Bioavailability assessment in activated carbon treated coastal sediment with *in situ* and *ex situ* porewater measurements

Songjing Yan [a], Magdalena Rakowska [b], Xiaolong Shen [b], Theresa Himmer [c], Cameron Irvine [d], Rachel Zajac-Fay [e], Jamie Eby [f], Danielle Janda [g], Sharon Ohannessian [h], Danny D. Reible [a,b,*]

[a] *Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, USA*
[b] *Department of Civil, Environmental and Construction Engineering, Texas Tech University, Lubbock, TX 79409, USA*
[c] *Jacobs Engineering, Boston, MA 02116, USA*
[d] *Robertson-Bryan, Elk Grove, CA 95624, USA*
[e] *Jacobs Engineering, Tampa, FL 33609, USA*
[f] *Port of Oakland, Oakland, CA 94607, USA*
[g] *Department of the Navy (DoN), Base Realignment and Closure Program Management Office (BRAC PMO) West, San Diego, CA 92014, USA*
[h] *Redhorse Corporation, San Diego, CA 92101, USA*

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ABSTRACT

Passive sampling and bioaccumulation assessments were used to evaluate the performance of activated carbon (AC) remediation of polychlorinated biphenyl (PCB) contaminated sediment offshore in Parcel F of the former Hunters Point Naval Shipyard (HPNS) (San Francisco, California). Two different composite AC materials, AquaGate+PAC[TM] (86 tons) and SediMite[TM] (24 tons) were placed on the sediment surface covering an area of 3200 m^2. PCB tissue concentrations in the clam *Macoma nasuta* were reduced 75 to 80% in pilot amendment areas after 8 months and 84–87% in non-lipid normalized tissues after 14 months during *in situ* monitoring, confirming the effectiveness of the AC at reducing bioavailability of the PCBs. Polydimethylsiloxane (PDMS) passive samplers were applied to evaluate and monitor freely dissolved concentrations (C_{free}) of PCBs in sediment porewater before AC placement (*i.e.*, during baseline) and at 8 months, 14 months and 26 months following placement. Although AC composite materials were placed only at the surface, 80% reductions were observed to a depth of 16 cm after 8 months and up to 26 cm after 26 months in AquaGate+PAC treatment area. Total PCB porewater concentrations in surface sediments (1–6 cm) were reduced 89 and 91% in the AquaGate+PAC and SediMite areas during final sampling. *Ex situ* passive sampling showed porewater concentrations 2–5 times larger than *in situ* measurements due to the absence of hyporheic exchange in laboratory measurements and near equilibration between sediment and porewater. Estimated post placement *ex situ* porewater concentrations were more consistent with a model of bioaccumulation using the octanol-water partition coefficient (K_{OW}) as a bioaccumulation factor leading to a hypothesis that the bioaccumulation factor in the deposit feeding clam is better estimated by equilibrium *ex situ* porewater measurements.

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1. Introduction

Contaminant flux and availability in sediments can be greatly reduced with activated carbon (AC) amendment technology. AC adsorbs hydrophobic organic species such polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dioxins present in sediment interstitial water and reduces risks of contaminant transfer to the food chain (Palermo, 1998; Wang et al., 1991). The first pilot-scale AC amendment studies were conducted

at former HPNS sediments with oversight by BRAC PMO West, and funded by the Department of Defense's (DoD's) Strategic Environmental Research and Development and Environmental Security Technology Certification Programs (SERDP/ESTCP) (Cho et al., 2012, 2009; Luthy et al., 2009). These early pilot studies were conducted in shallow intertidal areas of HPNS and were supported by parallel laboratory assessments (Janssen et al., 2011a; Tomaszewski and Luthy, 2008; Zimmerman et al., 2004). Cumulatively, HPNS is one of the most extensively studied areas with research of more than a decade in AC amendment trials and in passive sampling monitoring (Cho et al., 2012; Gschwend et al., 2011; Janssen et al., 2010; Oen et al., 2011; Zimmerman et al., 2005). Effective reduction of porewater and bioaccumulation during *in situ* sediment treatment

with pure AC particles has also been documented in multiple studies worldwide (Hilber and Bucheli, 2010; Patmont et al., 2015; Reible and Lampert, 2014).

Accurate placement of AC in aquatic systems is challenging, and AC losses are likely to occur in tidal or other dynamic areas (Abel and Akkanen, 2018). Consequently, AC is more often deposited as a composite material to aid in settling and retention at the sediment surface. Natural processes such as bioturbation are expected to incorporate carbon into the sediment (Ghosh et al., 2011; Kupryianchyk et al., 2015; Rakowska et al., 2012). Although the addition of composite material is more practical, especially in difficult areas (Kirtay et al., 2018), it is uncertain to what extent surficial placement of AC effectively reduces exposure concentrations in deeper sediment layers and whether the performance of different AC composite materials can be sustained throughout the mixing depth over longer periods of time.

Investigations assessing treatment effectiveness are generally supported by passive sampling techniques to measure freely dissolved contaminant concentrations (C_{free}). Vertical placement of polymer materials, such as polyethylene (PE) (Booij et al., 2002) and polydimethylsiloxane (PDMS) coated fibers or silicone sheets (Ghosh et al., 2014; Lampert et al., 2013; Mayer et al., 2014) into the sampling media *in situ*, enables quantitative determination of C_{free} in surface water and sediment porewater. It is generally understood that C_{free} is an indicator of chemical activity (Kraaij et al., 2003) and a suitable representation of bioaccumulation in aquatic organisms (Gomez-Eyles et al., 2012; Lu et al., 2003, 2011). Multiple studies have demonstrated the effects of AC on C_{free} and accumulation in laboratory-exposed benthic invertebrates and found a 70.9 to 99.9% reduction in PCB porewater concentrations and body burdens, respectively (Kirtay et al., 2018; Thomas et al., 2014; Wu et al., 2017). *In situ* studies have reported C_{free} and bioaccumulation reductions ranging from 35 to 80% and 13 to 50%, respectively (Cornelissen et al., 2012; Denyes et al., 2016; Janssen et al., 2011a; Kupryianchyk et al., 2013). Studies from HPNS are shown in Table S1. It is unclear, however, whether such reductions are feasible after placement of composite materials to the surface of the sediments in open systems subject to tides and storm events, where complex processes and factors such as advective transport play a role. It is also uncertain whether reductions in porewater concentrations are equally reflected in reduced bioaccumulation of HOCs in benthic organisms *in situ* and to what extent accurate predictions can be achieved through *in situ* porewater measurements. It is also unclear how well *ex situ* passive sampling can be used to indicate *in situ* porewater concentrations or bioaccumulation.

