FINAL REPORT

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

FEBRUARY 2016

Charles Menzie
Bennett Amos
Susan Kane Driscoll
Exponent

Upal Ghosh
University of Maryland, Baltimore County

Cynthia Gilmour
Smithsonian Environmental Research Center

REPORT DOCUMENTATION PAGE						*Form Approved OMB No. 0704-0188*
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1. REPORT DATE 09-26-2015			**2. REPORT TYPE** Final			**3. DATES COVERED** 2008 -2015
4. TITLE AND SUBTITLE Evaluating the Efficacy of a Low-Impact Delivery System for *In situ* Treatment of Sediments Contaminated with Methylmercury and Other Hydrophobic Chemicals						**5a. CONTRACT NUMBER** W912HQ-08-C-0017 **5b. GRANT NUMBER** **5c. PROGRAM ELEMENT NUMBER**
6. AUTHOR(S) Menzie, C 571-214-3648; camenzie@exponent.com Amos, B Kane Driscoll, S Ghosh, U Gilmour, C						**5d. PROJECT NUMBER** ER-200835 **5e. TASK NUMBER** **5f. WORK UNIT NUMBER**
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Exponent Inc., Alexandria VA and Maynard MA University of Maryland Baltimore County, Baltimore MD Smithsonian Environmental Research Center, Edgewater MD						**8. PERFORMING ORGANIZATION REPORT NUMBER** ER-200835
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Environmental Security Technology Certification Program (ESTCP), Alexandria, VA						**10. SPONSOR/MONITOR'S ACRONYM(S)** ESTCP **11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
12. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT: This report describes field demonstrations of *in situ* treatment of PCBs and mercury with activated carbon (AC) delivered using the SediMite® delivery system. The project involved two sites within Canal Creek at the Aberdeen Proving Ground (APG) in Edgewood, Maryland, that are contaminated with mercury and PCBs. The application of SediMite® to a third site—Bailey Creek at Fort Eustis in Virginia—is also described for comparison. Data are also included for a fourth site at which SediMite® was used to treat PCBs within a *Phragmites* marsh. The sites represent different types of habitats, and the synoptic evaluation provides insights into the performance of SediMite® as a delivery system for *in situ* treatment with AC across a range of biological and physical conditions. The demonstration projects showed that treatment of PCBs can be carried out in the field using AC delivered via SediMite®. The bioavailability of PCBs was typically reduced by >80% across these sites, with values >90% being achievable. Treatment was also demonstrated for DDx. Efficacy was related to the presence of target doses of activated carbon. Results were equivocal for treatment of mercury. Because most performance metrics for bioavailability rely on laboratory measures of field-collected samples, there is some uncertainty regarding extrapolation to the field. Effects of treatment on native biota were judged to be negligible. This remedial option falls within a range of costs for other remedial alternatives.						
15. SUBJECT TERMS In-situ remediation, activated carbon, PCB, mercury, treatment, ecological effects						
16. SECURITY CLASSIFICATION OF: Unclassified				**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGE**	**19a. NAME OF RESPONSIBLE PERSON** Charles Menzie
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**		UU	120 plus appendices	**19b. TELEPHONE NUMBER** *(include area code)* 571-214-3648

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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ACRONYMS

AC	activated carbon
APG	Aberdeen Proving Ground
BC	black carbon
BPW	Maryland Board of Public Works
BSAF	biota-soil/sediment accumulation factor
CCSA	Canal Creek Study Area
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act of 1980
DDx	dichlorodiphenyltrichloroethane and related degradation products
DOC	Dissolved organic carbon
DoD	U.S. Department of Defense
DOM	dissolved organic matter
EMNR	enhanced monitored natural recovery
ENR	enhanced natural recovery
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
Hg	mercury
ICP-OES	inductively coupled plasma-optical emission spectroscopy
Kd	partitioning coefficient
LCC	Lower Canal Creek
MeHg	methylmercury
MNR	monitored natural recovery
NIEHS	National Institute of Environmental Health Services
PAC	powdered activated carbon
PCB	polychlorinated biphenyl
POM	polyoxymethylene
QA/QC	quality assurance and quality control
RPM	Remedial Project Manager
SAOB	sulfide anti-oxidant buffer
SAV	submerged aquatic vegetation
SBIR	Small Business Innovative Research
SERC	Smithsonian Environmental Research Center
SERDP	Strategic Environmental Research and Development Program
SUVA280	specific UV absorbance at 280 nm
the Vortex	the Vortex TR-Aquatic system developed by Vortex Granular Systems, LLC
TOC	total organic carbon
UCC	Upper Canal Creek
UMBC	University of Maryland Baltimore County
USACE	U.S. Army Corps of Engineers
UXO	unexploded ordnance
WREC	Wye Research and Education Center

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ACKNOWLEDGEMENTS

The Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) has funded Exponent and its partners—the University of Maryland at Baltimore County and the Smithsonian Environmental Research Center—to conduct work under ESTCP Project No. ER-0835. As part of this effort, the Exponent team coordinated with ESTCP Project No. ER-2000825 led by the Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC) and its DoD partners: U.S. Army Public Health Command, Naval Facilities Engineering Command Atlantic Division (NAVFAC LANT), U.S. Air Force (USAF), Engineer Research and Development Center Waterways Experiment Station (ERDC WES), AECOM, and the University of New Hampshire (UNH). The Exponent team coordinated closely with many individuals at the U.S. Army's Aberdeen Proving Ground; in particular, the leadership of Allison O'Brien is acknowledged. Support for the effort was also provided by RMT, Inc., the University of Maryland Wye Research Institute, Eco Analysts, and Dr. Jeffrey G. Baguley of the Department of Biology, University of Nevada, Reno. Helpful advice was provided by the technical support team for the ESTCP environmental program. The report was prepared with the assistance of Eileen McAuliffe of Exponent.

EXECUTIVE SUMMARY

Objectives of the Demonstration

This report describes the efficacy of activated carbon (AC) delivered in the field using the SediMite® delivery system for *in situ* treatment of sediments contaminated with polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and related degradation products (DDx), and/or mercury. Performance objectives are related to how well SediMite® can be delivered at field sites, the degree of reduction in contaminant bioavailability and exposure, and the potential for environmental effects. Performance of SediMite® was examined for a variety of systems, including: (1) a mercury-contaminated tidal creek (Canal Creek) at the Aberdeen Proving Ground (APG) in Edgewood, Maryland (Environmental Restoration Project ER-200835); (2) a PCB- and DDx-contaminated freshwater tidal wetland at the head of Canal Creek (Environmental Restoration Project ER-200835); (3) a PCB-contaminated tidal creek (Bailey Creek) at Fort Eustis in Virginia (National Institute of Environmental Health Services Grant # 5R01ES16182 to Upal Ghosh at the University of Maryland Baltimore County); and (4) a PCB-contaminated *Phragmites* marsh at Berry's Creek in the New Jersey meadowlands (funded by the Dow Chemical Company). Finally, because different plots in the tidal wetland of Canal Creek at APG were treated with AC delivered by two different application methods—SediMite® under ER-200835 and AquaBlok® under ER-200825—a discussion is provided that contrasts these two studies.

Technology Description

The treatment material—SediMite®—is designed for *in situ* treatment of contaminants in sediments and wetland soils. It is pelletized agglomerate composed of the treatment agent (AC in this case), a weighting agent, and an inert binder. The pellets can be used to deliver fine particle treatment agents such as powdered activated carbon and are designed for ease of handling and application. Once the pellets are distributed on surface waters and settle to the sediments or onto wetland soils, the SediMite® pellets disaggregate and release the active treatment agent(s). This agent is mixed into the sediment or soil by natural physical processes, thus minimizing physical disturbance. Because the delivery results in a very thin initial layer, blanketing the substrate with a cap is also avoided.

Application and Retention of SediMite®-applied AC

The projects demonstrated that:

- SediMite® pellets were delivered effectively to wetland soils and aqueous sediments using either the Vortex blower system or the TurfTiger spreader system.
- Most of the applied AC was retained in wetland/marsh systems over the duration of the demonstration.
- Retention and/or AC concentrations for subaqueous tidal creek applications decreased to varying degrees over time. These variations are thought to reflect edge effects in the case of Bailey Creek and possible storm effects on resuspension or burial in the case of Canal Creek.

- Mixing of SediMite®-applied AC into sediments occurred throughout the targeted biologically active zone for applications to subaqueous sediments in tidal creeks. Vertical mixing of SediMite®-applied AC into wetland/marsh sediments was slower and to less depth than that observed for subaqueous sediments. This likely reflects differences in physical and biological processes between the aquatic and wetland systems evaluated.

<u>Reductions in Contaminant Bioavailability</u>

Treatment-related reductions in bioavailability were evaluated by comparing treatment and control plots with respect to contaminant levels in tissues of exposed invertebrates and porewater. These measurements were made primarily in the laboratory for field-collected sediments that had undergone treatment in the field for various lengths of time. While laboratory testing affords control over test conditions, laboratory conditions during the test can differ from those present in the field. For the *Phragmites* marsh at Berry's Creek, measurements of bioavailability were made in the field, as well as in the laboratory. The demonstration projects showed that:

- SediMite®-applied AC to treatment plots typically lowered the bioavailability and bioaccumulation of PCBs by >80%, and commonly by >90%, compared to control plots. These reductions were statistically significant. The reductions in PCB bioavailability were observed for all wetland/marsh and subaqueous sediments evaluated for the three study sites. Magnitudes of reduction in PCB bioavailability varied among locations and sample times and appear 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. There is evidence from the literature and from the observations at Upper Canal Creek that if AC is retained, treatment efficacy will increase with time. This is reflected in a decrease in bioavailability over time, as measured by bioaccumulation and porewater measurements.
- DDx bioavailability was reduced by 80% in field-collected wetland soils from treated plots in the Upper Canal Creek, as compared to untreated plots.
- Field-collected sediment cores from the treated plot in Lower Canal Creek exhibited significantly reduced bioaccumulation of methylmercury into laboratory test organisms six months after treatment; this reduction was ~50%. However, the AC was reduced to near-background levels at these plots 10 months after application, and the site could not be evaluated further.

<u>Potential for Biological Effects</u>

The demonstration projects showed that:

- Applications of AC via SediMite® did not adversely affect native benthic invertebrate communities in the tidal creeks at APG and Fort Eustis. Observations on benthic invertebrates were not made for the wetland/marsh environments.
- Benthic invertebrates colonized azoic sediments to which SediMite® was added, and adverse effects were not apparent after a 17-month colonization period. However, because AC was lost from these sediments over this time period, it was not possible

to determine whether a threshold AC concentration exists, above which colonization of treated sediments would be depressed.
- Based on visual observations, application of SediMite® did not appear to have adverse effects on wetland plants and submerged aquatic vegetation.

Comparisons between SediMite® (ER-200835) and AquaBlock (ER-200825) for Canal Creek

Project ER-200825 included an application of AquaBlok® to treatment plots, similar to the application of SediMite® under Project ER-200835, and also included comparisons of treatment efficacy for the two application methods by sampling the SediMite® plots. The results of treatment efficacy for SediMite® found in ER-200825 are not consistent with what is reported in this report. The reason for this is that the two methods sampled different sediment depths. ER-200825 used a fixed sample depth of 0–15 cm, whereas ER-200835 targeted the AC treatment zone within the upper few centimeters. Because AC mixing was restricted to the upper 5 cm, ER-200825 samples from 0–15 cm incorporated untreated native soils in the sample. Further samples taken with a 0- to 15-cm core from a SediMite® plot would contain more untreated native soil than a comparable sample from an AquaBlok® plot. PCB concentrations increased with depth in the plots, and this, together with the inclusion of deeper native soil for the SediMite® plots than for the AquaBlok® plots, would yield more untreated mass of PCBs in the former than in the latter. This is not a difference in treatment efficacy but rather a sampling artifact present within ER-200825. The result is that ER-200825 data cannot be used to compare the efficacy of the two application methods. However, each study provides insights into treatment efficacy, recognizing the associated limitations of the respective sampling approaches. Because ER-200835 generated depth-discrete information on treatment, as compared to the fixed-depth sampling of ER-200825, ER-200835 (the SediMite® study) provides a reliable means of assessing treatment efficacy for AC delivered via SediMite® for the actual treatment zone. However, ER-200835 sheds no light on performance of AquaBlok®.

