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Long-Term Stability and Efficacy of Historic Activated Carbon (AC) Deployments at Diverse Freshwater and Marine Remediation Sites

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Environmental Laboratory

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Long-Term Stability and Efficacy of Historic Activated Carbon (AC) Deployments at Diverse Freshwater and Marine Remediation Sites

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Final report

Abstract

A number of sites around the United States have used activated carbon (AC) amendments to remedy contaminated sediments. Variation in site-specific characteristics likely influences the long-term fate and efficacy of AC treatment. The long-term effectiveness of an AC amendment to sediment is largely unknown, as the field performance has not been monitored for more than three years. As a consequence, the focus of this research effort was to evaluate AC's long-term (6–10 yr) performance. These assessments were performed at two pilot-scale demonstration sites, Grasse River, Massena, New York and Canal Creek, Aberdeen Proving Ground (APG), Aberdeen, Maryland, representing two distinct physical environments. Sediment core samples were collected after 6 and 10 years of remedy implementation at APG and Grasse River, respectively. Core samples were collected and sectioned to determine the current vertical distribution and persistence of AC in the field. The concentration profile of polychlorinated biphenyls (PCBs) in sediment pore water with depth was measured using passive sampling. Sediment samples from the untreated and AC-treated zones were also assessed for bioaccumulation in benthic organisms.

The data collected enabled comparison of AC distribution, PCB concentrations, and bioaccumulation measured over the short- and long-term (months to years).

Contents

Report Documentation Page

Figures and Tables

Figures

Tables

Preface

This study was conducted for the Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) and funded the Engineer Research and Development Center (ERDC), the University of Maryland Baltimore County, and Exponent. to conduct work under ESTCP Project Number ER-2001580-PR. The technical monitor was Dr. David Moore.

The work was performed by the Environmental Risk Branch of the Environmental Processes Division, US Army Engineer Research and Development Center, Environmental Laboratory (ERDC-EL). At the time of publication, B.C. James Lindsay was Chief; D.C. Warren Lorentz Name was Chief; and T.D. Al Cofrancesco was the Technical Director for Technical Domain Name. The Deputy Director of ERDC-EL was Dr. Jack Davis and the Director was Dr. Edmond Russo.

The work would not have been possible without the cooperation and support from many individuals at the US Army's Aberdeen Proving Ground and Alcoa (Massena, New York).

The Commander of ERDC was COL Teresa A. Schlosser and the Director was Dr. David W. Pittman.

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Portions of this report have been modified and reprinted from Charles Menzie, Bennett Amos, Susan Kane Driscoll, Upal Ghosh, and Cynthia Gilmour. 2016. *Evaluating the Efficacy of a Low-Impact Delivery System for In Situ Treatment of Sediments Contaminated with Methylmercury and Other Hydrophobic Chemicals*. ESTCP Project ER-200835. Alexandria, VA: Environmental Security Technology Certification Program. https://serdp-estcp.org/content/download/39419/379369/file /Final%20Report%20ER200835%20February%202016.pdf. Public Domain.

Executive Summary

Introduction and objectives

Aquatic sediments serve as the ultimate repository for past and ongoing discharges of hydrophobic organic compounds (HOCs) such as PCBs, mercury, and other select contaminants. Sediment HOCs can be taken up by pelagic or benthic organisms through ingestion and absorption across dermal/respiratory surfaces and subsequently transferred via aquatic food webs to higher organisms and humans. For both of these pathways (that is, ingestion and absorption), the uptake depends on the bioavailability of contaminants in sediment (Luthy et al. 1997; National Research Council (NRC) 2003). Work in the last two decades has demonstrated that black carbon (BC), including soot, coal, and charcoal, strongly bind HOCs, and the presence of BC in sediments (both natural and anthropogenic) reduces bioaccumulation, often by an order of magnitude or more compared to natural organic matter (Luthy et al. 1997; Ghosh et al. 2000; Lohmann, Macfarlane, and Gschwend 2005). Contaminant sequestration in native sediments can be greatly enhanced by the addition of clean, manufactured BC materials such as activated carbon (AC) (Ghosh et al. 2011).

Despite multiple demonstrations in the field and full-scale AC applications, regulators and the parties conducting sediment clean-up at Department of Defense (DoD) and non-DoD contaminated sites continue to question the long-term efficacy of AC as an approach to in situ remediation. Long-term efficacy and permanence is one of the nine National Contingency Plan criteria (USEPA 2005) used in the evaluation and selection of remedies for contaminated sediment sites. One issue of concern in comparing dredging/removal to an in situ remediation strategy, such as AC treatment, is that in situ remediation is more vulnerable to changes in conditions that can compromise the performance of the remedy over time. The present study was designed to collect data from two pilot-scale studies, Grasse River, Massena, New York and Canal Creek, Aberdeen Proving Ground (APG), Aberdeen, Maryland, to inform an understanding of the long-term effectiveness and success of in situ remediation using AC.

The overall objective of this study was to assess the long-term (6–10 yr) performance of AC at multiple sites and determine the relative importance

of physical processes affecting long-term efficacy. Specifically, the individual objectives comprised the following:

- Determine the mass of AC present and its vertical distribution within the sediment following the initial introduction.
- Determine if the AC still retained its functional efficacy (PCB sorption, reduced bioavailability).
- Apply this information to develop lines of evidence for making conclusions on the long-term efficacy of in situ remediation using AC.
- Disseminate the study results to inform sediment remediation guidance.

The data collected enabled comparison of AC distribution, PCB concentrations, and bioaccumulation measured over the short and long term (months to years).

Technology description

Researchers have taken a range of technological approaches to amending AC into sediments. Early technological attempts involved placement of a slurry of AC on the sediment bed, with or without mechanical mixing into a target zone of surficial sediments. Several early pilot-scale studies, including the ones performed in Hunters Point, California (Cho et al. 2009) and in Grasse River, New York (Beckingham and Ghosh 2011), used this approach. AC amendment works best when the particle size is small, which allows more efficient mass transfer of the pollutants from the sediment to the AC (Zimmerman et al. 2005). The main challenge with direct application of an AC slurry underwater is the potential loss of fine-grained AC immediately after placement. Another challenge is the need for containment using a metal enclosure, as done in the Grasse River study, which adds to the cost of deployment. Subsequent technological advancement led to the development of pelletized AC large enough to fall through the water column without breaking up. These AC pellets slowly disintegrate in the sediments, releasing fine-grained AC over time for natural mixing within the bioactive zone of sediments (Ghosh et al. 2010). At the Canal Creek pilot study site, two commercially available technologies designed to deliver AC in a pelletized form into sediments were evaluated: SediMite, produced and marketed by Sediment Solutions, and AquaGate, manufactured and marketed by AquaBlok. In the Grasse River pilot study, mixed and layered carbon treatments were evaluated. In the mixed treatment, a tiller-like device mechanically mixed bituminous

coal–based AC (Carbsorb, Calgon Carbon) into surface sediments, while in the layered treatment a coconut shell–based AC (055C-CNS-V000, Calgon Carbon) was layered by broadcasting of the material over the water surface and allowing it to settle onto the sediment surface and mix into the sediments via natural processes (for example, bioturbation). Data collected at each of the demonstration sites enabled a comparison of AC distribution, PCB concentrations, and bioaccumulation measured over the short and long term under differing hydrologic regimes, AC amendment types, and application techniques.

Performance and cost assessment

A summary of findings from long-term assessment of the two pilot studies are provided below.*Grasse River Pilot Study*. The depth profile of AC in sediment cores measured in the present study, shown in the first figure below, was compared with historic data from the first three years of monitoring (Beckingham and Ghosh 2011). In the 10-year post-application samples collected as part of the present study, there was a pronounced change in the AC profile, where AC is seen primarily in the two deepest core sections (15–22.5 cm[1] and 22.5–30 cm) compared to the <15 cm during the initial three years of monitoring. The AC was stable in the flowing river environment when placed on the surface sediments without initial mechanical mixing and also when mixed into the sediments. The 10-year post-treatment assessment revealed that the Grasse River site had a sediment deposition rate of close to 2 cm/yr, which led to the burial of the AC treatment. The greatest impact of AC amendment is seen in the two lower sections, where most of the AC was present in 2016, as shown in the second graph below. The percent reduction in pore water PCB in these two sections was 96%–98% for both the mixed treatment area (MTA) and unmixed treatment area (UTA) and was similar to the reductions observed in the first three years after remedy. Therefore, the AC treatment continues to be effective after 10 years in reducing pore water PCB concentration in sediments. In addition to the deeper layer where most of the AC is present, the surface sediment layer also shows reductions in pore water PCB concentrations as shown in the inset table in figure ES-2. It is

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1. For a full list of the spelled-out forms of the units of measure used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 248–52, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

likely that the reductions of pore water PCB at depth is reducing the recontamination of the cleaner new deposits. Bioaccumulation studies using core sections of the AC-treated zone showed a greater reduction in PCB uptake in worms (84%) in the UTA site compared to the MTA site (56%). The greater effectiveness of the UTA site is likely due to a higher concentration of AC (6.8%) present in a narrower zone of 15–22.5 cm in sediments compared to a wider AC distribution in the deeper sediments of the MTA site, resulting in a much lower AC content in the 15–22.5 cm zone of 3.2%. Overall, the AC layer remained functional in reducing pore water PCB concentrations in the sediments and was effective at reducing accumulation in worms even after 10 years in the field.

Percentage black carbon (BC) measured in sediment core sections from Grasse River activated carbon (AC) pilot study collected 10 years post treatment. (BG: background site; MTA: mixed treatment area; UTA: unmixed treatment area).

% recovery AC after 10 years

MTA: 95%
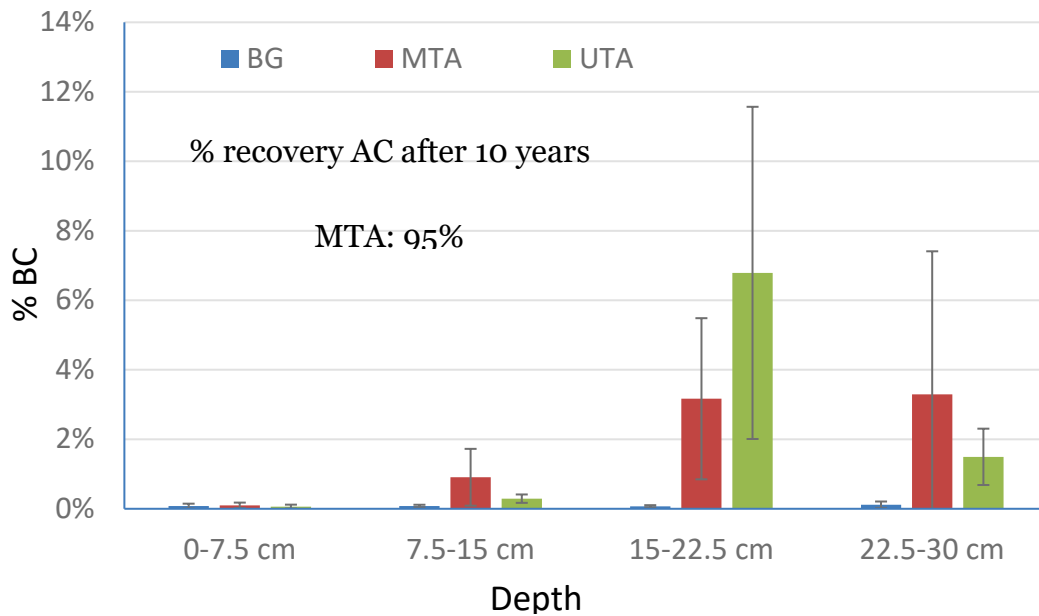
PCB concentration in sediment pore water by depth in Canal Creek Pilot demonstration study treatments.

% reduction compared to BG		
	MTA	UTA
0-7.5 cm	64	24
7.5-15 cm	80	73
15-22.5 cm	98	98
22.5-30 cm	98	96
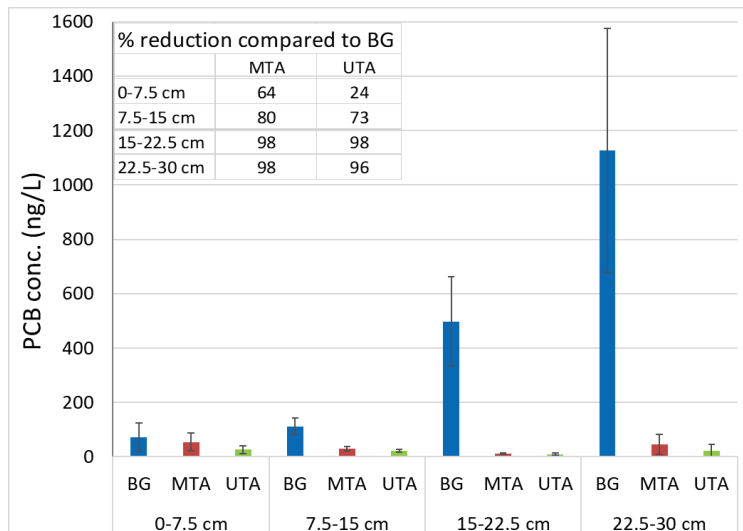
Canal Creek Pilot Study. The Canal Creek pilot study provided a very different hydrodynamic environment, within a tidal wetland, than the Grasse River study. Deposition of new sediment was much lower compared to Grasse River and was calculated to be about 1/3 cm/yr. This slow deposition rate resulted in a shallower penetration of the applied AC

material into sediments in Canal Creek than at Grasse River. For all AC treatments, the highest abundance of AC was found in the 2–5 cm layer after six years in the field. In this active hydrodynamic environment, AC placed using three different approaches (SediMite, AquaGate, and AC slurry) was found to be stable with near complete recovery of the applied dose of AC for all treatments. All AC treatments at Canal Creek continue to reduce pore water PCB concentrations six years after application and were likely effective in reducing PCB migration to the depositing surface layer of sediment. Pore water PCB concentrations measured in intact cores in the laboratory were greatly reduced in the treated plots compared to the untreated control plots at every depth, as shown in the first figure below. This was particularly notable in the treatments that included AC (Sedimite, AquaGate, and AC slurry) where the pore water PCB concentrations in the surface 0–2 cm sediments were 99% lower relative to the untreated control. The total pore water PCB concentrations in the 0–2 cm surficial sediments were 16 ng/L in the control site compared to 1.8 ng/L in the soil cover treatment, 0.4 ng/L in the AquaGate treatment, 0.01 ng/L in the SediMite treatment, and 0.06 ng/L in the AC slurry treatment. Reduced pore water concentrations in the treatment zone, also occurs in most of the in situ measurements except for the AquaGate plots, as shown in the second figure below. However, the pore water concentrations measured in situ are generally higher than those measured ex situ in the treatment zones. It is likely that the ex situ measurement with static water conditions is not able to capture the effect of groundwater movement in a tidally active site. The accumulation of total PCBs in worms was lower in all the treatment plots compared to the bioaccumulation in the untreated plot.

In-situ measured PCB concentrations in sediment pore water (from intact core samples). Samples were collected from the Canal Creek pilot study after six years of application of treatment amendments.
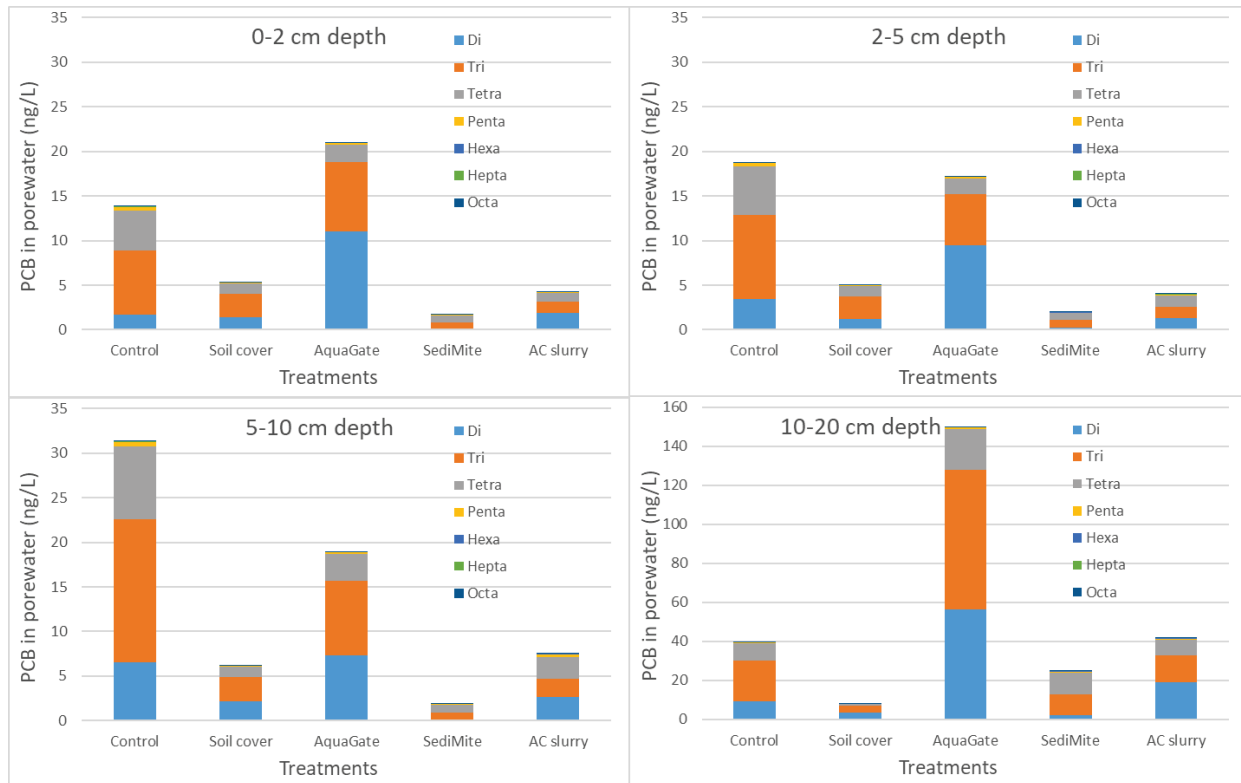
A cost assessment was not performed in this long-term monitoring study. Detailed cost assessments of the remedy implementation for the various treatments are available in the original Environmental Security Technology Certification Program (ESTCP) project final reports (Menzie et al. 2016; Ruiz et al. 2016).

Overall, the long-term monitoring at the two pilot-scale studies revealed that AC is stable in the sediment environment at two very distinct sites (that is, vegetated estuarine wetlands [Canal Creek, Maryland] and a riverine system [Grasse River, New York]) with different AC amendments deployed using different application technologies. Results from the present study provide the following key insights into the long-term performance of AC amendment to river sediments:

• AC applied directly into sediments is stable in a slow-flowing river system and could be found at or above target levels after 10 years in the field.

- AC applied on surface sediments using three different approaches was found to be stable in a tidal wetland environment after 6 years in the field.
- Deposition of new, cleaner sediments over time buried the AC-treated zone of sediments, which now functions as a barrier layer between the shallower, cleaner sediments and deeper, more contaminated sediments.
- The depth of penetration of the AC layer is a function of site characteristics. A higher rate of burial and mixing is observed in the river site compare to the tidal wetland.
- AC amended to sediments continues to reduce pore water PCB concentrations within the zone of application.
- Natural attenuation due to clean sediment deposition is high at Grasse River, which has resulted in a nearly one order of magnitude reduction in surface sediment PCB concentration over 10 years.
- Pore water PCB concentrations continue to be reduced in the zone where AC was found in each of the treatments.
- The presence of AC in sediments continues to reduce PCB bioavailability to benthic organisms.
- Initial mechanical mixing in the MTA plot resulted in a more diffuse layer of AC over time, as additional natural mixing spread out the AC through the depth. This finding suggests that the initial mechanical mixing may not be necessary for sites where natural mixing is anticipated.

Implementation issues

The study found an important issue with performing ex situ measurements for sediments from a tidally influenced marsh sites. Intact cores in the laboratory do not appear to accurately reflect the field exposure conditions after treatment for passive sampling or organism exposure when there is very active groundwater movement due to diurnal tidal pumping. This can be especially true where a major source of the pollutants lies deeper in the sediments and there is an active tidal pumping process as seen at the Canal Creek site.

1 Introduction

1.1 Background

Because there is no data on the long-term effectiveness of activated carbon (AC) amendments to contaminated sediments, this research effort collected data to analyze the long-term (6–10 yr) performance of AC treatments at two field sites. These sites, Grasse River in New York and Canal Creek in Maryland, represent diverse physical environments—a vegetated estuarine wetland and a riverine system—and are summarized in figure 1. This assessment sought to characterize the distribution, activity, and continued efficacy of the previously deployed AC in the context of the different physical, chemical, and biological processes occurring at each site.

This study hypothesized that if AC were present within each of the selected sites at comparable concentrations to the original deployment, it would continue to significantly reduce the bioavailability of sediment-associated polychlorinated biphenyls (PCBs). To test this hypothesis, this study collected data on AC distribution, PCB partitioning, and PCB bioaccumulation in order to develop lines of evidence concerning long-term efficacy of AC in reducing PCB bioavailability.

Figure 1. Maps and images of the study areas at Canal Creek, MD and Grasse River, NY
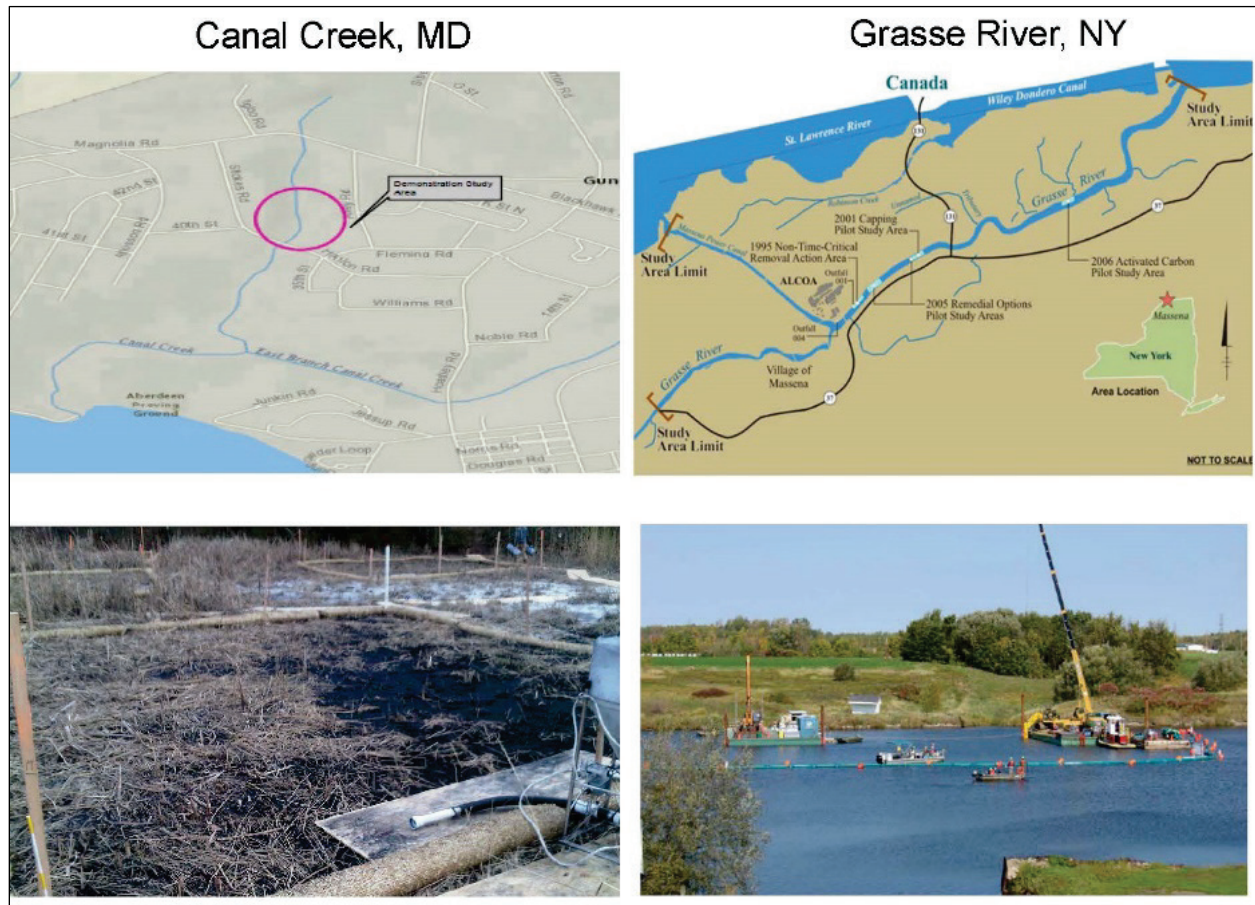
1.2   Objective of the demonstration

The team recognizes the challenges associated with assessing long-term effectiveness from small-scale pilot projects. The degree to which a remedy will be effective or successful over the long term will relate directly to the following:

- Spatial scale of the treatment vs. lateral mixing of sediments
- Adequate site-specific retention of AC and homogeneity (that is, via loss or dilution)
- Retention of AC sorptive properties
- Retention of AC effect on decreasing bioavailability and benthic bioaccumulation
- Absence of unacceptable AC-induced long-term negative effects on the benthic community or aquatic life

Further work, which is beyond the scope of the present study but could be pursued as a separate follow-on effort, should include modeling sediment deposition and mixing to scale up the observations from pilot-scale and predict site-wide performance.

