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Remediation and Restoration

Performance of an In Situ Activated Carbon Treatment to Reduce PCB Availability in an Active Harbor

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Abstract: In situ amendment of surface sediment with activated carbon is a promising technique for reducing the availability of hydrophobic organic compounds in surface sediment. The present study evaluated the performance of a logistically challenging activated carbon placement in a high-energy hydrodynamic environment adjacent to and beneath a pier in an active military harbor. Measurements conducted preamendment and 10, 21, and 33 months (mo) postamendment using in situ exposures of benthic invertebrates and passive samplers indicated that the targeted 4% (by weight) addition of activated carbon (particle diameter $\leq$74 μm) in the uppermost 10 cm of surface sediment reduced polychlorinated biphenyl availability by an average ($\pm$ standard deviation) of 81 $\pm$ 11% in the first 10 mo after amendment. The final monitoring event (33 mo after amendment) indicated an approximate 90 $\pm$ 6% reduction in availability, reflecting a slight increase in performance and showing the stability of the amendment. Benthic invertebrate census and sediment profile imagery did not indicate significant differences in benthic community ecological metrics among the preamendment and 3 postamendment monitoring events, supporting existing scientific literature that this approximate activated carbon dosage level does not significantly impair native benthic invertebrate communities. Recommendations for optimizing typical site-specific assessments of activated carbon performance are also discussed and include quantifying reductions in availability and confirming placement of activated carbon. *Environ Toxicol Chem* 2018;37:1767–1777. Published 2018 Wiley Periodicals, Inc. on behalf of SETAC. This article is a US government work and, as such, is in the public domain in the United States of America.

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INTRODUCTION

Active harbor areas pose a number of challenges to the effective use of traditional sediment remedies—especially in areas adjacent to or beneath permanent infrastructure such as marine bulkheads, docks, and overwater piers—where removal of sediments can be difficult or may compromise structural integrity. In addition, the use of isolation caps (which can be more than 1 m thick) in these areas is often impractical because their application reduces water depths necessary for adequate vessel berthing. Further, many areas in active harbors exhibit high surface sediment disturbance rates caused by vessel activity (e.g., propeller wash) that may not be conducive to monitored natural recovery.

The use of in situ active amendments such as the addition of activated carbon to surface sediment has emerged as an attractive and cost-effective sediment remediation strategy (Patmont et al. 2015). Activated carbon exhibits a high sorption capacity for hydrophobic organic compounds such that when it is placed on or mixed within surface sediment, the activated carbon can serve as a sink for available compounds, reducing the overall exposure of benthic organisms and transport to overlying water (Ghosh et al. 2011; Kupryianchyk et al. 2015; Patmont et al. 2015). Activated carbon is also able to overcome some of the practical limitations for sediment remedies in active harbor areas. For example, activated carbon can be applied in thin layers (30 cm or less) to achieve effective activated carbon dosage rates in sediment; however, it does not significantly reduce berthing depths at piers. Because activated carbon added to sediment is

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incorporated into deeper layers via bioturbation (Ghosh et al. 2011) or application approaches that can encourage deeper sediment penetration and partial armoring (see Supplemental Data, Section 2), activated carbon is likely to be retained in sediments (Choi et al. 2014a, 2014b), despite potential vessel-related physical sediment disturbances. Furthermore, if applied at full scale, a remedy could be engineered to allow for some mixing and redistribution of the activated carbon without sacrificing its overall effectiveness at reducing polychlorinated biphenyl (PCB) bioavailability and uptake into the biological food chain.

The goal of the 4-yr investigation described in the present study was to evaluate the placement and performance of a logistically challenging activated carbon remedy in PCB-impacted sediments. Consistent with many aspects of previous activated carbon studies (Ghosh et al. 2011; Kupryianchyk et al. 2015; Patmont et al. 2015), our evaluation focused on 3 goals. The first goal was to confirm the initial placement of the activated carbon and its degree of physical resilience in the sediment throughout the duration of the study because the placement and retention of activated carbon (or any in situ remedy amendment) is not necessarily guaranteed in sediment systems (Ghosh et al. 2011; Patmont et al. 2015). The second goal focused on quantifying the potential reduction in PCB availability after activated carbon placement. Reductions in availability of hydrophobic organic compounds of 90% or more are often observed for typical activated carbon amendments (Kupryianchyk et al. 2015), although there can be variability caused by dosage rate, activated carbon particle sizes used, and site conditions (Ghosh et al. 2011; Patmont et al. 2015). The third study goal was to identify potential changes in the benthic invertebrate community that could be associated with the activated carbon amendment. The potential for adverse effects of activated carbon on benthic invertebrates has been observed for some activated carbon treatments (Janssen et al. 2012), although generally effects were observed for finer grained activated carbon at higher dosage levels (i.e., $>$ 5% by weight; Kupryianchyk et al. 2015; Patmont et al. 2015).

The present study represents one of the first comprehensive field assessments of activated carbon performance in an active military harbor area characterized by the presence of infrastructure, ship and tug movements, and relatively deep water ($\sim$ 10- to 15-m water depth). At the time the present study was initiated, the scale of evaluation and challenging nature of the study area represented a novel endeavor in the field of activated carbon amendment research because activated carbon amendments had been primarily tested in pilot-scale efforts (Patmont et al. 2015) generally targeted to areas with shallow or protected waters and with minimal vessel traffic, infrastructure, or harbor activities. The present study also provides an additional example of activated carbon performance in marine sediments.