Implementation Issues

The following issues were identified as part of the demonstration projects:

- SediMite® can be used to deliver AC topically to wetland and open-water environments using various placement methods. Experience gained from the ESTCP project was subsequently used to design and implement a full-scale application at the 5-acre Mirror Lake.
- Mixing depths and retention of AC in surficial sediments varied among studies, indicating that site-specific physical factors are important determinants for treatment efficacy. The design and implementation of full-scale *in situ* remedies involving AC will benefit from comprehensive assessments of the physical factors that can affect the vertical and horizontal mixing of AC at various time scales (short and long term) and as a result of episodic events such as storms.
- The physical fate of applied AC varies among environments. Applications to two wetland areas indicate that AC is retained over the observation periods (10 and 21 months) but that vertical mixing into the wetland soils was slower than has been observed for sediments in open-water environments. Retention in open-water environments is likely

related to factors that affect sediment resuspension and flushing. Observations indicate that these processes should be better understood and planned for as part of designing full-scale implementations.

Uncertainties

There are uncertainties associated with the design and implementation of these pilot studies:

- The results related to UCC may have been affected by a change in the location and designation of control plots that occurred between pre- and post-application monitoring events.
- For UCC, AC in surficial sediments of the control plots were observed to be higher after AC was applied to the treatment plots indicating that some of the AC in the treatment plots may have gotten into the treatment plots. We believe this is due to slurry application of AC to other treatment plots as part of a companion project.
- Applications to UCC and LCC were made during the winter when ice was present. This may have influenced application efficacy.
- Mixing depths and retention of AC in surficial sediments varied among studies indicating that site-specific physical factors are important determinants for treatment efficacy. The design and implementation of full-scale *in-situ* remedies involving AC will benefit from comprehensive assessments of the physical factors that can affect the vertical and horizontal mixing of AC at various time scales (short and long-term) and as a result of episodic events such as storms. While the study was able to demonstrate the efficacy of AC amendments for *in-situ* remediation over the short-term, however, additional monitoring of the sediment, pore water, and biota within the study areas of Canal Creek and Bailey's Creek would be required to determine the long-term efficacy of AC for in-situ sediment remediation.

Cost Model

A cost model was developed based on the use of a spreader to distribute SediMite® over 1, 5, and10 acres. The cost model includes mobilization, travel, application, and the cost for SediMite
with 50% AC, and assumes sediment conditions similar to those at APG in terms of native TOC content, benthic community structure, and the distribution and concentrations of contaminants, which affect the amount of SediMite required to properly treat sediment. A treatability study was performed to determine the optimal dose of SediMite to treat the sediments of Canal Creek.Site characterization and monitoring are not included. Because mobilization costs are spread over the acreage, the overall cost per acre of treatment decreases with the application area. Based on data from the pilot study, the cost of SediMite® is approximately $74,600 per acre to treat an aquatic site to a depth of 10 cm. This cost includes production and shipment. Shipment cost is an especially important factor influencing the overall project costs for *in-situ* treatment with AC. The reason for this is that cost is very sensitive to weight. For equivalent treatment areas (e.g., per acre), SediMite® , which contains high (50%) AC content, would be less expensive to ship and store than products of equivalent size that have low AC content. Application costs will depend on the method of application and the size of the area to be treated. The costs of

SediMite® combined with application costs were calculated as follows based on data from the pilot study:

Cost Elements	Unit Costs			Site Size (acres)		
	Fixed per Project	Cost per Acre	Cost per Application Day	1	5	10
SediMite® material cost		$74,000		$74,600	$373,000	$746,000
Mobilization/ Demobilization	$23,000			$23,000	$23,000	$23,000
Application travel and staging based on data for contracting with a company that offers spreading technology (includes all labor and supplies)	$47,000			$47,000	$47,000	$47,000
Per diem application			$10,000	$10,000	$40,000	$80,000
			Project cost =	$154,600	$483,000	$896,000
			Cost/acre =	$154,600	$96,600	$89,600

Note: Costs do not include a feasibility study within which there would have been a $15,000 treatability study.
Costs do not include monitoring.

These above costs presume a 10-cm treatment depth for an aquatic site for which SediMite® is applied to the water surface. The cost per acre decreases with the size of the project. Based on these data, it is reasonable to expect that a multiple acre aquatic site can be treated with SediMite® at a cost of ~ $100,000/acre (covers production, shipment, and application). The investigators' previous experience indicates that marshes would benefit from a thinner treatment depth. Thus, the costs for treatment of marshes are likely lower per treatment than for aqueous sediments. If monitoring indicated that marshes or aqueous environments require additional treatment over time such costs could be included as part of longer-term operating and maintenance costs. The above costs do not include planning, consulting, or monitoring. Such costs are part of any remediation project. This analysis indicates that SediMite® is more expensive than a thin-layer sand cap but less expensive than other in-situ treatment options involving AC and is considerably less expensive than dredging.

1.0 INTRODUCTION

ESTCP Project ER-200835 involved a field demonstration using SediMite® to deliver activated carbon for the *in situ* treatment of polychlorinated biphenyls (PCBs), dichlorodiphenyl-trichloroethane (DDT) and related degradation products (DDx), and mercury. As part of ER-200835, SediMite® was applied to a tidal creek and a wetland within Canal Creek at the Aberdeen Proving Ground (APG) in Edgewood, Maryland. Data are also included for SediMite® applications at two PCB-contaminated sites to broaden the information on treatment performance: (1) Bailey Creek at Fort Eustis in Virginia funded under National Institute of Environmental Health Services (NIEHS) Grant # 5R01ES16182 to Upal Ghosh at the University of Maryland Baltimore Count, and (2) a *Phragmites* marsh at Berry's Creek in the Hackensack Meadows of New Jersey funded by The Dow Chemical Company. Collectively, these demonstration projects address the following questions:

- How effectively can AC be delivered using SediMite®?
- What is the fate of the delivered AC?
- To what degree is the bioavailability of contaminants reduced?
- Do the applications have adverse effects?

1.1 Rationale for *In situ* Treatment of Sediments

Hydrophobic chemicals such as methylmercury (MeHg), PCBs, DDT, other pesticides, and polycyclic aromatic hydrocarbons are present in sediments and wetland soils at many U.S. Department of Defense (DoD) sites (SERDP-ESTCP 2008). These chemicals pose risks to animals in the sediments and are also bioaccumulated and transferred to fish, wildlife, and humans via food webs. For those reasons, hydrophobic chemicals are particularly problematic and drive many remedial decisions. Excavation and dredging (essentially forms of environmental surgery) have been the primary approaches for addressing the presence of these contaminants. Capping has also been used to isolate contaminants and prevent exposures. While these technologies can be effective, they have limitations and can be costly. There has long been interest in *in situ* remedies that might fit situations where other concerns or practical constraints make excavation, dredging, and/or capping less desirable. Based on discussions with Remedial Project Managers (RPMs), state and federal regulatory agencies, and trustee agencies, the conditions for which *in situ* remedies can be attractive relative to excavation, dredging, and/or isolation capping include:

- The risks are low to moderate and do not pose acute toxic effects. This allows for a more moderate remediation that provides time for the remedy to be effective.
- There is an expectation that risks will continue to decline with time and that *in situ* treatment will serve to accelerate that process.
- The system is relatively stable and will allow for the treatment to work over time.
- Valuable habitats and ecological receptors are present that could be damaged by excavation, dredging, and/or isolation capping. Examples include vernal pools, marshes, vegetated wetlands, eel grass beds (and other types of submerged aquatic vegetation), reef systems (e.g., oysters, other mollusks, corals), fish spawning habitat, and proximity to sensitive wildlife areas or threatened and endangered species;

- Communities of people are present at and around the area to be remediated, and there is a desire to minimize the types of construction-related impacts associated with excavation, dredging, or isolation capping.
- Practical constraints increase the difficulty of excavation, dredging, or installation of isolation caps. Examples include contaminated areas under piers and against retaining walls, sediments with considerable debris or unknown distribution of unexploded ordnance (UXO), and areas where there is a desire to limit changes to bathymetry and associated hydrological patterns. For some sites, there can be concerns regarding the possible presence of UXO; this is an aspect of the Canal Creek demonstration site.

Remedial decisions that incorporate *in situ* remedies take into account many of the same factors that RPMs consider for monitored natural recovery (MNR) and enhanced monitored natural recovery (EMNR). The principal differences from a remedy perspective are that *in situ* remedies offer an opportunity to reduce exposures and risks at a more accelerated pace, and that the chemicals are treated in a manner that reduces their exposure. For each of these less invasive remedial measures—MNR, EMNR, and *in situ*—there is a recognition that contaminants are being left in place and that the goal is to reduce risks over time. The acceptability of this risk reduction approach involves balancing the positive aspects of alternative remedial actions against the potential negative consequences of those actions. This process involves a broader evaluation than the conventional perspective of focusing only on meeting a clean-up level. Discussions with RPMs indicate that there is often a desire to achieve a level of risk reduction for situations where other types of remedies are undesirable and that such reductions may or may not be related to concentration-based clean-up values.

1.2 Objectives of the Demonstration

The objectives of the field demonstrations were to:

- Field demonstrate applications of SediMite® with activated carbon that are scalable to full-scale applications
- Evaluate the efficacy of activated carbon delivered by SediMite® on reducing the bioavailability of several hydrophobic contaminants, including MeHg, PCBs, and DDx
- Evaluate the performance of activated carbon delivered by SediMite® for different types of habitat and physical conditions
- Assess whether applications of AC via SediMite® adversely affect biota.

1.3 Regulatory Drivers

Environmental restoration activities at DoD sites with contaminated sediments are being conducted in accordance with a variety of regulatory programs. Larger sites are often regulated under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) as amended by the Superfund Amendments and Reauthorization Act of 1986. Many smaller sites are being addressed as part of state and voluntary waste-site programs.

The sites being evaluated in the present program fall under CERCLA and are under active consideration for a remedy. A performance-based Record of Decision is in place, and this study has been coordinated with the facilities' environmental control authority. The results of this demonstration project have been generated in a timeframe that will enable SediMite® to be considered as an option for the site. The U.S. Environmental Protection Agency (EPA) and Maryland Department of the Environment have been kept aware of the program.

2.0 TECHNOLOGY

SediMite® was developed to address logistical challenges and potential impacts associated with previous efforts to implement *in situ* treatment. Because amendments such as powdered activated carbon (PAC) have particle sizes comparable to fine silts or sands and/or are buoyant when initially placed on or into water, a key challenge involves getting these amendments to the sediments and mixed into them. At two sites where AC was used to treat PCBs—Hunters Point in San Francisco Bay and the Grasse River in New York—mixing of AC into the sediments was accomplished primarily using mechanical devices (Cho et al. 2009; Oen et al. 2012). Other approaches for introducing treatment amendments have involved placement of a few to several inches of material, including the amendment, on top of sediments (U.S. EPA 2013).

The concept that led to the development of the SediMite® technology was to deliver treatment amendments to contaminated sediments with minimal impacts on biota and the physical system and with negligible release of sediment contaminants to overlying water that might result from physical disturbance such as mechanical mixing or dropping heavy clay or sand capping materials on the surface of the sediments. The SediMite® delivery system consists of pellets that contain treatment amendments such as activated carbon (Figure 1). The pellets provide a convenient way to broadcast amendments onto surface water or exposed sediment/soil, after which the amendment is released from the pellet. A distinguishing feature of the technology is that it can deliver small amounts (a thin layer, e.g., <1 cm thick) of highly concentrated amendment directly to the surface of the sediment or wetland soil.

