Evaluation of passive sampling polymers and non-equilibrium adjustment methods in a multi-year surveillance of sediment porewater PCBs

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ABSTRACT

Polymeric passive sampling devices are increasingly used to measure low-level, freely dissolved concentrations of hydrophobic organic contaminants in environmental waters. A range of polymers have been used for this purpose, and several different methods of accounting for nonequilibrium using performance reference compounds (PRCs) have been proposed. This study explores the practical impacts of these decisions in an applied context using results from a multi-year passive sampling surveillance of polychlorinated biphenyl (PCB) concentrations in sediment porewater at a contaminated marsh amended with activated carbon sorbent materials. In a series of five sampling events spanning almost two years, we deployed polyoxymethylene (POM) and polyethylene (PE) samplers and calculated porewater concentrations with five different PRC adjustment methods. The results provide a basis for evaluating amendment performance by showing reductions of 34–97% in amended sediment porewater concentrations. They also provide a quantitative underpinning for discussions of the differences between sampling polymers, selection of PRCs, generation of high-resolution vertical profiles of porewater concentrations, and a comparison of PRC adjustment methods. For unamended sediment, older methods based on first-order kinetics agreed well with a recently-developed method based on diffusion into and out of sediment beds. However, the sediment diffusion method did not work well for the sediments amended with activated carbon.

INTRODUCTION

Hydrophobic polymers are in wide use as passive sampling devices for organic pollutants like polychlorinated biphenyls (PCBs) in sediment porewaters. Their measurements of freely dissolved contaminant concentrations provide a useful metric of bioavailability to benthic organisms (Ghosh and others 2014). The advantage provided by passive samplers lies in their ability to sample target chemicals, which typically exist in extremely low aqueous concentrations, to analytically detectable levels, and to do so in a time-integrative fashion. During sampler deployment, contaminants diffuse into the polymer toward a thermodynamic equilibrium with the external water phase. This can be modeled as a diffusion process whose rate is controlled by the sampler's geometry, the concentration gradient between sampler and water, and an overall mass transfer coefficient representing the resistances to transfer in the sampling polymer and the external, aqueous boundary layer (Fernandez and others 2009). The relative importance of each source of mass transfer resistance can be described in terms of the target compound's octanol-water partitioning coefficient. When passive samplers are deployed in static sediments, mass transfer is limited by the sediment side (i.e., the aqueous boundary layer) for most hydrophobic compounds (Booij and others 2003). In practice, this means that samplers in stagnant sediments may be kinetically inhibited from reaching equilibrium with highly hydrophobic contaminants during a typical deployment time of months. To account for this nonequilibrium, performance reference compounds (PRCs) can be loaded into samplers prior to deployment.

PRCs are compounds with chemical characteristics similar to those of the target contaminants but not present in the field at detectable levels. Loss of PRCs from samplers is used to characterize sampler equilibration during the period of deployment, and to adjust measured contaminant concentrations accordingly (Huckins and others 2002).

Ideally, the kinetics of PRC desorption should be identical to those of target compound absorption. In practice, such isotropic kinetics may be realized by the use of stable isotope-labelled versions of each of the target compounds as PRCs. However, when this strategy is not viable (as in the present study, in which a suite of dozens of PCB congeners was measured and the use of an isotope-labelled version of each would have been cost prohibitive), desorption data from a small selection of PRCs must be extrapolated to estimate the equilibration state of all target compounds (Huckins and others 2006). Currently, there exists no standardized method of carrying out such extrapolations, with numerous variants having been reported in the literature. In the past, most of these relied on correlations (either linear or nonlinear) between measured sampler uptake rate (k_e) and a physicochemical property of the PRCs like molar volume (V_m), molecular weight (MW), octanol-water partitioning (K_{ow}) (Burgess and others 2015) or sampler-water partitioning (K_{pw}) (Rusina and others 2010). The latter two are to some extent interchangeable because K_{pw} values for most congeners are derived from literature-reported correlations with K_{ow} (Ghosh and others 2014). All of these methods are based on a first-order kinetics model of uptake in a polymer. Most investigators have found this approximation suitable for conditions in which contaminant mass transfer is controlled primarily by the aqueous boundary layer. This includes low-flow or stagnant sediments, thin sampling polymers (< 100 μm), and highly hydrophobic target compounds (log K_{ow} > 4.5; (Booij and others 2003; Lampert and others 2015). Recently, more general PRC adjustment methods have been proposed. These are based on modeling of Fickian diffusion by contaminants into and out of sediment beds and they take into account not only compound- but site-specific properties (Fernandez and others 2009; Tcaciuc and others 2015).

In the present work, passive sampling data were generated as part of a multi-year monitoring effort for a pilot-scale sediment remediation project, which is described in greater detail elsewhere (Sanders and others 2018). The goals of the passive sampling effort were as follows: (1) compare different sampling polymers in a remediated marsh setting; (2) compare different PRC adjustment methods; (3) evaluate PRC adjustment methods in the context of altered sediment K_d. Two widely-used sampling polymers were employed and their measurements are compared, including contrasting congener accumulation profiles and PRC desorption rates. Finally, a comparison is made of several of the most commonly used methods for adjusting measured porewater concentrations for nonequilibrium.