MATERIALS AND METHODS

Activated carbon amendment

The activated carbon amendment was placed in a 2000-m^2 area ($\sim$ 10- to 15-m water depth) located partially beneath and adjacent to Pier 7 of the Puget Sound Naval Shipyard and Intermediate Maintenance Facility, in Bremerton, Washington, USA (Figure 1; Supplemental Data, Section 1 and Figures S1 and S2), in October 2012. The specific location for the field experiment was identified as the southwest corner of Pier 7, located at the shipyard's eastern end, where PCBs are contaminants of concern in surface sediment. The amendment, AquaGate + PAC (AquaGate), is a dense, clay, mineral aggregate coated with powdered activated carbon (particle diameter $\leq$74 μm; Supplemental Data, Section 2 and Figure S3 Figure S3). The AquaGate amendment was broadcast from a barge-mounted conveyor belt to the water surface. The AquaGate particle has a high specific gravity ($\sim$ equal to that of limestone at 2.5 $\times$ the density of water) and was observed during application to sink rapidly ($<$ 1 min) through the water column. A 5-cm layer of AquaGate was applied to achieve an estimated activated carbon dosage of 0.04 g activated carbon/g sediment dry weight ($\sim$ 4% by weight) in the top 10 cm of surface sediment (Supplemental Data, Section 2 and Figure S4). As shown in the Supplemental Data (Figure S5), the activated carbon coating of the AquaGate is designed to slough off the aggregate within hours after hydration, enabling the activated carbon particle to mix with surface sediments. The activated carbon remedy functions via sorption of available organic chemicals to activated carbon, not bulk dilution of the surface sediment with added amendment materials.

Postamendment sediment profile imagery surveys indicated a successful placement of the AquaGate amendment, and additional surveys confirmed stability of the amendment within

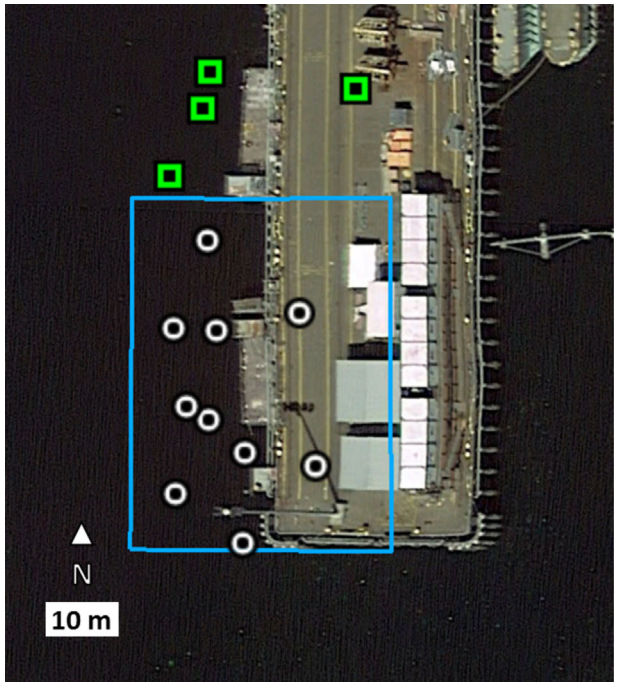

FIGURE 1: Sample station locations inside (white circles) and outside (green squares) the amendment area (blue outline) adjacent to and beneath Pier 7, Puget Sound Naval Shipyard and Intermediate Maintenance Facility, Bremerton, Washington, USA. (Image from Google Earth).

the placement area during the duration of the study (Supplemental Data, Section 2 and Figures S6–S10). Analysis of sediment core samples collected before the amendment (baseline) and at 0.5 month (mo) postamendment (Supplemental Data, Section 4 and Figure S12) confirmed the incorporation of activated carbon within the surface sediment because total organic carbon content of surface sediment increased from approximately 4 to 8% in the top 0 to 5 cm of sediment.

PCB availability measurement

The availability of PCBs in surface sediment was evaluated at baseline (2 mo preamendment) and 10, 21, and 33 mo postamendment using in situ exposures of organisms and passive samplers deployed at 10 stations located within the amendment area (Figure 1). Laboratory-provided *Nephtys caecoides* (polychaete worms) and *Macoma nasuta* (bent-nose clam) were housed in sediment ecotoxicity assessment rings (Zebra-Tech; Supplemental Data, Section 3 and Figure S13), an autonomous multichamber sampler used for in situ toxicity and bioaccumulation testing (Rosen et al. 2012; Burton et al. 2013; Rosen et al. 2017). Sediment ecotoxicity assessment rings were installed and retrieved by scuba divers so that organisms were exposed to approximately the top 15 cm of surface sediment for 14 d (Supplemental Data, Section 3). After retrieval of the sediment ecotoxicity assessment rings, *N. caecoides* and *M. nasuta* were recovered from the chambers by extruding chamber contents onto a 500-μm stainless steel sieve and sorting contents by hand. Organisms were allowed to depurate in clean seawater for 24 h. *Nephtys caecoides* (whole body) and *M. nasuta* (soft tissues) were homogenized, extracted, and analyzed for PCB congeners via US Environmental Protection Agency Method 8082A and for lipid content via a gravimetric approach (Honeycutt et al. 1995). Concentrations of PCBs in tissue were reported on a wet weight basis (ng/g wet wt) and normalized to a lipid weight basis (ng/g lipid wet wt) by dividing the concentration by lipid content (g lipid wet wt/g tissue wet wt) to account for differences in bioaccumulation potential caused by differential lipid contents of the organisms (Burkhard 2009). *Macoma nasuta* averaged 0.007 g lipid/g tissue wet weight (standard deviation [SD] = 0.003) and *N. caecoides* averaged 0.01 g lipid/g tissue wet weight (SD = 0.004).

Passive samplers were installed by scuba divers in the top 10 to 15 cm of surface sediment, co-located with the sediment ecotoxicity assessment rings (2 passive samplers were deployed at each of the amendment area stations; Figure 1). Each passive sampler consisted of a set of 12 to 16 solid-phase microextraction fibers (precleaned and spiked with rare PCB performance reference compounds) housed in a stainless steel mesh envelope (Supplemental Data, Section 6). Each fiber was 12.5 cm in length. After a 14-d exposure period, passive samplers were retrieved by scuba divers and stored at 4 °C until the solid-phase microextraction fibers could be cleaned with a moistened tissue and extracted in hexane. The 14-d period was not sufficient to achieve equilibrium for the PCB target analytes; thus nonequilibrium approaches using the performance reference compounds were used as described in Section 6 of the Supplemental Data. Extracts were analyzed for PCB congeners via US Environmental Protection Agency Method 8082A to provide concentrations of PCBs in the polydimethylsiloxane coating (sorptive phase) of the solid-phase microextraction fibers, which were utilized to calculate concentrations of freely dissolved PCBs (ng/L) based on techniques detailed in the Supplemental Data, Section 6.