Figure 1. SediMite® pellets containing powdered activated carbon (PAC). The pellet is an agglomerate that includes the treatment agent (PAC), a weighting agent (sand), and a binding agent. Once wetted, the pellet releases the fine-particle-size treatment agent to sediments or wetland soils. SediMite® can include PAC or any other treatment agent or mixture of agents that can benefit from pelletized delivery.

SediMite® was developed with support from an EPA Small Business Innovative Research (SBIR) grant. The SediMite® delivery process is covered under U.S. Patent # 7,824,129: A Low-Impact Delivery System for *In situ* Treatment of Contaminated Sediment. The use of activated carbon as an amendment for treating hydrophobic chemicals in sediments is covered under U.S. Patent 7,101,115: *In situ* Stabilization Of Persistent Hydrophobic Organic Contaminants In Sediments Using Coal- and Wood-Derived Carbon Sorbents.

2.1 Technology Description

2.1.1 Overview

SediMite® pellets are designed as a means of packaging amendments into an agglomerate that can be transported, readily handled, and delivered without the loss of amendment or the creation of dust. While the pellets can be produced in dimensions of 0.25 to 1 cm, they contain amendments that may be powders (i.e., microns in diameter). SediMite® makes it possible to deliver substantial quantities of these fine-diameter materials. Once delivered, the pellets take in water and begin to break down, releasing the amendment materials contained within them. The amendments are released over time (hours to days, but the rate can be adjusted), and as they are released, they mix into the sediment by natural processes such as bioturbation. To the extent that mixing is achieved via biological processes, the amendments are delivered to the depths in sediments or wetland soils that are occupied by benthic or soil invertebrates. As a result, the delivery system can target the sediment or soil strata most relevant for exposure to sediment-surface-dwelling organisms and the animals that feed on these organisms. In some cases, this can be a relatively thin layer (e.g., on the order of a few centimeters), while in other cases, the mixing depth may be greater. While not evaluated in this report, SediMite® can also be incorporated into thin-layer sand caps, materials applied for EMNR, and treatment mats. For these applications, SediMite® offers a means of handling AC or other amendments with a fine particle size.

2.1.2 Formulation

SediMite® used in this study is composed of AC as the active treatment agent, sand for weight, and a clay binder. The agglomerate was pelletized to form tubular pellets that are approximately 1 cm in length and 3 mm in diameter. The blend's moisture content and the compression strength, production rate, and drying temperature were manipulated during production to form pellets with the following properties:

- Sufficiently heavy to sink in water
- Sufficiently compact to minimize internal air space, which can cause re-suspension of and/or rapid degradation of the pellets
- Dried, to cure the binder, forming a solid pellet that will degrade slowly under water over time.

The SediMite® pellets are easily packaged and transported and can be broadcast on surface waters, under piers, and/or on exposed intertidal mudflats or the surfaces of marshes and wetlands. The demonstrations described in this report involve activated carbon, but the SediMite® delivery system can be used with other treatment agents and combinations of agents.

2.1.3 Application

SediMite® can be delivered by any method that can project and/or spread pellets. These can include blower-based approaches such as the Vortex TR-Aquatic system developed by Vortex Granular Systems, LLC (the Vortex), as well as various types of mechanical spreaders. Both types of devices were used in the demonstrations discussed in this report.

2.2 Technology Development

The concept behind using AC as an *in situ* remedy for contaminants in sediments began to be explored in ~2001 with applications to PCB-contaminated sediments at Hunters Point (Table 1). The concept of packaging AC into a pellet form was pursued by Charles Menzie, Upal Ghosh, and Bennett Amos in 2006 under an EPA SBIR to Menzie-Cura & Associates in ~2006. During the period of 2001 to the present, there have been a number of initiatives to employ AC as a sorptive amendment (Table 1, Ghosh et al. 2011; U.S. EPA 2013).

Table 1. Details of the Technology Development History Related to Activated Carbon and SediMite®

Development Phase	Time Frame	Funding Agency	Publications & Reports
Demonstration of reduced PCB aqueous availability from Hunters Point sediment treated with activated carbon	2001–2004	SERDP CU-1207	SERDP 2004
Demonstration of reduced PCB bioaccumulation in clams, polychaetes, and crustaceans from Hunters Point sediment treated with activated carbon	2001–2004	SERDP CU-1207	SERDP 2004
Demonstration of reduced PCB bioaccumulation in freshwater oligochaetes, with and without mechanical mixing of activated carbon into sediments	2005–2007	EPA GLNPO	Sun and Ghosh 2007
Ongoing pilot-scale study to evaluate the application of activated carbon in reducing PCB bioavailability in a tidal mudflat	2005–2008	ESTCP ER-0510	ESTCP 2008
Ongoing pilot-scale study to evaluate the application of activated carbon in reducing PCB bioavailability in river sediments	2007–2010	Alcoa and U.S. EPA	U.S. EPA 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	EPA SBIR EPD06029	U.S. EPA 2006
Pilot-scale research of novel amendment delivery for in-situ sediment remediation	2008–2011	NIEHS Grant 5R01ES16182	NIEHS 2012

2.3 Advantages and Limitations of the Technology

The advantages of SediMite® include:

- Ability to deliver *in situ* treatment amendments in a concentrated form that can be handled easily; the pellets are to be broadcast over the area of interest
- Higher treatment effectiveness of powdered activated carbon compared to larger-sized granular carbon
- Lower shipment costs because of the concentrated nature of the amendment
- Reduced cost per area of contaminated sediment compared to capping or dredging
- Reduced environmental impacts compared to capping or dredging
- Less labor intensive than other activated carbon placement techniques.

The primary advantage of the technology is the ability to remediate contaminated wetland soils or aquatic sediments in a low-impact manner. This can be especially attractive for areas that are considered sensitive habitats or where there are practical constraints on using other types of remedial approaches. The SediMite® technology is projected to be substantially less expensive than dredging. Comparative cost information is provided in Section 8.

A limitation of the technology as a topical application is that it is dependent on natural mixing processes. (SediMite® can be incorporated into sand caps, but that technique is not considered herein.) These processes vary from site to site, and thus, the depth and speed of mixing are variables that need to be understood. The technology is designed as a topical application, so it focuses on surface sediments and wetland soils. Contaminants below the surface treatment zone are not treated, and this could be a concern if the potential exists to expose these chemicals in the future. The limitation associated with leaving chemicals in place is shared by other technologies such as capping, MNR, and EMNR.

3.0 PERFORMANCE OBJECTIVES

Performance objectives are summarized in Table 2. While most objectives apply to more than one study area, some apply only to a specific study area. Performance is evaluated against sets of criteria. The results provided in the following subsections are summaries. Details with supporting data are provided in Section 6 and in the appendices.

Because of operational constraints, a few performance metrics put forward in the work plan needed to be modified. For the two Canal Creek demonstration sites, accumulations of contaminants from sediments into animal tissues was to be evaluated using both field chambers and laboratory bioaccumulation tests. However, the facility requested that chambers and other devices not be placed and left in the field. For this reason, our metrics for Canal Creek consist of measurements made in the laboratory on field-collected sediments that had undergone treatment in the field. These measurements were made either on bulk sediments that had been subjected to treatment or on intact cores that retained vertical structure. In all cases, the sediments had experienced the influences of meteorological events, natural mixing, other biotic factors, and field processes that might influence efficacy over time. The laboratory observations provide a greater degree of control than can be achieved in the field over the exposed organisms during the exposure periods used to judge the relative degrees of change in bioavailability and exposure. The use of laboratory tests to evaluate bioavailability and bioaccumulation for field-collected sediments and soils is consistent with standard practices used to evaluate sites and to assess ecological risks.

We have included data for Berry's Creek at which *in situ* and field measurements were made for PCBs in biota and porewater at a SediMite®-treated plot and at a control plot. Berry's Creek studies include many more elements, but the portion involving AC treatment of PCBs in marsh sediments complements work performed in the marsh that borders the upper portion of Canal Creek (UCC).

Table 2. Performance Objectives and Summaries of Results.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Effective placement and treatment levels for AC delivered via SediMite®	Measurements of AC in multiple cores to evaluate spatial distribution to evaluate vertical distribution	AC is present (i.e., retained) in the mixed treatment level during follow-up monitoring events at levels that provide effective treatment. The planned target range for AC in the treatment zone is 3% to 7% of sediment dry wt in the treatment zone.	For UCC, AC was present and largely retained in all plots for wetland soils throughout the monitoring period. Variability in the horizontal and vertical distribution of AC was noted initially, but diminished over time. Over the time period of 10 months, vertical mixing was limited to the upper 5 cm and the concentration of AC > 7% dry wt in this treatment zone. Vertical mixing occurs more slowly in wetland soils than in aquatic sediments. Two large storm events—Lee and Irene—occurred during this period, but retention in the marsh remained high. For LCC, the concentration of AC in tidal creek sediments was slightly greater than 1% dry wt six months after application and was only slightly greater than controls 10 months after application. The December 2010 application was followed by a large rainfall event in the spring. Following the June sampling event, Hurricane Irene and Tropical Storm Lee passed through the area prior to the October sampling. The diminishment of AC in LCC could reflect resuspension of sediments and washout, deposition of solids brought into the system, and/or greater than anticipated vertical mixing. For Bailey Creek, AC was within the target range for treatment 2 months after application; 70% of the mass of applied AC was estimated to be present. After 15 months, lateral mixing with

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
			untreated sediments (i.e., edge effects) had reduced AC to ~2.5% in upper 5 cm; 50% of the mass of the applied AC was present within the plots while the rest had been mixed laterally into areas outside the plots. Data are also included for a *Phragmites* marsh in Berry's Creek to provide additional insight into AC retention in a marsh plot treated with SediMite®. Retention of AC was high, despite the occurrence of a major storm event (Superstorm Sandy) that flooded the area.
Reduced bioavailability of PCBs, Hg, MeHg as revealed by reduced bioaccumulation into exposed invertebrates	Measurements of contaminants in tissues of invertebrates from either field, *in situ,* and/or laboratory exposures to SediMite®-treated wetland soils or sediments	Statistically significant or substantial (e.g., >50%) decrease in average concentrations of total Hg, MeHg, and PCBs, measured in tissues of exposed invertebrates. Significance testing was based on a test of mean concentrations using a t-test ($p < 0.05$)	**PCBs** Observations for UCC marsh and Bailey Creek are based on *ex-situ* exposures to field-collected treated and untreated wetland and creek sediments. The laboratory test methods for bioaccumulation are consistent with current approaches used to evaluate bioavailability and bioaccumulation at DoD sites. Bioaccumulation of total PCBs in worm tissues was reduced by 57% after 6 months (not statistically significant) and was reduced by 92% after 10 months (statistically significantly). Reductions in availability of PCBs as measured by worm concentrations normalized (i.e., divided by) soil concentrations (i.e., BSAF values) were all statistically significant in comparison with controls. For these normalized values, mean reductions of PCBs in tissues ranged from 60% for the pentachlorobiphenyls to more than 90% for trichlorobiphenyls. (Treatment effectiveness

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
			as judged by normalized data was likely greater, because the presence of AC will reduce measured concentrations of PCBs in soils due to the influence of AC on the measurement of the soil PCBs.) For Bailey Creek, PCBs in tissues were reduced by 90% after 2 months. Reductions were ~50% after 15 months, likely due to reduction in AC levels and influx of new PCBs from surrounding untreated sediments. These were statistically-significant reductions. Data from Berry's Creek provide additional insight into treatment efficacy for AC delivered by SediMite®. Relative to a control plot, PCBs in a treated plot were lower by 78% for native animals, 98% for caged animals (*in situ* exposures), and 84% for amphipods exposed *ex-situ* to field-collected soils in the laboratory. **DDx** The efficacy of AC treatment delivered by SediMite® was evaluated for UCC only. Following 10-months of treatment, the bio-accumulation of DDx in worms exposed to surface wetland soils (0-2 inches) from SediMite®-treated plots was 80% lower than worms exposed to wetland soils from controls. **Methyl Mercury** For LCC, MeHg in tissue of laboratory exposed organisms was significantly reduced by ~50% after 6 months. Measurements were not made at