1.3 Regulatory drivers

Estimated cleanup costs related to contaminated sediments for the DoD are projected to be as high as $1 billion. Developing the data and insights that enable wider use of in situ remediation could save the DoD hundreds of millions of dollars.

Regulatory drivers include The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), which is otherwise known as Superfund (US EPA 2005). CERCLA provides federal funds and oversight for cleanup of uncontrolled or abandoned hazardous waste sites as well as accidents, spills, and other emergency releases of pollutants and contaminants into the environment. In addition, the Superfund Amendments and Reauthorization Act (SARA) of 1986 (US EPA 2005) is an amendment and reauthorization of CERCLA to continue cleanup activities around the country. Several site-specific amendments, definitions clarifications, and technical requirements were added to the legislation, including additional enforcement authorities.

2   Technology

A number of laboratory evaluations using sediments from sites contaminated with persistent hydrophobic pollutants such as PCBs, PAHs, DDT, dioxins, and furans released to the environment decades ago have unambiguously demonstrated that AC amendment greatly reduces pollutant bioavailability and benthic bioaccumulation (Ghosh et al. 2011; McLeod et al. 2007; Millward et al. 2005; Sun and Ghosh 2007; Zimmerman et al. 2005). AC amendment in the range of 2%–5% of sediment dry weight reduces equilibrium pore water concentrations of these pollutants in the range of 70%–99%, thereby reducing the driving force for diffusive flux of pollutants into water and transfer into organisms (Ghosh et al. 2011). Most studies using benthic organisms show a 70%–90% reduction in bioaccumulation of pollutants in AC-amended sediment compared to unamended controls (Ghosh et al. 2011; McLeod et al. 2007; Millward et al. 2005; Sun and Ghosh 2007; Zimmerman et al. 2005). These studies have collectively demonstrated that engineered amendments reduce pollutant bioavailability and bioaccumulation in sediments. Several pilot-scale studies evaluated AC amendment and performance, typically over a period of 2–3 yr. Results from several of these pilot-scale demonstrations are summarized in a recent review article by Patmont et al. (2015). That review concluded that the extensive experimental studies and field trials demonstrate that, "when applied correctly, in situ treatment via contaminant sequestration and immobilization using AC amendment has progressed from an innovative sediment remediation approach to a proven, reliable technology" (Patmont et al. 2015, 9).

2.1   Technology description

The ESTCP pilot studies conducted at Canal Creek, Maryland tested both of these technologies as well as a direct slurry application.

2.2   Technology development

The technology of AC amendment to sediments has been developed through multiple research projects supported by several Strategic Environmental Research and Development Program (SERDP)/ESTCP programs as well as with funding from National Institute for Environmental Health Sciences (NIEHS), the United States Environmental Protection Agency (USEPA), and private industry as listed

in table 1. Original research in SERDP CU-1207 was conducted in the laboratory and subsequently demonstrated in the field through multiple field projects that tested the technology under a wide range of field conditions. As described by Patmont et al. (2015), AC amendment into sediment is now considered a mature technology available for use in full-scale projects.

Table 1. Active carbon sediment amendment technology development history (updated from Menzie et al. 2016, 7).

Development Phase	Time Frame	Funding Agency	Publications and Final Reports
Demonstration of reduced PCB bioaccumulation in clams, polychaetes, and crustaceans from Hunters Point, California sediment treated with AC	2001–2004	SERDP CU-1207	SERDP 2004
Demonstration of reduced PCB bioaccumulation in freshwater oligochaetes, with and without mechanical mixing of AC into sediments	2005–2007	USEPA Great Lakes National Program Office, (GLNPO)	Sun and Ghosh 2007
Pilot-scale study to evaluate the application of AC in reducing PCB bioavailability in a tidal mudflat	2005–2008	ESTCP ER-0510	Luthy et al. 2009
Pilot-scale study to evaluate the application of AC in reducing PCB bioavailability in river sediments	2007–2010	Alcoa, USEPA, SERDP	USEPA 2012
Selection of suitable sorbents for simultaneous stabilization of metals and organics in sediments	2006–2008	SERDP ER-1491	SERDP 2008
Development of SediMite as an efficient sorbent delivery mechanism to sediments	2006	USEPA Small Business Innovative Research EPD06029	USEPA 2006
Pilot-scale research of novel amendment delivery for in situ sediment remediation	2008–2011	NIEHS Grant 5R01ES16182	NIEHS 2012
Evaluating the efficacy of a low-impact delivery system for in situ treatment of sediments contaminated with methylmercury and other hydrophobic chemicals	2011–2015	ESTCP Project ER-200835	Menzie et al. 2016
Demonstration of in situ wetland restoration using a range of in situ amendment approaches	2011–2015	ESTCP Project ER-200825	Ruiz et al. 2016
Demonstration of in situ AC amendment in a PCB- and Hg[2]-affected phragmites marsh	2012–2015	Dow Chemical	Sanders, Andrade, and Ghosh 2018

2. For a full list of the spelled-out forms of the chemical elements used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 265, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

2.3   Advantages and limitations of the technology

In situ remediation of contaminated sediments offers several advantages compared to remediation via removal or dredging. In situ remediation costs substantially less, results in less disturbance to the environment, liberates less contamination through resuspension of sediment, and eliminates the risks and logistics related to handling and disposal of contaminated dredged sediments. To enable selection of alternatives that include AC, it is necessary to understand the long-term effectiveness of in situ remediation using AC. A number of pilot- and full-scale projects have implemented AC amendments over the last decade; however, there is a paucity of long-term monitoring data. The present study evaluated long-term effectiveness for projects as old as 10 years. In addition, the study included sites representing a range of distinct physical environments (nearshore estuarine, tidal wetland, river) enabling development of more robust conclusions regarding long-term effectiveness for extrapolating to potential DoD sites. Finally, the results of this study will inform development of more efficient and effective long-term monitoring plans for full-scale in situ remedies.

3   Performance Objectives

Table 2 summarizes the performance objectives and metrics chosen at the beginning of this project to judge the long-term efficacy of the previous AC deployment and remediation. Specific criteria defined the success of each AC deployment, as described in the conclusion section of this report.

Table 2. Performance objectives and evaluation metrics.

Performance Objective	Evaluation Metrics	Success Criteria*
Mass of AC retained within the site	-AC analysis	-Sediment core images show persistence of BC within test plots at intervals similar to those observed during post-placement monitoring. -Measured AC is statistically significantly greater than the control plots and is ≥50% of the target dose of the post-placement AC measurements on a per unit sampling area basis.
Vertical mixing and concentration of AC	-AC analysis at various core depths -Sediment core image profiles at various core depths	-Allowing for surface deposition and some vertical mixing, vertical distribution and quantity per unit surface area of AC is ≥50% to that observed during post-placement monitoring.
Horizontal dispersion, mixing, and concentration of AC	-AC analysis at multiple coring locations within treatment plot	-Measured AC is statistically significantly greater than the control plots and is ≥50% of the target dose of the post-placement -AC measurements on a per unit sampling area basis.
Functional performance of AC -Chemical performance using multiple chemical measures -Exposure reduction performance	-Physicochemical analysis of field sediment. -Ex situ assessment of PCB bioavailability reduction using intact cores	-Continued reduction (>50%) in PCB pore water concentrations. -PCB bioavailability within the treated zone is significantly reduced as compared to comparable untreated sediments on a bulk and normalized (to total PCB) basis. -Treatment efficacy scores according to % reduction: good: >80%; fair: 50%–79%; poor: <50%. Determination includes consideration of AC levels.

*Note: The success of this long-term monitoring project was based on the fulfillment of the monitoring tasks. Whether the in situ treatment implemented in the previous studies was successful was already determined on the basis of the monitoring performed as part of the original demonstration studies. In the long term, a small pilot demonstration is expected to be affected by ongoing mixing and deposition processes, the extent of which would be determined by the spatial scale of the pilot vs. the entire contaminated site. To adequately interpret whether the in situ treatment would have been effective in the long term after a full-scale implementation of the technology, this study considered the effect of scale of treatment on long-term sediment mixing and AC persistence. The measurements performed in this project provided initial observations used alongside sediment deposition and fate and transport models to predict whether a full-scale implementation of the remedy would be successful at that site.

4 Site Description

4.1 Grasse River

The Grasse River, a shallow freshwater tributary of the St. Lawrence River (Massena, NY), that is impacted by legacy sediment contamination of PCBs from historic industrial activity. The Grasse River is characterized by a shallow near-shoal area and steep banks going down to 4.5 – 8M (15–25 ft) deep in the mid-channel (figure 2). While the site is not adjacent to a DoD installation, the SERDP program supported part of the technology demonstration effort, largely because the proposed study provided important data regarding physical processes that are highly relevant to DoD sites. The previous pilot demonstration of AC amendments was in 2006. Additional site background information is provided in Section 5.1.1.

4.2 Canal Creek

The Canal Creek wetland site is located at the US Army Aberdeen Proving Ground-Edgewood Area (APG-EA) in Maryland. Canal Creek is a tidal creek with an associated wetland that flows into the Gunpowder River that in turn flows to the Chesapeake Bay. While the lower portion of the creek is brackish, the site sampled for this project is characterized by a freshwater wetland in the upper portion that is periodically inundated by high tides. Wetland soils and sediments in this upper portion contain elevated levels of PCBs, DDT and related isomers (DDx), and mercury (Hg). Additional site background The Canal Creek wetland site is located at APG's Edgewood Area in Maryland. Canal Creek is a tidal creek with an associated wetland that flows into the Gunpowder River, which in turn flows to the Chesapeake Bay. While the lower portion of the creek is brackish, the site sampled for this project is characterized by a freshwater wetland in the upper portion periodically inundated by high tides. Wetland soils and sediments in this upper portion contain elevated levels of PCBs, DDx and Hg. The section below provides additional background information about the site

5   Test Design

5.1   Grasse River assessment (2006–2016)

5.1.1   Site background

A full description of the pilot study location is given by Beckingham and Ghosh (2011). The pilot study site is located approximately 5.6 km downstream from a former industrial source of PCBs to the river. Sediments in the study area are composed primarily of sand and silt. PCB concentrations in surface sediments measured in 2006 were in the range of 2.0 to 3.9 µg/g dry weight and total organic carbon content averaged 5.8 ± 0.7% by dry weight (N = 13). In 2006, granular AC (particle size: 75–300 µm) was added to sediments at a target dose of 3.75% by dry weight to the top 15 cm of surficial sediment as a slurry by different modes of amendment. The sampling in 2016 included monitoring of the mixed and layered carbon treatments only. Bituminous coal–based AC (Carbsorb, Calgon Carbon) was amended in the mixed application, and a coconut shell–based AC (055C-CNS-V000, Calgon Carbon) in the layered application.

Figure 2. Study site maps. Top: Area map of the Grasse River 2006 Activated Carbon Pilot Study. Bottom: Typical cross sections in the portion of the river near the Village of Massena (left) and in the lower Grasse River (right). (From Comprehensive Characterization of the Lower Grasse River 2001).
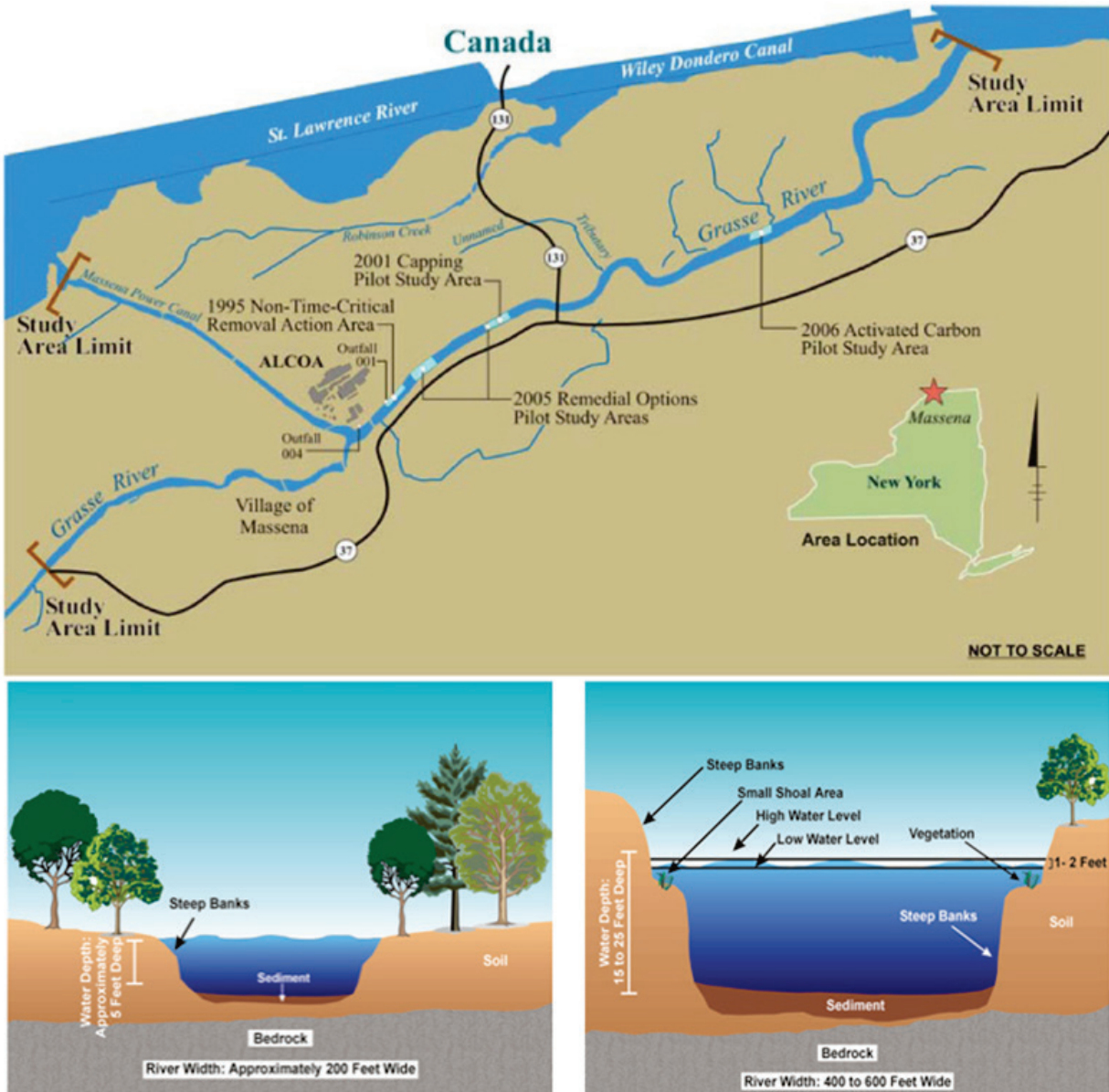
5.1.2 Summary of the previous pilot study

The Grasse River activated carbon pilot study (ACPS) began in September 2006 to evaluate the effectiveness of AC to sequester sediment PCBs and reduce PCB flux from sediments and PCB uptake by biota (United States Environmental Protection Agency [USEPA] 2012, 5). A review of recent laboratory and field studies (Ghosh et al. 2011) conducted by Stanford University, University of Maryland Baltimore County (UMBC), and others

have demonstrated that mixing AC into surface sediments successfully sequesters PCBs, effectively reduces PCB bioaccumulation in benthic organisms, and reduces release of bioavailable PCBs into the water column. An unanswered question addressed by the current project was if the previously applied AC remained in place in the river and continues to be effective in reducing pore water PCB concentrations.

The ACPS evaluated whether placement and mixing of AC (by mechanical or natural processes) into native sediments reduced the bioavailability of PCBs within Lower Grasse River sediments at the field scale. (USEPA 2012, 12). Other ACPS objectives regarding AC amendment included the following:

- Evaluate methodologies for delivering AC into existing sediments and determine the extent to which the application process releases PCBs and sediments into the river.
- Measure the change in PCB bioavailability to deposit-feeding benthic organisms.
- Evaluate changes in PCB equilibrium partitioning from sediments.
- Evaluate potential impacts to the benthic community structure.
- Evaluate whether AC amendment alters the erosion potential of the sediments. (USEPA 2008, 3)

In support of these objectives, Alcoa implemented a pilot demonstration project with oversight from state and federal agencies (Chang et al. 2012, 11). Beginning with laboratory studies and land-based equipment testing, the ACPS continued with field-scale testing of alternative placement methods then culminated in a field demonstration of the most promising AC application and mixing methods to a 0.2 ha (0.5 acre) pilot area within the Lower Grasse River (USEPA 2012, 5).

On the basis of the results of initial laboratory studies that evaluated bioavailability reductions achieved at different AC doses, a target application concentration of 2.5% AC (dry-weight basis) in the top 15 cm (6 in) of sediment after treatment was used in the Grasse River field demonstration. Alcoa implemented three application techniques within the pilot study area (figure 3):

- a 2.1 × 3.6 m (7 x 12 ft) enclosed device that first applied (that is, sprayed) AC onto the sediment surface and then mixed the material into near-surface sediments using a mechanical mixing unit (tiller);
- a 2.1 x 3 m (7 × 10 ft) tine sled that included direct injection of AC into near-surface sediments;
- an enclosed device that applied AC onto the sediment without the mixing devices; monitoring of the UTA allowed for an evaluation of the rate and extent of incorporation of the surficial layer of placed AC into near-surface sediments over time through natural processes (for example, bioturbation).

Figure 3. Activated carbon (AC) deployment for the Grasse River pilot study in 2006. Two different devices used to deploy AC included a steel box with an enclosed tiller (bottom left) and a sled with injection times (bottom right). (Modified and reprinted with permission from Beckingham and Ghosh 2011, 10569. Copyright 2011 American Chemical Society.)

To evaluate the different application techniques and mixing methods, the study divided the 0.2 ha pilot area into four separate test plots. These study plots included the initial testing area (tiller with and without mixing and tine sled), MTA (AC injected with tiller turned on), UTA (AC injected with tiller turned off), and tine sled–mixed treatment area (tine sled). table 3 below explains the study plot nomenclature is further. A single L-shaped silt curtain was installed adjacent to and downstream of the test plots during application.

Monitoring performed in 2007 and 2008 included in situ and ex situ PCB biological uptake studies, sediment sampling, erosion potential testing (via shaker studies), macroinvertebrate community studies, and in situ passive samplers. Additional monitoring in 2009 addressed specific questions raised from the 2007 and 2008 results. The 2009 monitoring included in situ PCB uptake studies, sediment sampling, macroinvertebrate community studies, and laboratory studies on the effects of AC on plant growth. A summary of results from the 2006–2009 monitoring activities is provided below:

- From 2006 to 2009, PCB concentrations in surface sediment decreased by 46% in the background site (BG) and by 54%–62% in the AC-treated sites.
- In the treated sediments, AC remained in place with no evidence of downstream migration.
- The 2008 and 2009 results indicated that AC was slightly deeper in the sediment profile than in the 2006 post-construction and 2007 sampling. This trend is likely due to recent sedimentation on top of the treated sediments since 2006. The average recovery of AC from the top 15 cm of sediment according to composite core analysis ranged 97%–156% for the mixed sites, 121%–192% for the layered sites, and 133%–189% for the injected sites over the 3 years of monitoring after AC application.
- Compared to baseline bioaccumulation measurements at each site, total PCB concentrations in worm tissues from sediment exposures in 2009 were reduced 85%–97% (field exposures) and 89%–98% (laboratory exposures) in sites where the AC was mixed with the sediment. Similar bioaccumulation reductions were observed at the layered application sites (92%–96%) and injected application sites (90%–95%).

- Aqueous equilibrium concentrations were reduced by 95% to >99% compared to BGs (and >93% compared to baseline) for all treatment sites with AC at the target dose or higher in each year.

  o "No differences in the benthic community composition (diversity, tolerance, or functional measures such as feeding mode or habit) or organism abundance were observed up to three years postapplication compared to unamended reference locations . . . . An increase in oligochaete biomass was observed following amendment at all monitoring sites . . . . Natural site fluctuations had a larger effect on the benthic community than the AC amendment itself" (Janssen and Beckingham 2013, 7601).

  o The AC amendments did not affect survival of submerged aquatic vegetation. However, "laboratory studies with submerged aquatic plants indicated reduced growth in sediments amended with ≥5% activated carbon, which [the studies] attributed to volume dilution of nutritional sediment or bulk density changes . . . [because reduced growth] was also observed when the sediment was amended with biochar and inert perlite" (Beckingham et al. 2013, 1504).

The 2006 pilot study demonstrated for the first time that primary exposure pathways to the aquatic food web can be restricted through pollutant binding in AC-amended river sediments. Furthermore, AC was successfully applied using both the enclosed tiller (mixed and unmixed) and injection tine devices (figure 2), and the amendment was stable over time. Previous laboratory work (Sun and Ghosh 2007) showed that application of AC without mixing is nearly as effective as application with initial brief mixing, especially when benthic organisms are present that induce mixing through bioturbation. Sediment core analysis showed that there was significant small-scale variability in AC dose achieved in sediments. Further improvements in engineering application are needed to reduce AC variability and improve efficiency. The delivered AC remained in the sediments at similar concentration throughout the three-year, postplacement monitoring period. Up to several centimeters of newly deposited sediment accumulated on the sediment surface in the pilot area over the three-year, postplacement monitoring period.

A number of unanswered questions remain with regard to the long-term performance of the AC placed during the initial pilot study:

- Did the AC remain in place in the river over the longer term?
- Did the AC remain effective in reducing pore water PCB concentrations?
- Did the AC continue to serve as a barrier between the underlying contaminated sediments and freshly deposited cleaner sediments?

