 pairs for five sites and three depths analyzed). The concentration difference between the duplicates C_{iA} and C_{iB} are normalized by their average, $\bar{C_i}$, to translate each value into a percentage. By doing this, all 15 duplicate pairs can be used to calculate a relative standard deviation (RSD) despite the samplers having concentrations that vary by an order of magnitude (Figure 1).

The RSD (σ) was calculated for each of the 35 congeners or co-eluting congener groups and for Σ_{35}PCBs (as ng/L_W) after the concentrations were equilibrium corrected. For the individual congeners, the RSD precision ranged from 22% to 43% with a median value of 27% and the highest values (i.e., poorest precision) associated with the octachlorobiphenyls (Table S10). Alternatively, the RSD can be calculated for Σ_{35}PCBs (as ng/L_W), which resulted in a RSD of 27% as well. The precision can also be demonstrated by comparing all of the duplicate pairs for all congeners (Figure 1A, n=522 pairs). Only 9% of duplicate pairs (n=47/522) show differences of greater than a factor of two. Most of these deviating pairs (n=36/47) are from the deeper samples at site 5 (purple diamonds in Figure 1B off the 1:1 line) which might simply be due to real differences in PCB concentrations at those neighboring samplers.

To put the calculated RSD values into context, we can compare them to the quality control criteria from EPA Method 1668C (measurement of PCBs by GC/MS), which sets a maximum acceptable RSD precision of 25%. Although our values of 27% are slightly higher, this represents the complete sampler precision (from preparation through GC/MS analysis and data corrections using standards) whereas the 25% outlined in the EPA method is for the analytical method precision only. Therefore, a sampler precision of 27% should be acceptable for remedial investigation work.

Furthermore, it should be highlighted that the sampler precision of 27% includes variability due to real-world spatial heterogeneity of contamination. An example of this is the observed differences between the duplicate samples at site 5 (10-20 cm and 20-30 cm) in this study (Figure 1B). At this site, the deeper duplicate samplers had similar PRC losses but accumulated substantially different amounts of native PCBs (Tables S8 and S25-S26). The PRC losses indicated that the transport kinetics to/from the duplicate samplers were similar; consequently, the most likely explanation for the observed sampler concentrations is differing PCB concentrations in the porewater. This is also supported by the fact that these samplers were deployed on the edge of a previously identified "hotspot" known as Terminal 117.

Comparing *In Situ* and *Ex Situ* Porewater Concentrations

There is currently limited work that compares the results from *in situ* passive samplers with other measures of porewater concentrations (Fernandez et al., 2014; Fernandez et al., 2009b). While it would be ideal to compare *in situ* passive samplers with direct measurements of *in situ* porewater, it is not practical to withdraw a representative *in situ* porewater sample in the field that is large enough to have detectable levels PCBs (or many other HOCs) while excluding dissolved/colloidal organic matter from the sample. Therefore, we chose the *ex situ* PE measurement of porewater concentrations for comparison (Apell and Gschwend, 2014; Fernandez et al., 2009a; Fernandez et al., 2009b).

For the five sites in this study, the porewater concentrations based on the *in situ* passive samplers were consistently less than the *ex situ* porewater concentrations for the top 0-10 cm of sediment (squares in Figure 2). Depending on the site, *in situ* Σ_{35}PCB concentrations equaled 28-77% of the *ex situ* concentrations (average 63±15%, n=10). Site 4 had the greatest disparity (28 and 46% for the duplicates, Figure 3 and Table S11). When the 95% confidence intervals are calculated using the RSD of 27% for the *in situ* samplers, some of the *in situ* and *ex situ* concentrations are statistically indistinguishable (Figure 3, both duplicates for sites 2 and 5, one of the duplicates for sites 1 and 3, and none for site 4). However, since all the *in situ* concentrations were lower and some *in situ*/*ex situ* comparisons were outside the 95% confidence interval calculated, this suggests that the observed differences are not due to measurement imprecision but instead that the *in situ* samplers are actually measuring lower porewater concentrations.