For both tissue and passive sampling results, PCBs were evaluated on the basis of the sum of PCB congeners (total PCBs) as well as the sums of trichlorinated, tetrachlorinated, pentachlorinated, and hexachlorinated biphenyl homologues. Only values that indicated detections were used in summations (nondetects were assumed to be zero), and samples in which all congeners were below detection limits were excluded from statistical comparisons among the monitoring events. This resulted in a conservative approach with regard to estimating the efficacy of the amendment, and the conclusions of the present study would be no different if nondetect data in the postamendment events were included via substitution approaches (i.e., assuming a value of one-half of the detection limit for nondetect data). Statistical comparisons and data summaries were evaluated on a logarithmic scale using geometric means as measurements of central tendency because data varied more than one to 2 (or more) orders of magnitude. Trichlorinated, tetrachlorinated, pentachlorinated, and hexachlorinated biphenyl homologue groups represented 92 to 99% of the PCBs detected in tissues and passive samplers, and 82 to 84% of the PCBs detected in bulk sediment among the monitoring events. Less chlorinated biphenyls (monochlorinated and dichlorinated biphenyls) were only detected in 2 of 141 instances. Heptachlorinated, octachlorinated, nonachlorinated, and decachlorinated biphenyls comprised 1 to 8% of the PCBs in tissues and passive samplers; however, results were considered to be of higher uncertainty given that these congeners may not have reached a sufficient proportion of equilibrium during the limited 14-d exposures for the organisms and passive samplers. Inclusion of these congeners in the summation of PCBs would not have affected the overall conclusions of the present study.

Benthic invertebrate community evaluation

The benthic invertebrate community was evaluated in preamendment and postamendment monitoring events via benthic census of surface sediment samples collected at 10 stations located within the amendment area and at 4 stations to the north of the amendment area (Figure 1), and via sediment profile imagery surveys of benthic invertebrate community successional stages at 6 to 20 locations in the amendment area and at 20 to 24 locations to the north of and surrounding the amendment area (Supplemental Data, Section 3 and Figures S6–S8). Benthic census and sediment profile imagery surveys were conducted for the baseline event (2 mo preamendment) and 10, 21, and 33 mo postamendment, with timing in late July through early August (midsummer) to minimize seasonal variability in results from year to year. An additional sediment profile imagery survey was performed 0.5 mo postamendment (in October, mid-autumn) primarily for the purpose of evaluating the presence of the amendment.

Benthic census was enabled by scuba diver collection of 5 4.8-cm diameter surface sediment cores at each station. The top 15 cm of surface sediment retained from each of the 5 cores were combined on retrieval from the scuba divers and stored at 4 °C before and during shipment to the taxonomic laboratory, where they were preserved with formalin immediately on receipt. The approximate maximum storage time of the sediment (before sieving and formalin preservation) was 24 h, to minimize potential degradation of invertebrate tissues or predation within the samples. Preserved sediments were sieved on 1000- and 500-μm sieves, and benthic invertebrates retained on the sieves were identified to the lowest possible taxonomic level and enumerated. Census data were used to calculate 6 benthic metrics (Supplemental Data, Section 7).

Benthic successional stages were identified by visual inspection of sediment profile imagery obtained using an underwater digital camera system mounted to a reflective prism inserted up to 15 cm into the sediment surface (Rhoads and Germano 1982), as shown in Figure S9 of the Supplemental Data. Images depict a profile view of the top 5 to 15 cm of sediment (depending on penetration depth) and were evaluated visually for the presence of dense assemblages of near-surface polychaetes and/or the presence of subsurface feeding voids under the assumption that organism–sediment interactions in fine-grained sediments follow a predictable sequence of successional stages after a benthic disturbance (Rhoads and Boyer 1982; Rhoads and Germano 1982, 1986). Data were evaluated according to the proportion of sediment profile imagery stations that showed evidence of stage 3 communities, which are mature, equilibrium communities composed of deep-dwelling, head-down deposit feeders (Supplemental Data, Section 3).

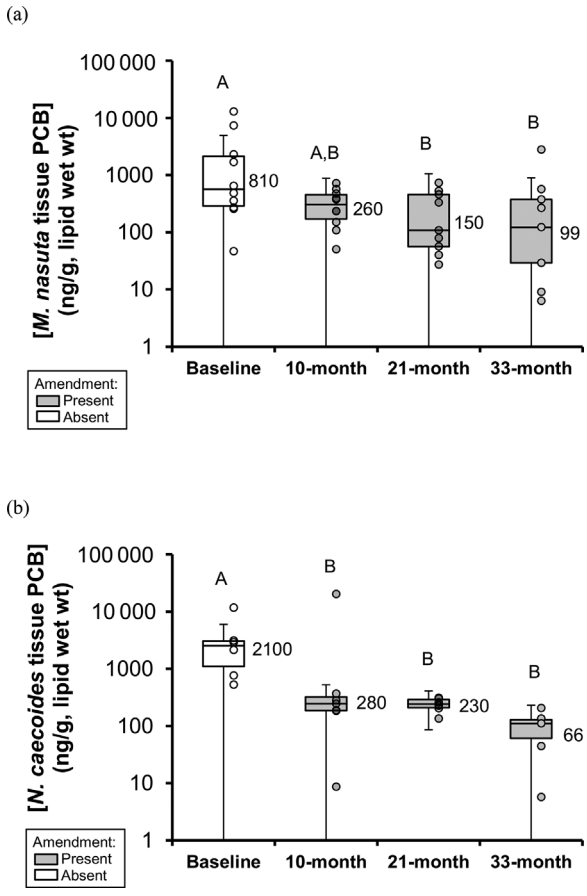

FIGURE 2: Concentrations of total polychlorinated biphenyls (PCBs; lipid-normalized, wet wt basis) in (a) *Macoma nasuta* and (b) *Nephtys caecoides* for the baseline and 3 postamendment monitoring events. Results are plotted as the median (horizontal bar), interquartile range (limits of boxes are 25th and 75th percentiles), 1.5 times the interquartile range (error bars), and individual data points (circles). The values shown to the right of each box indicate the geometric means. Events with the same letter in each plot are not significantly different ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Reductions in PCB availability as a result of the amendment