Consequently, the focus of the present study was to evaluate long-term performance of the 2006 pilot study initiated in the Grasse River. Sediment cores were collected and sectioned to analyze for AC and PCB content. In addition, the study measured PCB concentrations by depth interval in intact core samples and collected bioaccumulation data to evaluate the persistence of bioavailability reduction in sediments.

Table 3. Description of Grasse River plots, treatments, and nomenclature.

Treatment	Nomenclature	Description
Background	BG	No treatment
Mixed treatment area	MTA	Enclosed tiller/injector applied and mixed AC into a target depth of 15 cm
Unmixed treatment area	UTA	Enclosed tiller/injector only injected a layer of AC slurry with the tiller turned off

5.1.3   Methods: Long-Term Study Design

The present study assessed the long-term performance of the pilot study implemented in Grasse River in 2006. The study closely followed previous monitoring performed by UMBC in the original pilot-scale study. Sampling was conducted in the fall of 2016 using methods described below.

5.1.3.1 Sediment collection

Sediment collection was performed according to existing guidance (USEPA 2001; American Society for Testing and Materials [ASTM] 2003) with site-specific considerations. Each site used a stratified random sampling design, with care taken to sample away from the outer margins of the plots to avoid edge effects. Core samples were collected within 5 replicate locations from each of the selected control (BG) and AC-amended treatment areas (MTA and UTA), for a total of 15 sampling locations. Each core was 7.6 cm in diameter and 30 cm long. The concentrations of AC and PCBs in sediment was determined using samples collected from vertically sectioned, single and multiple co-located sediment cores.

5.1.3.2 Vertical distribution of activated carbon in sediment cores

For this analysis, sediment core samples were collected from treated and untreated (control) plots at each site. The 30 cm long cores were sectioned into four intervals to match prior work at this site. Each section was then homogenized and stored for analysis of PCBs and BC. The traditional measurement of total organic carbon (TOC) was confounded by the native organic carbon content in sediment. Previous work by Grossman and Ghosh (2009) showed that traditional BC measurement using low-temperature pre-oxidation (Gustafson et al. 1997) is not appropriate for the assessment of residual AC in sediments. The BC analysis used a chemical oxidation method to burn off most of the natural organic carbon while preserving most of the AC in the sample, a technique described in Grossman and Ghosh (2009). The BC analysis was performed at UMBC using a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). Carbon in the sample was combusted to form CO_2 which is detected by a nondispersive infrared gas analyzer (NDIR). The location of the AC layer identified by the carbon analysis informed the sampling of the cores with passive samplers as well as the bioaccumulation testing.

5.1.3.3 Benthic community sampling

Cores were taken from each sampling location within the biologically active zone (0–10 cm depth) for assessment of benthic macroinvertebrate composition to determine potential impacts of the original AC deployment on the benthos at the community level. The same method also directly compared each control and treatment plot. Four replicate samples were collected within each treatment with methods congruent to the original site assessment. Samples were collected away from the outer margins of AC-amended plots to avoid edge effects. Samples were sieved at 500 µm in the field using site water, preserved (4% formalin followed by 10% ethanol) and archived to compare differences in the community composition between amended and control areas. Preserved samples were postprocessed and macroinvertebrates sorted from debris and then archived. Further taxonomic identification was not executed at this time to preserve funding for the physical and chemical characterization objectives of the project, given the lack of impacts to the benthic community observed in the prior monitoring efforts (Cho et al. 2009; Beckingham et al. 2013).

5.1.3.4 PCB bioaccumulation in worms

Ex situ laboratory bioaccumulation tests were conducted using the oligochaete, *Lumbriculus variegatus*, a standard organism (ASTM 2000) previously used in investigations following the original AC amendment (Grasse River, Canal Creek). An ex situ assessment was used to avoid the complications of in situ bioaccumulation assessments (Luthy et al. 2009). Intact sediment cores were modified according to the location of the carbon layer. At Grasse River, natural deposition of sediment over the 10 years following placement formed a layer of approximately 15–20 cm containing very little AC (see section 5.1.4.1). Therefore, as illustrated in figure 4, the cores were modified by removing the top 7.5 cm of sediment, then extruding the next 7.5 cm upward, then allowing the remaining sediment to fall within the column, creating headspace for the worms to burrow while not being disturbed during water changes. Two 7.6 cm diameter cores were used, per replicate, to ensure sufficient surface area for colonization and adequate recovery of worms for analysis. The modified cores were placed into five replicate chambers (2–5 L), dechlorinated tap water was gently added, and the system was left undisturbed overnight. Organisms were added to each aerated replicate chamber to recover approximately 0.2 g needed for the PCB microanalytical method. Small tissue masses were analyzed for PCB congeners and lipids using published micromethod techniques previously described by Millward et al. (2005) and Jones et al. (2006). In addition, passive samplers were inserted into the sediment cores within each replicate chamber to estimate pore water concentrations, as described below. Assays were conducted in environmental chambers (23°C ± 1°C) for 28 days (USEPA 2000) while monitoring water quality (temperature, pH, conductivity, dissolved oxygen, ammonia), with 3 water exchanges per week according to existing guidance (USEPA / United States Army Corps of Engineers [USACE]) 1998; Kennedy et al. 2010; Lee et al. 1993 ASTM 2000). Following the exposure, organisms were transferred to clean water and allowed to purge undigested sediment for six hours (ASTM 2000). Tissue was then rinsed with reverse osmosis water, homogenized, and frozen (−20 ºC) for chemical analysis. An aliquot of tissue was analyzed for lipid content.

Figure 4. Core processing for Grasse River. Left: Core section extrusion process used for laboratory bioaccumulation testing. Right: PE strip to be inserted in an intact core from Grasse River.
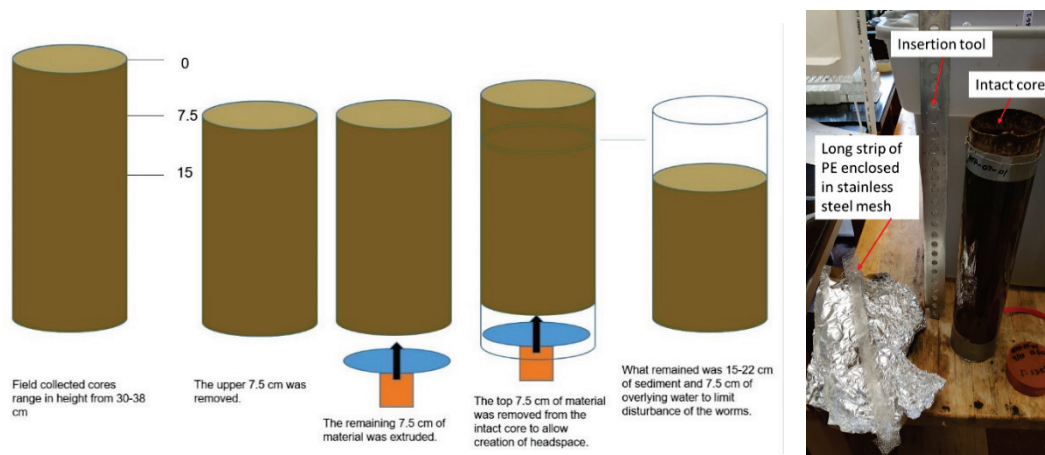
5.1.3.5 Sediment pore water measurement

For the Grasse River site, only ex situ, polymer-based pore water measurement was performed using intact sediment cores maintained in the laboratory underwater as illustrated in figure 4. Pore water PCB concentrations were measured using passive sampling. The sampling polymer used in this study was polyethylene (PE); (obtained from Husky, Bolton, Ontario) in 25 µm thicknesses. 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 et al. 2002). Spike levels were chosen to ensure analytically detectable masses in each congener after two months in sediment. Four PRCs were employed representing the tri- through hepta-substituted homologue groups: PCB BZ numbers (Ballschmiter and Zell [1980] numbers) 29, 69, 155, and 192. The PE strips were 2.5 cm wide and 30 cm long to allow sampling of the top 30 cm of the intact core. The strip was enclosed in a stainless steel mesh, inserted into the core using a metal bar, and allowed to equilibrate for about two months in the laboratory with the top of the core submerged underwater in a large tub. After the period of exposure, the passive samplers were retrieved from the core, cleaned to remove sediment, and then sectioned at 7.5 cm intervals to obtain four sections for each core. The passive sampler strips were stored in clean glass vials in a refrigerator until analysis.

Unadjusted pore water concentrations (Cpw) were calculated according to the equilibrium partitioning equation (Adams et al. 2007):

$$C_{pw} = \frac{C_{ps}}{K_{pw}} \tag{1}$$

where Cps is the measured concentration in the passive sampling material (g/kg polymer) and Kpw is the polymer-water partitioning coefficient specific to each congener/polymer combination (L/kg).

Kpw values for PE were derive d with the following empirical relationship (Smedes et al. 2009):

$$\log K_{pw} = 1.18 \times \log K_{ow} - 1.26 \tag{2}$$

PCB Kow values were taken from (Hawker and Connell 1988). Arithmetic average values were used for groups of two or more co-eluting congeners.

Pore water concentrations for nonequilibrium were adjusted using PRC depletion data according to the sampling rate approach, where the overall exchange rate of PCBs between sediment pore water and sampling polymers was approximated as a first-order kinetic process. An exchange rate coefficient (ke, PRC, d-1) was computed for each PRC in each sampler strip (that is, 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 Cps, PRC (0) is the measured concentration of PRC in the sampler prior to deployment, and Cps, PRC (t) is the measured concentration following deployment (Tomaszewski and Luthy 2008). Recent work by Sanders, Andrade, and Ghosh (2018) demonstrated that the first-order correction method is more appropriate to use for sediments treated with AC.

5.1.3.6 PCB analysis

5.1.3.6.1 PCB sediment analysis

PCB congeners in sediment were extracted using a Dionex 350 Accelerated Solvent Extraction system, following a modification of USEPA method 3545 (2007a). Briefly, sediment samples were weighed 15 ± 1 g (wet weight) and homogenized with hydromatrix drying agent into extraction vessels. Surrogate compounds, 2, 4, 5, 6-tetachloro-m-xylene and

decachlorobiphenyl, were added to provide extraction efficiency values. After extraction, the solvent was exchanged to hexane and adjusted to a final volume of 2 mL prior to analysis by Gas Chromotography with Electron Capture Detection (GC-ECD), following a modification of USEPA method 8082 (2007b).

5.1.3.6.2 PCB passive sampler analysis

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°C–40°C, treated with activated copper, and cleaned up using a miniaturized version of the silica gel procedure described in USEPA SW-846 method 3630C (1996), performed 146mm Pasteur pipettes. All samples were analyzed by gas chromatography with electron capture detection using an adaptation of USEPA SW-846 method 8082A (2007b) (Beckingham and Ghosh 2011). PCB BZ #30 and 204 were used as internal standards. Surrogate standards (PCB BZ number 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 according to the homologue groups or total PCBs. Average surrogate recoveries in passive sampler extracts were 92% ± 9.7% for PCB BZ number 14 and 88% ± 9.2% for PCB BZ number 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.

5.1.3.6.3 PCB tissue analysis

PCB congeners in tissues were extracted using a sonication bath for 16 h and maintained at room temperature during extraction using a water bath. Briefly, tissues samples were weighed 0.1 g ± 0.05 g and homogenized with hydromatrix drying agent. A solvent mixture of n-hexane and acetone (75:25) was then added to the sample vials. Surrogate compounds, 2,4,5,6-Tetachloro-m-xylene and decachlorobiphenyl, were added to provide extraction efficiency values. After extraction, the solvent was exchanged to hexane and adjusted to a final volume, 0.1 mL prior to analysis by GC-ECD, following a modification of USEPA method 8082 (2007b).

5.1.4 Results and Discussion

5.1.4.1 Activated carbon (AC) distribution in sediments

Sediment cores were anaerobic and dark in color, and the AC layer was not visually distinct enough for imaging and analysis. Thus, AC distribution assessment was based on actual AC analysis of sediment core sections.

For the Grasse River pilot study, sediment cores were sectioned into 7.5 cm intervals to a depth of 30 cm to match historic sampling specifications for this site. The depth profile of AC in sediment cores measured in the present study was compared with historic data from the first three years of monitoring (Beckingham and Ghosh 2011) in figure 5. In both treatment plots, progressive incorporation of AC into the deeper layers was observed in the first three years, as evidenced by the increasing level of AC in the 7.5–15 cm zone over time. Little AC migrated to the depth below the top 15 cm in the first three years postapplication. Greater migration was observed for the MTA compared to the UTA, likely due to the initial application to a deeper layer because of the mechanical mixing. The phrase *migration of AC* is being used here to describe the combined processes of burial due to new sediments and movement of the AC material due to initial mechanical mixing and natural bioturbation processes. The BG was not monitored by depth for AC content in sediment in the initial study.

In the 10-year postapplication samples collected as part of the present study, there was a pronounced change in the AC profile, where AC was seen primarily in the two deepest core sections (15–22.5 cm and 22.5–30cm) instead of the <15 cm described above during the initial three years of monitoring. The MTA plots showed a greater depth of penetration, possibly due to an initial deeper incorporation of the AC through the mechanical mixing. Using the observation of the high concentration of AC seen in the deepest core of the MTA locations, it is possible to conclude that some AC mixed into the zone deeper than 30 cm. For the UTA locations, the highest AC content was observed in the 15–22.5 cm zone and much less in the 22.5–30 cm zone. Thus, the added AC occurred in a much narrower band of sediment horizon in the UTA than the MTA. This is likely a result of the initial mixing during application in the MTA, which broadened the zone of AC amendment. In comparison, sediment core sections from the BG showed low levels of native BC (average of 0.1%) measured as AC.

On the basis of the observed dominant profile of AC in the deeper zones of the UTA and MTA plots, it is evident that the centroid of the amended AC lies close to the depth of about 20 cm. Thus, there is long-term deposition of new sediments in this section of the river that has brought in approximately 20 cm of new sediments over the 10-year period, of which the top 15 cm has <1% AC. This depositional depth is in agreement with the original anticipated sediment deposition rate in this section of the river of 2–3 cm/year of new sediments (Beckingham and Ghosh 2011; USEPA 2012). The AC profile measured after 10 years corroborates the anticipated rate of deposition.

Figure 5. Summary of activated carbon (AC) vertical migration. The graph on the left summarizes AC in the mixed treatment area (MTA) and the graph on the right summarizes AC in the unmixed treatment area (UTA).
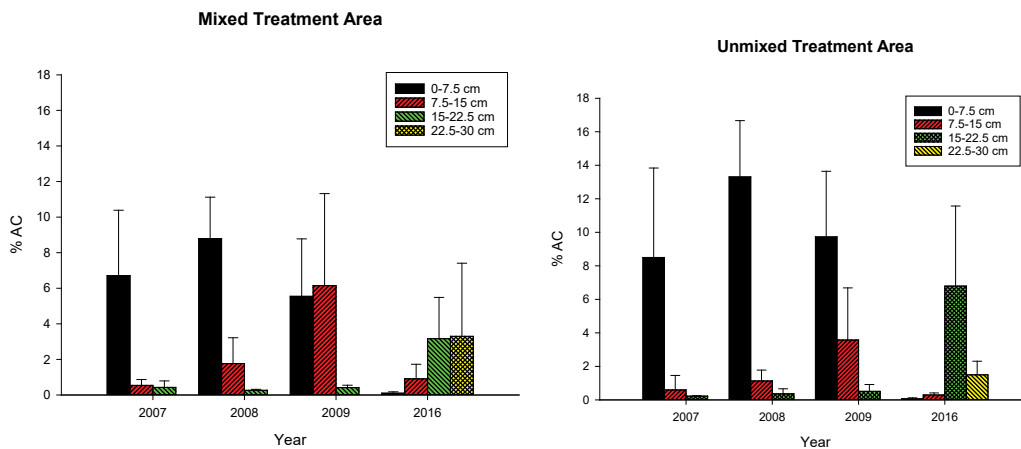
PCB concentrations in surface sediment taken from the two treatment areas 10 years after application are shown in figure 6, along with measurements performed earlier from 2006 to 2009. The top section (0–7.5 cm) in the sediment cores collected in 2016 are referred to as surface sediments in this analysis. These surface sediment concentrations were compared with surface sediments collected using a Petite Ponar grab sampler in the prior years (2006–2009), which collected an average of 10 cm depth of surface sediments. PCB concentrations in surface sediments of the study area ranged from 2–3.5 mg/kg in 2006 and decreased by approximately 10% annually for the first three years. The more recent 10-year data appear to fit the same trend, with about an order of magnitude decrease in PCB concentration for each of the treatment areas and the BG.

There is clear evidence of the natural attenuation process taking place in the river, primarily with the deposition of new, cleaner sediments over

time. This process is evident from the 20 cm of new deposit observed in the AC measurements presented above (figure 5) and the decrease in PCB concentration in surface sediments over time (figure 6) that have persisted at about the same rate over the 10-year study period. The attenuation of PCB concentration in sediments seen over the years is evident in all three study areas, indicating that the rate of sediment deposition and the nature of the new sediments were similar across each of the areas.

Sediment cores from 2016 were sectioned into four segments and analyzed for PCBs. As shown in figure 7, the depth profile for each of the three study areas provides a clear indication of sediment deposition over the years. Consistent with observations in prior years, the BG has higher concentrations of PCBs compared to the two treatment areas.

Sediment core sections from the MTA and UTA analyzed in the prior study at Grasse River are shown in figure 8. In any given year, PCB concentrations in sediments are the highest in the deepest layer with a gradual reduction in concentration to surface sediments. In both the treatment areas, surface sediment (0–7.5 cm) concentrations in 2016 were in the 0.2–0.3 mg/kg range; this is approximately 2–3 times lower than the concentration in the deepest layer. Similar results of 2–3 times lower concentration in surface sediments compared to the 22.5–30 cm zone were also observed in measurements conducted in 2006 (before construction), 2007, 2008, and 2009. In addition, the concentrations observed in 2016 were much lower than concentrations measured 7–10 years ago at every depth. In 2006–2009, PCB concentration in the 22.5–30 cm depth averaged at 6 mg/kg, while in 2016 the concentration at this depth had come down to close to 1 mg/kg. Similarly, in the surface sediments (0–7.5 cm), PCB concentration in 2006–2009 averaged about 2 mg/kg, which in 2016 was down to 0.2–0.3 mg/kg, as indicated above. Thus, the high-resolution core sections also reveal the same information as surface-grab samples, indicating a drop in concentration by about an order of magnitude in the last 10 years.

Figure 6. PCB concentration (average ± Standard Error (SE)) in surface sediment. This includes background and treatment plots in Grasse River activated carbon pilot study. Sediment samples were collected 2006–2009 using a Petite Ponar with an average collection depth of 10 cm Sediment cores were collected in 2016. The data presented above represents the top 7.5 cm of sediment.
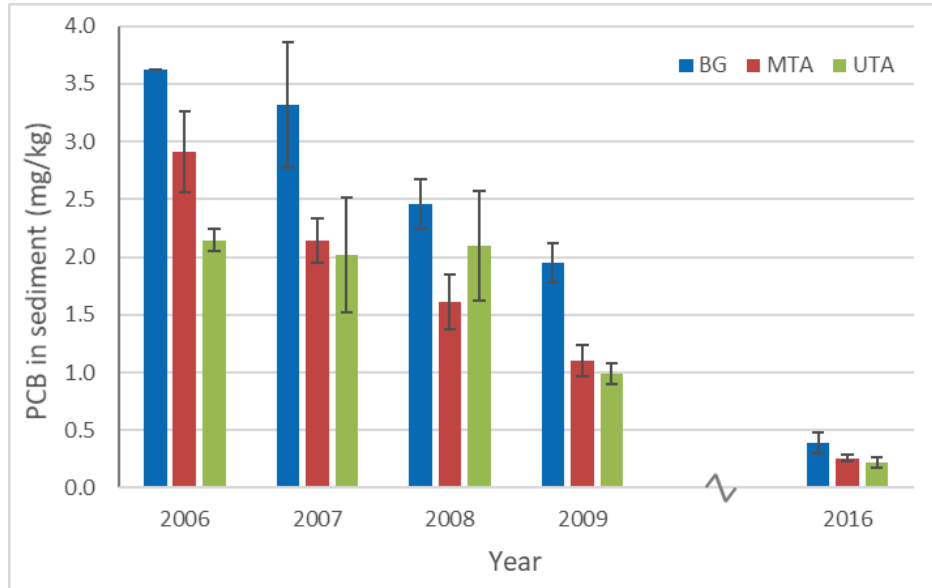
Figure 7. PCB concentration in sediment cores (average ± SE) 10 years
postapplication (2016) from the MTA, UTA, and BG of the Grasse River pilot study.
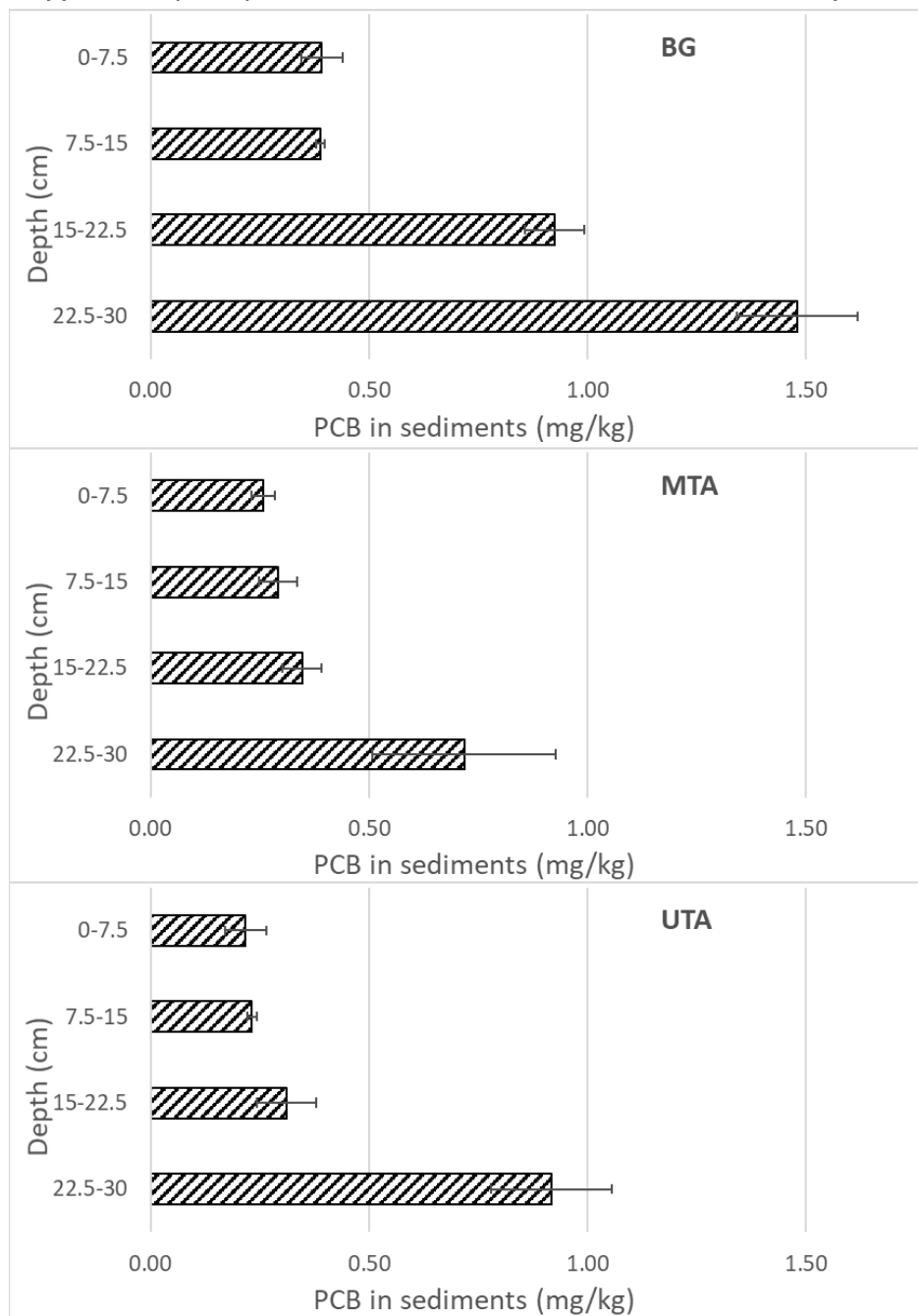
Figure 8. PCB concentration (average ± SE) in sediments collected 2006–2009. Concentrations are from high resolution core sections. Above: MTA. Below: UTA.
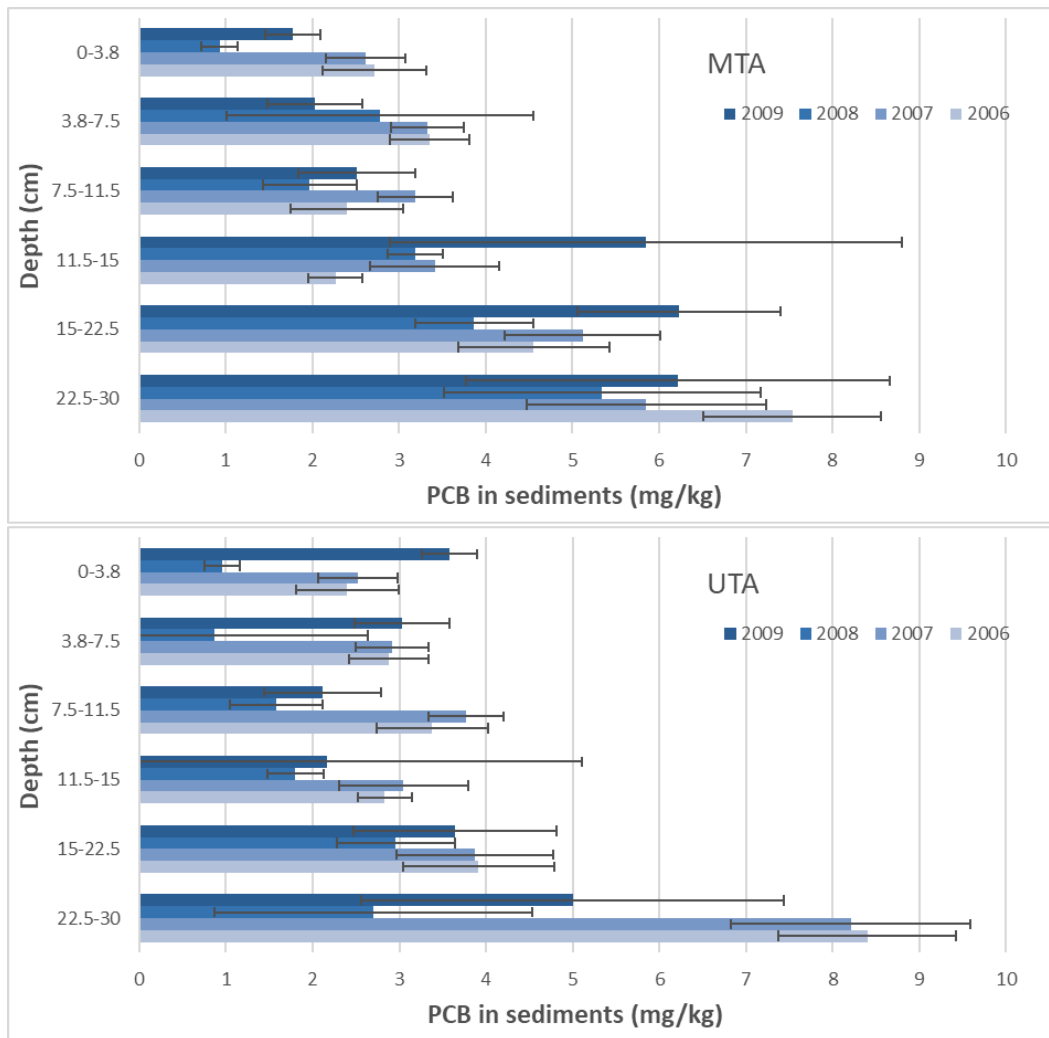
5.1.4.2 PCB concentration in sediment pore water