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
			10 months because of the low concentration of AC. The performance metric is relative and was derived for intact cores to maintain the vertical structure and geochemistry of mercury.
Reduced porewater concentrations of PCBs and MeHg	Laboratory equilibrium studies were used to evaluate the change in PCB and MeHg equilibrium partitioning from sediments after amendment with SediMite® in the field Polyoxymethylene (POM) samplers were placed in intact cores to examine vertical profiles Data for Berry's Creek include POM samplers placed into marsh sediment in the field.	Statistically significant or substantial (>50%) reduction in porewater concentrations Significance testing was based on a test of mean concentrations using a t-test ($p < 0.05$)	**PCBs** After 6 months of treatment, results for the slowly mixed samples showed that PCBs in porewater in SediMite®-treated surface (0–2 inch) wetland soils were 65% lower than the control soils, but this difference was not statistically significant; after 10 months of treatment, porewater concentrations in treated surface soils were 92% lower than the control soils, and this difference was statistically significant. POM samplers in intact cores from UCC showed strong vertical gradients in porewater, increasing with depth. This makes it difficult to discern the influence of AC-related treatment. When porewater concentrations are normalized to wetland soil concentrations, a treatment effect of AC with the treatment zone is evident. At Berry's Creek, the efficacy of SediMite® on reducing porewater concentrations of PCBs in the *Phragmites* wetland was evaluated *in situ* using passive samplers. After 21 months, porewater concentrations of PCBs in the SediMite®-treated plot were significantly lower than the untreated plot through the upper 10 cm. For LCC sediments in June 2011, porewater

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
			concentrations for MeHg were similar between control and treated plots.
Increased partitioning of Hg and MeHg to solid-phase sediment	Hg and MeHg were measured in bulk sediment and porewater, and partition coefficients were calculated	Statistically significant or substantial (e.g., >50%) increase in partition coefficients for Hg and MeHg in treated plot compared to control. Significance testing was based on a test of mean concentrations using a t-test ($p < 0.05$)	For LCC sediments in June 2011, partitioning coefficient (Kd) factors were significantly higher in the treatment plot as compared to the control plot by a factor of 2.5 for MeHg and 7.5 for inorganic Hg. (Analyses were not performed in October because of low AC.)
Potential for environmental effects	Benthic macrofauna abundance and community structure; benthic macrofauna colonization tests; laboratory bioassays for treatment agent; submerged aquatic vegetation (SAV) presence and general abundance (cover)	Community metrics and abundance are similar in the control plots and treatment plots; negligible adverse dose-response relationships are observed over the treatment range. Aquatic and wetland plants and general plant cover are similar between pre- and post-application	LCC and Bailey Creek exhibited no significant differences in composition or abundance of benthic invertebrates between the treatment and control plots. (There may have been a small effect on species richness at 15 months for Bailey Creek.) While AC was present in sediments of Bailey Creek throughout study, AC in LCC was diminished to a concentration of less than 1% prior to the end of the study in October 2011. All colonization trays exhibited a diverse community of invertebrates, with no differences among treatments. AC had decreased from levels as high as 20% to low levels (a few percent) by 17 months. Based on the age of clams, colonization of these animals occurred within a few months of placement of colonization trays, when AC presumably was at the higher end of the exposure range. Because AC declined over time, specific effects and no-effects thresholds cannot be determined.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
			Aquatic and wetland plants were present in the treated areas at 6 and 10 months following treatment.
Ease of application	Feedback from field personnel on effort of mobilization, movement, application, and demobilization	Field personnel able to apply SediMite® to treatment plots efficiently.	Application was easily performed rapidly by a few personnel.
Scalable to large-scale application	Feedback from field personnel on practicality and efficiency of application equipment	Equipment used for application could feasibly be used for large-scale application	Application methods could easily be used for large-scale application.

Prior to discussing performance, two issues will be covered as they relate to judging performance for the pilot study conducted in Upper Canal Creek. The first concerns the observed spatial and vertical variability in PCB concentrations in wetland soils. This variability can confound comparisons of treatment efficacy among plots. The second issue concerns comparisons between our study (Project ER-200835) of SediMite® applications and another concurrent study that applied AquaBlok® to which AC had been added (Project ER-200825).

3.1 Issue 1: Variability in PCB concentrations in Upper Canal Creek (UCC)

The study for UCC relied primarily on comparing treatment plots to control plots. Sampling revealed that the wetland soils and porewater in these plots exhibited considerable variability in PCB concentrations, as has also been noted in the ER-200825 study of this same area, and this confounds comparisons among treatments. Total PCB concentrations in samples of surface soils (0–5 cm) varied by a factor of ~4 across the plots. The implication of this variability is that the initial concentrations across plots were different prior to treatment. Thus, comparisons of performance metrics following treatment are subject to confounding by the initial variability. For this reason, comparisons are made using a variety of metrics, some of which dampen the influence of spatial variability.

Total PCB concentrations in soils also increased with depth. At the control locations, the PCB concentrations were generally less than 2 mg/kg in surface soils and increased up to 17 mg/kg at the 10- to 20-cm depth interval (based on samples collected 10 months after the SediMite® application). In contrast, for the SediMite® -treated locations, the PCB concentrations ranged from 1 to 11 mg/kg in the surface and increased to 730 mg/kg at 10–20 cm inches in soil depth at one of the treatment plots (based on samples collected at 10 months after application). The increasing vertical gradients in PCB concentrations have two implications for the study: (1) whole soil samples of differing depths would have different PCB concentrations, so sampling depth is critically important; and (2) because topically applied AC has a defined treatment layer, care must be taken to distinguish this layer from underlying untreated soil.

The spatial and vertical variability observed for soils was also reflected in porewater, as measured by passive samplers inserted into intact cores of wetland soils in the laboratory. Porewater concentrations for predominant PCB homologues typically increased by one to two orders of magnitude from the surface to a depth of 10–20 cm. A very high porewater concentration of 106,000 ng/L was observed at one location at, a depth interval of 10–20 cm, suggesting that there may be free-phase PCB oils at depth at some locations. All sampling locations showed substantially higher levels of PCBs in porewater at a soil depth of 10–20 cm, as compared to surface soils. Thus, inclusion of this particular soil depth horizon within the sample will influence the overall concentrations, as well as interpretations of treatment efficacy. This latter observation is important for the UCC wetland treatability studies, because AC treatments delivered via SediMite® did not penetrate to the 10–20 cm soil interval over the 10-month observation period.

3.2 Issue 2: Comparisons between SediMite® and Aquablock® treatments

It is not possible to use the results of studies from either ER-200825 or ER-20035 at Upper Canal Creek (UCC) to compare the treatment efficacy of AC delivered by SediMite® and AquaBlock®. This is because of differences in sampling between these two studies and because the sampling performed as part of ER-200825 yielded samples that included treated as well as untreated wetland soil, which differed in relative amounts between the two types of application. The primary difference between ER-200825 and ER-200835 is that a fixed soil depth of 0–15 cm was used for all plots as part of the AquaBlok® study (ER-200825), while the upper few centimeters was sampled for the SediMite® study, representing the observable treatment zone. The SediMite® study also included evaluations of intact cores and discrete core depths, which were not part of the AquaBlok® study. These differences in sampling depths and analyses of depth intervals influence results and confound interpretations of data within and between the two studies, because: (1) AquaBlok® and SediMite® are applied at different thicknesses, and (2) PCB concentrations increase with depth in the wetland soils.

Topical applications of AquaBlok® and SediMite® differ in thickness when applied to a wetland soil surface; AquaBlok® is composed mainly of aggregate and clay with 5% added AC, and it was delivered at a thickness of 5.3 $\pm$ 1 cm; SediMite® is composed of ~50% AC, and it was delivered at a thickness of ~0.25 cm. This difference in initial treatment thickness results in differences in the amount of native soil collected when a fixed sampling-depth interval is employed. The 15-cm sampling cores used for the ER-0825 study would include the ~5 cm of inert surface material that was delivered. As a result, some dilution of underlying native soils with overlying non-native material would be expected with non-native AquaBlok® material itself composing much of the surface soil. In contrast, a 15-cm core taken in a SediMite® plot would be composed primarily of native soils. In addition, cores into the native material from a SediMite® plot would penetrate deeper into native soil (by ~5 cm) than those for an AquaBlok® plot. This is because the thickness of SediMite® is initially only 0.25 cm, compared to the 5.1-cm thickness for AquaBlok®. Because PCB concentrations increase in soil with depth at the Canal Creek marsh, a SediMite® sample taken with a 15-cm core would contain a greater mass of untreated PCBs than the same-size sample from an AquaBlok® plot. This sampling artifact confounds reliable comparisons of the relative efficacy of two treatment methods. This project (ER-200835) did not include AquaBlok sampling but did target the treatment zone that contained AC delivered by SediMite®. This report presents the results of efficacy for this targeted sampling effort.

3.3 Performance Objective 1: Retention of Applied AC at Desired Treatment Levels

Retention was judged in terms of how much AV was present within a treatment plot relative to what was applied. The desired treatment dose was in the range of 3% to 7% AC in the treatment zone. The treatment zone was operationally defined as the strata into which the AC was mixed by natural processes.

Retention of AC varied among the studies, depending on the nature of the environment. Wetlands and marshes appear to do well at retaining AC delivered by SediMite®. High retention was observed for Upper Canal Creek (UCC) and Berry's Creek marshes, even though major storm events occurred for each during the observation periods. Hurricane Irene and Tropical Storm Lee occurred during the study of UCC marsh, while Superstorm Sandy occurred during the study at Berry's Creek.

In contrast to UCC, much of the applied AC was diminished over time in LLC, a tidal creek. During earlier site visits, LCC appeared benign and depositional, because it exhibited a soft bottom and was populated by a dense stand of submerged aquatic vegetation (SAV). However, due to temporal constraints associated with site logistics, SediMite® was applied to LCC in the winter (December 2011), after the SAV had died back. This is a time of year when there is low biological activity for sediments, because benthic invertebrate organisms tend to be dormant. A relatively large rain event occurred in March 2011, prior to the June 2011 sampling event, and two other large storm events—Irene and Lee—resulted in large runoff events in August and September 2011, prior to the October 2011 sampling event. It is believed these runoff events could have contributed to either washing the applied AC from this system or causing deposition of new sediment to this area. Because of the heavy plant growth in the creek, there could also have been high levels of decaying organic matter on the bottom of the creek, and movement of this material could have contributed to burial of sediments; loads of solids from the surrounding watershed could also have resulted in a dilution effect for AC.

In contrast to LCC, AC was better retained within Bailey Creek. Two months after application, 70% of the applied AC was still present in the plots for Bailey Creek, with levels within the desired dose range. A difference between the LCC and Bailey Creek applications is that the Bailey Creek application was made during the summer months, when substantial biological activity was available to create natural mixing, and no major storm events occurred immediately following the application. Because pilot studies for fine-particle amendments such as AC involve small plots in large systems, they can provide insight into success for short periods of time as they are continually diluted with new sediments and by lateral mixing. Such time-dependent edge effects would presumably diminish as the scale of treatment increases (e.g., from fractions of a treated acre to multiple acres of aquatic sediments or marsh).

Doses in excess of the sediment target range (7% AC per dry wt) were observed for UCC where AC concentrations were high in the upper few centimeters of wetland soils, because vertical mixing processes were slower than what has been observed previously for aquatic sediments. The study results for UCC show that vertical mixing continues to progress and that the lateral variation in AC concentrations decreases over time (results of October 2011 compared to June 2011); i.e., the AC is spread more evenly throughout the surface.