Concentrations of total PCBs in all 3 measures of PCB availability significantly decreased as a result of the activated carbon amendment (Figures 2 and 3). Concentrations of total PCBs in *M. nasuta* significantly decreased from the baseline characterization to the 21- and 33-mo monitoring events ($p < 0.05$; Figure 2a). This reflected a reduction in availability of 81 and 88%, respectively, as calculated using geometric means (Supplemental Data, Table S1). Concentrations at the 10-mo monitoring event indicated a 68% reduction in PCB availability from the baseline, which was not statistically different from the baseline. Postamendment concentrations of PCBs in *N.caecoides* were significantly lower ($p < 0.05$) from baseline at all monitoring events, with average reductions from the baseline of 87, 89, and 97%, for the 10-, 21-, and 33-mo events, respectively (recovery of *N. caecoides* was limited; see *Optimization of PCB availability measurement approaches* section). Postamendment concentrations of freely dissolved PCBs were also significantly lower ($p < 0.05$) from the baseline at all monitoring events, with average reductions of 88, 90, and 86% from baseline for the 10-, 21-, and 33-mo events, respectively. The average (± SD) percentage PCB availability decreases for the 3 availability measurements were 81 ± 11%, 87 ± 5%, and 90 ± 6% for the 10-, 21-, and 33-mo events, respectively (Supplemental Data, Table S1).

The approximate 80 to 90% decrease in hydrophobic organic chemical availability as a result of the 4% addition of activated carbon of this particle size (≤74 μm) is consistent with reductions in availability observed by other field and mesocosm experiments using similar application rates and activated carbon particle sizes (Beckingham and Ghosh 2011; Janssen et al. 2011; Beckingham et al. 2013; Kupryianchyk et al. 2013, 2015; Patmont et al. 2015; Thompson et al. 2016). In contrast to many of the field studies of activated carbon efficacy (Patmont et al. 2015), which have generally been conducted under relatively quiescent conditions, the present study showed that the decrease in PCB availability was sustained over a 33-mo period, despite being in a high-traffic, active harbor featuring a wide variety of surface vessels including tugboats, ships, and submarines that affected the area during the present study. The PCB availability data were supported by additional lines of evidence—including measurements of total organic carbon content in sediment and visual observations (via divers and sediment profile imagery survey) of the amendment over time—that indicated the activated carbon

amendment remained in place throughout the 33-mo evaluation period (Supplemental Data, Sections 3 and 4). In addition, as noted in previous studies with activated carbon sediment amendment (Ghosh et al. 2011; Kupryianchyk et al. 2015; Patmont et al. 2015), reduction in availability is primarily driven by the sorption of PCBs by activated carbon, not physical dilution of sediment with amendment or transformation of PCBs. This was confirmed via measurement of PCBs in surface sediments, which were not significantly different ($p > 0.05$) from the baseline geometric mean of 61 ng/g dry weight (Supplemental Data, Figure S11).

The activated carbon amendment was effective in reducing PCB availability within 10 mo or less (Figures 2 and 3). Empirical studies and models (Beckingham and Ghosh 2011; Cho et al. 2012; Choi et al. 2014a) with comparable activated carbon particle sizes to those used in the present study ($\leq$74 μm) indicate that the time scale needed for an 80 to 90% reduction in availability is expected to be on the order of magnitude of a few months for pentachlorinated and less chlorinated biphenyls, whereas hexachlorinated biphenyls may require longer periods (e.g., 1–2 yr). Because sorption kinetics are slowest for more hydrophobic organic compounds (Choi et al. 2014a, 2014b; Thompson et al. 2016), we evaluated the reductions in the availability on the basis of 4 PCB homologue groups (Figure 4). Concentration reductions varied by homologue for trichlorinated and hexachlorinated biphenyls in *M. nasuta* (Figure 4A). Concentrations of trichlorinated biphenyls did not differ significantly ($p < 0.05$) among the events, although concentrations of tetrachlorinated and pentachlorinated biphenyls decreased significantly ($p < 0.05$) from baseline to the 10-, 21-, and 33-mo events by an average reduction of 71 to 94%. A significant decrease in hexachlorinated biphenyls was observed from baseline to the 10-mo event; however, concentrations in the 21- and 33-mo events were not significantly different. As with *M. nasuta*, concentration reductions varied by homologues in *N. caecoides* (Figure 4B). Concentrations of trichlorinated biphenyls in *N. caecoides* did not differ significantly ($p < 0.05$) between the baseline and 10-mo event, although concentrations at the 21- and 33-mo events were significantly lower by an average reduction of 44 to 77%. Concentrations of tetrachlorinated and pentachlorinated biphenyls in *N. caecoides* decreased significantly ($p < 0.05$) from baseline to the 10-, 21-, and 33-mo events (average decreases ranged from 87–98%). Concentrations of hexachlorinated biphenyls decreased significantly ($p < 0.05$) from baseline to the 10- and 33-mo events (88 and 89%, respectively); nevertheless, decreases observed in the 21-mo event (79%) were not significant. Concentrations of freely dissolved tetrachlorinated and pentachlorinated biphenyls in surface sediment (Figure 4C) decreased significantly from the baseline event to the 10-, 21-, and 33-mo monitoring events by an average of 59 to 97%. Trichlorinated biphenyls were not detected above the approximate detection limit of 0.05 to 0.2 ng/L. Freely dissolved hexachlorinated biphenyls were significantly lower than baseline (82 and 92%) in the 10- and 21-mo events, and were not detected above an approximate detection limit of 0.002 to 0.01 ng/L in the 33-mo event.