PCB concentrations in sediment pore water measured in the laboratory using intact cores are shown in figure 9. There was some variability among individual core samples taken from the same treatment area as indicated by the error bars in figure 9 and also in the individual plots for each core shown by depth section in figure 10. There was a pronounced difference in the pore water PCB profile between the BG and treated sites. For the BG, PCB concentrations in pore water gradually increased with depth below the surface, reflecting increasing PCB concentrations in deeper sediments, and following the overall trend of increasing total PCB concentration with increasing depth for the BG. The PCB congener pattern in sediment pore water with depth differs slightly, possibly as a consequence of the greater mobility and degradability of the lighter congeners. For example, in the

near surface sediments, monochloro biphenyls comprised 8% of total PCBs in pore water compared to 28% of total PCBs in the deepest core section (figure 10 and figure 11). It is likely that the lighter PCB congeners in near-surface sediments are being exchanged with surface water and possibly aerobically degraded near the surface. In contrast, the MTA and UTA sites have very little monochloro biphenyls (<1%) in the pore water at any depth, potentially due to reduced migration of the lighter congeners from the lower depths in the AC-treated sites. Thus, in the presence of AC in the treated zone, there is less recontamination of the new sediments in these areas caused by the migration of dissolved PCBs from depth.

As shown in figure 9, the two AC-treated sites display a flat profile for pore water PCBs with depth. There is no gradient in pore water concentration with depth for the treated sites even though the PCB concentration in sediments increase by a factor of two to three with depth. The greatest impact of AC amendment is seen in the two lower sections where most of the AC was present in 2016. The percent reduction in pore water PCB in these two sections was 96–98% for the MTA and UTA sites, similar to the reductions observed in the first three years after remedy. Thus, even after 10 years, the AC treatment continues to reduce pore water PCB concentration in sediments. In addition to the deeper layer where most of the AC is present, the surface sediment layer also shows reductions in pore water PCB concentrations (inset table in figure 9). It is likely that the reductions of pore water PCB at depth is reducing the recontamination of the cleaner new deposits.

Figure 9. PCB concentration in sediment pore water by depth according to laboratory measurements with intact sediment cores collected in 2016. Inset table shows % reduction in pore water PCB concentration at each depth compared to the corresponding depth in the BG site.
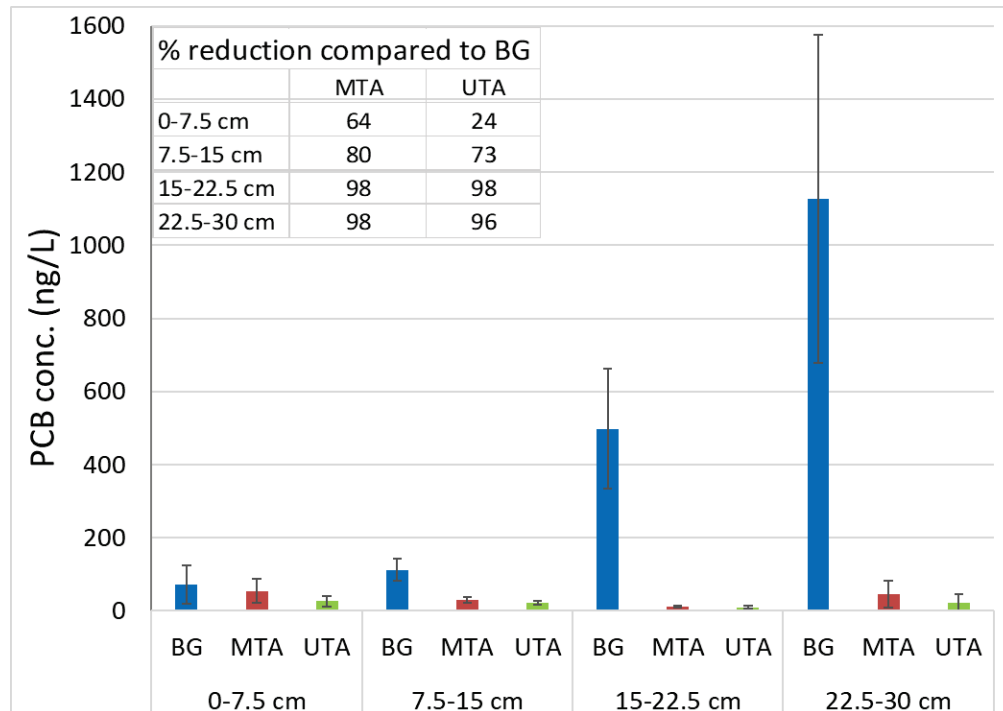
Figure 10 and figure 11 show the variability observed among individual core samples collected in 2016. Figure 12 compares the total PCB concentration in surface sediment pore water in each of the plots measured in 2016 with prior measurements from 2006–2009. The comparison shown in figure 12 is for aqueous equilibrium measurements performed with surface-sediment grab samples (target depth of top 10 cm where the treatment was present in 2006–2009), with pore water PCB measured in 2016 in the sediment core section of 15–22.5 cm (the treated zone as seen in 2006). The method used for pore water measurement was different in 2016 from the method used in 2006–2009. In the 2006–2009 period, the sediment pore water was measured directly by equilibrating the sediments with water in a batch setup in the laboratory followed by alum flocculation to remove colloidal interference (Beckingham and Ghosh 2011). As seen in figure 12, the pore water concentration in the BG has remained high over the 10 years. The pore water concentration in the two AC-treated sites decreased dramatically after treatment and remained reduced by nearly two orders of magnitude over the 10-year period.

Figure 10. Pore water PCB concentrations in intact sediment cores (0–7.5 top panel; 7.5–15 cm bottom panel). Samples were collected from the field in 2016. Concentration (ng/L) for each sediment core are for the top two depth intervals. Data are shown as individual replicates as well as averaged for each treatment (indicated by blue box at right).

Figure 11. Pore water PCB concentrations in intact sediment cores (15–22.5 top panel; 22.5–30 cm bottom panel). Samples were collected from the field in 2016. Concentrations (ng/L) for each sediment core are for the bottom two depth intervals. Data are shown as individual replicates as well as averaged for each treatment (indicated by blue box at right0.
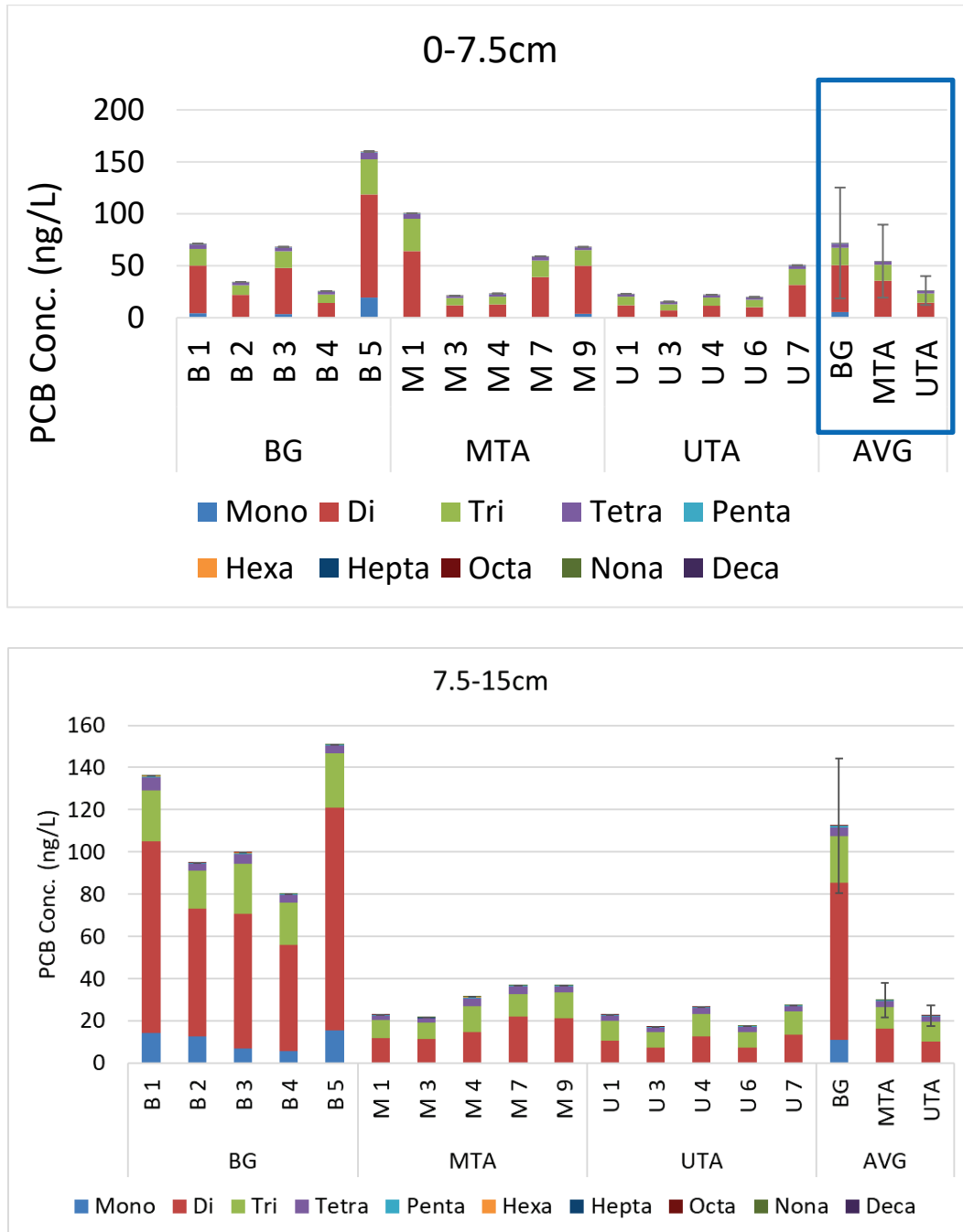
Figure 12. Pore water PCB concentration in sediments from the AC-treated zone. Concentrations were measured in 2016 and compared to measurements performed in the first three years post treatment. Pore water concentration in sediments measured 2006–2009 were based on batch equilibrium and alum flocculation to remove colloidal particles (Beckingham et al. 2011). The 2016 measurement was performed using passive sampling with polyethylene.
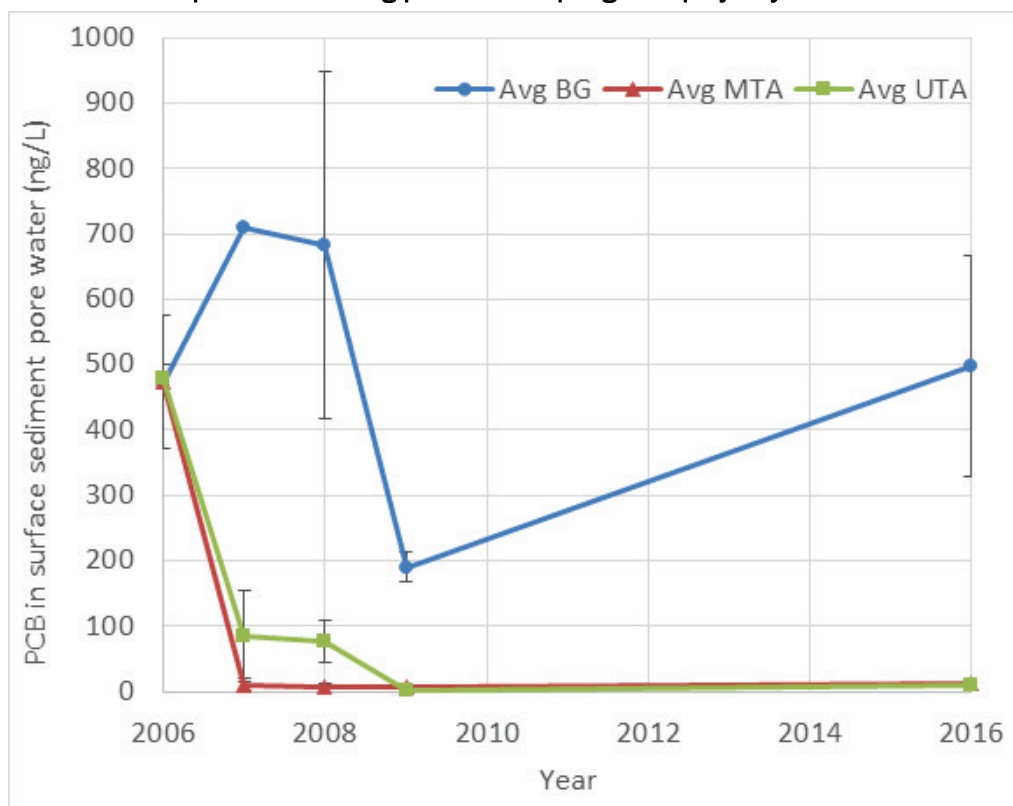
5.1.4.3 PCB accumulation in worms

PCB bioaccumulation in worms was the highest in the sediment cores from the BG. Both AC-treated sites showed reductions in PCB bioaccumulation in worms. As shown in figure 13, greater reduction in PCB uptake (84%) was seen in the UTA site compared to the MTA site (56%). The greater effectiveness of the UTA site is likely due to a higher concentration of AC (6.8%) present in a narrower zone of 15–22.5 cm in sediments compared to a more spread out AC distribution into the deeper sediments in the MTA site, resulting in a much lower MTA AC content in the 15–22.5 cm zone of 3.2%. We see a reflection of this differential AC distribution also in the greater reduction in pore water PCB concentration in the UTA site. A possible conclusion from this long-term observation is that initial mechanical mixing may not be necessary at sites like Grasse River where natural mixing and sediment deposition processes are anticipated to be high. Initial mechanical mixing ends up spreading the AC into a wider

zone of sediments in the long term and may not be necessary. This is an important finding, because at the time of the pilot study implementation, researchers anticipated that AC may not be stable in the sediments of a flowing river unless quickly incorporated into the surface sediments. Results of this long-term monitoring suggest that this concern of AC stability may be unwarranted.

As shown in figure 14, PCB accumulation in worms has continued to be suppressed in the AC treated areas over the 10 years of observation. It is important to remember that in 2016, the top 15 cm of the new sediment layer in the core samples was removed prior to testing. Thus, the comparison here is for the sediment zone that was treated with AC.

The percent reductions observed for accumulation in worms (56% and 84%) were lower than the 96–98% reductions seen in the pore water concentrations (see figure 9). Normalization of worm uptake to sediment PCB concentration does not explain this difference in worm tissue residues relative to pore water concentrations and only increases variability. Prior work at Grasse River demonstrated that bioaccumulation in freshwater oligochaete worms (*L. variegatus*) was reduced 69 –99% compared to preamendment conditions, and concentrations of PCBs in water at equilibrium with the sediment were reduced by greater than 93% at all treatment sites for up to three years of monitoring (Beckingham et al. 2011). The observation of overall lower tissue reduction in the present study could be a consequence of disturbance to each core during sectioning and extruding (only done for bioaccumulation studies), potentially resulting in cross contamination of the cleaner upper layers by the underlying layers, reducing the apparent effectiveness of the treatment. Also, AC content and PCB concentrations in each core varied, as seen in figure 5 and figure 7, and reflected the variable bioaccumulation of PCBs in each core, as shown in figure 13. Neither AC nor PCBs were measured in the specific cores used for the bioaccumulation studies; rather, performing those measurements required sacrificing additional cores.