In this work, we build on previous pilot trials conducted on PCB-contaminated sediment at HPNS, San Francisco, California, and provide results of a 3200 m^2 site demonstration of two composite materials, AquaGate+PAC^{TM} and SediMite^{TM}, placed in deeper, open water, within an area several hundred meters offshore where the Navy may use the full-scale technology. Specific objectives of this study were: (i) evaluate the effectiveness of the two activated carbon *in situ* treatment remedies by employing passive sampling methods to determine PCB porewater concentration over time and depth; (ii) evaluate the effect of two commercially available composite materials on PCB bioaccumulation in clams, and (iii) assess bioaccumulation in biota exposed in AC amended scenarios by comparing with predictions from measured porewater concentrations using both *in situ* and *ex situ* passive sampling methods.

2. Materials and methods

2.1. Activated carbon composite materials

AC materials consisted of AquaGate+PAC^{TM} (AquaBlok, Ltd, Toledo, OH) and SediMite^{TM} (Sediment Solutions, Ellicott City, MD)

to support placement and allow the sorptive material to disintegrate and blend with sediment under natural conditions (Fig. S1). The target AC dose was 4 to 6 percent (mass carbon /mass dry sediment). Target total amendment mass was calculated based on a sediment treatment thickness of 15 cm and a dry sediment bulk density of 600 kilograms per cubic meter. Details on composite materials and applied quantities are provided as Supporting Information (Table S2).

2.2. Demonstration study

The study was conducted at the South Basin of Parcel F (37°44′N, 122°22′W), located in the offshore area at the former HPNS in San Francisco, California (Fig. 1A). Earlier work conducted by various research teams have shown the potential of sorbent amendments (Cho et al., 2009, 2007) in the area and this work expands on these efforts in terms of scale and monitoring timeframe. The site is intertidal with typical water depths at high tide ranging from approximately 0.6 to 1.8 m with weak tidal currents. Within the 3200 m^2 test site, two distinct areas were chosen for amendments (ca. 1560 m^2 each) and an approximately 14 m wide buffer zone between both treatments (Fig. 1B and C). AquaGate+PAC^{TM} was introduced as amendment A (plot 1) with designated sampling stations (STN 1, 3, 5, 7, 9, 12, and 15), and SediMite^{TM} was placed as amendment B (plot 2) with sampling locations STN 28, 30, 33, 36, 38, 40, and 42. The buffer zone consisted of six sampling locations (STN 17, 19, 21, 22, 24, and 26). Additional reference stations (STN 43A, 45A, and 48A), were positioned approximately 10 m north of the AC amendment areas (Fig. 1C). A more detailed map of sampling locations is provided as Fig. S2 (Supporting Information). The composite materials were loaded on a barge, and incorporated into the sediment using a truck-mounted Telebelt radial conveyor. A spreader was placed at the discharge end of the Telebelt and a global positioning system was used to monitor the placement positions (CH2M HILL Kleinfelder, 2018) (Fig. S3).

2.3. Sampling design

Sampling efforts were initiated prior to AC placement (May 2015) to examine baseline conditions at the site and provide a reference to changes post-placement. Baseline monitoring was conducted at twenty stations of the intended amendment area (Fig. 1C, Fig. S2) and comprised of C_{free} measurements, bioaccumulation assessments with clams (*Macoma nasuta* and *Macoma secta*), surface sediment sampling (10–15 cm), sediment profile imaging (SPI) and hydrodynamic measurements. Reference stations were also located outside of the amendment area to provide an additional benchmark for assessing the response of benthos to the composite material addition. Post-application monitoring (8, 14, and 26 months) included surface sediment sampling for bulk chemistry, and remaining endpoints at all locations and reference stations, respectively.

2.4. Passive samplers (PS)

Polymeric passive samplers with polydimethylsiloxane (PDMS) coating of 36.4 μm and a core diameter of 486 μm (Polymicro Technologies, Phoenix, AZ) were applied to measure dissolved PCBs in sediment porewater (C_{pw}) during *in situ* and *ex situ* exposures (Lampert et al., 2013; Thomas et al., 2014).