Lessons learned from the demonstration are that:

- AC can be applied effectively to wetland and aquatic sediments
- The nature of these areas can influence how the AC is distributed over space and time
- Information can and should be gathered that can help predict that behavior (physical and biological conditions of soils and sediments, along with potential for high-velocity runoff and/or solids loads and deposition within the watershed)
- A multiple-application approach with smaller amounts of SediMite® might be an appropriate *in situ* remedial approach for vegetated marsh environments

- SediMite® is best applied to aquatic sediments during summer months or at times when historical records indicate low potential for major storm events.

3.4 Performance Objective: Reduced Bioavailability of PCBs, Hg, and MeHg, as Revealed by Reduced Bioaccumulation in Exposed Invertebrates

This performance objective was planned to be addressed by a combination of *in situ* and *ex-situ* (i.e., laboratory) bioaccumulation tests. However, because of the sensitivity associated with the historical presence of ordnance at Canal Creek, APG environmental personnel indicated that leaving and retrieving *in situ* devices at Canal Creek was not permissible. Effort was expended on laboratory *ex-situ* measures of bioaccumulation for sediments collected in the field at various time periods following treatment. The collected sediments still experienced all the in-field physical, biotic, and chemical factors over the time period, and the biological measure indicated changes in bioavailability for those field conditions combined with the presence of AC. The laboratory evaluation of contaminant bioaccumulation from sediments is consistent with what is typically done to evaluate the bioaccumulation of contaminants in soils and sediments, and such measures provide insight into the performance of AC with respect to changes in bioavailability.

The results indicate that AC applied in the field by SediMite® can reduce the bioavailability of PCBs, DDx, and MeHg, and the bioaccumulation of these chemicals into biota. Performance objectives were met with respect to the relative change in bioavailability and bioaccumulation between treated and untreated wetland soils and sediments for all these contaminants during the first round of post-application monitoring for all sites: UCC (PCBs and DDx), LCC (MeHg), and Bailey Creek (PCBs). Reduction of the bioavailability and bioaccumulation over time was directly related to the presence of AC. The UCC wetland retained AC and continued to demonstrate the reduction in bioavailability of PCBs and DDx over the 10-month study period; AC in LCC was diminished over time, so the treatment lost effectiveness at this location. Bailey Creek continued to demonstrate effectiveness commensurate with the amount of AC present after 15 months. At Bailey Creek, AC dose levels had declined by approximately 50% due to lateral mixing with untreated sediments. It is believed that this reflects edge effects for plots located within a dynamic tidal system. At the Berry's Creek *Phragmites* marsh site, all three measures of invertebrate bioaccumulation (field collections of native amphipods, *in situ* chambers containing amphipods, and laboratory tests) showed that bioaccumulation of PCBs was substantially reduced in the SediMite®-treated plot compared to the control.

Lessons learned are:

- AC delivered by SediMite® in field applications can reduce bioaccumulation in invertebrates to specified performance levels based on laboratory exposures of sediments that are field collected at various intervals following treatment; where possible, the results of laboratory determinations can be supported further by data from *in situ* exposures as an additional line of evidence. However, based on our experience at APG, *in situ* measurements may not always be possible, and there may be sites for which such measurements have a practical limitation.
- The long-term effectiveness for a particular environment will depend on the retention of the applied AC at desired dose levels.

3.5 Performance Objective: Reduced Porewater Concentrations of PCBs, DDx, and MeHg

Ex-situ measurements with passive samplers on intact cores and bulk sediments indicate that AC delivered by SediMite® reduced PCBs in porewater within the treated sediment/soil layer for UCC and Bailey Creek. Results from *in situ* passive samplers for the Berry's Creek site in New Jersey indicate that porewater concentrations of PCBs were reduced in the SediMite®-treated layer of a *Phragmites* marsh. The results for UCC and Berry's Creek suggest that a layer of AC treatment delivered by SediMite® created a treatment zone that could attenuate PCBs present in deeper soil strata. The results for MeHg in the LCC test area were more equivocal—approximately the same levels of MeHg in porewater were observed in the treated and control plot 6 months after treatment. However, the plots appeared to have different amounts of Hg in bulk sediment, and the partitioning coefficient (Kd) values discussed below suggest that much of the MeHg pool was bound in the treated plot.

The results for porewater mirror those for bioaccumulation with respect to reductions of potential for exposure. Lessons learned are similar to those discussed for bioaccumulation.

3.6 Performance Objective: Increased Partitioning of Hg and MeHg to Solid-Phase Sediment

Kd was increased significantly (i.e., bioavailability was reduced) by the addition of AC, and by a factor much greater than the performance criterion. This observation was made for the sediments at 6 months following treatment at LCC, when a small amount of AC was still present. Although there was a difference between the control and treatment plots at 6 months, there was no significant difference between pretreatment and post-treatment plots.

3.7 Performance Objective: Potential for Environmental Effects

Pre- and post-application benthic studies were performed in LCC and Bailey Creek. These were detailed abundance and community composition studies from which various metrics were derived. No treatment-related adverse effects—reduced abundance or a shift in the benthic community—were observed in these studies. There was a small reduction in species richness at 15 months between controls and treatment plots for Bailey Creek, but there was no difference between pre- and post-treatment conditions. Evidence for lack of adverse effects in the field is strongest for Bailey Creek, because AC was retained in the sediments for two rounds of post-application benthic studies. For LCC, the AC was progressively lost, such that there was low exposure (<1%) to added AC at the end of the study when the benthic invertebrate samples were taken.

The effects of AC in SediMite® on invertebrate colonization of sediment were examined over a 17-month period using field-collected sediment that was rendered azoic prior to amendment with SediMite®. Initial doses of AC for the experiment were 0%, 2.5%, 5%, 10%, and 20%. All colonization trays developed invertebrate macrofauna and meiofauna communities, and no differences were observed across the treatments. However, the interpretation of a dose-response relationship was obscured because of the reduction in AC levels within the exposures over the 17-month period. Analysis of the ages of clams present in the trays indicated that larvae were settling in the trays within a few months of deployment, when AC was presumably at the higher exposure levels. Because of the change in AC concentrations over time, specific effects thresholds cannot be derived.

Qualitative observations of plant growth at UCC indicated that the addition of SediMite® did not have an adverse effect on species composition or cover of submerged aquatic or emergent marsh plants.

3.8 Performance Objective: Ease of Application

The ease of application was evaluated using feedback from the field crew that applied SediMite® to the Bailey Creek, UCC, and LCC study areas.

SediMite® was applied to the UCC study area using a Vortex TR Aquatic applicator, which was moved by hand to and around the treatment plots. SediMite® was transferred to the four treatment plots by hand in 5-gallon buckets from a bulk bag of SediMite® placed in a staging area outside of the UCC marsh. Sufficient SediMite® to treat one quarter of each treatment plot was loaded into the Vortex unit's hopper and distributed over that area, before moving the unit to the next quadrant, re-loading the hopper, and applying to that quadrant. The field team of three was able to apply SediMite® evenly to each of the four treatment plots in an average of 40 minutes. The team reported that moving the Vortex unit and SediMite® by hand was not labor intensive. One person was able to fill, move, and stage sufficient SediMite® in 5-gallon buckets to treat an entire plot before the remaining two personnel had completed application to a single quadrant of one treatment plot. The application of SediMite® to the four treatment plots, taking into account mobilization (i.e., staging equipment and material and installing wood walkways in the marsh), moving the Vortex unit between treatment plots within the marsh, moving SediMite® into the marsh, applying it, and demobilizing (i.e., removing walkways, decontamination, and site cleanup) took three people less than 6 hours. The layer of SediMite® was <1 cm thick above the treatment plot.

The Vortex unit was also used for application to the Bailey Creek treatment area. In this case, the Vortex was mounted on the bow of a 21-foot Carolina Skiff. The boat was maneuvered into position outside one of the treatment-area subplots and held that position using anchors or by typing lines to poles that had been driven into the sediment to mark the plots. The amount of SediMite® required to treat each subplot was loaded into the Vortex unit's hopper and then distributed evenly onto the subplot. The Bailey Creek treatment area included areas of both intertidal salt grass marsh and subtidal creek channel, and could be accessed by boat only during mid- to high tide. Therefore, the SediMite® was broadcast over the surface water covering the treatment plots and settled to the sediment surface thereafter. The application required three people: a boat operator, an operator of the Vortex power unit, and an operator of the Vortex nozzle. The application was completed over two days due to the falling tide on the first day. The total amount of application time was approximately 4 hours. Sediment cores collected on day two from the area treated on day one showed that some intact SediMite® pellets had penetrated the sediment to a depth of approximately 1 cm, effectively mixing into the surficial sediment by the inertia built during the descent through the water column.

SediMite® was applied to the LCC study area using a turf spreader mounted on a barge. The application to LCC was confounded by extremely low temperatures which had frozen the creek and caused several inches of ice to form on the southern bank of the treatment area. The SediMite® could not be applied to approximately one-third of the designated treatment area, so the spreader was filled with sufficient SediMite® to treat approximately one-third of the treatment area, and a bulk bag containing the remaining third was placed onto the barge. Using three boats, the barge was moved from a staging area at the mouth of Canal Creek upstream to the treatment plot. Once on station, the spreader was activated as the boats moved the barge along a length of the treatment area. The material was applied to the treatment area in thirds, to ensure accurate and even distribution, including rotating the barge 90° to broadcast SediMite® perpendicularly to the creek, in order to treat the northern bank of the creek. The application of SediMite® to the LCC treatment plot took a crew of eight 2 days to complete, with the first day being dedicated to staging the boats, barge, and heavy equipment. The second day included the application, which was completed in approximately 4 hours, and demobilization of the site. Observations of the sediment conditions after application were not made.

Both applications were deemed successful by the field crew in terms of the ease of application.

3.9 Performance Objective: Scalable to Large-Scale Application

The application techniques used to apply SediMite® to the UCC and LCC test areas could be readily employed together for a large-scale application in a combined open-water/wetland site. In particular, considerable experience has been accrued with applications of sand for thin-layer caps, such as those used for EMNR. These application techniques can be used to deliver SediMite® pellets. The equipment used for the LCC application, including loader, barge, spreader, and generator, are available for rent in nearly all areas of the United States. Other considerations, such as access to the waterway, would be included in planning the site-specific logistics and are inherent to every such project. Limitations to the use of the barge would include rivers with high flow rates or unprotected bays. However, modifications to the application platform would overcome these limitations.

The use of the Vortex allows for highly mobile and highly accurate application of SediMite® in nearly all environments. The Vortex applicator is easily packaged for commercial shipment and can be deployed by minimal personnel to areas that could not be reached by heavier equipment, such as marshes or shallow open water.

A full-scale application of SediMite® has been implemented at Mirror Lake in Delaware (http://www.dnrec.delaware.gov/News/Pages/New-DNREC-video-Mirror-Lake-One-year-later-finds-significant-improvement-in-lakes-health.aspx). That project involved several methods for delivering SediMite® pellets. These included use of a tele-belt combined with two Vortex-like devices.

4.0 DESCRIPTION OF CANAL CREEK SITES

Canal Creek was selected as a demonstration site, because sediments of the creek and bordering wetlands were contaminated with low to moderate levels of Hg/MeHg and PCBs (EA 2008). Additional sediment sampling was performed in Canal Creek as part of a treatability study associated with this field demonstration (Appendix A). Chemical analysis confirmed low to moderate concentrations of PCBs, DDx, and Hg in sediments and/or wetland soils. In addition to the chemical characteristics, the preliminary site visits to the area indicated that Canal Creek exhibits the necessary physical and biological characteristics for the test site. These characteristics include soft, fine-grained sediments, low-energy tidal fluctuation, favorable salinity regimes, good access, and evidence of biological activity in the sediments.