Figure 13. PCB concentration in wet tissue of worms. Worms were exposed to intact sediment core with the top 15 cm depth of new sediment removed. Data are shown as individual replicates in homolog groups (A) and as total PCBs averaged for each treatment (B).
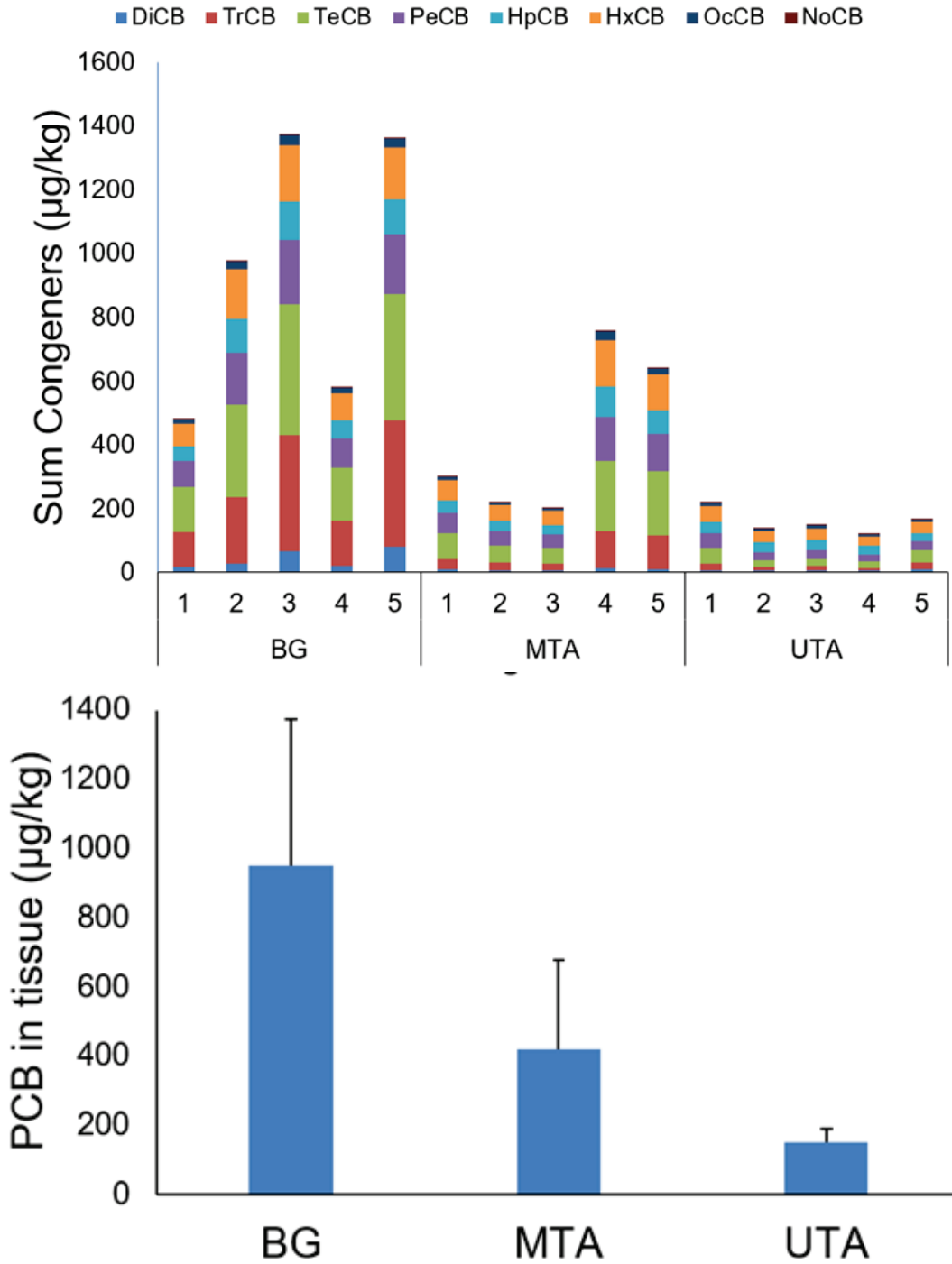
Figure 14. PCB concentration in wet tissue over 10 years. Tissues were exposed to sediments from treatment and background plots.
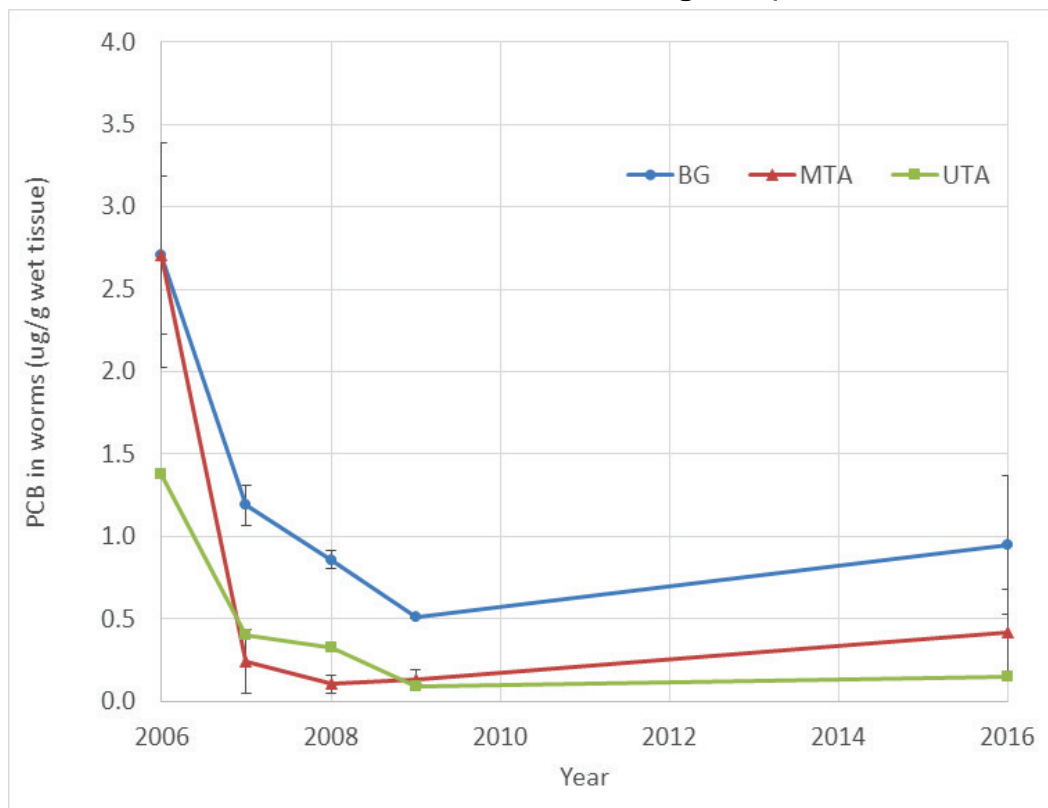
5.1.4.4 Key findings from the Grasse River long-term monitoring

Results from the present study provide the following key insights into the long-term performance of AC amendment to river sediments:

- AC applied directly into sediments is stable in a slow-flowing river system and could be found at or above target levels after 10 years in the field.
- AC amended to sediments continues to reduce pore water PCB concentrations within the zone of application.
- Deposition of new, cleaner sediments over time buried the AC-treated zone of sediments, which now functions as a barrier layer between the new, cleaner sediments and deeper, more contaminated sediments.
- Natural attenuation due to clean sediment deposition is high at Grasse River and resulted in a nearly one order of magnitude reduction in surface sediment PCB concentration over 10 years.
- The presence of AC in sediments continues to reduce PCB bioavailability to benthic organisms.

Initial mechanical mixing in the MTA plot resulted in a more diffuse layer of AC with time as additional natural mixing spread out the AC through the depth, suggesting that the initial mechanical mixing may not be necessary for sites where natural mixing can be anticipated.

5.2 Canal Creek assessment (2009–2016)

5.2.1 Site background

The Canal Creek wetland site (figure 1) is located at the APG Edgewood Area in Maryland. Canal Creek is a tidal creek with an associated wetland that flows into the Gunpowder River, which in turn flows into the Chesapeake Bay. While the lower portion of the creek is brackish, the site sampled for this project has a freshwater wetland in the upper portion periodically inundated by high tides. Wetland soils and sediments in this upper portion contain elevated levels of PCBs, DDx, and Hg.

Canal Creek ranges from nontidal to tidal oligohaline along its approximately 3.2 km length and is bordered by a number of wetlands. The salinity of the creek ranges from freshwater to approximately 5 ppt, and the headwaters are drainages and small streams north of Magnolia Road fed by overland runoff and seeps (EA 2008). Tidal marsh emergent vegetation with small areas of scrub-shrub and forested wetland borders the creek, which receives some input from contaminated groundwater seeps (EA 2008). The previous studies differentiated distinct habitat types, with the wild rice wetland designated as high-value wetland and the areas of *Phragmites sp*. low-value wetland.

Pilot studies involving in situ remediation with AC were implemented in the upper wetland portion of Canal Creek via two ESTCP projects: ER-200835 (Menzie et al 2016) and ER-200825 (Ruiz et al 2016). These pilot-scale studies are described in more detail in the following section.

5.2.2 Overview of previous pilot demonstrations

As described above, follow-up assessment monitoring was conducted at two previous ESTCP pilot-scale demonstrations (*ESTCP Project ER-200835* and *ESTCP Project ER-200825* [Menzie et al 2016; Ruiz et al 2016, respectively]). Menzie et al, 2016 examined the efficacy of in situ treatment of sediment contamination with AC delivered using the SediMite delivery system (Menzie et al. 2016). Ruiz et al. (2016) field

demonstrated and validated in situ wetland remediation technologies, including a powder AC slurry, pelletized AC product (AquaGate), and an engineered manufactured soil cover system (sand/soil treatment) designed to sequester contaminants in wetlands (Ruiz et al, 2016). Untreated control plots (control) were also used in the demonstration for comparative purposes. Slurry AC was only applied in the low-value wetland. SediMite was applied only in the high-value wetland. A list of the treatments and acronyms used for this study and subsequent tables and figures are summarized in table 4.

Table 4. Summary and nomenclature used for the comparative treatments for Canal Creek.

Treatment	Abbreviation
Control	C
AquaGate	AG
SediMite	SM
Sand Control	SC
AC Slurry	ACS

Previous studies used PCB pore water and tissue residue concentrations (pre- and post-treatment and relative to control plots) to evaluate the efficacy of the technologies that treat hydric soils affected by PCBs. For this project, performance was evaluated with respect to application and retention of applied AC, reduction in the bioavailability of chemicals as a result of treatment with AC, and potential for adverse effects from application of AC. Performance sampling conducted during 2011 generally indicated that the applications were reducing the bioavailability of PCBs (Ruiz et al. 2016, Menzie et al. 2016) as well as DDx (evaluated in the Menzie et al. study (2016)) using SediMite.

5.2.2.1 Summary findings from ER-200825 Final Report Executive Summary

Average total PCB pore water concentration generally decreased following treatment within the slurry and AquaGate treatment plots. Pore water concentrations, except for AquaGate, were not statistically significantly different between pre- and post-treatment. However, AquaGate and Slurry post-treatment pore water concentrations were statistically significantly lower than the post-treatment control plots. The temporal and spatial heterogeneity of PCBs measured in bulk sediment and a sample depth that exceeded designed treatment depth may explain why reductions in pore

water concentrations were not more clearly definitive as to the effectiveness of treatment. *L. variegatus* tissue concentrations were statistically significantly lower in AquaGate post-treatment plots compared to pre-treatment concentrations. *L. variegatus* tissue concentrations in the Slurry and the Sand Control were arithmetically lower, but not statistically different when post-treatment data were compared to pre-treatment data. However, AquaGate and Slurry post-treatment *L. variegatus* tissue concentrations were statistically significantly lower than the post-treatment Control plots. Post-treatment tissue concentrations in the SediMite and Sand Control treatments were also arithmetically lower than the post-treatment Control.

While the ER-200825 project findings suggest that additions of AC can sequester PCBs, the field demonstration findings did not conclusively demonstrate effective reductions in bioavailability (Ruiz et al, 2016). The overall program results do suggest that the active in situ remediation technologies tested in this project could be effective for the remediation of contaminated wetland sediments. Bench-scale testing of the AC treatments during the treatability study confirmed PCB sequestration. Equipment to deploy the amendment products was readily available and adapted easily to the task, resulting in effective placement of all AC products over the treatment plots. It also appears that cold weather may limit the degree to which high moisture products may be deployed successfully.

Confounding issues associated with the field-monitoring program included the large PCB heterogeneity in the field, small sample sizes, the short period of postapplication monitoring, the unexpectedly slow mixing of the placed AC with the underlying contaminated sediments, and the overall design of the sampling and monitoring program to measure PCB sequestration in situ. Two additional potential confounding factors are that BC was present in the system prior to treatment application and that migration of placed carbon into or out of the treatment area may have occurred; these factors also potentially affected the demonstration of treatment efficacy.

*5.2.2.2 Summary findings taken from ER-200835 Final Report Executive
        Summary*

For the wetland soils, the AC was retained (>90%) but mixing into the
soils was slower than observed for aqueous sediments. As a result, AC was
concentrated in surficial soils of the upper 5 cm.

Bioavailability was evaluated by measuring and comparing concentrations
of contaminants in invertebrate tissues and pore water. While uncertainty
exists in extrapolating from laboratory measurements to actual field
conditions, these comparisons between post-treatment sediments
collected in the field using grabs or cores were made primarily in the
laboratory to better control exposure conditions. However, this
uncertainty can be reduced by performing in situ measurements. The
demonstration projects showed that field-collected sediments from plots
that were treated with SediMite-applied AC exhibited significantly lower
bioavailability for PCBs than sediments from control plots.
Bioaccumulation of PCBs into invertebrates was reduced 60–90% over the
treatment period depending on PCB homolog. The reductions in PCB
bioavailability were observed for all wetlands and marshes, and
subaqueous sediments evaluated for the three study sites. However, the
magnitude of reduction in PCB bioavailability varied among locations and
appears to be related to retention of AC, contact time between PCBs and
AC-treated sediment, and mass transfer rates for PCBs with different
degrees of chlorination. Field-collected sediment from treated plots in the
Upper Canal Creek wetland exhibited reduced bioavailability of DDx as
compared to untreated plots and field-collected sediment cores from the
treated plot in

5.2.3   Methods: Long-term study design

5.2.3.1 Sediment collection

At the Canal Creek wetland site, AC treatments were applied to high- and
low-value wetland sediments in 2010. The treatments used included
AquaGate, AC slurry spray, and SediMite, along with sand and untreated
controls. Short-term performance sampling occurred in 2011, and long-
term performance sampling occurred in 2017.

Field sampling was performed from 21–22 February 2017 to avoid heavy
vegetation coverage of test plots. Initially, 14 plots were sampled, which

included 11 plots in the high-value wetlands and 3 in the low-value wetlands, as shown in figure 15. Two of each of the control plots were sampled, along with four AquaGate plots, three SediMite plots, and three AC slurry spray plots. Replicate 30.5 cm (12 in) depth cores were collected from each plot, using 10 cm (4 in) diameter clear polycarbonate rigid tubing. Cores were pushed into sediment by hand; when not possible, cores were hammered into the sediment using a rubber mallet and wood block to prevent damage of the core liner. New core liners were used for each sample.

Figure 15. Map of Canal Creek study site. Left: Map of study area showing 24 treatment plot locations. Red squares around numbers indicate plots sampled in the long-term evaluation in 2017. Top right: Image of site. Bottom right: Image of core samples collected from the field.
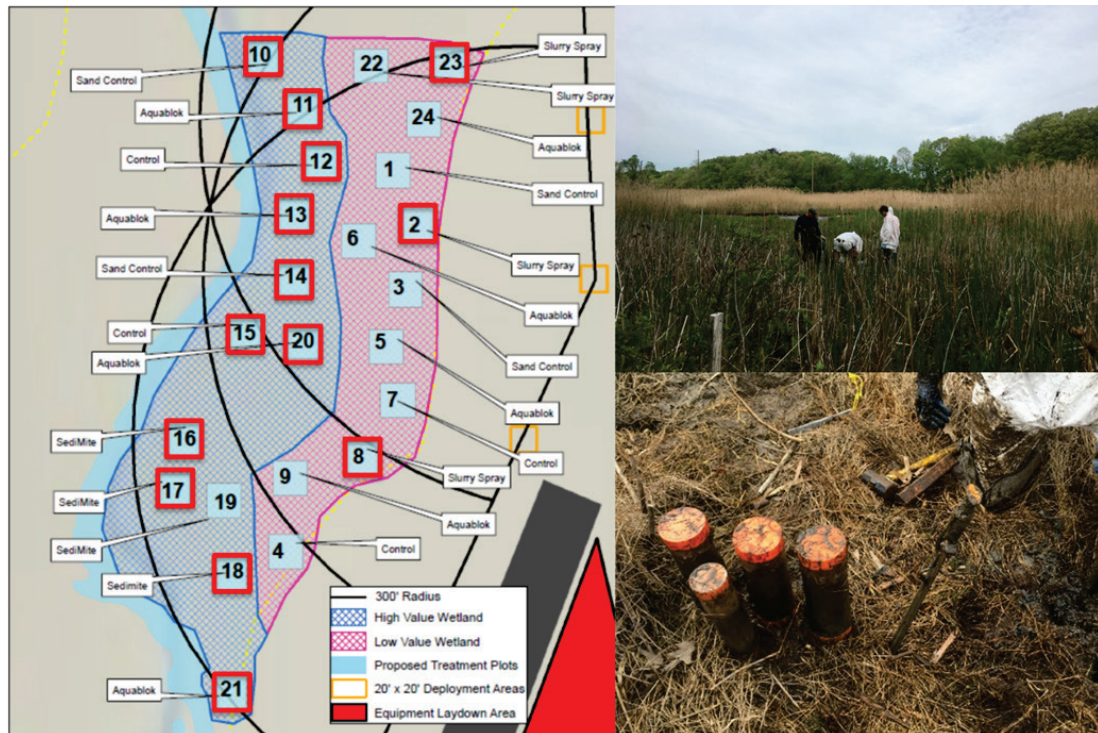
Plot boundaries were generally difficult to identify in the field. Many of the wooden stakes and hay bales that delineated the boundaries of the plots were badly decomposed or missing. GPS coordinates from the original study were used to delineate plot boundaries (included in the supplemental data appendices). Regrowth of *Phragmites sp.* was substantial in some areas of the wetlands, particularly in the low-value wetlands (so designated for being largely a monoculture of *Phragmites sp.*). Plots were redelineated (according to original GPS coordinates) and flagged prior to sampling in February of 2017, in one instance, the field

crew was unable to confidently identify the boundaries of a test plot (plot 22, AC slurry, at northern edge of site), and a different plot (plot 2, approximately two plots south of plot 22) with the same treatment was sampled as a substitute. This was the only instance where a plot was substituted from the original sampling plan. Even in late winter, when live vegetation was largely absent from the site, the dead stalks of *Phragmites sp.* remained in many areas and made traversing the site difficult.

Due to the timing of the field sampling (late February), benthic and sediment-dwelling macroinvertebrates were largely absent from the treatment plots. Collection of sediment cores in late winter was expected to be easier than sampling when plots were covered with dense stands of live vegetation. Sampling in late winter made collection of sediment cores more manageable.

Evidence of the experimental treatments was obvious in some of the test plots. For example, the layer of AquaGate was still visible at the surface, and gravelly material was still present in plot 11, directly southwest of plot 22. On many, but not all, sediment cores, a distinct treatment layer was obvious when the core was extracted. In some cases, it was noted that *Phragmites sp.* roots were evident through and below the treatment layer, indicating that some level of vertical mixing was taking place. On many plots, collection of cores had to take place around existing *Phragmites sp.* root balls; attempts to push core samplers through *Phragmites sp.* roots were not always successful.

Finally, due to historic activities at the site (for example, weapons and munitions testing), assistance from an unexploded ordinance support specialist was critical. Sample locations were relocated on several occasions due to the identification of potential subsurface hazards. Any potential hazards were left in place and avoided.

5.2.3.2 Vertical distribution of AC in sediment cores

The location of the AC layer identified by the carbon analysis was used to inform the sampling of the cores with passive samplers as well as the bioaccumulation testing.

5.2.3.3 Benthic community sampling

See section 5.1.3.3 for description.

5.2.3.4 Passive sampling characterization of pore water

For the Canal Creek site, both ex situ and in situ pore water measurements were performed. Pore water PCB concentrations were measured using passive sampling.

Ex situ measurement was performed using intact sediment cores maintained in the laboratory under water as illustrated in figure 16. The PE strips were 2.5 cm wide and 20 cm long to allow sampling of the top 20 cm of the intact core. The strips were enclosed in stainless steel mesh and inserted into the core using a metal bar and allowed to equilibrate for 1 month in the laboratory with the top of the core submerged under water in a large tub. After the period of exposure, the passive samplers were retrieved from the core, cleaned to remove sediment, and then sectioned from the top into the following depth intervals: 0–2.5 cm, 2.5–5 cm, 5–10 cm, and 10–20 cm to match depth intervals used in the prior benthic study at this site. The passive sampler strips were stored in clean glass vials in a refrigerator until analysis.

In situ measurement followed a similar procedure for the preparation of the passive sampler as described above. For in situ placement, the passive sampler was additionally enclosed within a metal bracket to allow insertion in the field as shown in figure 16.

Figure 16. Passive samplers used at Canal Creek. Left: Ex situ pore water measurement within intact cores take from the Canal Creek site. A passive sampling strip enclosed in stainless steel mesh is shown being inserted into the core. Right: In situ passive sampler retrieved from the field. The passive sampling sheet was enclosed in a stainless steel mesh and frame.

Pore water were adjusted concentrations for nonequilibrium using PRC depletion data according to the sampling rate approach, where the overall exchange rate of PCBs between sediment pore water and sampling polymers was approximated as a first-order kinetic process. PRC correction was performed for all samples where fractional loss of PRCs was less than 80%. An exchange rate coefficient (k_e, PRC, d-1) was computed for each PRC in each sampler strip (that is, each PRC at each depth interval in each sampler location) with the following equation:

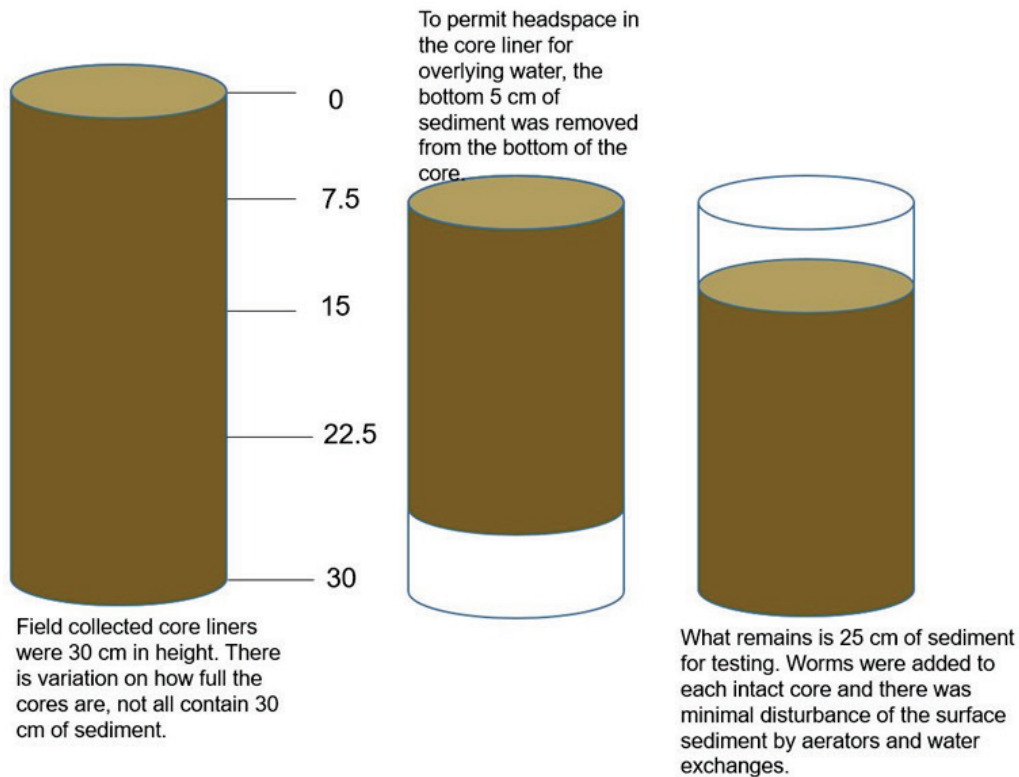$$k_{e,PRC} = \ln\left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)}\right)\left(\frac{1}{t}\right) \tag{3}$$

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).

Recent work by Sanders, Andrade, and Ghosh (2018) demonstrated that the first order correction method is more appropriate for sediments treated with AC.

5.2.3.5 PCB bioaccumulation in worms

Ex situ laboratory bioaccumulation tests were conducted using the oligochaete *L. variegatus*, a standard organism and test method (ASTM 2000) for bioaccumulation assessments that was previously used in investigations following the original AC amendment (Grasse River, Canal Creek). An ex situ assessment was used to avoid the complications of in situ bioaccumulation assessments (Luthy et al., 2009). Intact sediment cores were modified based on the location of the carbon layer. New deposition of sediment at the Canal Creek plots with very little AC was determined to be less than 2 cm over the 6 years following placement. To provide applicable test material for the bioaccumulation assessment, the cores were modified by removing approximately 5 cm sediment from the base of the core, then and allowing the remaining sediment to fall within the column, creating headspace for the worms to burrow while not being disturbed during water changes (figure 17). The modified cores were placed into 5 replicate chambers (2 L), dechlorinated tap water was gently added to avoid disturbance of the intact sediment core and the material allowed to equilibrate overnight. Worms were added to each aerated replicate chamber to recover approximately 0.2 g needed for the PCB micro-analytical method. Small tissue masses were analyzed for PCB congeners and lipids using published micromethod techniques (Millward et al 2005, Jones et al 2006). In addition, passive samplers were added to the sediment cores within each replicate chamber as described earlier to estimate pore water concentrations. Assays were conducted in environmental chambers (23 ± 1 $^{\circ}$C) for 28 days (USEPA 2000) while monitoring water quality (temperature, pH, conductivity, dissolved oxygen, ammonia), with 3 water exchanges per week according to guidance (USEPA / USACE 1998, Kennedy et al 2010, Lee et al 1991, ASTM 2000). Following the exposure, organisms were transferred to clean water and allowed to purge undigested sediment for 6 hours (ASTM 2000). Tissue was then rinsed with reverse osmosis water, homogenized and frozen (-20 $^{\circ}$C) for chemical analysis. An aliquot of tissue was analyzed for lipid content.