These results are in line with the limited previous work that compared *in situ* passive samplers with *ex situ* measurements of porewater. In Boston Harbor, use of an *in situ* PE passive sampler led to estimated polycyclic aromatic hydrocarbon (PAH) concentrations that were 5.8 ± 3.4 times lower (n=6) than were measured in the *ex situ* porewater concentrations (Fernandez et al., 2009b). At the Palos Verdes shelf, the concentrations of p,p′-DDE were close at one site (170 vs. 160 ng/L for *ex situ* and *in situ* samplers), but the *in situ* concentration was only 61% of the *ex situ* at the second site (84 vs. 51 ng/L for *ex situ* and *in situ* samplers) (Fernandez et al., 2014). It is also worth noting that no evidence of water flow through the sediments was found at the Palos Verdes shelf; therefore, sorptive equilibrium between the sediments and porewater would be expected (Palermo et al., 1999).

A possible explanation for the observed differences is that a bias is introduced by the use of the *in situ* passive sampling methodology. However, previous research that used passive samplers in the laboratory (with the use of PRCs to correct for equilibrium) did not find this discrepancy between passive and active (equilibrium) *ex situ* sampling, which indicates that the passive sampling methodology (e.g., the use of PRCs) is not responsible for the differences observed here (Apell and Gschwend, 2014; Fernandez et al., 2009a). Additionally, the discrepancies between *in situ* and *ex situ* concentrations cannot be from temperature and salinity differences. While *in situ* samplers were exposed at lower temperatures (~10°C) and higher salinity than *ex situ* samplers, both of these environmental differences would cause higher values of K_{PEW} (approximately 0.2 log difference assuming an enthalpy of -10 kJ/mol and a Setschenow constant of 0.35) and consequently even lower estimates of *in situ* porewater concentrations (Lohmann, 2012).

Since *in situ* concentrations were consistently lower than the *ex situ* concentrations, it is possible that the PCB concentrations in the porewaters are under-saturated with respect to the corresponding sediment. This hypothesis is supported by previous research that has found porewaters to be under-saturated in silicate with respect to silica dissolution and to exhibit ^{222}Rn levels that were not in secular equilibrium with its parent, ^{226}Ra. These observations are thought to be caused by natural processes such as tidal pumping or bioirrigation (Benoit et al., 1991; Emerson et al., 1984; Kristensen and Hansen, 1999; Martin and Sayles, 1987). Moreover, laboratory observations and modeling efforts indicate that upper horizons of sediments experiencing bioirrigation or tidal pumping can lower porewater concentrations and cause a sorptive disequilibrium between the porewater and the surrounding sediment (Berg et al., 2001; Deane et al., 1999; Lampert et al., 2013; Lick, 2006; Lohse et al., 1996; Work et al., 2002).

Previous work in the Lower Duwamish Waterway has found ample evidence of bioturbation using sediment profile imaging, which counted an average of 13 voids, small tubes, or burrows in the camera's viewing area (≈15 cm × 20 cm) that reached the maximum viewing depth of the camera (≈16 cm) (Washington State Department of Ecology, 2007). Two surveys of the benthic communities in the LDW also found tens of thousands of polychaetes, oligochaetes, and nematodes per m^2 (Tables S30-S31) (Cordell et al., 1996; Cordell et al., 2008). Additionally, the Lower Duwamish Waterway, which undergoes up to 4.3 m of water height change during the tidal cycle, likely experiences tidal pumping in at least some parts of the sediment bed. Thus, it is plausible that one or both of these processes are serving to flush porewater from the upper sediment layers of the Lower Duwamish Waterway causing a sorptive disequilibrium between the sediments and porewater.