2.4.1. In situ *passive sampling*

Prior to deployment the samplers were cut into 30 cm lengths and loaded with performance reference compounds (PRCs), $^{13}C_{12}$ labeled PCB-28, −52, −101, −153, −138, −180 and −209. Details of sampler preparation, loading, extraction and C_{pw} calculations are
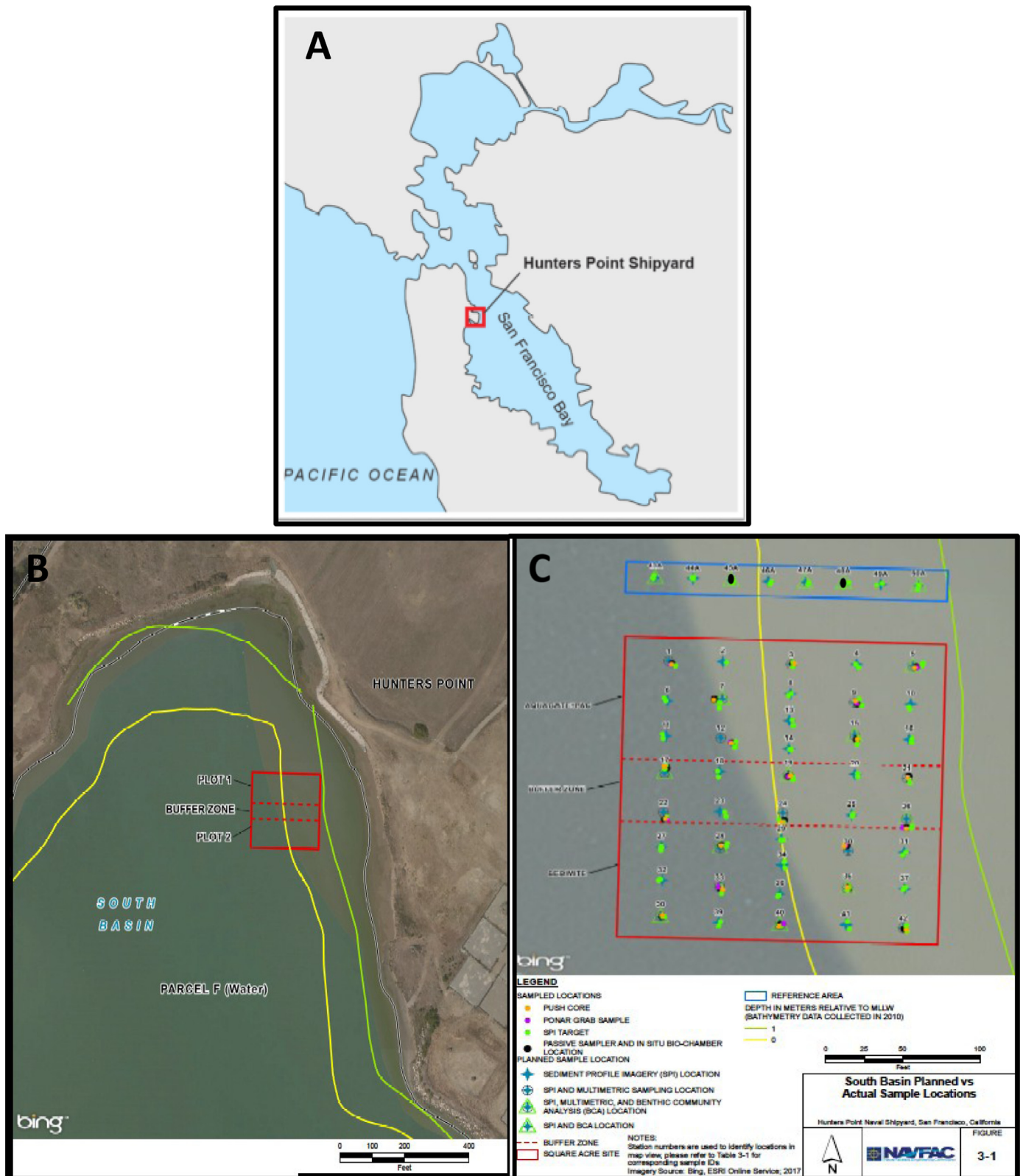
Fig. 1. (A) Sampling location map of former HPNS San Francisco Bay; (B) former HPNS Parcels; and (C) Actual sampling locations within two AC treatment areas and reference plot. Amendment A refers to AquaGate+PAC™ treatment plot while Amendment B refers to SediMite™ treatment plot.

provided as Supporting Information. The PDMS fiber was loaded onto slots with vertical steel rods as an insertion tool, covered with food grade aluminum foil and transported to HPNS in sterile and cold conditions. During deployment, three steel rods with PDMS loaded were attached to a triangular frame and placed into the sediments at 20 locations to a depth of 30 cm. The samplers were placed adjacent to bioaccumulation chambers at each sampling location (Fig. S4). All tripods were connected via nylon cords to surface-deployed floats marked with station numbers. The triangular frame provided 30 cm spacing between replicates and allowed the evaluation of spatial variability at each station and between stations. Details of the statistical analysis will be discussed in a separate study.

Passive sampling devices were retrieved after 28 days. PDMS fibers were carefully removed from the steel rods, wiped with damp lint-free tissue to remove sediment particles and sampled in 5 cm segments from top to bottom. The sampled segments corresponded to 1–6, 6–11, 11–16 cm sediment depths in the upper biologically active zone to aid comparison with bioaccumulation results. PDMS segments extending further from the surface (*i.e.*, 21–26 cm depth) were used to evaluate deeper contamination or potential for migration into the biologically active zone.

Sediment samples were collected immediately after passive sampler retrieval for *ex situ* PCB porewater concentrations (STN 17, 19, 22, 24, 28, 30, 33, 36, 38, 40 and 42), bulk sediment concentrations, and total organic carbon (TOC) analysis. Details of sediment extraction procedures for PCB and TOC analysis are provided as Supporting Information.

2.4.2. Ex situ *passive sampling*

For *ex situ* passive sampling of baseline sediments, 5 cm PDMS segments were washed and preloaded with PRCs as described in the Supporting Information. Sediment grab samples collected from 10 to 15 cm depth from each location were initially dosed with sodium azide (NaN_3) at a concentration of 100 mg/L to prevent biological activity and homogenized. Approximately, 40–42 g of wet sediment subsamples from individual locations were weighed into 40 mL vials in triplicate for measurement of C_{pw} *ex situ*. The cleaned and PRC loaded SPME fibers were introduced to the individual vials containing sediment subsamples and tightly closed. Sediment was exposed with PDMS vertically for 28 days at 20ºC with gentle motion on a shaker table. For *ex situ* samples obtained after 8-months AC placement, the volume of PDMS in the 5 cm segments was insufficient to quantify PCBs. Trifold increase in PDMS volume during subsequent monitoring events did not improve PCB detection *ex situ*. Approximate *ex situ* porewater concentrations were estimated by using the correction ratio between *in situ* and *ex situ* under baseline conditions under the assumption that this better reflects the kinetics of surficial exchange with the kinetics of sediment contaminant desorption in defining porewater concentrations.