4.1 Site Locations and History

Canal Creek is located in the Edgewood Area of APG, a 72,000-acre installation controlled by the U.S. Army. Canal Creek is part of the Canal Creek Study Area (CCSA), which was identified as an Army Environmental Database-Restoration site due to historical discharges and disposal practices. Parts of the CCSA have been used for chemical warfare research and development activities since 1917, including laboratory research, field testing, and pilot- and full-scale chemical materials manufacturing (EA 2008). Other activities within the CCSA included operation of machine and maintenance shops and garages, metal parts fabrication, degreasing, and metal plating. Prior to the late 1960s and early 1970s, almost all municipal and industrial wastewater generated by CCSA facilities was discharged into Canal Creek and its marsh (EA 2008). Portions of the Canal Creek marsh were used for landfilling of sanitary wastes and production waste disposal (EA 2008). The CCSA, including sediments of Canal Creek, is currently being evaluated for remediation.

Canal Creek no longer receives wastewater. Canal Creek is considered “off limits” for all recreational and commercial use because of the presence of ordnance, and is posted as such by the U.S. Army. No use of the Creek is allowed unless approved by APG and under the escort of a UXO support team that clears areas with regard to ordnance.

4.2 Site Geology/Hydrogeology

Canal Creek ranges from non-tidal to tidal oligohaline along its approximately 2-mile length. It is bordered by various 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). The creek is bordered by tidal marsh emergent vegetation with small areas of scrub-shrub and forested wetland, and receives some input from contaminated groundwater seeps (EA 2008).

The site geology and hydrogeology are not expected to have interfered with the demonstration project. However, during the course of the project, three major storm events occurred that could have influenced flows across wetland soils and within Canal Creek. Precipitation for 2011 is shown in Figure 2. There were several significant storm events. The February 2011 storm created significant runoff and river flows in the region, while Hurricane Irene and Tropical Storm Lee were significant historical storm events. One of these occurred between the SediMite® application and the June 2011 post-application sampling event. Irene and Lee preceded the October 2011 post-application monitoring event.

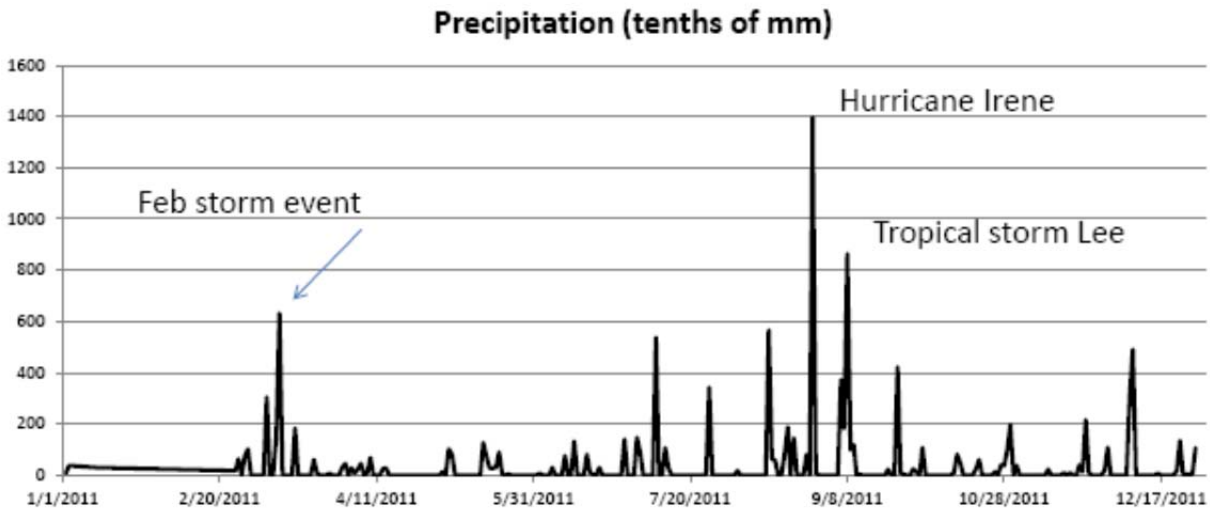


Figure 2. Precipitation in 2011 for Edgewater, Maryland

4.3 Contaminant Distribution

Canal Creek was sampled extensively by EA Engineering as part of the performance of an ecological risk assessment (EA 2008). The baseline ecological risk assessment showed that concentrations of PCBs and DDx in the desired range for the field demonstration were found in sediments of the northern portion of Canal Creek, while concentrations of Hg in the desired range for the field demonstration were found in sediments of the southern portion of Canal Creek. This case was confirmed during the treatability study (Appendix A). Therefore, the field demonstration was performed entirely at Canal Creek, with the PCB/DDx-contaminated wetland area in the northern portion of the creek being designated the Upper Canal Creek (UCC) study area, and the Hg/MeHg-contaminated tidal creek area in the southern portion of the creek being designated the Lower Canal Creek (LCC) study area.

Canal Creek and its associated freshwater wetlands were sampled in December 2008 for a treatability study to identify potential locations to perform the demonstration project. The treatability study report is included as Appendix A. Figure 3 provides a summary of these sampling data for the creek.

Figure 3. Preliminary sampling data for Canal Creek

The key contaminants in UCC are PCBs and DDx. PCBs were detected in eight of the twelve samples, at concentrations ranging from 740 to 5,700 μg/kg total PCBs, with an average concentration of 1,960 μg/kg. DDx was detected in nine of the twelve samples, with a concentration range of 87 to 6,920 μg/kg in those nine samples (average concentration of 1,308 μg/kg). In LCC, Hg was detected in each of the six samples. Total Hg concentrations ranged from 0.1 to 18.54 mg/kg, with an average concentration of 6.83 mg/kg.

As discussed elsewhere in this report, analysis of cores from UCC revealed that PCB concentrations increase greatly with depth in the wetland soils (by up to two orders of magnitude in some locations), and the porewater concentrations might actually be close to saturation at depth in some locations.

5.0 TEST DESIGN FOR CANAL CREEK

This section provides a detailed description of the SediMite® deployment and all associated monitoring related to the performance objectives described in Section 3.0.

5.1 Experimental Design

The field demonstration involved the distribution of SediMite® over two study areas in Canal Creek on APG. The efficacy of the *in situ* treatment by AC delivered by SediMite® was evaluated by measuring relative changes between treated and control plots in each of the study areas. Treatment effectiveness is judged by the degree to which exposure is reduced in the treatment, compared to the untreated plots and to pretreatment conditions. Treatment effectiveness is also evaluated by normalizing to bulk concentrations of contaminant in the sediments. Measures of exposure include analysis of chemical concentrations and composition in the sediment, porewater, and benthic organisms. These measurements are supported by measures of AC retention in sediment over the study period.

The study also examined the potential effects on biota of applying AC via SediMite®, including effects on benthic invertebrates that inhabit aquatic sediments, as well as effects on plants.

5.2 Baseline Characterization for Canal Creek

Baseline conditions were characterized by collecting sediment samples from LCC and wetland soil samples from UCC (Appendix A). These data were used, along with data from remedial investigations, to develop an understanding of the levels of contamination present in the study areas. In addition, as part of planning the design for UCC, a set of samples was collected from various plots. Sediment samples were used to evaluate the treatability of Hg in LCC; wetland soil samples were collected to evaluate the treatability of PCBs and DDx in UCC. These results are presented in Appendix A. In addition to chemical characterization, observations were made of sediment texture, salinity regime, evidence of biological activity in sediments, relative energy (low, high) of tidal fluctuation, surrounding habitat (e.g., wetlands, slope), and accessibility for future deployment and sampling.

Several comments were received regarding the initial study design and the potential for environmental effects during the baseline characterization period of the study (i.e., prior to application and monitoring at the site). One comment related to the potential for the application of SediMite® resulting in an anaerobic condition that would impair the ability of benthic organisms to mix the SediMite® into the sediments. Based on information available when baseline conditions were evaluated, this was not expected to be an issue, for the following reasons:

- Some initial layering and mixing would occur, based on observations of the sediment of the Fort Eustis application on the day after application, where SediMite® pellets were observed to have settled into the upper centimeter of sediment
- The initial layer is not particularly thick: a single layer of SediMite® pellets would measure less than 1 cm thick. Mixing into the sediments will be facilitated by animals

living within the sediments, as well as by epibenthic organisms that would not be covered by the layer

- Limited movement of the material by tidal fluctuations would further mix the surficial layer.

Another comment was related to whether the applied SediMite® layer would limit diffusion of oxygen. This could be the case if the organisms remained buried beneath the layer. However, given information on the types of benthic macroinvertebrates in LCC (e.g., worms, amphipods, and insect larvae) it is more likely that the organisms would move upward into the layer, to ensure a supply of oxygen, which is one of the primary processes of bioturbation. LCC was observed to be depositional. It is known that organisms in depositional environments are mobile and adapted to sedimentation, and are therefore expected to be able to handle a relatively small degree of sedimentation associated with the SediMite® application. Therefore, if the initial layer were to change the depth of the redox layer to some degree, the community would be expected to reestablish that zone through their movement and mixing. In other words, SediMite® applied to the sediments of LCC and the wetland soils of UCC was not expected to create an impervious "seal," but rather, a heterogeneous layer with small open spaces among the settled agglomerates. Thus, oxygen would be available to the sediments through this process, and the organisms will work to secure oxygen as needed.

5.3 Treatability Study Results for Canal Creek

Treatability studies were performed with wetland soils from UCC for PCBs and for sediments from LCC for Hg (Appendix A). Prior to initiating the treatability study, two tests with *Lumbriculus variegatus* were performed to ensure viability of the test organism when exposed to sediment from the site. In the first test, the salt tolerance of *L. variegatus* was tested by exposing worms to various salinity regimes; *L. variegatus* was found to be tolerant to a salinity of 2 ppt, and, therefore, the overlying water salinity was lowered to 2 ppt by adding local spring water for the treatability study. In the second test, 10-day toxicity tests for *L. variegatus* were conducted to ascertain baseline toxicity at Station CC-SD-02 in lower Canal Creek. The results indicated that there was no acute toxicity in Station CC-SD-02 sediment; worm recovery from the sediment mesocosms was more than 100%. A similar toxicity test was conducted with sediment from Station 1A in UCC. Survival of *L. variegatus* under current conditions is an important observation because incorporation of SediMite® into site sediment will be accomplished by the existing invertebrate community.

The treatability experiment for evaluating efficacy was carried out in half-gallon plastic buckets containing 750 mL wet sediment and an equal volume of overlaying water. Five replicates were prepared for each treatment (Figure 4). SediMite® was applied on top of sediments in the buckets, allowed to absorb water, and then stirred. Air stones were installed prior to worm addition. About 1 g wet weight of the worms (*L. variegatus*) was slowly deployed to each mesocosm after the sediment slurry had settled. After 2 weeks of exposure, samples of bulk sediment, porewater, and worms were taken from each of the five replicate mesocosms for analysis. Sample extraction and analysis methods were performed as described in Appendix A.

The treatability study for wetland soils from UCC was performed using two SediMite® dosing levels: 0.5× and 1× the total organic carbon (TOC) levels in the soils. These levels were selected based on previous experience with PCB-contaminated sediments. The results of these studies are shown in Figure 5 for PCBs and Figure 6 for DDx.

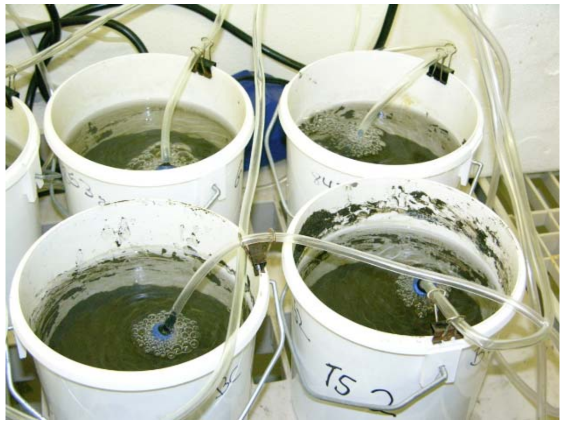


Figure 4. Setup for treatability test.