Therefore, it is reasonable to surmise that the lower *in situ* Σ_{35}PCB concentrations that were measured reflect an actual difference in dissolved porewater concentrations between the field (*in situ*) and the laboratory (*ex situ*) at our study site. In order to identify the presence of porewater flushing and the potential cause(s) of porewater disequilibrium, future efforts should capture simultaneous measures of HOCs and geochemical tracers like ^{222}Rn and ^{234}Th. This is especially important when using passive sampling to determine bed-water fluxes as the presence of porewater flushing would enhance the chemical transport of HOCs from the near-surface sediments (Thibodeaux and Bierman, 2003).

Comparing Estimates from EqP Theory with *In Situ* and *Ex Situ* PE Samplers

Traditionally, and as part of the LDW remedial investigation, porewater concentrations were estimated using the sediment concentration (C_{sed}) , the organic carbon content of the sediment (f_{OC}), and equilibrium partitioning theory. However, previous research has shown that calculating the sediment-water partition coefficient (K_d, equation 2) with EqP theory often results in an overestimation of the porewater concentrations ($C_{porewater}$) (Apell and Gschwend, 2014; Fernandez et al., 2009a; Fernandez et al., 2009b). Similar results were also found in this work (triangles in Figure 2). Using organic carbon-water partition coefficients (K_{OC}) from the literature (Hansen et al., 1999) yielded overestimates of PCB porewater concentrations with Σ_{35}PCB equaling 380% to 530% of the *ex situ* porewater concentration (Table S11).

$$C_{porewater} = {C_{sed}}/{K_d} = {C_{sed}}/{f_{OC}K_{OC}} \quad (2)$$

For all of the sites, the porewater concentrations measured *ex situ* were closer to the concentrations measured with *in situ* passive sampling (*ex situ* Σ_{35}PCB = 1.3-3.5 × *in situ* Σ_{35}PCB) than the porewater concentrations estimated using EqP theory (Eq 2 Σ_{35}PCB = 3.8-5.3 *ex situ* Σ_{35}PCB). Furthermore, if the *in situ* porewater concentrations are actually undersaturated with respect to the sediments, then the premise of equilibrium partitioning theory is not valid since the system is actually in disequilibrium.

Implications and Use of *In Situ* Passive Samplers

Although the *in situ* passive PE samplers and *ex situ* active PE samplers generally agreed within a factor of two, the *in situ* measurements of Σ_{35}PCB were consistently lower than *ex situ* measurements. In some cases, *ex situ* (equilibrated) porewater concentration data could be preferred since the equilibrium concentrations are the highest possible porewater concentrations if the sediment is a source of contamination. Therefore, it would be a complementary, and likely conservative, value to use when assessing the potential risk of contaminated sediments. However, *ex situ* measurements may not accurately represent the concentrations that are freely-dissolved in the porewater in the field. This discrepancy would, in turn, affect some applications such as estimating bed-to-water fluxes or the dose of HOCs experienced by benthic organisms (Fernandez and Gschwend, 2015; Fernandez et al., 2014; Janssen et al., 2011; Lick, 2006; Liu et al., 2013b). If *ex situ* porewater concentrations were used instead, then estimated bed-to-water fluxes based on porewater-bottom water gradients and estimated bioaccumulation by benthic organisms based on lipid-water partitioning would be expected to be overestimated.

Furthermore, *in situ* passive samplers can provide other insights into sediment bed contamination. The passive samplers can be sectioned at different depth intervals to determine HOC concentration profiles (Figure S5), which can inform remediation decisions. Similarly, *in situ* passive samplers can be used to evaluate the performance of remedial designs (e.g., sand caps and sorbent amendments) after installation while minimally disturbing the sediment bed and cap (Lampert et al., 2013; Lampert et al., 2011; Oen et al., 2011; Thomas et al., 2014; Tomaszewski and Luthy, 2008).