MATERIALS AND METHODS

Study Site. All measurements were performed at the Berry's Creek Study Area (BCSA) in Bergen County, NJ. The area chosen is a tidal marsh overrun by *Phragmites australis* reeds and impacted by legacy contamination with mercury and PCBs. The marsh study area was divided into four plots, designated A–D. Plot A was amended with SediMite™, a pelletized agglomerate of 50% powdered activated carbon (Siemens regenerated AC, < 30 mesh), sand, and clay (www.sedimite.com); Plot B served as an unamended control; Plot C was amended with coconut-shell based granular activated carbon (GAC; OLC WW 20 x 50 mesh from Calgon Corp.) topped by a 2–3 cm layer of sand; and Plot D was amended with GAC only. Passive sampling was performed at five different time points, which for simplicity will be referred to by the number of months before or after amendment application: t_{-1}, t_{+2}, t_{+11}, t_{+15}, and t_{+21}.

Passive Sampling. Sampling polymers used in this study include polyethylene (PE; Husky, Bolton, Ontario) in 17.7 and 25 µm thicknesses, hereafter denoted PE-18 and PE-25, and polyoxymethylene (POM; CS Hyde, Lake Villa, IL) in 38 and 76 µm thicknesses, hereafter denoted POM-38 and POM-76. Prior to use, polymer sheets were cut into strips and cleaned by soaking in a 1:1 mixture of hexane and acetone for approximately 12 h. Strips were impregnated with performance reference compounds (PRCs) in a 4:1 mixture of methanol and deionized water for at least 24 h (Booij and others 2002). Spike levels were chosen to ensure analytically detectable masses in each congener after 28 d in sediment. Initially, five PRCs were to be employed: PCB BZ #s 29, 69, 103, 155, and 192, representing the tri- through hepta-substituted homolog groups. However, in early chromatographic tests, PCB BZ #103 was found to coelute with another compound present in BCSA sediment and was excluded from subsequent work. After impregnation, strips were removed from solution and blotted gently. For the t_{-1}, t_{+2}, t_{+11}, and t_{+15} deployments, one strip from each impregnation solution was removed and analyzed, with the results used as a proxy measure of initial PRC concentrations in all other strips from that solution. For t_{+21}, a 4-cm portion of each PE sheet to be deployed was cut off, placed in 25 mL 1:1 hexane:acetone, and refrigerated for subsequent extraction and direct measurement of initial PRC concentrations.

POM samplers were assembled by enfolding the strips with stainless steel mesh and placed in a frame assembled by fastening two 8” galvanized steel corner brackets (Home Depot model #16077) with 3/8” screws and nuts. For t_{-1}, t_{+2}, t_{+11}, and t_{+15}, two 2.5 cm strips of POM-76 were fixed horizontally across the 14.5 cm width of the frame’s open area and arranged to sample the 0–2.5 cm and 5–7.5 cm depth intervals discretely (Figure 1). PE samplers for t_{+21} were assembled in a similar fashion with two corner brackets, but with an additional 10” zinc mending plate (Home Depot model #15390) to create an inner open area 18 cm wide x 14.5 cm high. One contiguous sheet of PE-25 was fixed across this entire area (Figure 1). For t_{+15}, one strip each of PE-18 and POM-76 were arranged side by side across the 14.5 cm open width and spanning the 0–2.5 cm depth interval. After assembly, all samplers were wrapped in aluminum foil and kept refrigerated or on ice prior to deployment. One field blank sampler was transported in the same fashion as the deployed devices, briefly exposed to the air at the site, and returned to the lab for analysis. Each sampler was placed in one of nine subsections of a plot, and sampler locations were varied between events. Each device was deployed by cutting a slot into the root mat with a hacksaw, placing the sampler into the slot, and gently tapping it down until the polymer strips were aligned with the intended sampling depth (Figure 1). Sampler locations were changed for each sampling event. After 28 d of exposure, samplers were removed from sediment and disassembled. All strips were gently rinsed with deionized water, blotted dry with paper towels, placed in individual borosilicate vials, and kept cold until processing. Contiguous PE sheets used at t_{+21} were sectioned into five 1-cm strips corresponding to the uppermost 5 cm of sediment, and one 5-cm strip corresponding to the 5–10 cm depth interval.

Chemicals. PCB solutions were prepared using individual congener and Aroclor standards in hexane purchased from Ultra Scientific (Kingstown, RI). All other chemicals and solvents were purchased from Fisher Scientific (Pittsburgh, PA). Hexane and acetone were pesticide grade (CAS Nos. 110-54-3 and 67-64-1). Anhydrous sodium sulfate was ACS grade (CAS No. 7757-82-6). Silica gel was 644 or 923 grade (CAS No. 112926-00-8 or 63231-67-4). Copper powder was lab grade (CAS No. 7440-50-8).

Analytical Methods. Passive sampling polymers were extracted three times overnight in 1:1 hexane:acetone with 60 rpm orbital shaking. The pooled extracts were reduced to 2 mL with a gentle nitrogen stream in a water bath at 35–40 °C, treated with activated copper, and cleaned up using a miniaturized version of the silica gel procedure described in U.S. EPA SW-846 method 3630C, performed in 5.75" Pasteur pipets. All samples were analyzed by gas chromatography with electron capture detection using an adaptation of U.S. EPA SW-846 method 8082A (Beckingham and Ghosh 2011). PCB BZ #30 and 204 were used as internal standards. Surrogate standards (PCB BZ #14 and 65) were added prior to all sample extractions to assess loss during processing. The analytical method measured 87 target congeners/congener groups that were summed based on homolog groups or total PCBs (hereafter denoted ΣC).