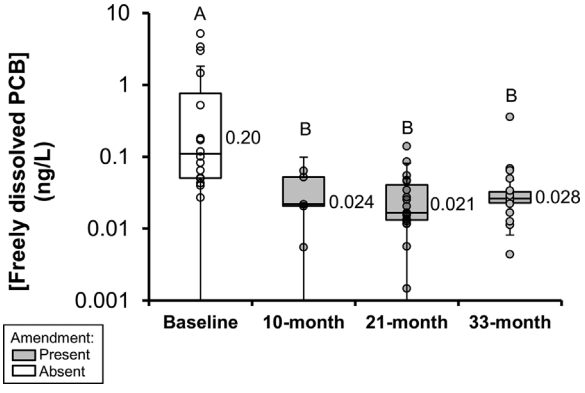

FIGURE 3: Concentrations of freely dissolved total polychlorinated biphenyls (PCBs) in surface sediment for the baseline and 3 postamendment monitoring events. Results are plotted as the median (horizontal bar), interquartile range (limits of boxes are 25th and 75th percentiles), 1.5 times the interquartile range (error bars), and individual data points (circles). The values to the right of each box denote the geometric means. Events with the same letter in each plot are not significantly different ($\alpha = 0.05$).

Overall, the relative contribution of total PCB homologues in tissues of both organisms appears to have stabilized by the 21- and 33-mo events at an approximate PCB homologue profile of 5 to 10% trichlorinated, 10 to 20% tetrachlorinated, 40 to 50% pentachlorinated, and 30 to 50% hexachlorinated biphenyls (Figure 4A and B). The homologue profile evident in these 2 events appears to have shifted slightly to a more chlorinated profile as a result of the amendment because the baseline profile was proportionately higher in tetrachlorinated and pentachlorinated biphenyls (20–30% and 50–60% of total PCBs, respectively) and lower in hexachlorinated biphenyls (10–20% of total PCBs).

Among the homologue groups, trichlorinated and hexachlorinated biphenyls indicated mixed results with respect to reductions in availability compared with the less hydrophobic tetrachlorinated and pentachlorinated biphenyls. Trichlorinated biphenyls in both *N. caecoides* and *M. nasuta* were very low in baseline and postremedy events and data were affected by a high proportion of nondetects. Freely dissolved trichlorinated biphenyls were not detected. Hexachlorinated biphenyls in *N. caecoides* (Figure 4B) indicated slightly lower levels of reduction from the baseline in the 21- and 33-mo events, with an 85% reduction for hexachlorinated biphenyls compared with 92 and 96% reductions for tetrachlorinated and pentachlorinated biphenyls, respectively. Freely dissolved hexachlorinated biphenyls displayed slightly higher average (90% or more) reduction in hexachlorinated biphenyls compared with *N. caecoides*. In contrast, hexachlorinated biphenyls in *M. nasuta* (Figure 4A) did not reflect a significant difference in availability at the final 33-mo event compared with baseline.

It is expected that the availability of the more hydrophobic hexachlorinated biphenyls may have indicated a slower response to the amendment in contrast to the less hydrophobic PCBs. For example, Choi et al. (2014b) found that a hexachlorinated PCB required a longer time period (a factor of $\sim$ 5 to 10 times the time period) to reach 90% reduction in PCB availability in an activated carbon–amended sediment, as compared with a

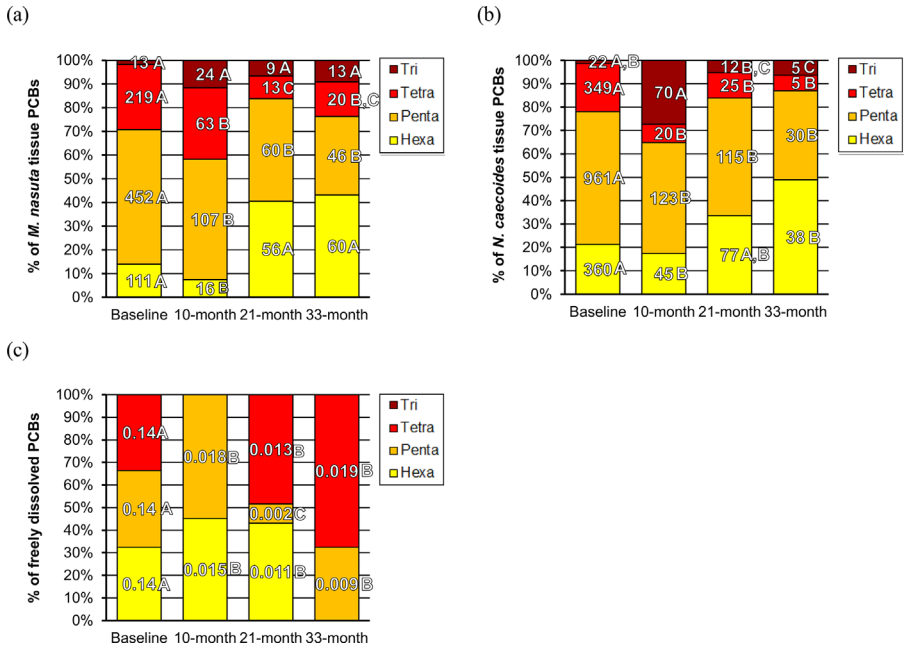

FIGURE 4: Distributions of trichlorinated, tetrachlorinated, pentachlorinated, and hexachlorinated biphenyl homologues in (**a**) *Macoma nasuta*, (**b**) *Nephtys caecoides*, and (**c**) freely dissolved measurements. Numerical labels in the center of each homologue proportion identify the geometric mean of the lipid-normalized concentration in tissue (ng/g lipid wet wt) or the geometric mean of the concentration of freely dissolved polychlorinated biphenyls (PCBs) in surface sediment (ng/L). Means with the same letter in each plot (proceeding horizontally for each homologue group) are not significantly different among the events ($\alpha = 0.05$). For example, the mean concentration of pentachlorinated biphenyls in *M. nasuta* for the baseline is labeled with an A, whereas the means for the other events are labeled with a B, showing that the baseline was statistically different from the postamendment events and that the postamendment events were not statistically different from one another.

pentachlorinated PCB. However, in the present study, hexachlorinated biphenyls were only a small proportion of the total available PCBs at the baseline (~ 10–30% of available PCBs). The approximate 2- to 3-yr period needed for availability reduction to be fully or mostly realized is reasonable, considering the rapid (i.e., ≤10 mo) time period needed for reductions in the tetrachlorinated and pentachlorinated biphenyls that comprised approximately 70 to 80% of the available PCBs. Further evaluation of the kinetics of the reduction of PCBs as a result of activated carbon amendment would be helpful because kinetics are influenced by activated carbon particle size (smaller particle reaching equilibrium more quickly; Choi et al. 2014a, 2014b). This information would be especially useful for cases in which larger particles of activated carbon are used (e.g., 200–1000 μm), compounds more hydrophobic than the PCB homologues focused on in this evaluation are targeted for amendment, or the time scale of several weeks to months is relevant to site-specific goals.