Most importantly, this study, along with the other studies reported in the literature, has shown that *in situ* passive sampling in sediment beds can provide precise and more accurate estimates of porewater concentrations compared to traditional approaches using sediment concentrations. The *in situ* passive samplers allowed for measures of individual HOCs (e.g., 35 PCB congeners/co-eluting congeners) that spanned a large range of physicochemical properties and were present at only pg/L levels. Hence, the passive sampler-measured porewater concentrations may provide better insight into the fate and effects of HOCs that continue to influence the ecological quality of waterbodies all over the world. Given that the remediation and ongoing monitoring of Superfund sites is associated with large costs, which are USD$40 million for the site investigation and an estimated USD$342 million for the remediation of the Lower Duwamish Waterway, the best available methods should be used to identify the areas where remediation would result in the greatest environmental improvement (United States Environmental Protection Agency, 2014). Therefore, investigators should be encouraged to use *in situ* passive sampling methods to determine better measures of fluxes, bioaccumulation potential, contamination distribution, and remediation effectiveness.

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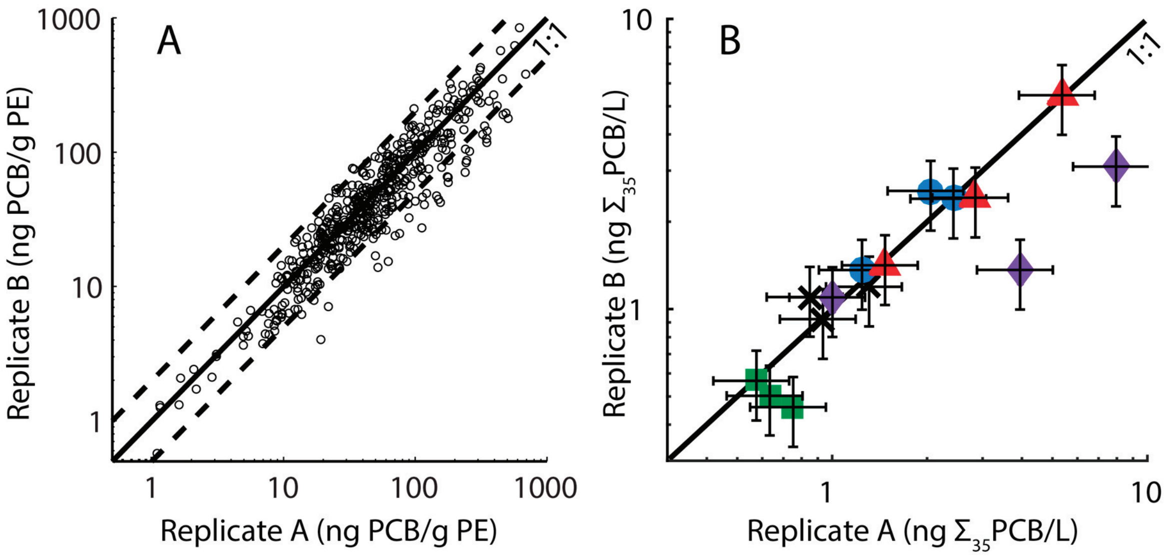

Figure 1. Comparison of porewater concentrations of individual PCB congeners estimated using replicate *in situ* passive PE samplers. In Figure 1A, each circle represents a congener pair from the duplicate samplers after equilibrium correction using PRC data (n=522) with the dashed lines representing a factor of 2 difference. In Figure 1B, symbols represent the sum of 35 PCB congeners or co-eluting groups for site 1 (black x), site 2 (blue circle), site 3 (red triangle), site 4 (green square), and site 5 (purple diamond) (n=15). Error bars represent ±1σ of calculated sampler precision. The solid black line is the 1:1 line.