Quality Assurance/Quality Control. Average surrogate recoveries in passive sampler extracts were 92 ± 9.7% for PCB BZ#14 and 88 ± 9.2% for PCB BZ#65 (n = 167). PCB samples with less than 60% recovery of each surrogate compound are not reported. No values were adjusted to account for surrogate recoveries.

Calculation of PCB Porewater Concentrations. Unadjusted porewater concentrations (C_{pw}) were calculated according to the equilibrium partitioning equation:

$$C_{pw} = \frac{C_{ps}}{K_{pw}} \qquad (1)$$

where C_{ps} is the measured concentration in the passive sampling material (g kg^{-1} polymer) and K_{pw} is the polymer-water partitioning coefficient specific to each congener/polymer combination (L kg^{-1}). K_{pw} values for POM were derived using an empirical relationship with octanol-water partitioning coefficients (K_{ow}; (Hawthorne and others 2009):

$$\log K_{pw} = 0.791 \times \log K_{ow} + 1.018 \qquad (2)$$

PCB K_{ow} values were taken from (Hawker and Connell 1988). Arithmetic average values were used for groups of two or more coeluting congeners. K_{pw} values for PE were derived with the following empirical relationship (Smedes and others 2009):

$$\log K_{pw} = 1.18 \times \log K_{ow} - 1.26 \tag{3}$$

K_{pw} for PE has been found to be independent of polymer thickness, so one set of values was used for both PE-18 and PE-25 (Lohmann 2012).

PRC depletion data were used to adjust porewater concentrations for nonequilibrium using four different methods (summarized in Table 1). The first three are based on the sampling rate approach where the overall exchange rate of PCBs between sediment porewater and sampling polymers was approximated as a first-order kinetic process. An exchange rate coefficient ($k_{e,PRC}$, d^{-1}) was computed for each PRC in each sampler strip (i.e., each PRC at each depth interval in each sampler location) with the following equation:

$$k_{e,PRC} = \ln\left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)}\right)\left(\frac{1}{t}\right) \tag{4}$$

where $C_{ps,PRC}(0)$ is the measured concentration of PRC in the sampler prior to deployment and $C_{ps,PRC}(t)$ is the measured concentration following deployment (Tomaszewski and Luthy 2008). In this work, t = 28 d for all experiments. The first adjustment method consisted of establishing log-linear correlations between measured $k_{e,PRC}$ and K_{pw}, and extrapolating k_e for target PCBs (Booij and others 1998). In the second method, log k_e values were extrapolated from linear correlations with molar volume (V_m, cm^3 mol^{-1}). V_m was taken from published values or homolog group averages for unreported congeners (Choi and others 2013). With k_e values for each congener or congener group, adjusted porewater concentrations (C_{pw}') can be computed:

$$C_{pw}' = \frac{C_{ps}}{K_{ps}(1-e^{-k_e t})} \quad (5)$$

The third method was the molar volume adjustment (MVA) procedure, which is based on an empirically derived, nonlinear relationship between apparent sampling rate (R_s, L d^{-1}) and V_m (Huckins and others 2006). $R_{s,PRC}$ for each PRC was calculated as follows (Tomaszewski and Luthy 2008):

$$R_{s,PRC} = k_{e,PRC} K_{ps} M_{ps} \quad (6)$$

where M_{ps} is the mass of the sampling material. This sampling rate was adjusted for the V_m of target PCBs with the following relationship (Huckins and others 2006):

$$R_s = R_{s,PRC} \left(\frac{V_{m,PRC}}{V_m}\right)^{0.39} \quad (7)$$

With R_s and k_e, C_{pw}' for target PCBs can be calculated as above. For all methods mentioned thus far, PCB BZ #29 was used to adjust mono- through tri-CBs, BZ # 69 was used for tetra- and penta-CBs, BZ # 155 was used for hexa-CBs, and BZ # 192 was used for hepta- and higher CBs.

The final adjustment method applied was a diffusion-based model (Fernandez and others 2009). Calculations were carried out using the associated PRC Correction Calculator software (Tcaciuc 2014). The software's compound database was updated to include coeluting PCB congener groups with averaged literature values for K_{ow} and diffusivity in PE (Hawker and Connell 1988; Rusina and others 2010). A porosity value of 0.72, representing an average of volumetrically measured sediment samples, was used in the calculations.

RESULTS AND DISCUSSION

PCB Concentrations in Sediment Porewater. At t_{-1}, unadjusted concentrations of freely dissolved total PCBs (ΣC_{pw}) measured with POM were in the range of 1.0–4.0 ng L^{-1} in all plots and in both the 0–2.5 cm (Figure 2) and 5–7.5 cm depth intervals. At t_{+2}, ΣC_{pw} in the upper interval had decreased by 97% in Plot A, 48% in Plot B, 76% in Plot C, and 86% in Plot D ($n = 5$ for Plots A, B, and D, $n = 3$ for Plot C). In all subsequent sampling events up to t_{+15}, upper-interval ΣC_{pw} in amended plots remained low relative to both pre-amendment levels in the same plots and concurrently measured levels in the unamended plot. At t_{+15}, the smallest reduction was observed in the granular AC and sand-treated plot (34%). The largest relative upper-interval reductions were measured in Plot A, where ΣC_{pw} was 91–97% lower than the initial value at all sampling events throughout the study. In the 5–7.5 cm depth interval, significant reductions in ΣC_{pw} were only observed in Plot A, where they were significant at all sampling events ($p < 0.05$). Significant reductions relative to pre-application values ($p < 0.05$) were observed in all three amended plots and at all time points except the 38-μm POM measurement at t_{+15} in Plot C

Observed changes in ΣC_{pw} in the amended plots generally remained consistent throughout the study period. Following amendment application, within-plot variability from one sampling event to another was modest and can be explained by some combination of experimental error, temperature effects (sampling events occurred in summer and fall alternately), and the fact that sampling devices were placed in different locations within plots for each event. This means that any spatial variations in AC levels, microbial dechlorination activity, sediment geochemistry, hydrology, and other variables potentially influencing porewater concentrations were not controlled across sampling events.