It is notable that at the final 33-mo event, the levels of total PCB availability were below conservative risk-based screening and ambient levels of PCBs in aquatic systems. For example, the final geometric mean concentrations in tissue on a wet weight lipid basis (99 ng/g wet wt for *M. nasuta* and 66 ng/g wet wt for *N. caecoides*; Figure 2) were below target tissue PCB levels for protection of direct acute toxicity to aquatic life (1400 ng/g lipid wt; US Army Corps of Engineers et al., 2009). The geometric mean concentrations of freely dissolved PCBs in surface sediment in the 33-mo event (0.028 ng/L) were also several orders of magnitude lower than the 4090 ng/L median lethal concentration for aquatic invertebrates and other more conservative, no-effect thresholds identified by Finkelstein et al. (2017), confirming that PCB exposures are not expected to cause direct toxicity to benthic invertebrates. In terms of potential risks to higher trophic levels, PCB availability was also below screening thresholds or contaminated site management levels for wildlife and human health risk considerations. For example, the final geometric mean concentrations in *M. nasuta* tissue on a wet weight basis (0.37 ng/g wet wt) were also below a nonurban background value of 0.42 ng/g wet weight for clams derived from a nearby superfund site located in the Seattle, Washington, US Environmental Protection Agency area (2014). In addition, the geometric mean concentrations of freely dissolved PCBs in surface sediment in the 33-mo event (0.028 ng/L) were below even the US Environmental Protection Agency human health-based National Recommended Water Quality Criteria for PCBs (0.064 ng/L; US Environmental Protection Agency, 2017).

Optimization of PCB availability measurement approaches

Although all 3 PCB availability measurements indicated 80 to 90% reductions from the baseline as a result of the amendment, biological differences in the test organisms may explain the slightly lower availability decrease indicated by *M. nasuta*. *Macoma nasuta* is a facultative filter feeder that may siphon water from surface water (in addition to sediment porewater); thus its exposure is derived from both surface water and benthic sources. The US Army Corps of Engineers (2017) also noted that

in experiments with sand and activated carbon amendments, decreases in PCB concentrations of infaunal organisms as a result of sediment amendments were more readily observed compared with those of bivalves. Moreover, in controlled studies that evaluated overlying water and sediment exposures to various organisms separately, the US Army Corps of Engineers (2017) found that a bivalve species accumulated approximately 10 to 20 times more overlying water-derived PCBs (PCB-24 and PCB-104) relative to a polychaete species exposed to the same conditions. It is likely that surface water could have served as a partial source of PCBs to *M. nasuta*; and it is unlikely that the amendment could completely reduce this exposure because surface water–associated PCBs could originate from local unamended Pier 7 area sediments (at most, stations were within ~ 15 m of unamended sediment) or other sources that affect available PCBs in surface water. Thus a potentially minor but constant source of PCBs from the water column could dampen or obscure a strict assessment of the effectiveness of an activated carbon amendment at some contaminated sediment sites. Hence, although bivalves such as *M. nasuta* provide useful information and signal a reduction in PCB availability caused by the amendment, in limited-scope evaluations or situations in which significant, uncontrolled surface water sources may be present, use of an infaunal deposit feeder (e.g., polychaete, oligochaete, or larval infaunal arthropod) likely supplies a more relevant measurement of the effect of the sediment amendment on benthic sources of contaminants.

The in situ passive sampling measurements of freely dissolved PCBs in surface sediment reinforced observations utilizing the biological measurements of in situ PCB availability. As noted in Figure 3, passive sampling provided an additional line of evidence regarding PCB availability, supplying assurance of obtaining PCB availability measurements at all of the stations regardless of the survival or recovery of the organisms deployed in the bioaccumulation evaluations. For example, only 60% of the 40 *N. caecoides* measurements (10 stations; 4 monitoring events) were successful as a result of complications with low organism recovery (caused by potential escape and other logistical complications; Supplemental Data, Section 5). In contrast, 95% of *M. nasuta* measurements were possible, although losses of organisms were still observed in individual stations. Moreover, 100% of the 80 passive samplers deployed during the present study were recovered, and the samplers required much less logistical support than was needed for the biological measurements.

Effects of the amendment on the benthic community

Benthic invertebrate census metrics (Supplemental Data, Section 7) were examined among the 4 monitoring events within the amended area to investigate potential differences as a result of the amendment; and metrics in the unamended area were also evaluated for potential disparities because of ecological shifts in the study area over time. There were no statistically significant dissimilarities in any of the 6 benthic metrics among the 4 monitoring events ($p > 0.05$) in either the amended or unamended areas (Figure 5). In general, abundance, diversity, and evenness for the amended stations suggested similar or healthier benthic conditions than those found at a benthic census station with similar water depth and sediment texture characteristics monitored within the Puget Sound Ambient Monitoring Program (Washington State Department of Ecology, 2009). However, the Swartz Dominance Index and the richness values in the amended and unamended stations were approximately 40 and 75% lower, respectively, signaling that the Pier 7 benthic communities (in both the amended and unamended areas) were generally dominated by fewer taxa. Disparities between the amended and unamended conditions were not observed using these 2 indices.

It should be noted that the results for the 6 benthic metrics indicated that statistical differences among the events could not be detected (Figure 5), not necessarily that there were no differences. Given the 10 samples per event in the amended area, a post hoc statistical power analysis (Sokal and Rohlf 1995) suggested that the data for the benthic invertebrate census metrics (Figure 5) would be able to detect an average approximate 50% (or greater) difference in metrics between the baseline and postamendment monitoring events. For the least variable benthic metric (evenness, Figure 5D) an approximate 30% (or greater) decrease from baseline could have been detected with the data from the amended area. In contrast, for the most variable benthic metric (abundance, Figure 5A) only an approximate 70% (or greater) decrease from baseline could have been detected. The lack of detectable, ecologically significant level of benthic impairment for the present study (more than ecologically significant thresholds of ~ 30 to 70%) is consistent with observations of many laboratory, mesocosm, and field studies that have analyzed the responses of individuals and benthic communities to activated carbon. In general, these studies have found that adverse effects are not expected for activated carbon dosages below approximately 5% by weight in surface sediment (Rackowska et al. 2012; Janssen and Beckingham 2013; Kupryianchyk et al. 2015; Patmont et al. 2015).