2.5. In situ *and* ex situ *bioaccumulation exposures*

Bent nose clams (*Macoma nasuta*) were used in field deployments to evaluate bioaccumulation of PCBs in both AC placement areas, with the exception of baseline monitoring, where white sand clams (*Macoma secta*) were applied. High mortality of these clams limited data recovery and the switch to *Macoma nasuta* led to increased recovery. At each sampling location 5 clams were exposed to sediment for 28 days inside 15 cm diameter PVC *in situ* bioaccumulation chambers based on the design described by Cho et al. (2007). The chambers were pressed firmly 15 cm into the sediment and attached to surface-deployed markers (Fig. S4). *In situ* bioaccumulation was measured at 10 locations in each AC

treatment area, at 2 reference locations, and in duplicate during each monitoring event.

Laboratory (*ex situ*) exposures were performed at Pacific EcoRisk (Fairfield, CA) concurrent with field exposures during each monitoring event. Bioaccumulation was measured over 28 days in sediments collected from the upper 15 cm at 5 locations from each treatment area, 2 reference area locations, and in duplicate. Ten clams were exposed to each sample in these laboratory exposures. At the end of exposures, the surviving clams were placed inside a 500-milliliter wide-mouth amber glass jar with unbleached paper towels that were wet with site surface water and maintained in a cooler at field temperature (16 °C) for 24 h to depurate (ASTM, 2010). After depuration, whole clams were wrapped in baked-out aluminum foil, placed in re-sealable plastic bags, and shipped to the analytical laboratory (Vista Lab, El Dorado Hills, California) where they were frozen prior to chemical analysis. Unexposed tissue from clams maintained at the bioassay laboratory during the field deployment was also sent for laboratory analysis after each monitoring event as a tissue/source blank.

3. Results and discussion

3.1. TOC analysis and correlation with AC dosage

The average thicknesses of the AquaGate and SediMite layers were found to be 5.5 ± 0.4 cm and 2.5 ± 0.3 cm, respectively. These observed thicknesses were slightly greater than the actual effective placement thicknesses of 4.3 cm and 1.8 cm determined based on the mass of amendment deployed. The total organic carbon (TOC) in the post-amendment sediments compared to the TOC during baseline sampling was used to estimate the amount of AC in the sediment samples. In the baseline study, the sediment samples had an average TOC of 1.4 ± 0.08 wt.%. The averaged TOC content in surficial sediment (10–15 cm) at 8-months after placement of the composite materials increased substantially to 11.7 ± 7.1 and 13.8 ± 8.8 wt.% in AquaGate+PAC and SediMite areas, respectively (Fig. S5). The larger variations in TOC content may be explained by the non-uniform placement of AC across the site and/or differences in the rate of AC vertical mixing. AC represented 9% of sediment in the AquaGate+PAC amendment and 10% in the SediMite treated area. The difference between the post-amendment TOC value (TOC%p) and the TOC percentage at baseline (TOC%b) was used to estimate the AC amount added in both amendments. Higher TOC content and corresponding AC dosage after 8-months compared to targeted masses of AC reflect the higher concentration in the surficial layer prior to intermixing over the design depth. Sampling after 26 months showed that the TOC was reduced to 4% and 5% in the 10–15 cm depth (Fig. S5), due to both intermixing into the sediments and potentially some AC loss.

3.2. In situ *PCB porewater concentrations*

The *in situ* porewater concentrations of target PCBs during baseline monitoring were measured in June 2015. In total, 78 PCB congeners were detected and the ΣPCB porewater concentration during baseline monitoring averaged 2.6 and 2.3 ng/L in the AquaGate+PAC and SediMite areas, respectively (Fig. 2). Corrections for temperature and salinity were not applied to the C_{pw} data. The C_{pw} across both amendment areas and all depths averaged 2.4 ng/L with a low standard deviation (SD) of 0.2 ng/L. The ΣPCB congener concentration (ng/L) of at 21–26 cm depth was 2.8 ± 0.6 ng/L, and generally higher than at 1–6 cm and 11–16 cm, where C_{pw} was 2.2 ± 0.2 ng/L.

8 months after amendment application, the *in situ* ΣPCB porewater concentration was reduced by $81 \pm 10\%$ in AquaGate+PAC
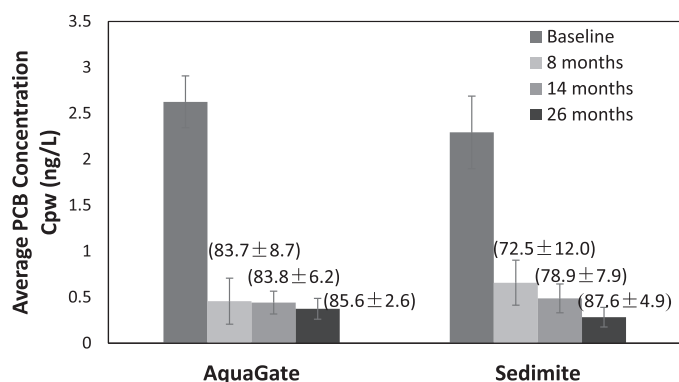
Fig. 2. Measured *in situ* porewater concentrations of ΣPCB across the two different AC treatment plots. The data bars represent the average of ΣPCB concentrations across amendment plot and measured depths (1–6, 6–11, 11–16 and 21–26 cm) and the error bars represent one standard deviation (SD). Numbers in brackets represent% reduction $\pm$ SD for C_{pw} relative to baseline data.

treatment plot and 73$\pm$10% reduction in the SediMite amendment area (Fig. 2). As expected, the effect of the amendment on C_{pw} at surface layer (1–6 cm) was greater than in deeper layers (21–26 cm). Passive sampling monitoring at 14 months and 26 months generally showed a similar or slightly lower C_{pw} in the near-surface samples (Fig. S6). Although the average amount of sorbent in the surficial sediments declined due to intermixing with depth or due to loss, AC treatment resulted in a relatively rapid C_{pw} reduction in the first 8 months and sustained that reduction throughout sampling.