When initial PRC concentrations in POM strips were obtained from a separate strip taken from the same impregnation solution, $C_{0,PRC}$ was more variable and, in a few cases, lower than $C_{f,PRC}$ for the two heaviest PRCs. In these cases, PRC adjustments were not possible. The use of a small piece cut off of each sampling strip to represent $C_{0,PRC}$ for that strip led to much more predictable patterns of PRC loss. This highlights a potentially significant degree of variability in the extent of PRC loading among POM strips loaded together in a single solution jar, even with orbital shaking, and may owe to the spatial configuration of the strips and/or attachment within the jar. Because reliable PRC loss measurements were available for some, but not all, sampling events, only unadjusted ΣC_{pw} values were used to compare porewater concentrations among sampling events and compute fractional decreases following AC amendment. While these unadjusted concentrations are likely substantially lower than the true values in an absolute sense, their use for comparison between plots and across sampling events is still instructive. This is because, when PRC data were applied, the relative magnitudes of the resulting adjustments were reasonably consistent between plots, thereby preserving the proportionality of the C_{pw} data (Figure 3). To the extent that sub-equilibrium values might bias such comparisons, it would be toward a slight underestimation of amendment efficacy as described later.

High resolution depth profile of porewater PCBs. Data from contiguous PE samplers collected at t_{+21} enabled generation of 1-cm vertical profiles of freely dissolved PCBs in porewater for Plots A and B (Figure 3). Plots C and D were not sampled for this event. This deployment produced useful PRC data which enabled calculation of adjusted C_{pw} values. In Plot B, ΣC_{pw} values (computed using the k_e-K_{pw} adjustment method) were in the range of 11–16 ng L^{-1} (n = 3) at all depth intervals, and in Plot A ΣC_{pw} values were in the range of 0.52–3.7 ng L^{-1} (n = 3). No trend with depth was apparent in Plot B. In Plot A, ΣC_{pw} values were higher at each successive depth interval below 1 cm, suggesting a profile in loose accord with that of black carbon, measured separately (Sanders and others 2018). However, no statistically significant trend with depth could be determined due to variability in the data. In both plots, passive samplers were more completely equilibrated in the uppermost 2 cm of sediment (Figure 3), potentially due to increased mobility of surficial porewater. At each depth, ΣC_{pw} values were significantly lower in Plot A than Plot B (t-test, $p < 0.05$). Because black carbon concentrations at depths greater than 3 cm did not differ significantly between the plots, reduced PCB concentrations in these intervals invite closer scrutiny. It is possible that during installation, surficial black carbon was inadvertently introduced into the slots cut to accommodate passive sampling devices, leading to artificially reduced concentrations immediately adjacent to the samplers. This may also explain the decreased ΣC_{pw} in the 5–10 cm interval found in prior sampling events. As described above, this was not observed in Plots C and D, perhaps owing to the coarser (and thus both less mobile and less sorptive) granular AC applied in those plots. Thus, care must be taken when placing in situ passive samplers within a layered treatment zone such as reactive caps or in situ amendments.

Nonequilibrium assessment with performance reference compounds. While the adjustment for nonequilibrium for total PCBs was typically less than 50% (Figure 3), the extent of nonequilibrium varied greatly by congener hydrophobicity. In all deployments, PCB 29 and 69 (tri- and tetra-substituted congeners, respectively) were depleted from passive sampling strips to a greater extent than were PCB 155 and 192 (hexa- and hepta-). This is to be expected regardless of whether diffusion was under water- or polymer-side control, because heavier PCBs are less diffusive than lighter ones in either medium (Rusina and others 2010; Schwarzenbach and others 2003). At t_{+21}, PRCs were depleted by 92 ± 8.7% (PCB-29), 84 ± 16% (PCB-69), 29 ± 7.1% (PCB-155), and 30 ± 6.1% (PCB-192) in Plot A ($n = 18$), and 69 ± 6.8%, 58 ± 7.1%, 25 ± 8.4%, and 23 ± 7.0% in Plot B ($n = 18$). This indicates that the samplers were far from equilibrium with respect to more hydrophobic PCBs after their 28-d deployments. By extension, this also implies a larger adjustment of C_{pw} for larger PCBs regardless of the PRC adjustment method employed, and a concomitantly larger degree of uncertainty in C_{pw}'. For example, with the k_e-K_{pw} method, mono-CBs were adjusted upward by 7.4%, while deca-CB was adjusted upward by 2300% as illustrated in Figure 4. However, even after PRC adjustment, hepta- through deca-chlorinated congeners accounted for only 2.1% of ΣC_{pw}'. This can be attributed in part to their much lower water solubilities, and also to the compositions of the original contaminant mixtures; Aroclors up to 1254 comprise less than 3% by weight hepta-substituted or higher congeners (Faroon and Olson 2000). In this sampling, tri-, tetra-, and penta-CBs accounted for 98% of ΣC_{pw}' (Figure 4). Since the objective of amendment was to decrease total PCB concentrations in porewater, the incremental error from PRC adjustments of the heaviest PCB congeners was of negligible importance. However, when the target reductions are for benthic organism tissue concentration, the higher chlorinated homologs gain significance due to the strong partitioning into lipids. In general, selection of PRCs should be made in consideration of the expected congener distribution in the medium to be sampled. However, heavier, less diffusive PRCs can be problematic if they don't dissipate to a quantifiable extent (Söderström and Bergqvist 2004).