Figure 17. Illustration of core section extrusions used in bioaccumulation testing.

To permit headspace in the core liner for overlying water, the bottom 5 cm of sediment was removed from the bottom of the core.

0

7.5

15

22.5

30

Field collected core liners were 30 cm in height. There is variation on how full the cores are, not all contain 30 cm of sediment.

What remains is 25 cm of sediment for testing. Worms were added to each intact core and there was minimal disturbance of the surface sediment by aerators and water exchanges.

5.2.3.6 PCB analysis

5.2.3.6.1 PCB analysis of sediment

See section 5.1.3.6.1 for description

5.2.3.6.2 PCB analysis of passive samplers

See section 5.1.3.6.2 for description

5.2.3.6.3 PCB tissue analysis

See section 5.1.3.6.3 for description

5.2.4   Results and discussion

5.2.4.1 AC distribution in sediments

As shown in figure 18A, about 2% BC was measured in the control plot through the sediment depths analyzed. These values are higher than the average BC content measured in the control plot samples in 2011 (Ruiz et al. 2016). The natural organic carbon in sediments at this site is high, with

a mean of 17.3% TOC (range of 4.2%–31.2%; which may be partly responsible for the high native BC measurement. It is also possible that over the six years, there has been some spreading of AC from the treatment plots to the control plots. Menzie et al (2016) noted an increase in BC in control plots from pre-application to postapplication sampling and speculated on a small migration from treatment cells. BC levels in soil cores from the SediMite treated plots are shown in figure 18B. In the first two post application samplings conducted in 2011, most of the applied AC was found in the surface 2 cm of the core, with a small penetration to the 2–5 cm zone and virtually no penetration of the AC to the zones deeper than 5 cm (Menzie et al. 2016). This low mixing into deeper layers of sediments was attributed to a slow bioturbation rate in the marsh soils with extensively rooted vegetation. The six-year postapplication sample for SediMite indicates a similar slow trend of penetration of the AC layer. However, in the six-year sample, the majority of the AC is present in the 2–5 cm zone of sediments and the next deeper layer of 5–10 cm depth also shows some penetration of the AC. The surface 2 cm layer is likely affected by a slow deposition of new sediments, which partly mixes with the AC layer as it is buried deeper down. While the apparent rate of natural mixing appears to be slow in the vegetated marsh soil embedded with plant roots, there is still evidence of mixing to a depth of 10 cm after six years at this site. Thus, topical application of an amendment in a marsh setting appears to have technical efficacy by gradual mixing with freshly deposited sediments for integration into the deeper layers.

Results of AC from soil cores taken from soil cover, AC slurry, and AquaGate are shown in figure 19. See, for example, the photo logs provided in Ruiz et al (2016) for a visual indication of the AC placement with depth. Prior monitoring at these treatment locations did not measure AC with depth. In Ruiz et al (2016), one representative sample was collected per test plot which was a composite of eight subsamples collected using a hand soil auger from the upper 0–15 cm of the soil profile. Multiple depth intervals were not measured. Thus, the prior measurements of AC in soil from Ruiz et al (2016) are not directly comparable to the soil-core sections measured in the present study.

The soil cover placement resulted in a 5 cm thick cap of new material on the sediment surface. The soil cover treatment shows a remarkably reduced BC level in the 2–5 and 5–10 cm depth, likely indicating the zone where the placed soil cover now lies. It also indicates that the placed soil

cover has distinctly low BC content compared to the native soil. It is also interesting to note the low rate of deposition of new sediment in this site, about 2 cm in six years, or one-third of a centimeter per year. This rate of deposition is markedly smaller than the 2 cm/yr seen in the Grasse River activated carbon pilot study (Beckingham and Ghosh 2011).

The AC slurry application plots show the highest concentration of BC in sediment-core sections, averaging 24% in the 2–5 cm zone. This high value is attributable to pure AC application in this treatment compared to composite pelletized application in both the SediMite and AquaGate treatment plots, where the %AC in the starting material is 50% and 5% respectively. Similar to the observations from the SediMite treatment, the AC slurry treatment shows the highest concentration of AC in the 2–5 cm zone followed by the surface 2 cm zone. There is also evidence of penetration of AC to the deeper 5–10 cm zone. Thus, in this treatment, while the penetration into deeper sediments is slow, there is evidence of integrating to a depth of about 10 cm in six years after application.

The AquaGate treatment resulted in a much deeper thickness of cap (5.5 cm) compared to the other AC treatments and was comparable to the thickness of the soil cover cap of 5 cm. The AC slurry and SediMite applications resulted in a barely measurable thickness of new material of 0–0.3 cm. As observed for the other AC treatments, after six years the AquaGate treatment also resulted in the highest concentration of AC in the 2–5 cm zone. The next highest concentrations of AC were observed in the deeper cores of 5–10 cm and 10–20 cm. The surface layer of 2 cm also contained some residual AC. Thus, among the AC treatments, the AquaGate treatment resulted in a deeper placement of the amendment caused mainly by the additional thickness of 5.5 cm introduced by the amendment layer itself.

5.2.4.2 AC recovery

The measured %BC for each core section was first corrected for background level of AC found in the core sections form the control plots. The corrected percent BC values were then converted to %AC for each of the AC treatments according to an 89% BC measurement in coconut shell AC reported by Grossmann and Ghosh (2009). The %AC values were used to calculate the mass of AC present per square meter of a plot and compared with applied AC loading for each treatment. A measured dry bulk density of sediment from the site of 0.338 g/ml was used for the dry

soil mass calculations. For the SediMite treatment, the carbon recovery was estimated to be 115% using the application rate of 4.5 kg SediMite/m2. There are significant errors propagated in these calculations due to the variability of BC measurement across samples from the plot (relative standard deviation, or RSD, of 51% for SediMite) and uncertainty associated with the soil dry bulk density assessment (not measured in each plot).

For the AC slurry treatment, the calculated recovery of AC was 169% according to the reported application rate of 112 kg (300 lb) AC per plot or 2.13 kg AC/m². The RSD for AC measurement in the AC slurry plot was 70% which could lead to an uncertainty in the calculation of AC recovery. For the AquaGate treatment, the percent recovery of AC was 89% according to the reported application rate of 2444 kg (6550 lbs) /plot or 47 kg AquaGate/m². The RSD for AC measurement in the AquaGate treatment plots was 45%. Overall, each of the AC treatment plots showed high levels of AC retention. However, variability of the residual AC among each replicate plot was high.

Figure 18. Black Carbon (BC) in sediments. Panel A: BC levels in sediment core sections for untreated control site. Panel B: BC levels in sediment core sections in treatment site with SediMite.
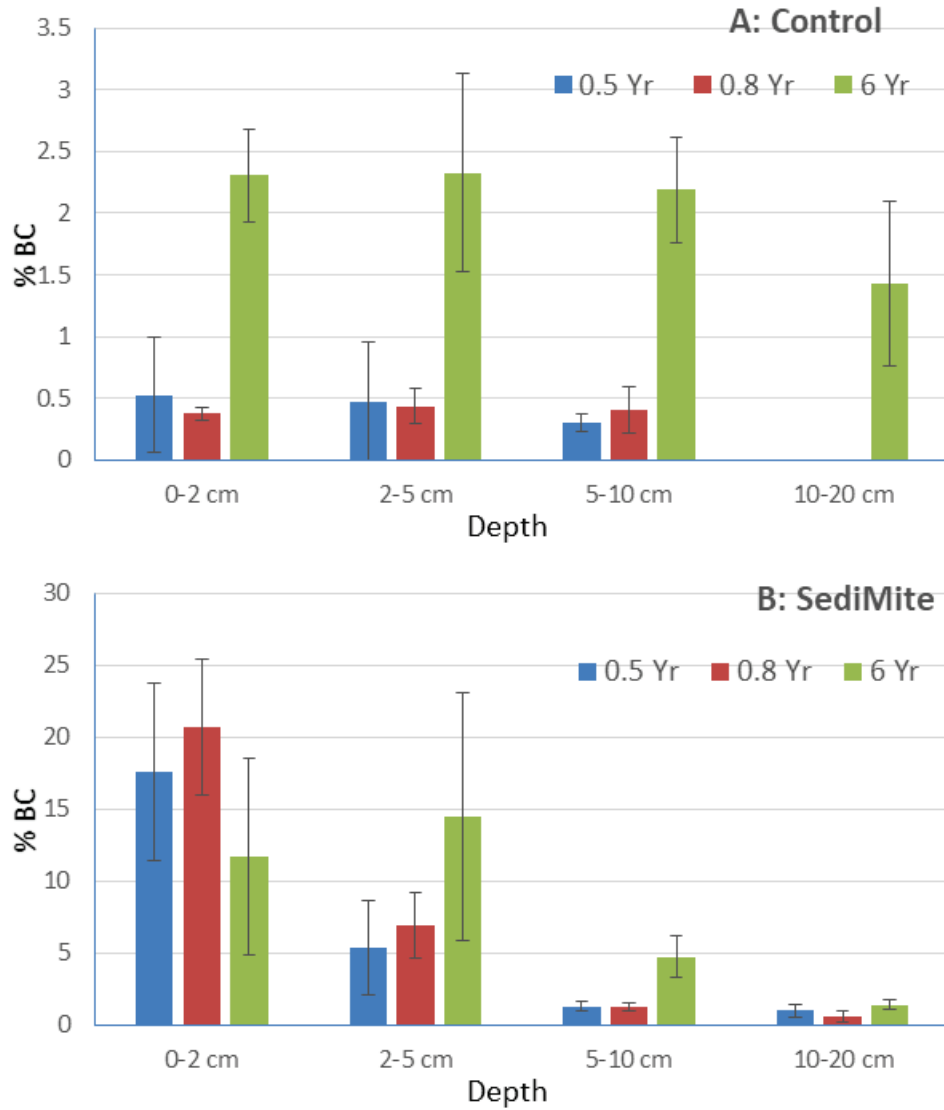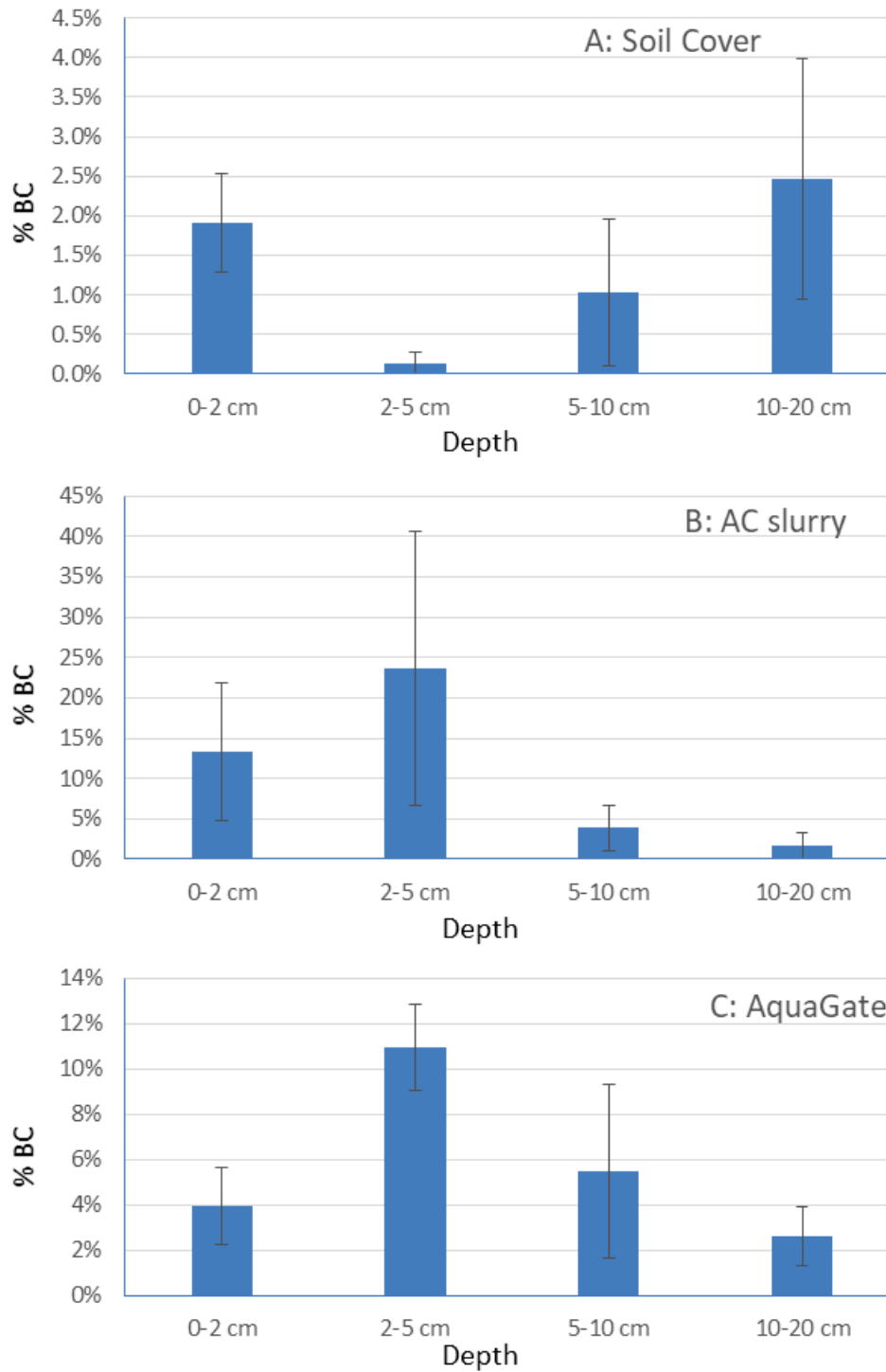
Figure 19. Percent BC measured in core sections from treatment plots six years after application. Panel A: Soil cover. Panel B: AC slurry. Panel C: AquaGate.

5.2.4.3 PCBs in sediment

PCB concentration in sediment was highly variable as also observed in prior sampling at this site. Variability by an order of magnitude or more was observed through the vertical depth of a core section of 0–20 cm depth and also spatially across the sites. This native variability makes robust interpretation of the PCB results difficult.

For each treatment location, the PCB concentration in sediment generally increases with depth with the highest concentration seen in the deepest core. In the soil cover and AquaGate treatments that placed a 5–5.5 cm thick layer of amendment, a reduction in PCB concentration was observed in the 2–5 cm layer, where the amendment caps were expected to lie on the basis of the observed BC measurements (figure 20). These reductions in PCB concentration in sediment in the treated zones for soil cover and AquaGate are caused by dilution of the native PCBs in that sediment with the large mass of amendment placed as a cap. For example, the application rate of AquaGate was 47 kg/m2. This marked decrease in PCB concentration in sediment in the 2–5 cm depth was not observed in the SediMite and AC slurry treatments due to the relatively small mass of amendments placed in these two treatments (4.5 kg SediMite/m^2 and 2.13 kg AC/m^2 respectively).

5.2.4.4 PCB concentration in sediment pore water

Pore water PCB concentrations measured in intact cores in the laboratory were greatly reduced in the treated plots compared to the untreated control plots at every depth (figure 21). This was particularly notable in the treatments that included AC (AquaGate, SediMite, and AC slurry), where the pore water PCB concentrations in the surface 0–2 cm sediments were 99% lower relative to the untreated control. The total pore water PCB concentrations in the 0–2 cm surficial sediments were 16 ng/L in the control site compared to 1.8 ng/L in the soil cover, 0.4 ng/L in the AquaGate treatment, 0.01 ng/L in the SediMite treatment, and 0.06 ng/L in the AC slurry treatment.

Reduced pore water PCB concentrations in the treatment zone, especially for the AC-treated plots, also occurred in the in situ measurements (figure 22). However, the PCB pore water concentrations measured in situ are generally higher than those measured ex situ in the treatment zones. A

more detailed discussion of the differences observed in PCB pore water concentrations measured in situ and ex situ follows this section.

Greatly depressed pore water PCB concentrations were observed in the entire treated depth section, down to 10 cm for each of the AC treated plots. Comparing directly among the treatment plots is challenging due to the spatial heterogeneity in PCBs across plots. However, as indicated before, the surface 0–2 cm sediments were freshly deposited sediments in the pilot-testing area and were likely to have a similar level of PCBs when deposited on the surface of all plots in the vicinity. PCB concentrations in the surface sediments of the control plot appeared to be higher compared to the other treated plots (figure 20). It is likely that the surface sediments deposited on the untreated area were more prone to further contamination from the PCBs migrating upwards from the untreated contaminated sediments. In the treated plots, a barrier was created between the existing highly contaminated sediments and the freshly deposited less contaminated sediments. The elevated pore water concentrations migrating upwards were likely able to influence the surface sediments more in the control plot compared to the treatment plots, where the migration is severely hindered, especially in the AC-treated plots. However, new sediments deposited at each site also have different PCB concentrations to start with, reflecting variability in PCB concentrations in native sediments in the vicinity of each treatment plot.

Figure 20. PCB concentration in sediment core sections. Error bars show ± 1 standard deviation.
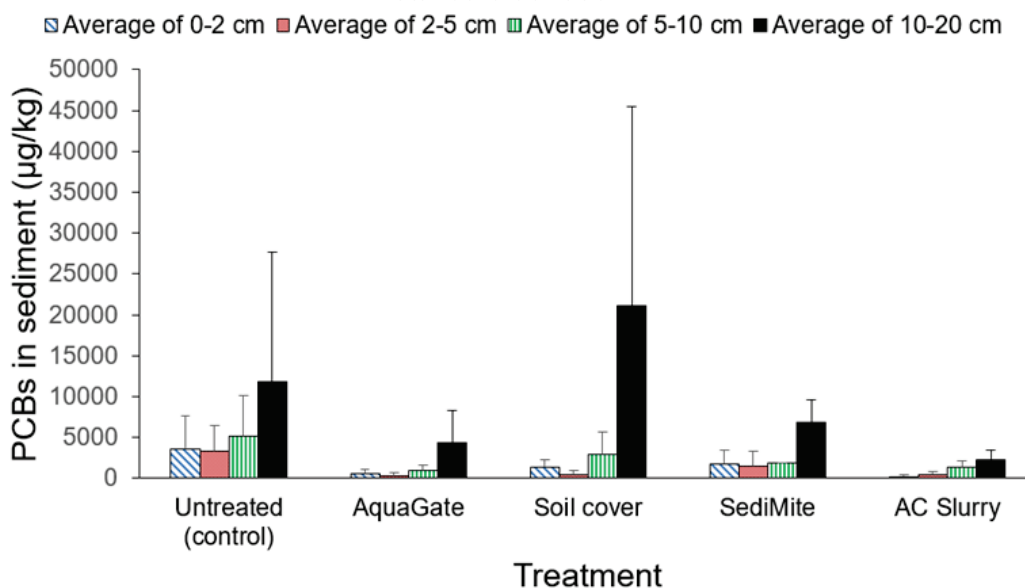
Another way to evaluate the effectiveness of the treatment plots is to analyze the depth profile of the pore water PCB concentrations across plots and compare reductions seen in the surface layers with the deepest layer. As shown in figure 23, the reduction in pore water PCB concentration from the deepest section to the surface was modest for the untreated control (about 60%) and soil cover treatment (about 35%). However, for each of the AC treated plots, the pore water concentration in the surface layer was reduced by about 90% compared to the deepest section. Thus, the soil cover treatment, while very effective in reducing PCB concentrations in sediments (through mass dilution; figure 23), was not very effective in reducing pore water PCB concentrations compared to the AC treatments