The measured average ΣPCB porewater concentrations 26 months after AC placement at the surface (1–6 cm) was 0.24$\pm$0.08 ng/L (89% reduction) in the AquaGate+PAC treatment and 0.19$\pm$0.09 ng/L (91% reduction) in the SediMite amendment (Fig. S6).

At both AC amendment areas, the largest concentration reductions were observed in the low molecular weight PCB homologs (mono-, di-, tri-), which is consistent with earlier AC treatment studies (Hale et al., 2010; Kupryianchyk et al., 2012; Rakowska et al., 2014). The lower decrease of high molecular weight PCBs in the porewater compared to low molecular weight congeners (Fig. S7) can be explained by slow desorption from the solid matrix, slow transfer of the former compounds onto the AC surface and/or pore blocking by dissolved organic matter (DOM) fouling (Oen et al., 2011). In the baseline study, the mean concentration weighted congener in the porewater, defined by $\Sigma(\#_i)(C_i)/\Sigma C_i$ was PCB 66 at baseline sampling, and PCBs 98–104 after AC treatment, depending upon treatment and time. The PCBs in the porewater shifted towards a heavy molecular weight compound in the post-treatment sampling events due to the more rapid sorption of the low molecular weight congeners to AC and the relatively slow sorption of higher molecular weight congeners. The PCB congeners were grouped into homologs for comparison to bioaccumulation data. Approximately, 99% of monochloro- PCBs were removed from the porewater by the AC after 8 months, while a 70% decline was observed for heptachloro-PCBs after 26 months. The distribution of PCB homologs at the surface (1–6 cm) and deeper layer (21–26 cm) at AquaGate+PAC and SediMite plots are shown in Fig. S7. Smaller but significant reductions in porewater concentrations were also noted at the deeper intervals. An 83% reduction of PCB porewater concentration was ultimately observed at 26 months between 21 and 26 cm below sediment surface in the AquaGate+PAC plot, while SediMite treatment led to approximately 85% decrease of PCB C_{pw} at the same depth.

3.3. Ex situ *porewater measurements*

In general, baseline monitoring with passive samplers showed that C_{pw} determined *ex situ* was 2–5 times higher compared to C_{pw} determined *in situ* (Fig. S8). Similar observations were reported for *in situ* and *ex situ* C_{pw} measurements using passive samplers at five locations in Lower Duwamish Waterway (Apell and Gschwend, 2016). The *in situ* C_{pw} of PCBs were consistently lower (within a factor of two) than the *ex situ* C_{pw} measured in the 0–10 cm sediment depth (Apell and Gschwend, 2016). In a study conducted in Boston Harbor, *ex situ* PAH concentrations determined by passive samplers were typically higher compared to *in situ* C_{pw} (Fernandez et al., 2009a,b). The higher porewater concentrations *ex situ* are likely related to the absence of dilution effects as a result of bioirrigation, tidal pumping and hyporheic exchange. *Ex situ* samplers would be expected to be more reflective of true equilibrium between the sediment particles and surrounding media (Fernandez et al., 2009a,b; Lampert et al., 2013; Lick, 2006; Work et al., 2002).

Differences were also observed between the cumulative C_{pw} per homolog group in the *in situ* and *ex situ* measurements during the baseline assessment. Tetrachlorobiphenyls (C_{pw}=1.2 ng/L) were the dominant homolog in *ex situ* porewater measurements while trichlorobiphenyls (C_{pw}=0.6 ng/L) were dominant *in situ* C_{pw}. Low chlorine number congeners, like monochloro- and dichloro-, showed greater differences between *in situ* and *ex situ* compared to heavier molecular weight compounds (Fig. S8), which may reflect larger loss of the lower molecular weight congeners from sediments in the more dynamic *in situ* environment due to flushing.

The ratio of *ex situ* to *in situ* concentration obtained during baseline monitoring was further used to characterize the dilution associated with *in situ* hyporheic exchange processes. During post-amendment sampling events, sediment samples collected for *ex situ* analysis were taken from the surficial layer, which contained more AC than even shallow buried sediments. The mass of PDMS employed in the *ex situ* samples did not compensate for the high AC content and resulted in C_{pw} measurements below quantification limits.

3.4. The effect of composite materials on bioaccumulation reduction

During baseline monitoring, tissue bioaccumulation was conducted with white sand clam (*Macoma secta*) that were collected at a nearby reference location. Exposures of the white sand clams in the field and laboratory resulted in poor recoveries (<20%) and baseline tissue concentration data represent a composite of the surviving organisms from *in situ* exposures. The white sand clams, locally sourced by the contract lab, were not as tolerant of testing conditions as bent-nosed clams. Therefore, bioaccumulation of PCBs after AC placement was monitored with bent nose clams (*Macoma nasuta*). Both species have similar feeding preferences and reside in mid to low intertidal zones. *Macoma nasuta* has been applied successfully for assessing AC efficiency in earlier field trials (Janssen et al., 2011b).

Post-amendment monitoring with bent nose clams (>90% survival) found 75 to 80% reductions of *in situ* PCB tissue concentration after 8 months and 84–87% after 14 months relative to the reference locations (Fig. 3A). The *ex situ* bioaccumulation monitoring showed higher reduction than *in situ*, which agrees with previous studies at the former HPNS (Table S1). Tissue PCBs declined by approximately 85% following 8 months post-treatment in the 28-d laboratory exposures and the reductions remained unchanged throughout the entire monitoring period (Fig. 3B).