Greater PRC loss was observed in AC-amended sediment than in unamended sediment. This is to be expected, since amendment with AC increases sediment-water partitioning coefficient (K_d), resulting in faster kinetics of desorption (Fernandez and others 2009). This may imply that unadjusted C_{pw} values tend to underestimate amendment efficacy because the difference between amended- and unamended-plot concentrations is made larger by PRC adjustment. PRC loss data also pointed to differences in polymer uptake behavior. At t_{+11}, PE-18 equilibrated with lighter PCBs much more quickly than did simultaneously and adjacently deployed POM-76. Because the bulk of PCB contamination in BCSA porewater comprises mono- through tetra-substituted congeners, this contrast in kinetic profiles led to sharp differences in total uptake between the two polymer types: the unadjusted estimate of ΣC_{pw} given by the POM samplers ($n = 5$) was 30% of the PE value ($n = 4$). However, accounting for kinetic differences by applying the k_e-K_{pw} PRC method brought the POM-reported value of ΣC_{pw}' to 83% of the PE value (Figure 5). While ΣC_{pw}' was comparable between the two polymer types, it is likely that the PE value is more accurate, not because of an inherent superiority in the polymer but because the degree of uncertainty in each measurement is related to the degree of polymer-porewater nonequilibrium and the magnitude of the resulting PRC adjustment. Oen and others reported agreement within a factor of two in PRC-adjusted porewater concentrations of PCBs measured by 51-μm PE and 17-μm POM. Notably, their POM-measured values were still lower than the PE-measured values, despite the advantage of thinner POM and thicker PE relative to those used in the present work (Oen and others 2011). Another group observed a similar factor-of-two discrepancy between the two polymers' measurements in ex situ sediments. They proposed the use of a PE/POM correction factor in lieu of PRCs, but noted that POM hadn't fully equilibrated even after 96 d in their experimental systems (Endo and others 2017).

Considering ease of use, equilibration rate, and reproducibility of PRC desorption, PE proved to be the most effective among the sampling materials evaluated in the present study.

Comparison of PRC adjustment methods. The k_e-K_{pw} correlation method was applied to sampling events for which the average coefficient of regression among samplers was 0.7 or greater. In most cases r^2 was greater than 0.85. At t_{+15}, r^2 for POM-38 averaged 0.76 ± 0.30, but only 0.42 ± 0.21 for POM-76. This was due to slower desorption of PRCs from the thicker polymers, resulting in larger relative error in pre- vs. post-deployment measurements. At t_{+21}, a comparison of results using two sets of K_{pw} values revealed a large influence of K_{pw} on both the strength of correlation with k_e and the magnitude of adjustment to C_{pw}. In this deployment, r^2 for k_e vs. K_{pw} averaged 0.68 ± 0.13 using K_{pw} values derived from a published correlation with K_{ow} (Smedes and others 2009). A SETAC Pellston Workshop recommended that these values be used for consistency across laboratories (Ghosh and others 2014). However, as an exercise, we also computed C_{pw}' using K_{pw} either taken directly or, where necessary, interpolated from another set of published values (Choi and others 2013). With these K_{pw} values, r^2 for k_e averaged 0.91 ± 0.08. Further, ΣC_{pw}' in Plots A and B was on average 20% higher using the values from Choi and others than with those from Smedes and others. Nonetheless, the relative effect of the amendment was independent of the choice of K_{pw} values; ΣC_{pw}' in Plot A was 86% lower than in Plot B using either set. In cases where greater certainty in absolute C_{pw} measurements is needed, the accuracy of K_{pw} and K_{ow} values would be more critical. K_{pw} for PRCs is the largest source of error in C_{pw}

measurements. An interlaboratory variability of 0.2–0.5 log units has been found in PCB K_{pw}, potentially leading to errors in C_{pw} up to a factor of three (Booij and others 2016).

Correlation coefficients for the k_e-V_m method were similar to, and in most cases slightly higher than, those for k_e-K_{pw}. ΣC_{pw}' values calculated with this method were also quite similar, including comparable homolog distributions. The molar volume adjustment (MVA) method produced similar ΣC_{pw}' values, with homolog distributions shifted slightly away from lighter PCBs in favor of penta- and hexa-substituted congeners.

The diffusion-based adjustment method was applied to the t_{+21} porewater data. The calculated relationships between K_d and K_{ow} were consistent among samples from Plot B (unamended), with an average correlation coefficient of 0.89 ± 0.09. The average slope was 1.6 ± 0.2 and the average intercept was -4.4 ± 1.1. The resulting fractional equilibration values produced remarkably similar C_{pw}' results to those obtained with the other methods, including both total concentration and homolog distribution (Figure 6). Thus, the first-order, rate-based methods are able to provide a reasonably accurate adjustment for nonequilibrium, comparable to the more rigorous diffusion based method.