Results of the sediment profile imagery surveys conducted within and adjacent to the amended area (Supplemental Data, Figures S6–S8) also showed that the benthic community was not impaired as a result of the activated carbon amendment. Slight impairment in both unamended and amended areas was noted in the 10- and 33-mo surveys, although the results indicate that impairment was not because of the activated carbon amendment. Results showed that less than 80% of the locations surveyed during the 10-mo (both amended and unamended areas) and 33-mo events (amended area) exhibited a mature, equilibrium stage 3 benthic community composed of deep-dwelling, head-down deposit feeders (Figure 6). Given that 88% (95% confidence interval [CI] of 76–100%) of the locations exhibited stage 3 benthic communities in the amended area at the 21-mo event, it is unlikely that the lower proportion of stage 3 observations at the 10- and 33-mo events were caused by the amendment. Rather, the sediment profile imagery data suggest that the lower proportion of stage 3 benthic communities observed at the 10- and 33-mo events appear to reflect local, year-to-year ecological variability that could be caused by a wide

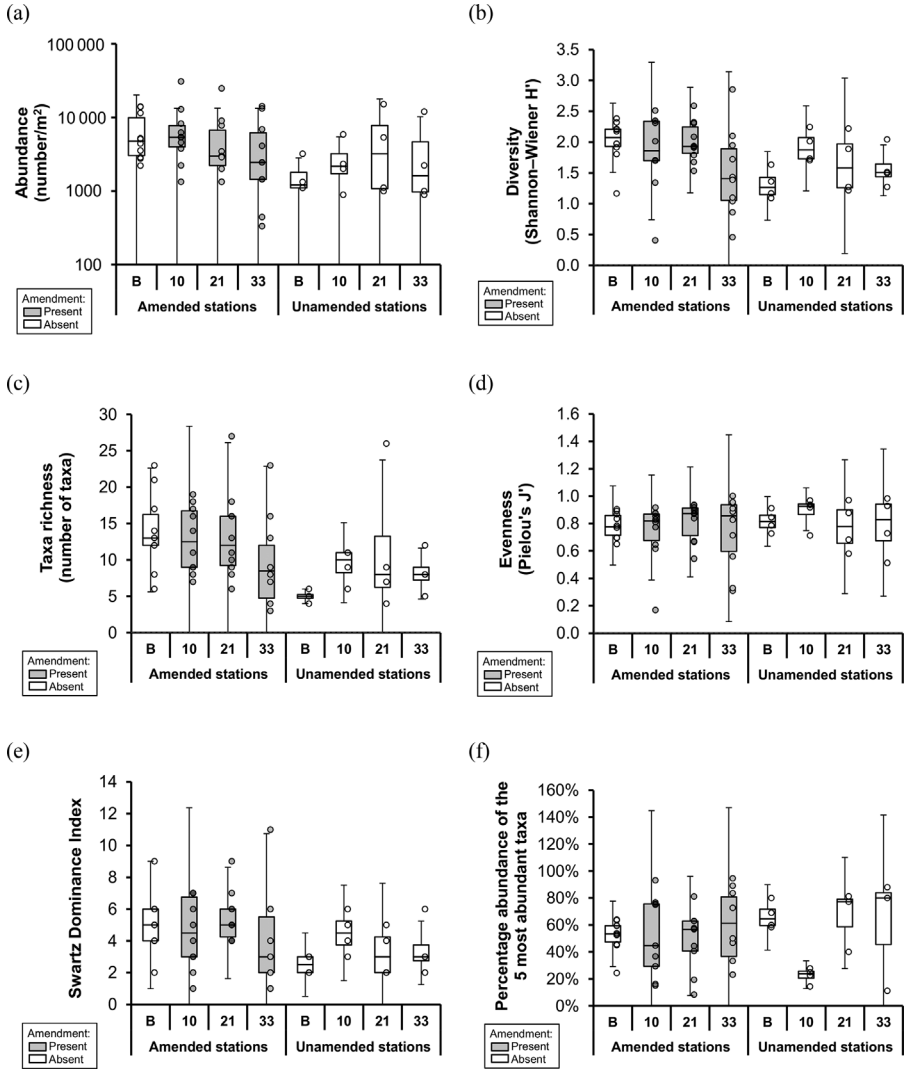

FIGURE 5: Benthic invertebrate census metrics for amended and unamended (reference) stations measured before the amendment was placed at B (baseline) and 10, 21, and 33 mo after amendment. Results are plotted as the median (horizontal bar), interquartile range (limits of boxes are 25th and 75th percentiles), 1.5 times the interquartile range (error bars), and individual data points (circles).

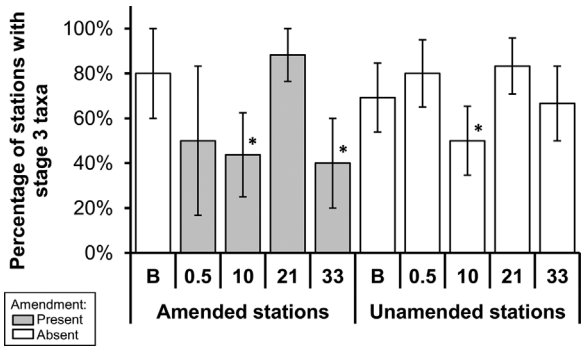

FIGURE 6: The percentage of sediment profile imagery stations displaying benthic invertebrate community successional stage 3 in amended and unamended (reference) areas, as measured before the amendment was placed at B (baseline) and 0.5, 10, 21, and 33 mo after amendment. Results are plotted as the percentage of stations (95% confidence interval). For columns labeled with an *, the percentage is significantly less than 80% ($\alpha = 0.05$).

variety of biotic and abiotic variations (pathogens affecting certain categories of invertebrates, water temperature, salinity, etc.). The percentage of locations exhibiting a stage 3 benthic community was significantly reduced during the 10-mo event in the unamended area (50% [95% CI of 35–65%]) and nearly significantly ($p = 0.05$) reduced during the 33-mo event in the unamended area (67% [95% CI of 50–83%]). Hence local conditions unrelated to the amendment were likely affecting benthic successional stages in both the unamended and amended areas before the 10- and 33-mo events. Overall, the sediment profile imagery results confirm the conclusion reached by the benthic census metrics (Figure 6) regarding the absence of an ecologically significant adverse effect of the activated carbon amendment on the benthic invertebrate community.