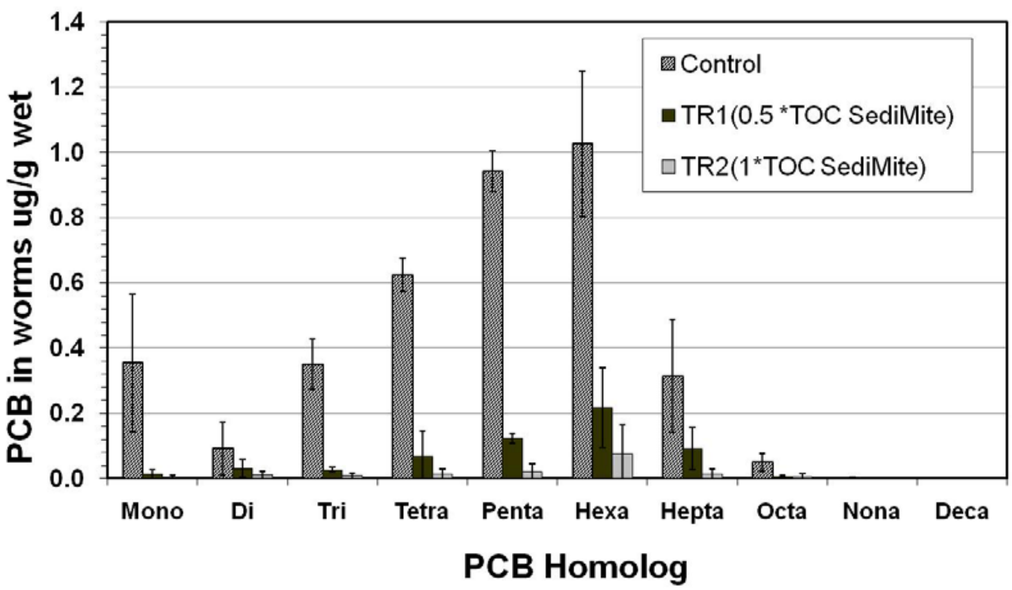


Figure 5. Treatability results for PCBs in wetland soils from UCC at two dose applications of SediMite®.

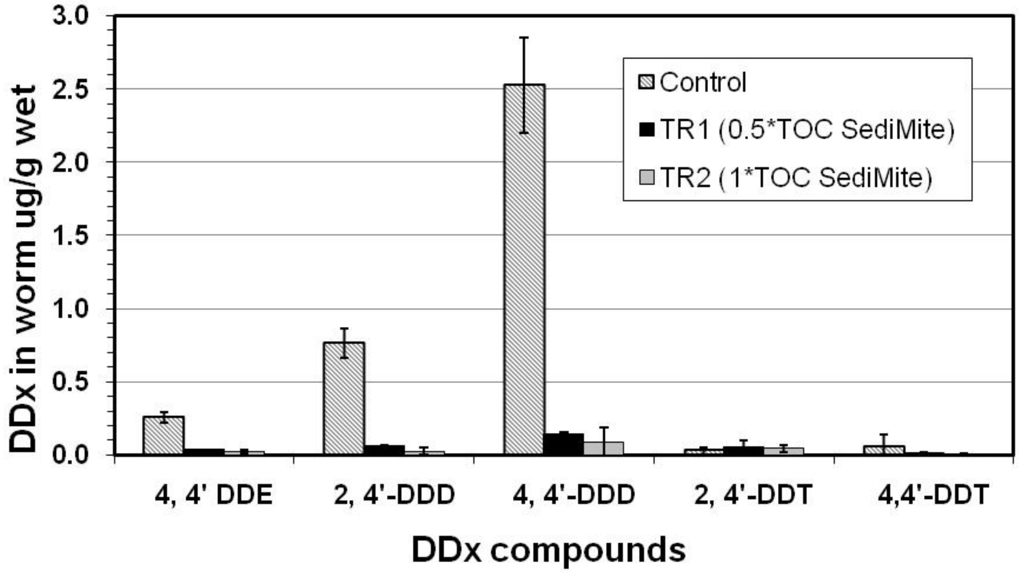


Figure 6. Treatability results for DDx in wetland soils from UCC at two dose applications of SediMite®.

The results of the treatability study show that, over a 14-day exposure period in the laboratory test system with field-collected soils from UCC, AC delivered by SediMite® reduced the bioaccumulation of PCBs and DDx in worm tissue. The results are similar to what has been seen in treatability studies for other sites (Appendix D, Ghosh et al. 2011; U.S. EPA 2013) and indicate that AC has a high potential for reducing the bioavailability of PCBs and DDx in the wetland soils of UCC. For example, for this short-term treatment duration, the bioaccumulation of tri-, tetra-, penta-, and hexa-chlorinated biphenyls were reduced by >80% at a SediMite® dose level of 0.5× TOC. Slightly greater reductions were achieved at a dose level equivalent to the TOC.

The treatability study for sediments in LCC was conducted with three different dosages of SediMite®: 0.5×, 1×, and 1.5× the TOC level in the soils (6.6% TOC dry weight). The results are shown in Figure 7.

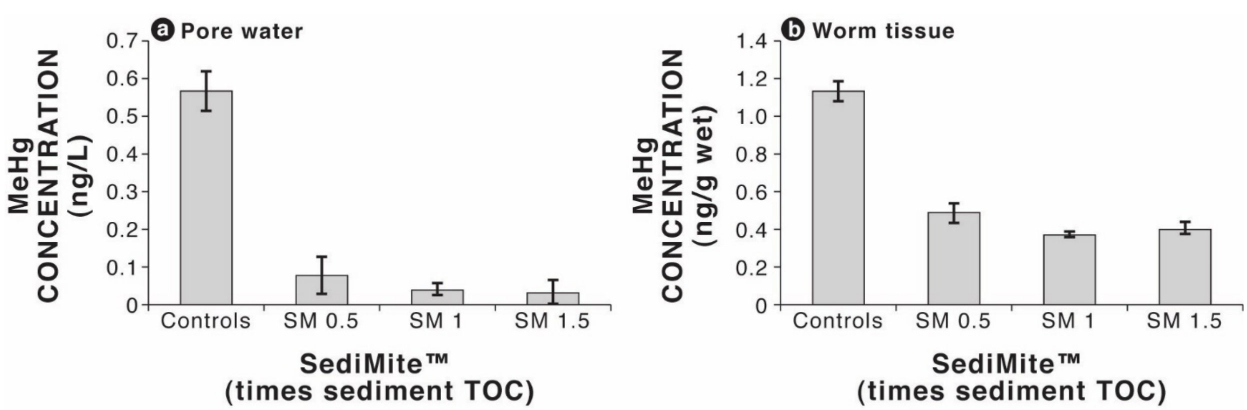


Figure 7. Treatability results for MeHg in sediments from LCC at three dose applications of SediMite®.

For sediment from LCC, the treatability study showed that at a dosing rate equal to the TOC of native sediment (1× TOC), the MeHg concentration in porewater was reduced by ~90% of control untreated sediment, and the bioaccumulation of MeHg in worm tissue was reduced by ~70% of the control. The next highest dosing rate (1.5× TOC) did not result in proportionally higher reductions in MeHg concentrations in either porewater or worm tissue compared to the 1× TOC results. The treatability results indicated that AC delivered by SediMite® has the potential for reducing MeHg in porewater of LCC sediments and in the bioaccumulation of MeHg into benthic invertebrates.

Based on the treatability studies, a SediMite® dose level of 1× TOC was used to calculate the loading rate of SediMite® (i.e., the mass of amendment required per unit area) for both UCC and LCC. The dosing rate was calculated as 4.5 kg SediMite®/m^2 based on 10 cm (4 in.) of bioactive surficial sediment, 1× TOC, and a 25% safety factor. The amount of SediMite® to deliver was then calculated by multiplying the treatment plot's surface area by the loading rate. For example, for a 1,000-m^2 (0.25 acre) treatment area, approximately 4,500 kg or 10,000 lb of SediMite® is required.

5.4 Technology Components

The production and distribution of SediMite® at APG involved three components: production of SediMite® at a pellet mill and distribution of SediMite® via two application systems. The applications systems included a blower system (Vortex) and a spreader system (TurfTiger).

5.4.1 Pellet Production

SediMite® pellets were produced at Carolina Pelleting and Extrusion, Inc. in Newton, North Carolina, a toll-manufacturing pellet mill. Pellets were prepared according to the composition and moisture content specifications that have been determined through materials testing at UMBC. The pellet blend was prepared in an industrial mixer. The mixture was then passed through a pellet mill, which uses a set of rollers to press the mixture through a die. The die contains several hundred holes of the desired pellet diameter. A stationary knife is located on the back end of the die. The extruded blend is cut by the knife to produce the pellets. The revolutions of the auger and die were manipulated to produce pellets of the desired length and strength. The pellets were then moved by conveyor belt through a fluid-bed dryer, which dried the pellets. The temperature and bed speed were manipulated to ensure the pellets were dried to the appropriate final moisture content. The finished pellets were then moved by conveyor to a set of sieves followed by a packaging chute, where they were loaded into buckets, bags, or bulk sacks for shipment. Production testing determined an average production rate of 1,000 pounds per hour, and drying rate of 800 pounds per hour. For the pilot study, SediMite® was packaged in two ways (Figure 8).

30 lb buckets for "light" transfer into delicate wetlands or light craft

1,800 lb bulk bags for transfer via barge

Figure 8. Packaging for SediMite® for use in Canal Creek pilot studies.

5.4.2 Vortex TR Aquatic System

Figure 9. Vortex TR Aquatic system.

The Vortex TR Aquatic system (Figure 9) was used for land-based application of SediMite® to wetland soils in UCC. The Vortex is a modular system composed of a 250-pound capacity polyethylene inductor hopper and a 2-stroke gasoline-powered blower unit. Pellets are loaded into the hopper, and an electric articulating valve releases the pellets from the bottom of the hopper and into a manifold. The pellets are blown from the manifold and through tubing that is aimed at the target area of application.

5.4.3 TurfTiger System

A barge-mounted TurfTiger soil spreader (Figure 10) was used for application in LCC. The TurfTiger consists of a wheeled, steel-frame rectangular hopper. The bottom of the hopper is a conveyor belt that moves the contents of the hopper to a rotating series of paddles that distribute the materials. The application rate can be adjusted by manipulating the belt and auger speeds. The TurfTiger was mounted onto a barge. Three boats were used to move the barge to the project site and while the SediMite® was being applied to the test area.

Figure 10. **Barge-mounted TurfTiger spreader. The picture on left shows on-land delivery trial for SediMite®; picture on right shows a thin-layer sand cap spreading operation that was essentially the same deployment approach used for SediMite® delivery to LCC.**

5.5 Field Testing Overview

The field testing for this study included five separate components: a treatability study, pre-application sampling, SediMite® application, post-application sampling, benthic invertebrate sampling, and a sediment re-colonization study. There were multiple sampling events associated with most of these field components. Table 3 details the field events that occurred for each of the study's components, the dates on which the field events occurred, and the tasks that were performed during each event. A Gantt chart illustrates the work flow of the project (Figure 11).

Table 3. Field Event Timeline for Canal Creek Studies.