By contrast, the diffusion based method did not work well when applied to the sampler data from Plot A (SediMite™). An average log K_d-log K_{ow} correlation coefficient of 0.50 ± 0.31 was obtained, with wildly varying slopes and intercepts among individual samples. The method was therefore not used to calculate C_{pw}' for this plot. The distinction was most likely due to the presence of activated carbon amendment in Plot A. On average, the amendment increased sediment K_d by one to two log units. However, this effect was stronger for the lower molecular weight compounds because mass transfer into AC can be faster compared to the strongly hydrophobic compounds as observed previously (Beckingham and Ghosh 2011). Thus, the altered K_d observed after fresh amendment of AC has a weaker relationship with compound log K_{ow}. This likely confounded PRC calculations across sampler locations and depth intervals in the presence of AC.

CONCLUSIONS

This three-year surveillance program demonstrated a sustained reduction of porewater PCBs in *Phragmites* marsh sediments after amendment with activated carbon. Apart from the challenges with the diffusion method for the AC-amended sediments, ΣC_{pw} values from all PRC adjustment methods agreed closely with one another and preserved trends in unadjusted ΣC_{pw} measurements and homolog distributions across all plots, sampling times, and depth intervals (Figure 6). This is perhaps unsurprising as all are based on intrinsic physical properties of PCB molecules either directly (molecular volume) or indirectly (diffusivity or sorption affinity for a polymer, which themselves depend on characteristics such as molecular volume, flexibility, planarity, and hydrophobicity) (Booij and others 2003; Rusina and others 2010). While the "true" porewater concentrations cannot be established, the extent of agreement among all methods lends confidence in both the absolute values of ΣC_{pw}' and the ratios among plots in the study, enabling comparison of the efficacy of tested amendments. However, the difficulty we experienced in applying the diffusion method to the AC-amended plot highlights the importance of interpreting PRC results carefully to ensure that they make physical and chemical sense. Here, the use of multiple, complementary PRC adjustment methods proved helpful. The use of four PRCs spanning the predominant homolog range present at the site strengthened all of the adjustment calculations and minimized the error associated with extrapolating fractional equilibration. Of the two polymers used, PE provided the most fully equilibrated porewater concentration measurements. While further confirmations are needed in a range of field conditions, especially at less tidally influenced sites, results from the present study suggest that first-order adjustment methods may perform equally well compared to the more elaborate and time-consuming diffusion-based methods. Under conditions where sediments are amended with AC, the first-order method performed better than the diffusion-based method. Recent work also found that a first-order adjustment method is preferred under conditions of significant porewater advection (Apell and others 2018). Given their observed performance and relative simplicity, renewed attention should be given to first-order adjustment methods as an alternative to diffusion-based methods.

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Table 1. Summary of PRC adjustment methods employed.

Abbrevation	Summary	Relevant Equation	Reference
k_e-K_{pw}	linear regression of exchange rate vs. sampler partitioning	$k_{e,PRC} = \ln\left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)}\right)\left(\frac{1}{t}\right)$	(Booij and others 1998; Tomaszewski and Luthy 2008)
k_e-V_m	linear regression of exchange rate vs. molar volume	$k_{e,PRC} = \ln\left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)}\right)\left(\frac{1}{t}\right)$	(Booij and others 1998; Tomaszewski and Luthy 2008)
MVA	adjustment of sampling rate based on empirical molar volume dependence	$R_s = R_{s,PRC}\left(\frac{V_{m,PRC}}{V_m}\right)^{0.39}$	(Huckins and others 2006)
diffusion	fixed-bed diffusive mass transfer model	$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2}$ for $-l < x < l$	(Fernandez and others 2009)

Figure 1. Passive samplers enclosed in metal frames for deployment in marsh sediment. Top left: POM strips arranged to sample two discrete depth intervals; top right: contiguous PE sheet for high resolution measurement of vertical pore water concentration profiles; bottom: passive sampling frame (denoted with arrow) embedded in sediment alongside in situ organism exposure cages.