Thus, the overall reduction in organism bioaccumulation of PCBs was mirrored by the reductions in porewater concentrations. The dynamics were somewhat different depending upon whether
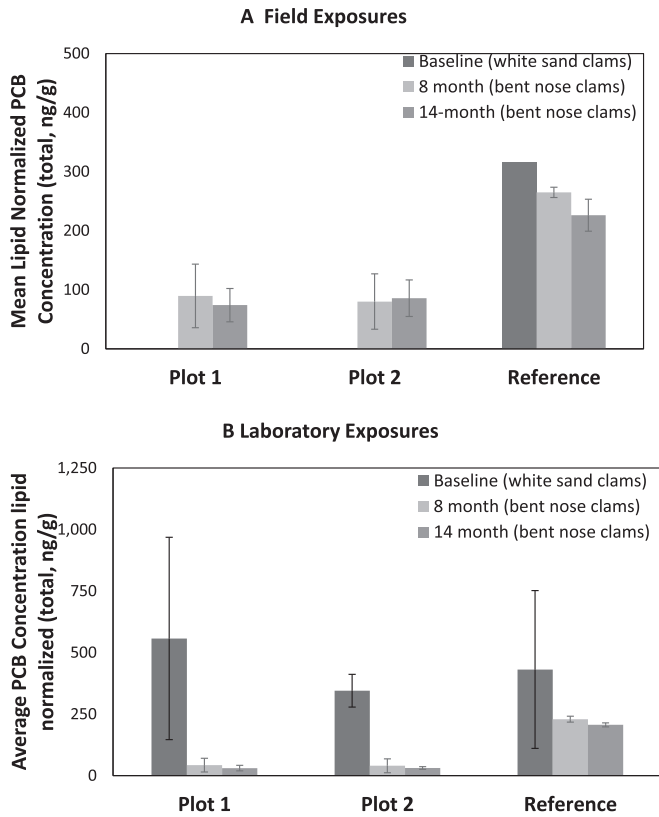
A Field Exposures

B Laboratory Exposures

Fig. 3. Lipid-normalized PCB bioaccumulation reduction in tested clams among AC treatments: AquaGate+PAC (Plot 1), SediMite (Plot 2) and reference site at different sampling times in (A) Field exposures and (B) Laboratory exposures.

the bioaccumulation occurred during laboratory exposures or *in situ*, likely as a result of the dynamics of hyporheic exchange and AC mixing over the near surface sediment column *in situ*.

3.5. Conceptual model of contaminant availability

The above discussion focused on overall PCB reductions in porewater and bioaccumulation. The porewater concentrations and bioaccumulation were explored further to evaluate the effects of *in situ* and *ex situ* measurements and the influence of different homolog groups. Because *in situ* porewater is lower in PCB concentration than *ex situ* (Fig. S8) due to hyporheic exchange and other mixing processes, the differences between *ex situ* and *in situ* porewater values can be used to obtain information about the disequilibrium between the porewater, sediment and/or biota. The exposure of deposit feeding organisms would be governed by C_{free} as an indication of the available contaminants in the sediment. We hypothesize that the bioaccumulation in sediment ingesting organisms is likely related to the equilibrium availability of sediment contaminants, and thus better reflected by *ex situ* porewater measurements of C_{free}. For filter feeding organisms, however, exposure occurs directly through the water phase and *in situ* measurements of C_{free}, perhaps influenced by hyporheic exchange and other mixing processes, likely better reflects that exposure.

The concentration in the organism via bioaccumulation can be written as:

$$\frac{W_b}{f_l} = (BAF)C_w = \frac{(BAF)W_s^l}{K_{sw}} \tag{1}$$

where W_b is the PCB concentration in biota (ng/kg), f_l is the fraction of lipids and W_b^l is the lipid-normalized concentration of contaminant in the organism (ng/kg lipids). *BAF* is a biota-water accu-

mulation factor (BAF, L/kg lipids) expressed by:

$$BAF = \frac{W_b^l}{C_{pw}} \tag{2}$$

The magnitude of the BAF is expected to be of the order of the octanol-water partition coefficient, K_{ow}.

For deposit feeding organism, *ex situ* concentrations (C_{pw}^{eq}) in water reflect equilibrium with the solid:

$$C_{pw}^{eq} = \frac{W_s^l}{K_{sw}} \tag{3}$$

where K_{sw} is the equilibrium partition coefficient (L/kg), and W_S^l is the labile concentration of contaminant in the solids (ng/kg). Assuming that this concentration defines bioaccumulation in deposit feeders and using K_{ow} as an estimate of the approximate bioaccumulation factor:

$$\frac{W_b^l}{K_{ow}C_{pw}^{eq}} \sim 1 \tag{4}$$

Under *ex situ* passive sampling conditions, the porewater is in equilibrium with the labile fraction of the solids, as long as the characteristic time for sorption/desorption is smaller than characteristic time for passive sampling (τ_{ps}). The release of contaminants from the solids to the *ex situ* porewater in such a scenario C_{pw}^{eq}, can be described by the equation:

$$(dV_W C_p w^e q)/dt = k_s a_s (W_s^l - K_s w C_p w^e q)\rho_s \tag{5}$$

where the intrinsic rate constant $k_s a_s$, the product of a mass transfer coefficient, length/time, and an sorption area per unit volume, 1/length, represents the inverse of the characteristic time for sorption/desorption ($1/\tau_s$) to or from the labile fraction of the sediment, ρ_s representing the dry bulk density of the sediment solids (g/cm³) and V_w water volume (cm³)

In instances of disequilibrium between the porewater and labile concentration of contaminants on the solid particles, *e.g.* due to hyporheic exchange and flushing of the pore space, the exposure of filter feeding organisms accumulating contaminants directly from the water is expected to be given by the *in situ* measured C_{pw}^{in}. Inclusion of the volumetric flushing rate (Q, m³/s) in Eq. (5) gives an estimate of C_{pw}^{in}:

$$\frac{dV_W C_{pw}^{in}}{dt} = k_s a_s (W_s^l - K_{sw}C_{pw}^{in})\rho_s V - QC_{pw}^{in} \tag{6}$$

which under quasi-steady conditions can be written in terms of a characteristic time for water exchange, τ_w as:

$$0 = k_s a_s (W_s^\ell - K_{sw}C_{pw}^{in})\rho_s \frac{V}{V_w} - \frac{Q}{V_w}C_{pw}^{in}$$
$$= \frac{1}{\phi_w \tau_s}(W_s^\ell - K_{sw}C_{pw}^{in})\rho_s - \frac{1}{\tau_w}C_{pw}^{in} \tag{7}$$

and the *in situ* porewater concentration is:

$$C_{pw}^{in} = \frac{W_s^\ell}{\left(K_{sw} + \frac{\phi_w \tau_s}{\rho_s \tau_w}\right)} \tag{8}$$