CONCLUSIONS

The present study successfully evaluated the performance of an activated carbon amendment in an active harbor area

throughout a multiyear monitoring period. The results showed a sustained reduction in PCB availability during a 33-mo evaluation period as a result of a 4% (by weight) addition of activated carbon (particle size $\leq$74 μm) into the uppermost approximately 10 cm of surface sediment. Polychlorinated biphenyl availability was reduced significantly before the first monitoring event (i.e., within 10 mo postamendment), although minor components of the PCB mixture (more hydrophobic PCBs) did not indicate the most significant reductions in availability until the 21- and 33-mo monitoring events. At the final 33-mo monitoring event, an average ($\pm$ SD) reduction of 90 $\pm$ 6% was found among the 3 PCB availability measurement approaches, with PCB availability levels that would meet typical risk-based screening or management expectations for surface sediments at many contaminated sediment sites. This achievement is especially significant given that traditional sediment remedies (e.g., dredging and capping) would be challenging or infeasible for this location, which includes an area adjacent to/beneath a pier and within a vessel berth with specific water-depth requirements. The performance of the amendment shown in the present study will ideally encourage the consideration of activated carbon amendments for similar logistically challenging settings in contaminated sediment sites and as an alternative to traditional sediment remedies.

The monitoring tools employed in the present study could be considered for contaminated site monitoring programs to examine the performance of activated carbon amendments to reduce the availability of organic compounds in surface sediment. Measuring the reduction in PCB availability from preamendment to postamendment is likely a relevant effort for many programs, given the wide variety of site- and application-specific variables that may affect the performance of activated carbon amendments (e.g., dosage rate, source of carbon, carbon particle size, application method, and hydrodynamic conditions). Use of organisms (especially infaunal deposit feeders, which likely better reflect amendment efficacy) and/or passive samplers to measure freely dissolved concentrations of PCBs in sediment are effective devices for evaluating availability, and both approaches can be adapted for analysis within most site-specific, remedial management frameworks. At some sites, multiple measurements of availability (biological and passive sampling) may be warranted; nevertheless, as activated carbon amendments are more widely applied and as confidence in the ability of passive sampling to predict biological uptake (Greenberg et al. 2014; Mayer et al. 2014; Joyce et al. 2016) builds among stakeholders, routine monitoring may focus more on the utilization of passive sampling because of its logistical simplicity and cost effectiveness.

In terms of timing measurements to evaluate activated carbon performance, the present study suggests that significant, order-of-magnitude reductions in organic compound availability can be observed as quickly as several months to a year after activated carbon amendment addition. At most sites, a postamendment monitoring event targeted for the approximate 1-yr postamendment time frame should allow sufficient time for absorption of the organic compound to the activated carbon, as well as for site-specific hydrodynamic and biological processes to physically integrate the amendment with surface sediment. The present study and others reviewed in Kupryianchyk et al. (2015) and Patmont et al. (2015) have shown that performance of activated carbon continues to improve with longer time periods (~3 yr). Additional monitoring of activated carbon pilot studies should continue to evaluate the performance on longer term monitoring time scales such as 5 and 10 yr postamendment, which are more commonly used in regulatory monitoring programs.

Benthic invertebrate census and sediment profile imagery surveys did not indicate significant differences in benthic community ecological metrics among the preamendment and 3 postamendment monitoring events, confirming the findings of most (i.e., ~ 80%; Janssen and Beckingham 2013) scientific studies proposing that adverse effects on benthic invertebrates are not expected as a result of activated carbon amendments, especially when activated carbon dosage rates remain below approximately 5% by weight in sediment (Rackowska et al. 2012; Janssen and Beckingham 2013; Kupryianchyk et al. 2015; Patmont et al. 2015). Site heterogeneity, local physical and hydrodynamic conditions, and year-to-year ecological variations were likely the driving forces affecting benthic community health in the present study area. Even if slight adverse effects caused by the activated carbon are possible at sites, the reduction of organic contaminant available from potentially toxic levels likely results in a net positive outcome on benthic communities, adding to the beneficial reductions in chemical exposures to wildlife and human consumers higher in the food web (Ghosh et al. 2011; Patmont et al. 2015).

It should be mentioned that other sediment remedy approaches (i.e., dredging, capping, and enhanced natural recovery) also contribute to adverse benthic impacts (Merritt et al. 2010). Benthic invertebrate community health is rarely analyzed as a part of routine postremedy monitoring unless the goal remedy itself is meant to reduce chemical-induced adverse effects on benthic invertebrates. In specialized cases in which postremedy benthic monitoring is of concern, monitoring programs should consider preremedy (baseline) measurements and nearby (reference area) measurements to account for the considerable variability inherent in benthic invertebrate data because year-to-year variability can be significant. Nonetheless, even with sampling programs that include more than one postremedy monitoring event and dozens of samples, only larger magnitude effects (e.g., average of 50% adverse effect levels in the present study) are likely to be possible to observe with statistical certainty. Accordingly, the need for and complication of benthic invertebrate sampling should be weighed against site-specific concerns and low likelihood of adverse effects for typical activated carbon remedies. At most contaminated sediment sites that are amended with low dosages of activated carbon, an ecological examination of the effects of activated carbon on the benthic community is likely not warranted.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.4121.

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Data availability—Data, associated metadata, and calculation tools are available from the corresponding author (jconder@geosyntec.com).

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