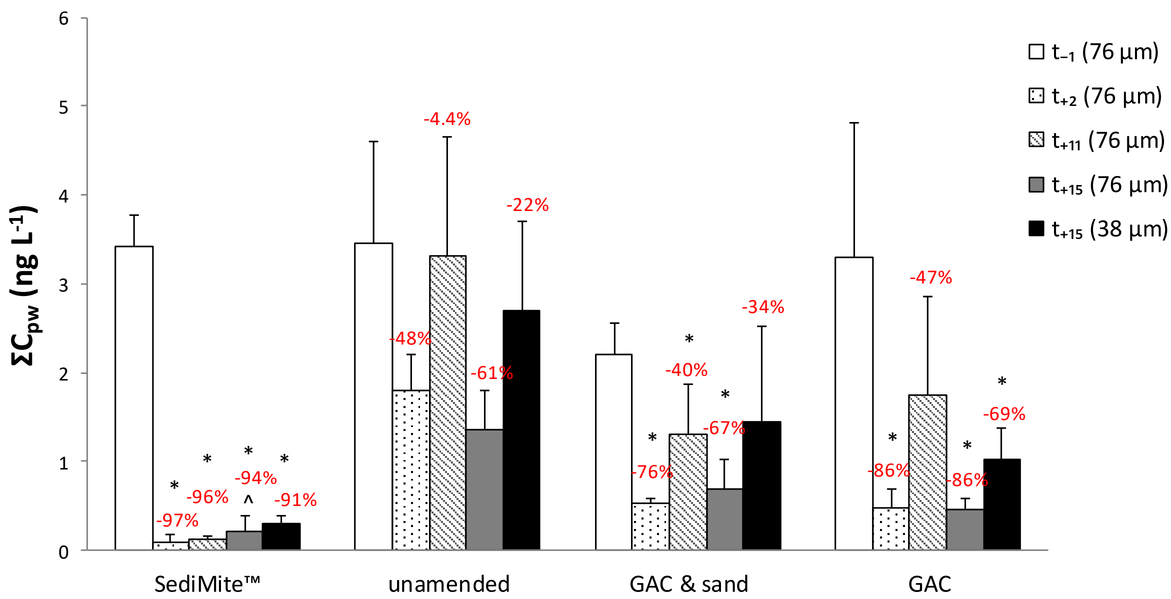

Figure 2. Average total PCB concentrations measured in sediment pore water using POM passive samplers in the 0-2.5 cm depth interval at BCSA. Values are unadjusted for fractional PRC loss. Error bars show one standard deviation among samplers in each plot ($n = 5$ except ^ ($n = 4$)). Percent decreases from each plot's pre-amendment value are shown. *Statistically significant decrease from pre-amendment value (t-test, $p < 0.05$).

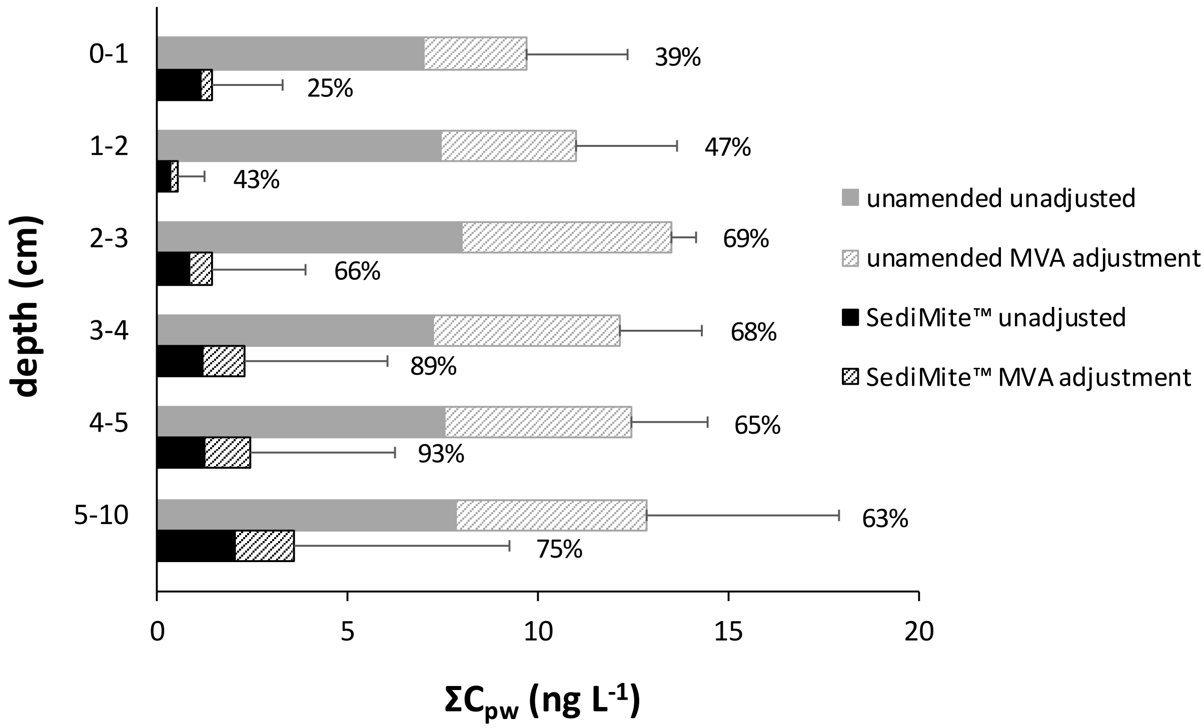

Figure 3. Total PCB concentrations in BCSA sediment pore water measured in situ at discrete depth intervals using PE passive samplers (t_{+21}). Solid bars show unadjusted ΣC_{pw}. Hatched bars show adjustments for PRC loss using the MVA method. Error bars show standard deviation in total adjusted values among samplers in each plot ($n = 3$). Percentages represent magnitudes of PRC adjustment relative to unadjusted values.

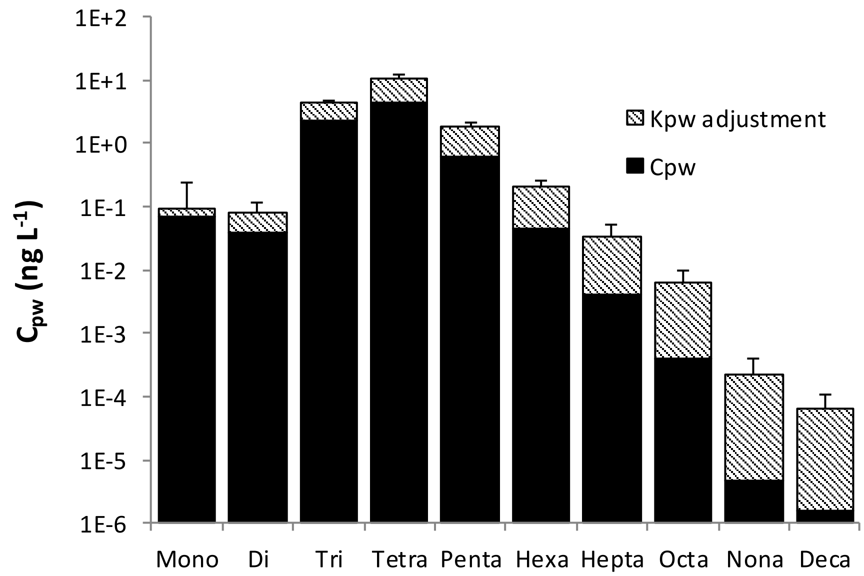

Figure 4. Vertically averaged (0–10 cm) PCB pore water concentrations in unamended BCSA sediment at t_{+21} as measured by PE passive samplers, shown by degree of chlorination. PRC adjustments made using k_e-K_{pw} linear regression. Error bars show standard deviation in adjusted value among samplers (*n* = 3). Note logarithmic scale.