As a result, the *in situ* porewater measurement obtained with passive samplers will be smaller than equilibrium porewater concentration and lower than *ex situ* porewater concentration measurement and the difference primarily dependent on the ratio of characteristic times (τ_s / τ_w). Note, that typically $\tau_w < \tau_s$. Given our hypothesis that deposit feeding organisms will equilibrate with solids and will not be influenced by porewater flushing, the bioaccumulation of a deposit feeding organism will be underestimated by the *in-situ* porewater concentration by the ratio:

$$\left(\frac{W_b^l}{K_{ow}C_{pw}^{in}}\right) = \frac{K_{sw} + \frac{\phi_w \tau_s}{\rho_s \tau_w}}{K_{sw}} = 1 + \frac{\phi_w \tau_s}{K_{sw}\rho_s \tau_w} \tag{9}$$

and the slope of the correlation between W_b and $K_{ow}C_{pw}$ for deposit feeders would be greater than unity. During *ex-situ* passive sampling, $\tau_w \to \infty$ and the correlation should have slope near unity (Eq. (4)). These relationships were tested using the measured porewater concentrations and the bioaccumulation data.

Note however, that the ratio between the porewater and overlying water in the field is likely controlled by the exchange between the sediment organic carbon and porewater due to the slower dynamics of the AC. Thus, the ratio of the *in situ* to *ex situ* in the baseline (pre AC addition) may be a better indicator of the ratio between equilibrium with the sediment and the porewater-sediment disequilibrium caused by hyporheic exchange. In addition, the effect of the temperature change relative to the field may have influenced kinetics of AC uptake such

that greater apparent uptake occurred at the higher laboratory temperatures.

3.6. Correlation of bioaccumulation with C_{pw}

Post-amendment monitoring of C_{pw} *ex situ* resulted in non-detects in passive sampler extracts due to the use of insufficient mass of PDMS for quantitation. To better understand the importance of *in situ* and *ex situ* porewater in bioaccumulation predictions we applied the ratio of *ex situ* C_{pw} and *in situ* C_{pw} obtained from baseline measurements (Table S4) as an estimate of post-treatment *ex situ* porewater concentrations for the reasons identified above. We assumed that the ratio of *in situ* to *ex situ* for each homolog group was approximately constant and applied this ratio
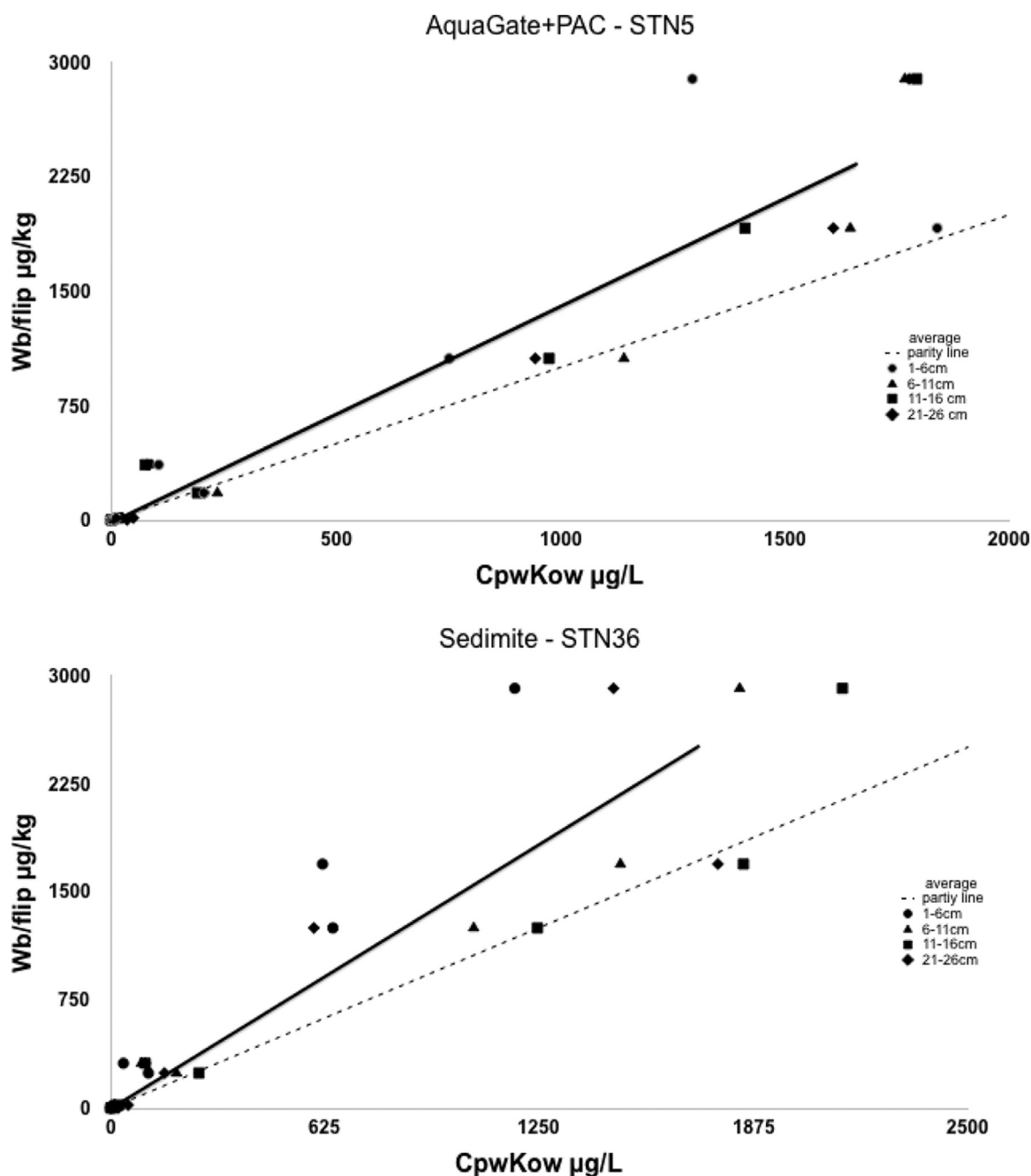