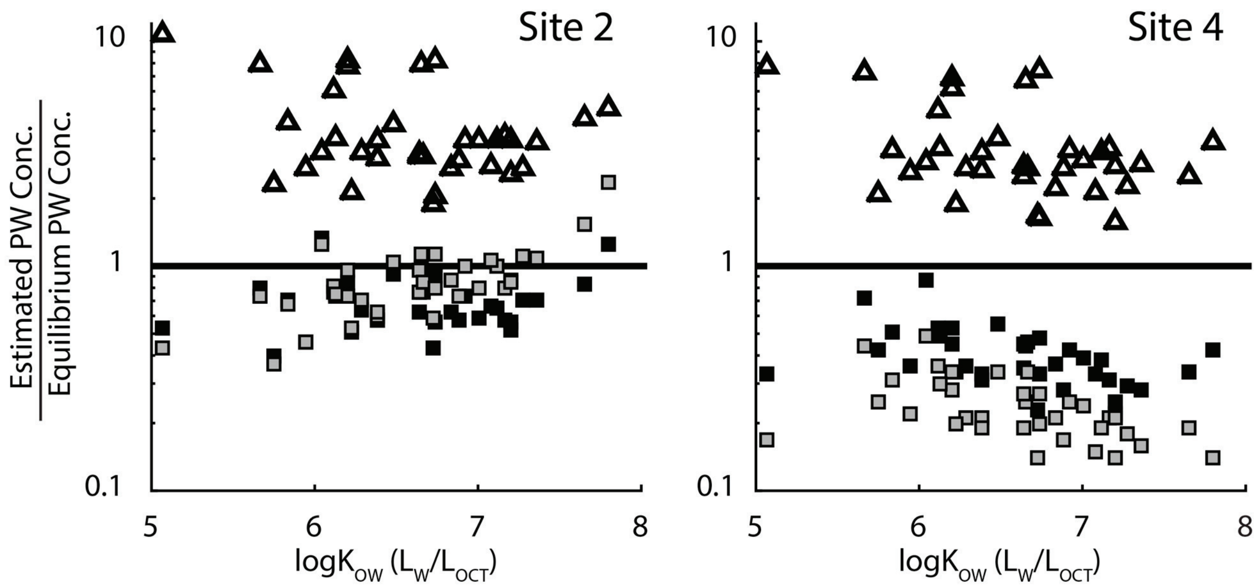

Figure 2. Comparison of porewater concentrations for PCB congeners, plotted as a function of their log K_{OW} values, measured with *in situ* passive sampling (■, grey and black squares each represent data from one of the duplicate samplers) and estimated using sediment concentrations normalized by equilibrium sorption coefficients given by $f_{OC}K_{OC}$ (Δ, equation 2). Sites 2 and 4 are representative of the range of results from the five sites.

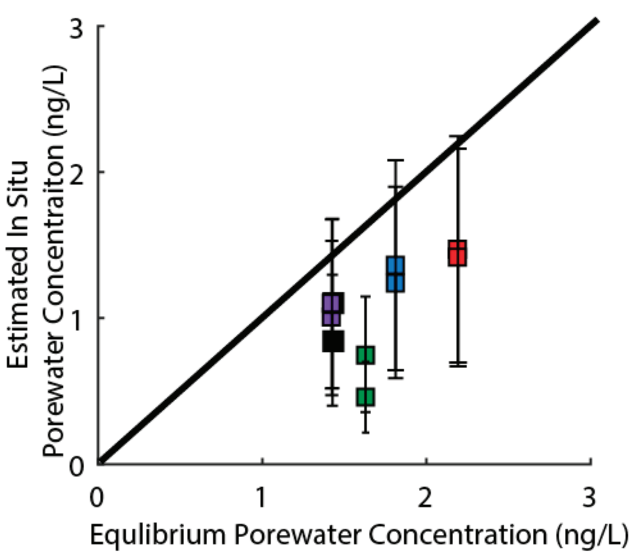

Figure 3. The Σ_{35}PCB concentrations measured using *ex situ* PE samplers that were equilibrated with sediment cores from the 0-10 cm depth interval compared with the Σ_{35}PCB concentrations measured using *in situ* PE passive samplers for the 0-10 cm depth interval at sites 1 (black), 2 (blue), 3 (red), 4 (green), and 5 (purple). The solid black line represents the 1:1 line and error bars represent the 95% confidence interval based on the calculated *in situ* sampler precision (RSD=27%).

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Abstract Graphic