Figure 21. PCB concentration in sediment pore water (ex situ in intact core samples). Samples were collected from the Canal Creek pilot study after six years of application of treatment amendments.
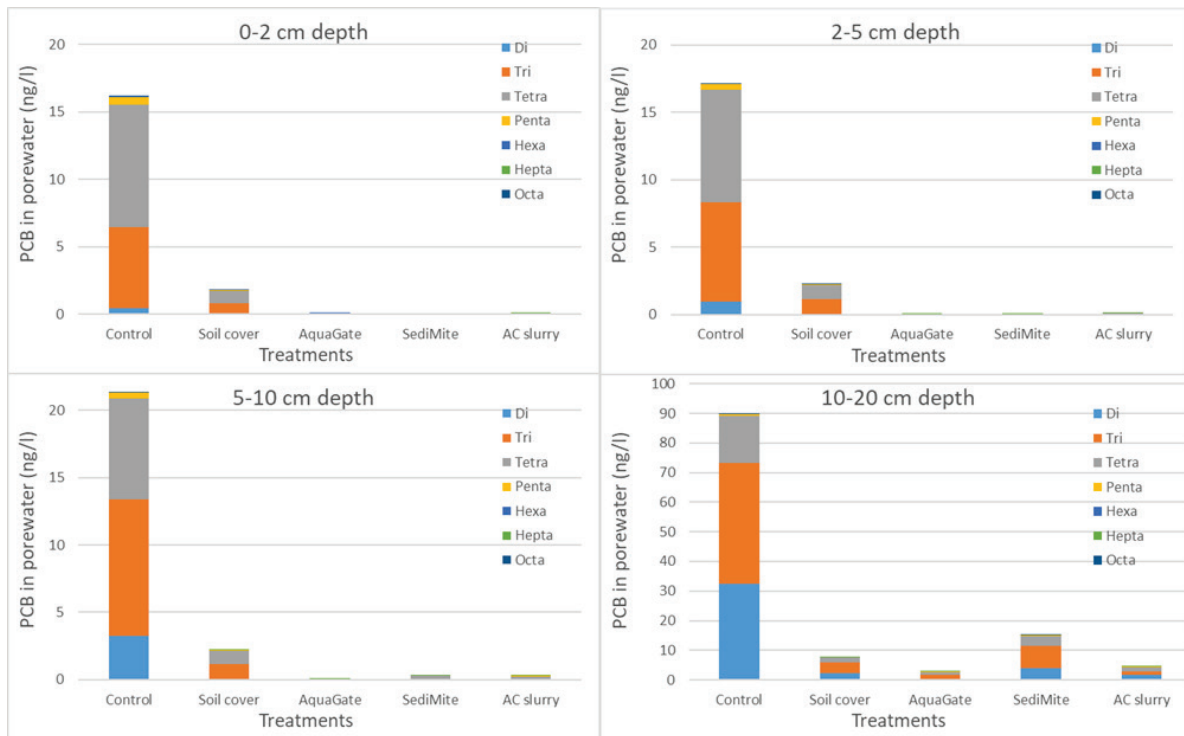
Figure 22. PCB concentrations in sediment pore water (in situ in intact core samples). Samples were collected from the Canal Creek pilot study after six years of application of treatment amendments.
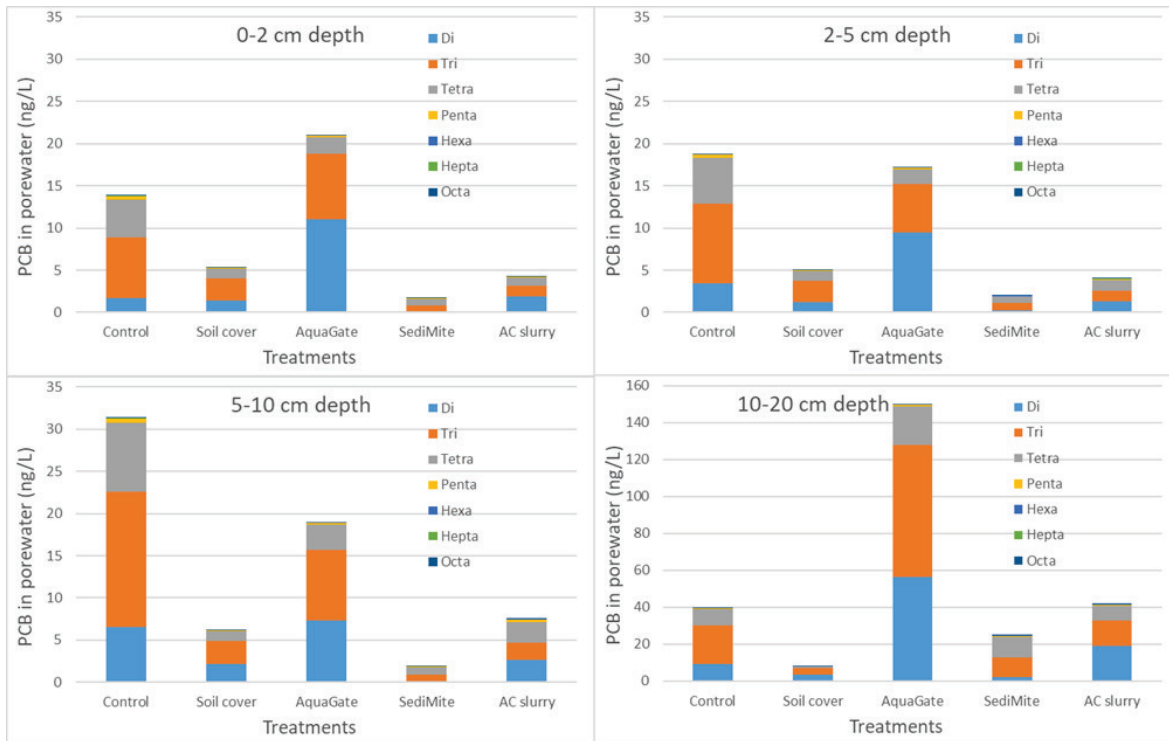
Figure 23. Percent reductions in sediment pore water PCB concentrations. Measurements were in situ at the two surficial layers compared to the pore water concentration measured in the 10–20 cm layer.
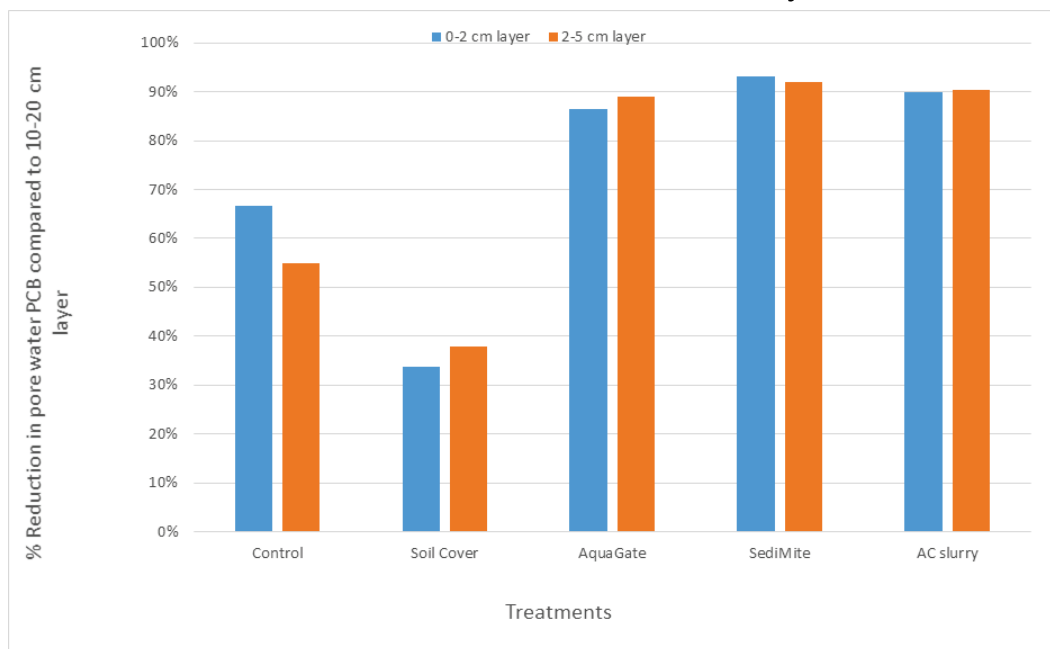
5.2.4.5 Comparison of in situ vs. ex situ passive sampling measurements

For the long-term assessment, pore water PCB concentrations were measured both in the field by in situ deployment of passive samplers as well as ex situ in the laboratory using intact soil cores collected from the treatment plots in the field. The goals were to confirm the measurements using both field and lab measurements and to compare the results obtained from in situ measurements with ex situ measurements. A major difference in the laboratory setup was that the cores were maintained in static water with minimal pore water exchange. In contrast, in situ measures were affected by naturally occurring tidal pumping processes. Additionally, the intact cores used for laboratory testing were processed in the laboratory to remove the bottom 5 cm, which likely removed the most contaminated section in the core. As shown in figure 24, the increasing trend of pore water PCB concentrations with depth is evident in both the in situ and ex situ deployments of the passive samplers. For the untreated control plots, the surface 0–10 cm depth sections gave similar measurements of pore water in situ and ex situ. For the 10–20 cm section, the ex situ measurements were greater by factor of two. Thus, the ex situ laboratory measurement of sediment pore water is acceptable for undisturbed native sediments, and the method should be considered for site investigations. For the soil cover plot, the 0–10 cm sections showed pore water PCB concentrations that were greater by a factor of two to three for the in situ measurements than the ex situ measurements. Additionally, the dichlorobiphenyls seen in the in situ measurements are not seen in the ex situ measurements. It is likely that the ex situ measurements with static water conditions were not able to capture the effect of groundwater movement in a tidally active site. This phenomenon is especially evident for the more soluble dichlorobiphenyls, which are more mobile and prone to transport with groundwater movement. As discussed earlier, the in situ measurements report little effectiveness of the soil cover treatment in reducing pore water migration compared to the ex situ measurements. The pore water concentration in surface sediments was barely 35% lower compared to the pore water concentration at 10–20 cm depth. Thus, the soil cover treatment is not effective in reducing PCB concentrations in sediment pore water, according to the field measurements. As described above, this is likely a consequence of differences in pore water exchange affecting in situ vs. ex situ measures.

For the three AC-treated plots shown in figure 23, figure 25, and figure 26 the ex situ pore water measurement in the top 10 cm shows nearly two

orders of magnitude reduction in pore water concentration compared to the pore water concentration in the 10–20 cm depth section. However, the in situ measurement shows less reduction, about one order of magnitude reduction compared to the respective 10–20 cm depth section. There are several possible reasons for this difference: (1) upward migration of sediment pore water via tidal pumping is likely in the field site, which would affect the in situ measurement, while migration of PCBs in the ex situ setup would be driven almost entirely by slow molecular diffusion; (2) contaminated surface water probably influences the surface sediment pore water measurement in the field site, whereas, in the laboratory exposure, clean artificial water was used; (3) spatial variability resulted in differences in PCB concentrations in sediment collected for ex situ measurements compared to locations where in situ measurements were performed. However, this third explanation is very unlikely to have occurred to all the samples of all three AC treatments.

On the basis of the observation of differences in pore water measurement performed in situ vs. ex situ, it is likely that the ex situ intact core measurements of pore water and bioaccumulation were not able to replicate the real exposure scenario in a tidally influenced marsh environment, where groundwater pumping may have a dominant role in influencing exposure of PCBs present in deeper sediments. The extensive presence of plant matter within the sediment in a marsh environment also likely increases hydraulic conductivity and facilitates the transport of water during tidal pumping. This phenomenon is likely to be of less significance in river sediments, where density of plant matter is less and there is an absence of tidal pumping. Previous work at Grasse River demonstrated similar bioaccumulation observations performed in situ and ex situ (Beckingham and Ghosh 2011). However, parallel in situ vs. ex situ measurements of bioaccumulation has not been performed for a tidal marsh environment, and it is not clear if ex situ measurements in such an environment would reflect in situ exposures.

Figure 24. Comparison of ex situ (top) and in situ (bottom) sediment pore water PCB concentrations. Analysis used passive sampling for the untreated and soil cover treatment. *Note the two different* y-*axis scales for the untreated and soil-cover plots.*
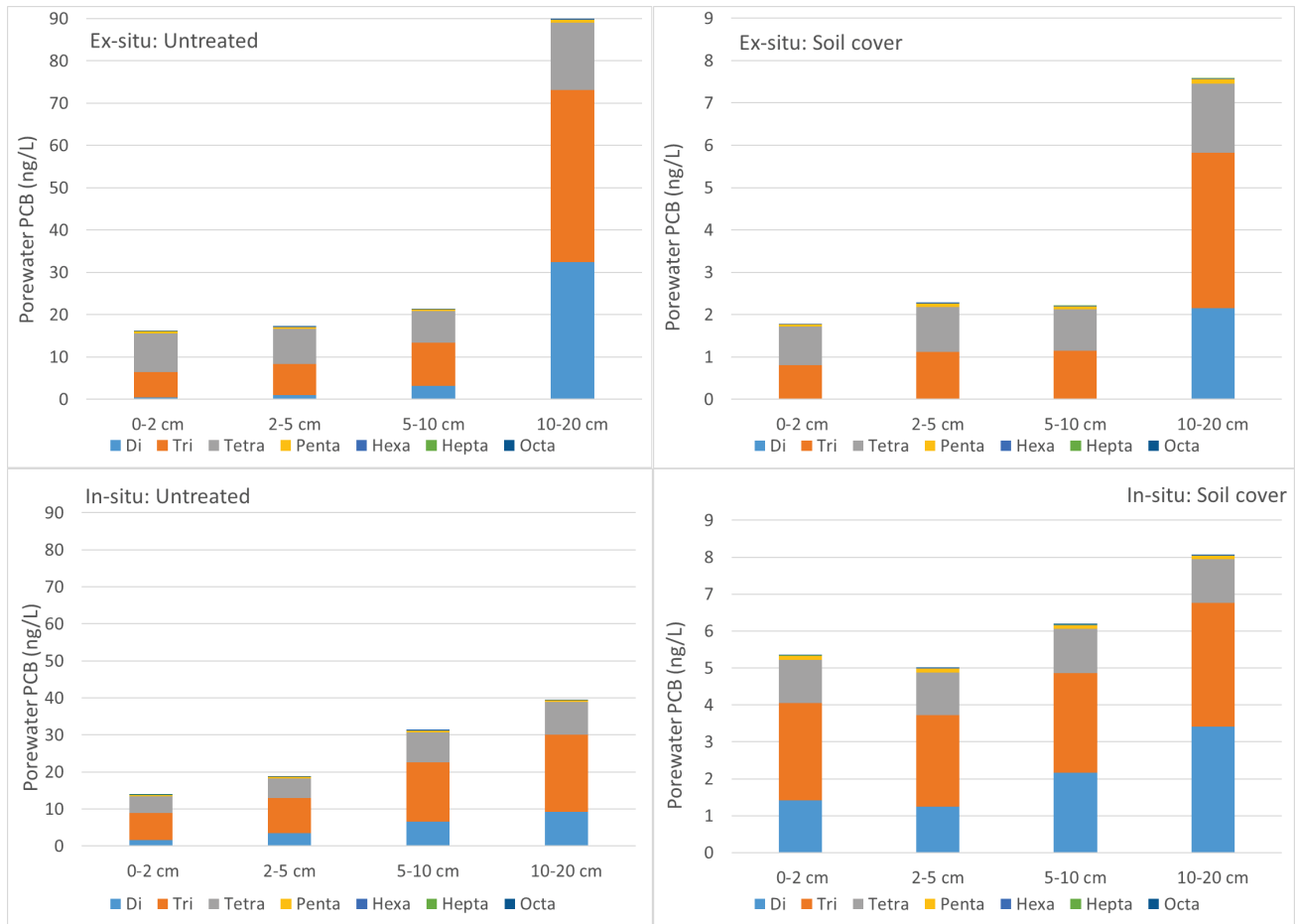
Figure 25. Comparison of ex situ (top) and in situ (bottom) sediment pore water PCB concentrations. Samples were measured using passive sampling for the AquaGate and SediMite treatments. *Note the different* y-*axis scale for the in situ AquaGate plot.*
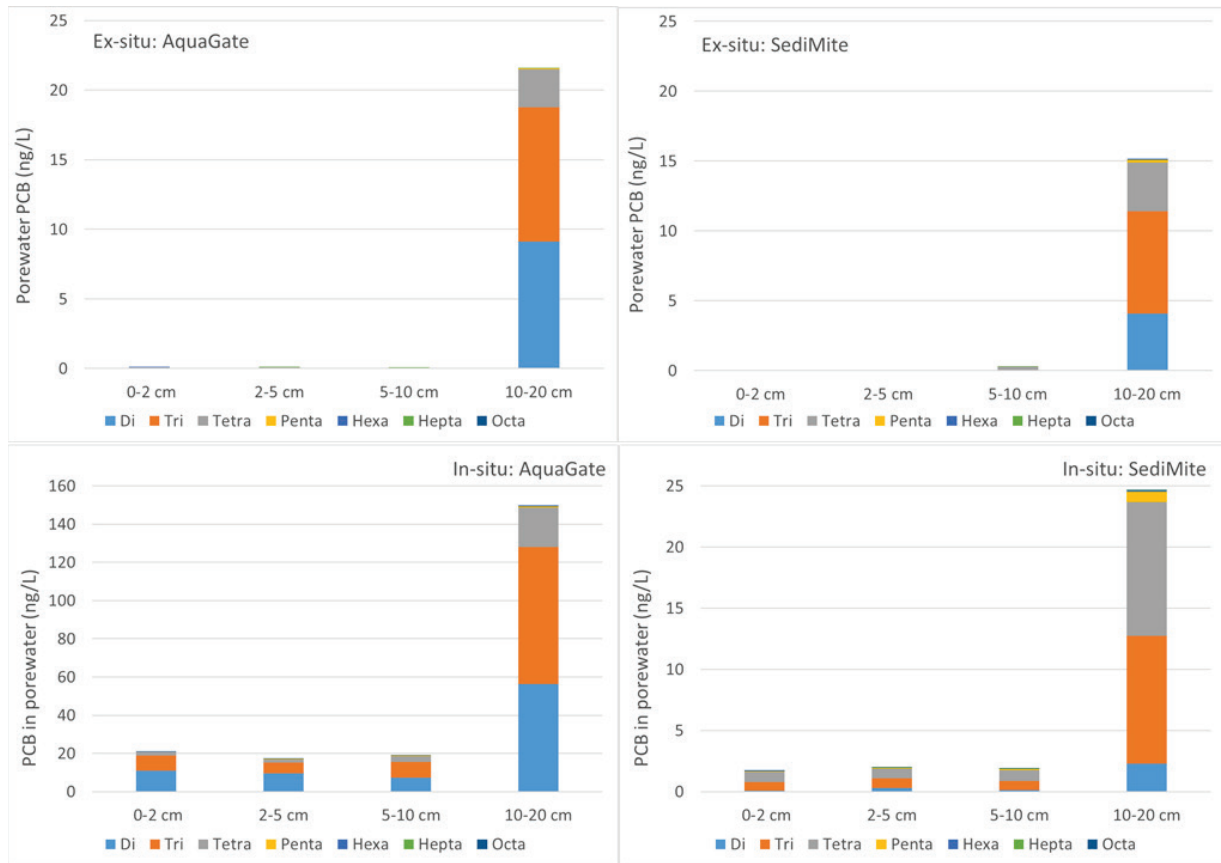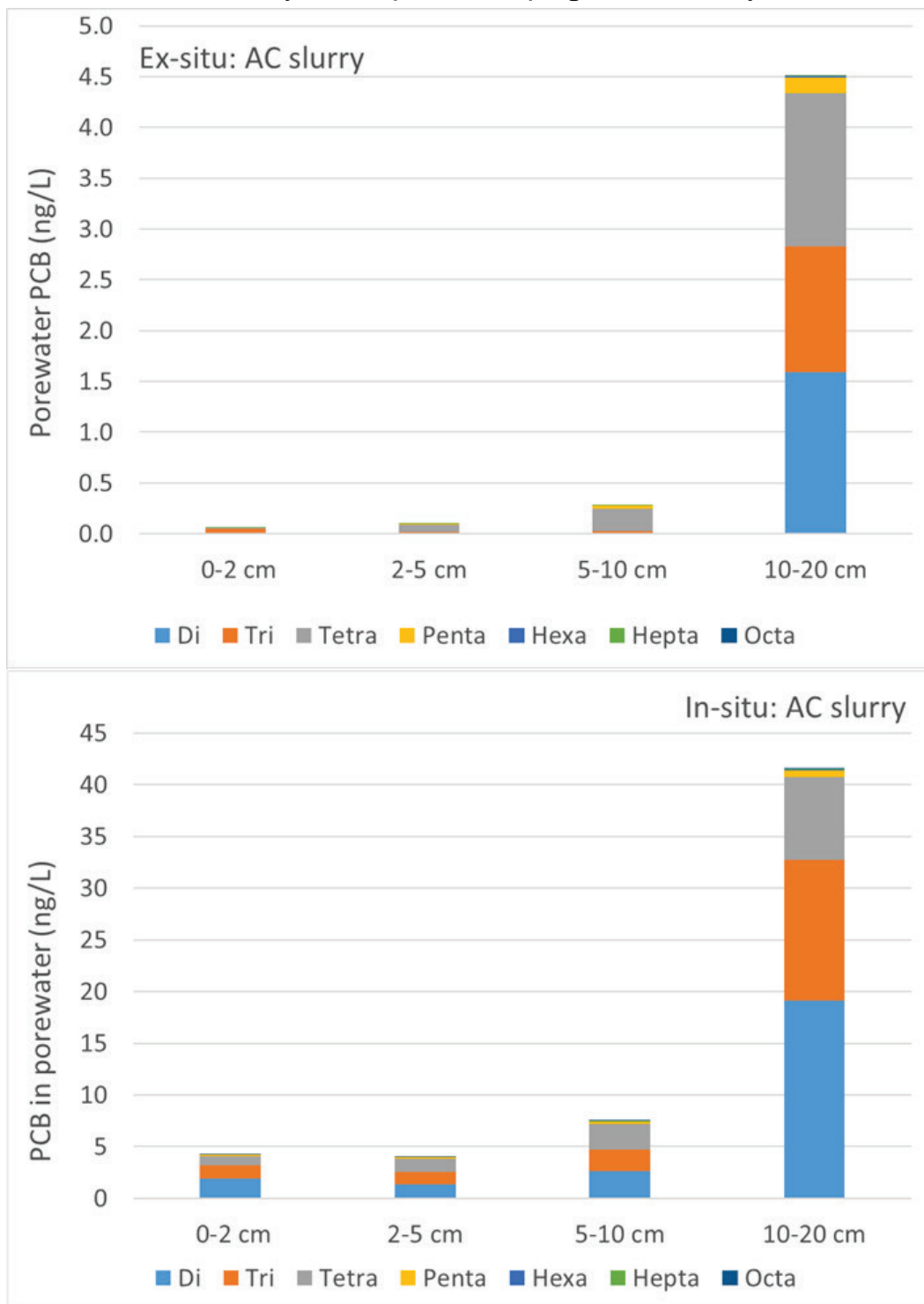
Figure 26. Comparison of ex situ (top) and in situ (bottom) sediment pore water PCB concentrations. Analysis used passive sampling for the AC slurry treatment.

5.2.4.6 PCB bioaccumulation in worms

In addition to assessing bioavailability of contaminants through the use of passive sampling (both in situ and ex situ), bioavailability was also assessed in laboratory bioaccumulation tests in this study using the freshwater oligochaete *L. variegatus*. The accumulation of total PCBs in worms was lower in all the treatment plots compared to the bioaccumulation in the untreated plot (figure 27). The box-and-whisker plots (figure 27A) clearly show greater variability in tissue residues in the untreated plot relative to the AC-amended plots. One of the five replicates in SediMite treatment showed high PCB bioaccumulation compared to very low values in the remaining four replicates. Similarly, there was some variability in the soil cover treatment, with two of the replicates showing high PCB bioaccumulation compared to low bioaccumulation for the remaining three. These inconsistencies could be due to local variability in PCB concentrations in sediment or variability in the applied dose of amendments to the location where the individual core was collected from. Among the treatments, The SediMite and soil cover treatment areas had higher starting PCB concentrations in sediment compared to the AC slurry and AquaGate plots (figure 20). For AquaGate and AC slurry treatments, all five replicates showed similar low PCB bioaccumulation. Despite the variability, bioaccumulation of total PCBs was significantly reduced in all treated plots. The average reduction in sum congener concentrations relative to untreated for AquaGate, AC slurry, soil cover, and SediMite treatments was 91%, 96%, 83%, and 82%, respectively.

Significant trends developed between some homolog groups. Monochlor biphenyls were not detected in tissue. For di and trichlor biphenyls, there were no significant differences between treatments (p = .054). There were significantly lower concentrations of tetra, penta, hexa, hepta, and octachlor biphenyls in worms exposed to all treatment plots (p< .009) relative to worms exposed to the untreated plot. The average concentration of these homolog groups in tissues ranged 78–98% lower than the worms exposed to the untreated plot. Trace levels of nonochlor biphenyls were detected in worm tissue in the untreated plots, while no nonochlor biphenyls were detected in treatment tissues (exception soil cover).

Some of the difference in bioaccumulation across plots can be explained by the differences in PCB concentration in sediment at the various treatment plot locations. As shown in figure 20, the average PCB concentration in the

bottom 10–20 cm of sediment ranged from a low of 1.8 ppm in the AC slurry treatment to a high of 21 ppm in the soil cover treatment. PCB concentration in the new sediment in the top 2 cm of sediment also ranged across plots and varied from 0.2 ppm in the AC slurry treatment to 3.6 ppm in the untreated plot—a nearly one order of magnitude difference. These differences in surface sediment PCB concentrations likely affected the observed bioaccumulation in worms. To evaluate the effect of surface sediment concentration, the concentration in tissue was normalized to the concentration in the top 2 cm of sediment for each treatment (figure 28). After accounting for the differences in sediment PCB concentrations, the differences across treatments in tissue residue concentrations are less obvious. For example, the AC slurry treatment that showed the biggest reduction in PCB accumulation in worms compared to the untreated sediment also had the lowest PCB concentration in surface sediments and does not appear to have a treatment effect after six years when normalized to the sediment PCB concentration. After normalization to total PCB in sediment, the SediMite and soil cover treatments still show >50% reduction in PCB accumulation in worms, while the AquaGate and AC Slurry treatments show less than <50% reduction. To the extent that the surface sediment PCB concentrations are affected by the treatment's reduction of recontamination from deeper sediments, the treatments can still be considered to be effective. Thus, normalization of bioaccumulation to total PCB concentration in surface sediment may not lead to the correct assessment of the treatments.