Fig. 4. Modeled correlations of PCB homolog bioaccumulation with homolog C_{pw} at different depths at two different AC amendment locations: (A) AquaGate+PAC-STN5 and (B) SediMite-STN36. Solid lines represent averaged C_{pw} throughout the measured depths with $y = 1.414$ and $R^2 = 0.922$ for AquaGate+PAC and $y = 1.463$ and $R^2 = 0.953$ for SediMite.

Table 1

Average measured lipid normalized bioaccumulation and biota concentrations predicted from equilibrium partitioning as a product of the octanol-water partition coefficient and estimated porewater concentration and their ratio for each homolog group by AC amendment. *In situ* porewater data were used as input.

Homolog	$LogK_{ow}$	AquaGate+PAC ™				SediMite ™			
		W_b^l µg/kg lipid	$K_{ow}C_{pw}$ µg/L	Ratio	Std Dev	W_{bl} µg/kg lipid	$K_{ow}C_{pw}$ µg/L	Ratio	Std Dev
Monochloro	4.09	3	0	–		4	1	3.6	
Dichloro	5.13	3	11	0.26	0.53	3	23	0.13	0.29
Trichloro	5.55	19	30	0.64	0.24	21	40	0.51	0.19
Tetrachloro	5.98	289	178	1.62	0.73	261	262	1.00	0.5
Pentachloro	6.40	1930	805	2.40	1.01	1510	1030	1.47	0.66
Hexachloro	6.80	4050	1250	3.25	1.01	3700	1470	2.51	1.43
Heptachloro	7.17	2300	1070	2.15	0.65	2220	1270	1.76	1.04
Octochloro	7.52	373	57	6.55	1.97	388	68	6.10	3.50

by each homolog group. The biota-lipid concentrations were plotted against biota concentrations predicted from equilibrium partitioning using the octanol-water partitioning coefficient as a bioaccumulation factor (Lu et al., 2011). The ratio of lipid normalized biota accumulation to estimated ex-situ porewater concentration divided by the octanol-water partition coefficient for each homolog varied from 1 to 5 with excellent correlations (R^2 by location ranging from 0.898–0.998). The average results for 1–16 cm depth by homolog group are summarized in Table 1. Porewater concentrations of mono-, di- and trichlorobiphenyls as well as octochlorobiphenyls were very low and the ratios deviated substantially from unity, although perhaps simply due to uncertainty in those concentrations. The ratios for the remaining homologs were in the range of 1–3 suggesting that the octanol-water partition coefficient multiplied by the estimated equilibrium porewater concentration ($K_{ow}C_{pw}^{eq}$) provided a good estimate of the lipid normalized bioaccumulation in the deposit feeding clam. The correlation of $K_{ow}C_{pw}^{eq}$ with lipid normalized bioaccumulation for locations containing AquaGate+PAC (STN 5), and SediMite (STN 36) is provided in Fig. 4A and 4B, respectively. Each homolog group at each depth is shown on the figure, which illustrates that the porewater concentration at the 1–6 cm depth tends to be more variable than other depths but that the slope (effectively the ratio as defined above) was near unity for all depths, particularly immediately below the surface layer.

4. Conclusions

The results from the activated carbon post-treatment analysis at the former HPNS demonstrated high performance of AquaGate+PAC and SediMite in reducing risks in PCB contaminated sediment. Effective reduction in C_{pw} (83.7–85.6%) was noted in the first 8 months following amendment and these strong reductions continued throughout the remainder of the study period. The decline of low molecular weight PCBs (mono-, di-, and tri-) in the porewater was most prominent in both activated carbon placement scenarios. Largest reductions of available PCBs were observed in the surficial layer (1–6 cm depth), which implies lower flux to the overlying water column and lower availability to benthic organisms. Smaller but significant reductions in porewater concentrations were also noted at the deeper intervals (up to 26 cm) particularly at later sampling periods due to intermixing of the AC downward. *Ex situ* measured porewater concentrations were 2–5 times larger than *in situ* during baseline sampling due to the greater hyporheic exchange *in situ*.

The reduction of PCB bioaccumulation in bent nose clams was approximately 75–80% during the *in situ* pilot study 8 months after activated carbon addition. The effectiveness of AC in reducing bioaccumulation did not change during the monitoring period including 26 months after AC deployment.

A conceptual model was built based on the *in situ* and *ex situ* results to assess bioaccumulation in biota exposed in AC treatment period by using the octanol-water partition coefficient as the estimated bioaccumulation factor. The model hypothesizes that *ex situ* passive sampling would better indicate bioavailability and bioaccumulation in deposit feeding organisms such as the bent nose clams applied here. The use of *ex situ* porewater concentrations estimated from the observed ratio of *ex situ* to *in situ* porewater concentrations for specific homolog groups appeared to better predict bioaccumulation if the bioaccumulation factor is assumed to be the octanol-water partition coefficient of PCBs.

Overall, this study demonstrates the significant PCB reductions and shows the feasibility of deploying activated carbon materials for PCB contaminated sediment management and remediation. These results suggest the activated carbon treatment can be effective and that AC can be retained at the sediment surface in an open water tidal environment until it has mixed relatively deeply into the sediments. The effectiveness of the AC is therefore, likely to continue well beyond the 26 months of the monitoring.

Supporting information

Additional information on the steady state fraction analysis, placed activated carbon materials, tables and figures are provided as Supporting Information.

Declaration of Competing Interest

The authors declare they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2020.116259.

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