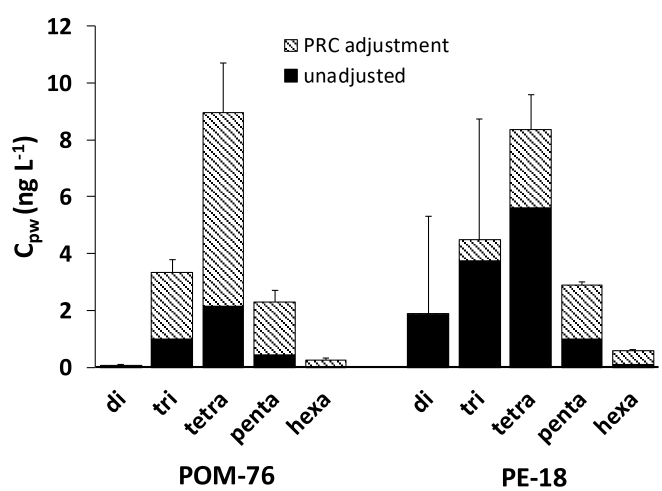

Figure 5. PCB homolog concentrations in the uppermost 2.5 cm of unamended BCSA sediment pore water measured at t_{+11} in a simultaneous deployment of 76-µm POM and 18-µm PE. PRC adjustments were performed using the k_e-K_{pw} method. Error bars show standard deviation of total adjusted values among samplers (n = 5 for POM-76, n = 4 for PE-18).

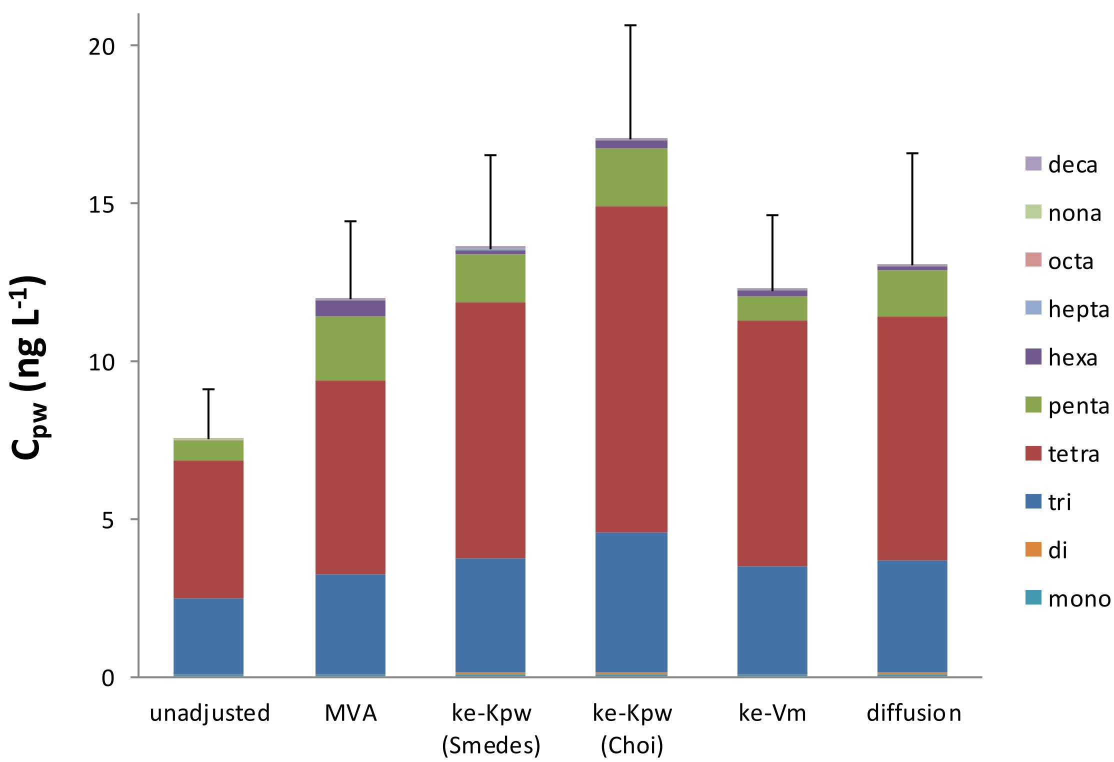

Figure 6. Comparison of PRC adjustment methods. Bars show vertically averaged pore water PCB concentrations in the uppermost 2.5 cm of unamended BCSA sediment, arranged by homolog group. Concentrations were measured in situ with PE passive samplers at t_{+21}.

Included are unadjusted values and values adjusted with each of the PRC methods discussed.

Error bars show standard deviation in ΣC_{pw} among samplers (n = 3).