Figure 27. PCB bioaccumulation in worms. Worms were exposed to sediment in intact cores in the laboratory. Panel A summarizes the sum PCB congener concentrations for the different plots (dashed lines = means; solid lines = median). Boxes represent 25th to 75th percentiles, while bars indicate 5th and 95th percentiles. Asterisks denote a statistically significant difference relative to the control (Holm-Sidak method (Ryan 1960); data were square-root transformed). Panel B summarizes the homolog variability between replicates. The analytical quality control (QA) plot was included as the fifth replicate so that each plot comparison had a total of five replicates. Panel C shows averages homolog concentrations on a linear scale to show relative differences. Panel D provides the data from panel C on a log scale to more clearly show differences between groups.
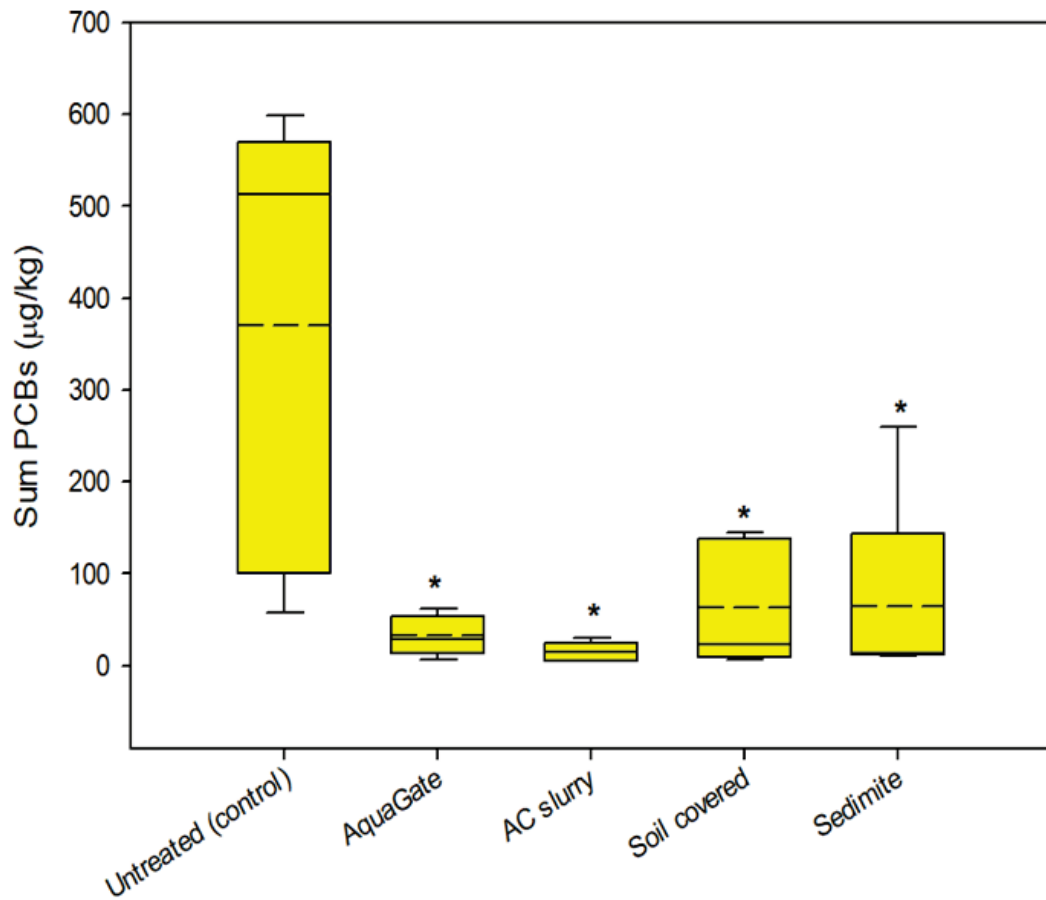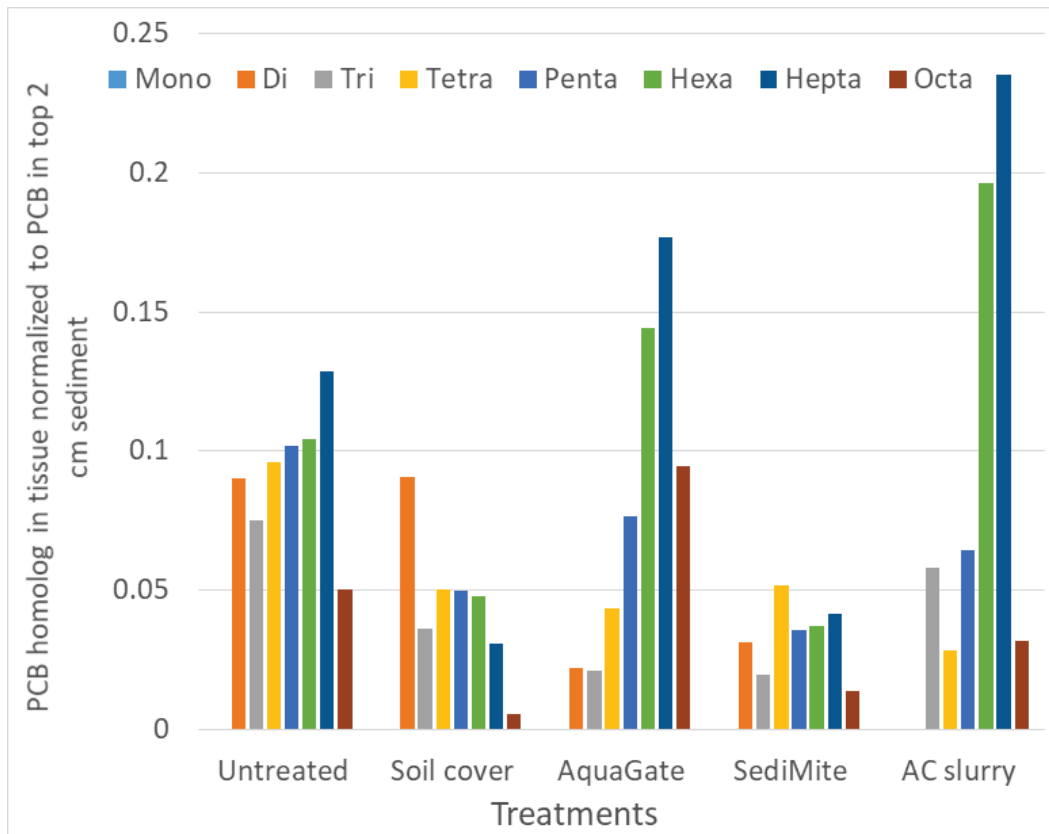

A
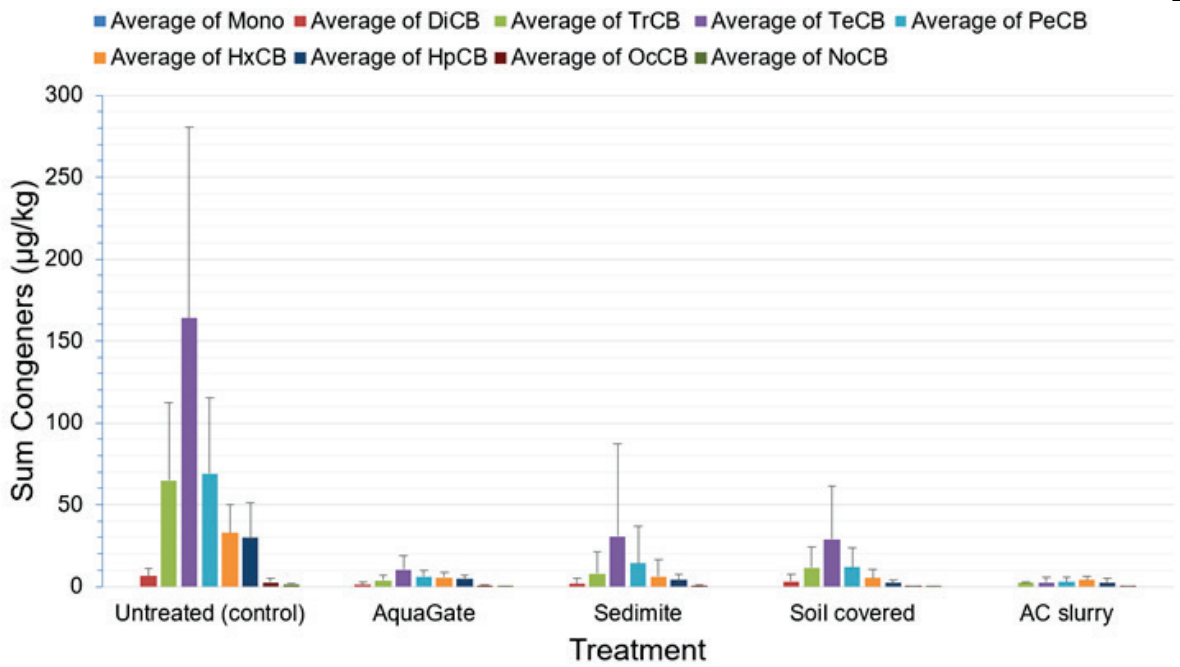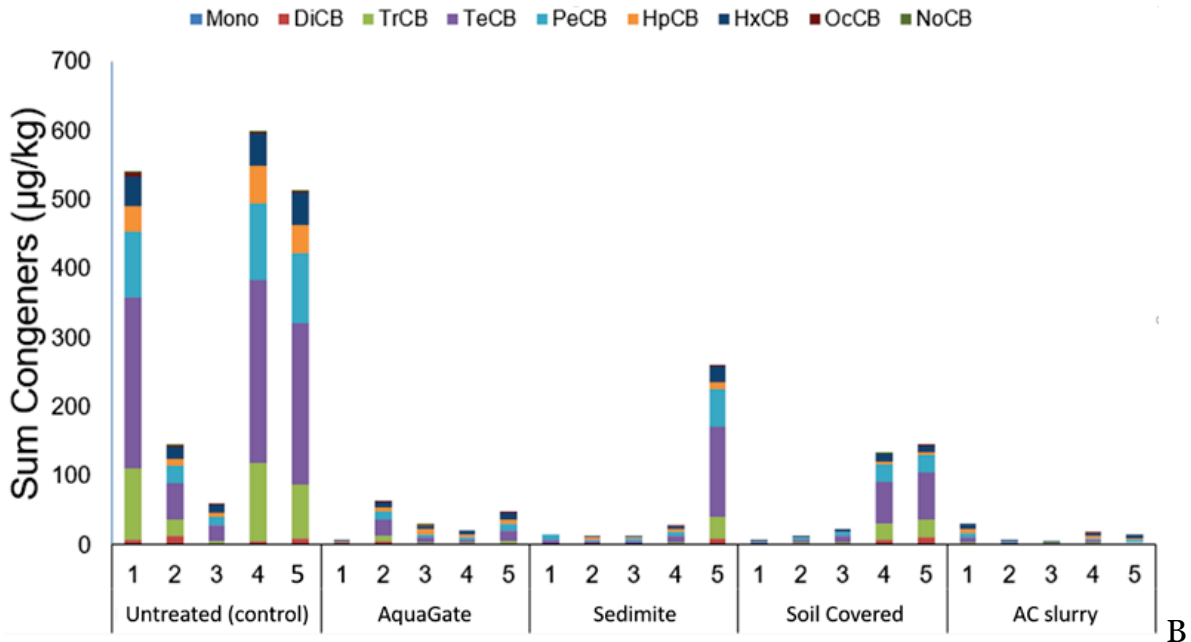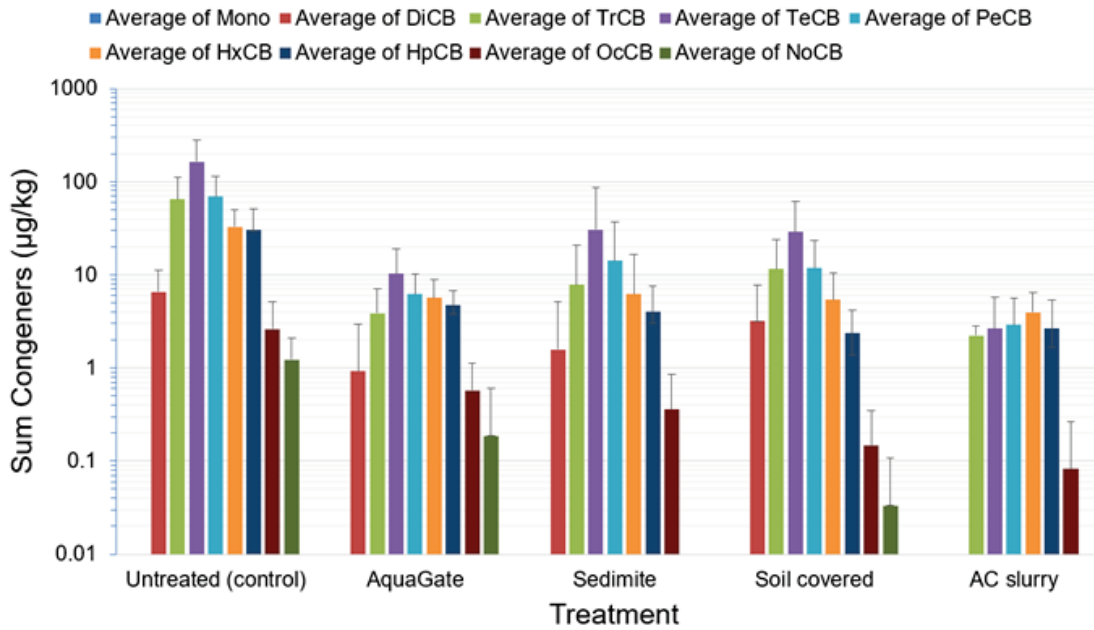
D

Figure 28. PCB homolog concentration in worms normalized to PCB concentration in surface 2 cm of sediments.

6 Performance Assessment

Overall, the long-term monitoring at the two pilot-scale study sites revealed that AC was stable in the sediment environment at two hydrodynamically very different sites. In the Grasse River pilot study, the AC was stable in the flowing river environment when placed on the surface sediments without initial mechanical mixing and also when the AC was mixed into the sediments. The 10-year post-treatment assessment revealed that the Grasse River site had a sediment deposition rate of close to 2 cm/yr, which led to the burial of the AC treatment. The AC layer remained functional in reducing pore water PCB concentrations in the sediments and was effective in reducing accumulation in worms even after 10 years in the field. The Canal Creek pilot study provided a very different hydrodynamic environment: a tidal wetland. Deposition of new sediment was much lower compared to Grasse River and calculated at about 1/3 cm/yr. In this active hydrodynamic environment, AC placed using three approaches (SediMite, AquaGate, and AC Slurry) was found to be stable with near complete recovery of the applied dose of AC for all treatments. All AC treatments at Canal Creek continued to reduce pore water PCB concentrations six years after application and was likely effective in reducing PCB upward migration of sediment pore water via tidal pumping to the depositing surface layer of sediment. An assessment of the proposed performances matrices is provided in table 5 below. All performance objectives were met.

Table 5. Performance metrics.

Performance Objective	Evaluation Metric	Success Criteria*	Result
Mass of AC retained within the site	AC analysis	-Sediment core images show persistence of BC within test plots at intervals similar to that observed during postplacement monitoring. -Measured AC is statistically significantly greater than the control plots and ≥50% of the target dose of the postplacement AC measurements on a per unit sampling area basis.	-Core images were not taken due to difficulty in imaging the AC layer within dark anaerobic sediments. -AC measured in core sections revealed the presence of AC in sediment at or above the target dose in both Grasse River and Canal Creek pilot studies.
Vertical mixing and concentration of AC	AC analysis at various core depths -Sediment core image profiles at various core depths	-Allowing for surface deposition and some vertical mixing, vertical distribution and quantity per unit surface area of AC ≥50% to that observed during postplacement monitoring.	-Vertical mixing was higher at the Grasse River site compared to the Canal Creek site. At both sites, AC recovery was >50% of target dose.
Horizontal dispersion, mixing, and concentration of AC	AC analysis at multiple coring locations within treatment plot	-Measured AC is statistically significantly greater than the control plots and ≥50% of the target dose of the postplacement AC measurements on a per unit sampling area basis.	-Measured AC in the treated zone was statistically greater than in the control plots at both sites. -AC recovery from the treatment plots at both pilot studies was >50% of target dose.
Functional performance of AC Chemical performance using multiple chemical measures Exposure reduction performance	-Physicochemical analysis of field sediment -Ex situ assessment of PCB bioavailability reduction using intact cores	-Continued reduction (>50%) in PCB pore water concentrations. -PCB bioavailability within the treated zone is significantly reduced as compared to untreated sediments on a bulk and normalized (to total PCB) basis. Treatment efficacy judged as >80% good; 50 – 79% fair; <50% poor. Determination includes consideration of AC levels.	-PCB pore water concentration reductions in the AC treated zone was >80% in both Grasse River and Canal Creek pilot studies. -For Grasse River, reduction in PCB bioaccumulation was >80% for the UTA site and >50% for the MTA site. After normalization to sediment total PCB, only the UTA site showed >50% reduction in bioaccumulation in worms. -For Canal Creek, reduction in PCB bioaccumulation was >80% for all treatments. After normalization to sediment total PCB, only the SediMite and soil cover sites showed >50% reduction in bioaccumulation in worms.

7   Cost Assessment

A cost assessment was not performed in this long-term monitoring study. Detailed cost assessments of the remedy implementation for the various treatments are available in the original ESTCP project final reports (Menzie et al. 2016, Ruiz et al. 2016).

8   Implementation Issues

The long-term monitoring program was implemented successfully as described in this report. Full descriptions of the technology implementation are available elsewhere for the Grasse River Site (Beckingham et al. 2011) and Canal Creek site (Ruiz et al. 2016, Menzie et al. 2016). This project provides novel results of long-term performance of AC treatments in two pilot-scale projects. Overall, the results indicate persistence of the applied AC in both studies. In addition, the applied AC continues to reduce pore water PCB concentrations in the treated zones 6–10 years after application. PCB bioavailability continues to show reductions in the treated sediments. These findings address stakeholder concerns of lack of long-term data for in situ treatments with AC.

The study also found an important issue with performing ex situ measurements for sediments from a tidally influenced marsh site. The evidence indicates that intact cores in the laboratory do not accurately reflect the field exposure conditions after treatment for passive sampling or organism exposure when there is very active groundwater movement. This can be especially true where a major source of the pollutants lies deeper in the sediments and there is an active tidal pumping process, as seen in the Canal Creek site.

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David Moore	3909 Halls Ferry Rd Vicksburg, MS 39180-6199	601-634-4199 601-634-2263 david.w.moore@usace.army.mil	Lead, oversight and development of deliverables
Jim Leather	SPAWAR (US Navy) 53475 Strothe Road San Diego, CA 92152-6325	619-553-6240 619-553-6305 leather@spawar.navy.mil	Consultant and coordinator to related navy projects
Upal Ghosh	University of Maryland Baltimore County Baltimore, MD 21250	410-455-8665 410-455-6500 ughosh@umbc.edu	Lead, physiochemical studies
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Federal

ERDC: Todd S. Bridges, Dr. Sandra Brasfield Newell, Mr. Alan J. Kennedy, and Dr. David Moore

Dr. Todd Bridges is the principal investigator for the ESTCP project. He is the army's senior scientist for environmental science. He provided expertise and

guidance to the project manager in the development and implementation of the demonstration plan. His team at ERDC (Dr. Newell, Mr. Kennedy, and Dr. Moore) was responsible for assessment of proposed carbon application by AEI and CEI, deployment of semipermeable membrane devices (SPMDs), analysis of sediment PCB concentrations, and analysis of aqueous equilibrium PCB concentrations.

Dr. Sandra Brasfield Newell served as the project manager. Dr. Newell, a team leader and researcher at ERDC, coordinated field efforts outlined in the demonstration plan between the various groups involved in the project. She coordinated the overall preparation of the study's plan documentation, the demonstration plan and supporting documents. She also coordinated technical activities as a liaison between the ESTCP's environmental restoration manager, ERDC, and other partners. She was responsible for ensuring that communication of all decisions that affected field or laboratory activities were dispatched in real time. Finally, she responded to quality assurance reports and implemented corrective action to address systematic problems.

Mr. Al Kennedy served as project bioaccumulation quality assurance and data manager.

Dr. Moore, a senior team leader, researcher at ERDC, and director of the ERDC Center for Emerging Contaminants of Concern provided additional oversight and facilitate development of deliverables.

US Navy SPAWAR (Dr. Jim Leather)

Dr. Leather has worked in the oil industry, academia, the DOE, and navy research laboratories for 25 years. He served as a consultant for this project, but once the program eliminated Hunters Point from the project scope, his role was minimized.

Academia

University of Maryland Baltimore County: Upal Ghosh

Dr. Upal Ghosh served as the physiochemical studies leader. He has been involved in demonstrations at all of the selected sites and provided the details of prior treatments. He and his staff also conducted laboratory tests to assess the change in PCB availability for desorption to the aqueous phase. He implemented these tests in coordination with the project manager. Dr. Ghosh assisted the preparation of this report and made himself available for presentations to the program, user community, regulatory community, and industry.

Industry

Exponent: Dr. Charles Menzie

Dr. Charles Menzie is a principal scientist with Exponent and brought invaluable experience to the project team. Dr. Menzie was involved in the demonstrations performed at Canal Creek and is the coinventor of SediMite, a low-impact method for remediating contaminated sediments.

Acronyms

AG   AquaGate

AC   Activated Carbon

ACS   activated carbon slurry

ACPS   activated carbon pilot study

APG   Aberdeen Proving Ground

BC   black carbon

BG   background site

BSAF   biota sediment accumulation factor

BZ   Ballschmiter and Zell (1980) PCB identification number C
              control

CERCLA   Comprehensive Environmental Response, Compensation,
              and Liability Act

DDT   dichlorodiphenyltrichloroethane

DDx   DDT and related isomers, including
              dichlorodiphenyldichloroethylene (DDE) and
              dichlorodiphenyldichloroethane (DDD)

DoD   Department of Defense

ERDC   Engineer Research and Development Center

ESTCP   Environmental Security Technology Certification Program

GC-ECD   gas chromatography/electron capture detection

GLNPO   Great Lakes National Program Office

HOC	hydrophobic organic compounds
MTA	mixed treatment area
NIEHS	National Institute of Environmental Health Sciences
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PE	polyethylene
PRC	performance reference compound
SARA	Superfund Amendments and Reauthorization Act (1986)
SC	sand control
SE	standard error
SERDP	Strategic Environmental Research and Development Program
SM	SediMite
TOC	total organic carbon
UMBC	University of Maryland Baltimore County
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
UTA	unmixed treatment area

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14. ABSTRACT

A number of sites around the United States have used activated carbon (AC) amendments to remedy contaminated sediments. Variation in site-specific characteristics likely influences the long-term fate and efficacy of AC treatment. The long-term effectiveness of an AC amendment to sediment is largely unknown, as the field performance has not been monitored for more than three years. As a consequence, the focus of this re-search effort was to evaluate AC's long-term (6–10 yr) performance. These assessments were performed at two pilot-scale demonstration sites, Grasse River, Massena, New York and Canal Creek, Aberdeen Proving Ground (APG), Aberdeen, Maryland, representing two distinct physical environments. Sediment core samples were collected after 6 and 10 years of remedy implementation at APG and Grasse River, respectively. Core samples were collected and sectioned to determine the current vertical distribution and persistence of AC in the field. The concentration pro-file of polychlorinated biphenyls (PCBs) in sediment pore water with depth was measured using passive sampling. Sediment samples from the untreated and AC-treated zones were also assessed for bioaccumulation in benthic organisms.

The data collected enabled comparison of AC distribution, PCB concentrations, and bioaccumulation measured over the short- and long-term (months to years).

15. SUBJECT TERMS

Water – pollution Aquatic habitats	Contaminated sediments Carbon, Activated	Environmental protection

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