Component	Field Event Dates	Field Event Task
Treatability Study	12/9/2008–12/11/2008	Collection of sediment samples from Canal Creek and Kings Creek for use in a sediment treatability study.
Pre-Application Sampling	9/1/2009–9/2/2009	Collection of sediment samples from LCC study area: bulk sediment for chemistry, bioaccumulation, and benthic community.
	9/15/2009–9/17/2009	Collection of sediment samples from LCC study area: sediment cores for MeHg production and TOC/black carbon (BC) content.
	11/19/2009–11/20/2009	Collection of sediment samples from UCC study area: bulk sediment for chemistry and bioaccumulation, intact sediment cores for laboratory POM analysis, sediment cores for TOC/BC content.
Sediment Re-Colonization Study	3/17/2010–3/18/2010	Initiation of sediment re-colonization study at WREC.
SediMite® Application	12/7/2010–12/9/2010	Application of SediMite® to UCC and LCC treatment plots.
Post-Application Sampling (6-month)	6/1/2011–6/2/2011	Collection of sediment samples from UCC study area: bulk sediment for chemistry and bioaccumulation, intact sediment cores for laboratory POM analysis, sediment cores for TOC/BC content.
	6/21/2011–6/23/2011	Collection of sediment samples from LCC study area: sediment cores for MeHg production and TOC/BC content, bulk sediment for chemistry, intact sediment cores for bioaccumulation.
Sediment Re-Colonization Study	8/23/2011–8/24/2011	Retrieval of sediment re-colonization trays at WREC.
Post-Application Sampling (10-month)	10/4/2011–10/7/2011	Collection of sediment samples from UCC study area: bulk sediment for chemistry and bioaccumulation, intact sediment cores for laboratory POM analysis, sediment cores for TOC/BC content.
		Collection of sediment samples from LCC study area: sediment cores for MeHg production and TOC/BC content, bulk sediment for chemistry and benthic community, intact sediment cores for bioaccumulation.

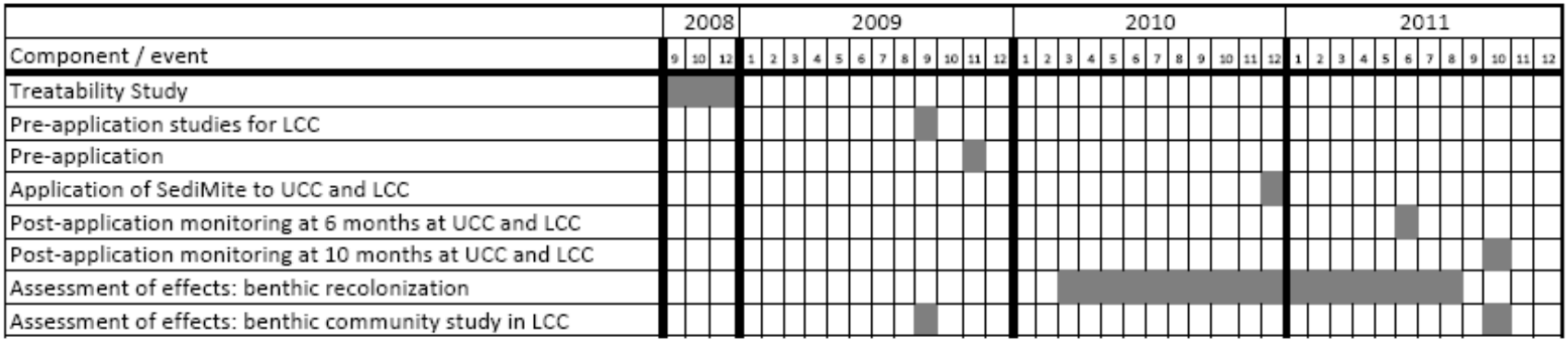


Figure 11. Gantt chart illustrating the flow of major work elements for Canal Creek. The schedule was influenced by the need to secure permits prior to application, which resulted in a delay following the 2009 pre-application studies. The schedule was also influenced by the need to avoid windows of time when bald eagles were nesting in the area.

The basic design included collections of treated and control plots. These were slightly different from one another as described below.

5.5.1 Design for UCC

Figure 12. High-value wetland in UCC used for pilot studies with SediMite®.

The treatment design for UCC was coordinated with another ESTCP program (ESTCP Project ER-0825). For the SediMite® portion of the work, the study was conducted only in the high-value wetland, which is typified by freshwater marsh plants (Figure 12). The study included four treatment plots (16, 17, 18, 19) and two control plots (12 and 15) that were subdivided (identified as A and B) to provide four control sampling locations (Figure 13). For ESTCP Project ER-0825, the work included applications to high-value marsh as well as low-value marsh which was characterized by the presence of the common reed *Phragmites.* SediMite® was not applied to any areas of low-value marsh, and no samples were collected from plots within the low-value wetland area, as shown in red on Figure 13.

The UCC study design inadvertently experienced three confounding factors. The first is that the locations of application and control plots were changed by a project coordinator after the pre-application sampling was conducted. Thus, because of the variability in PCB concentrations among plots, before and after treatment comparisons must be made with the recognition that variability may confound such comparisons. To address uncertainties arising from this confounding factor, data were analyzed not only based on raw measurements but also by normalizing the data on bioaccumulation to measures of the PCB and DDx content of the soils on a plot-specific basis. This normalization enabled comparisons over time, as well as with untreated sites prior to the application. The use of normalized values is influenced by an additional factor that tends to underestimate treatment performance. The presence of AC in wetland soils and sediments results in a lower efficiency of extracting chlorinated organic chemicals from the soil/sediment matrices; the magnitude of this effect can be as much as 40% (Beckingham et al. 2011). The effect of this factor is that the performance estimates tend to be underestimated.

The second confounding factor arises from the observation that the control plots assigned to the SediMite® project were likely influenced to varying degrees by the application of AC from a slurry treatment at nearby plots. AC is measured as black carbon (BC). Levels of BC were slightly higher in three of the four control plot sediment samples collected in June 2011 than was observed prior to treatment. BC levels in the control plot samples were in the range of 0.6–1.0%, where pre-application samples were around 0.2% BC. The control plots for the SediMite® project were in the northern portion of the study area and down-gradient of the treatment plots that received slurry spray (Plots 2, 8, 22, 23). We believe that runoff related to the application of the slurry may have influenced the BC levels in some of the controls assigned to the SediMite® project. To address this uncertainty, we considered the presence of BC in plots as a factor that may influence performance and possibly confound comparisons.

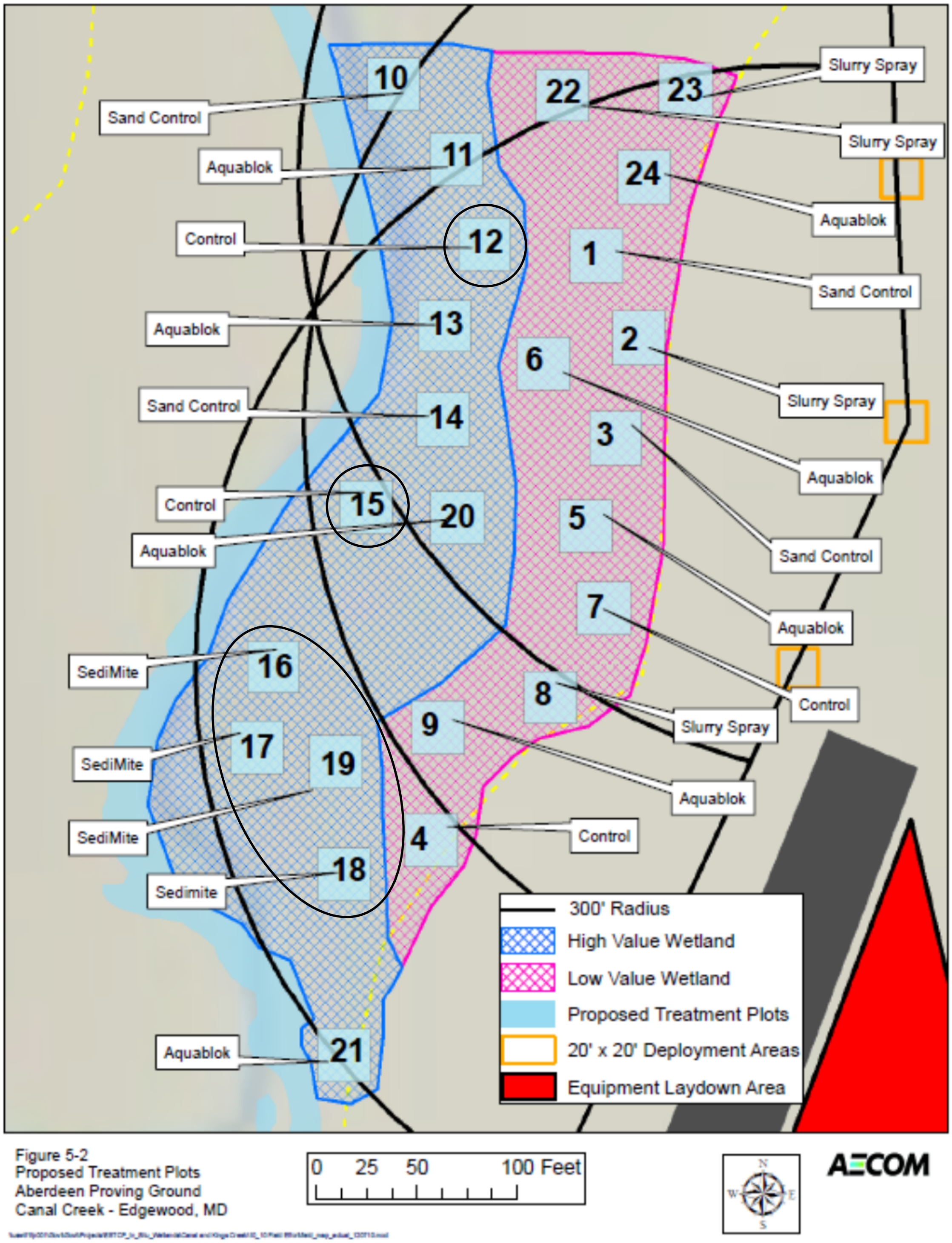


Figure 13. Locations of the treatment plots for UCC. There are four SediMite® plots (16, 17, 18, 19) and and two control plots (12 and 15) located in high value wetland.

The third confounding factor present in the wetland soils is the large horizontal and vertical variability of PCB concentrations in the soils described earlier. This variability in PCB concentrations across the study area confounds the interpretation of post-application data. The sharp vertical gradients in PCB concentrations with depth also make it essential that the treatment zone for SediMite® be clearly distinguished from deeper areas that were not treated. This was addressed in the current study by sampling the treatment zone rather than an arbitrary depth and by the collection of core samples to evaluate vertical distribution. Observations were made over a 10-month period in 2011. Future observations could be used to determine long-term mixing and efficacy.

Single composite samples of treated wetland soil were taken from the treatment zone in the various plots at which SediMite® was applied; a comparable depth was sampled in the control plots. Cores were also taken to evaluate porewater concentrations and the vertical distribution of AC, PCBs, and DDx.

5.5.2 Design for LCC

The study design for LCC involved two 0.25-acre plots that were established in Canal Creek (Figure 14). Each of these was divided into five sub-plots for pre- and post-application sampling.

Sediment samples were collected from each of the sub-plots pre- and post-application. Composite samples were made for each sub-plot on each date yielding five samples per plot for comparison on each date. Intact cores (five per plot) were collected for the assessment of bioaccumulation at each location where the collection of cores was made for porewater and sediment. These intact cores were evaluated in the laboratory using the oligochaete worm, *Lumbriculus variegatus*, as the test organism for assessing changes in mercury bioavailability and bioaccumulation following treatment of the field sediments under field conditions.

Analysis of treatment effects for LCC is limited to the first post-treatment sampling (June 2011) during which treatment-related effects were observed despite the low level of AC present in surficial sediments. Analysis of the second post-treatment samples (October 2011) was not performed due to an apparent lack of AC in sediment, which is discussed in detail in Section 6.1.2.

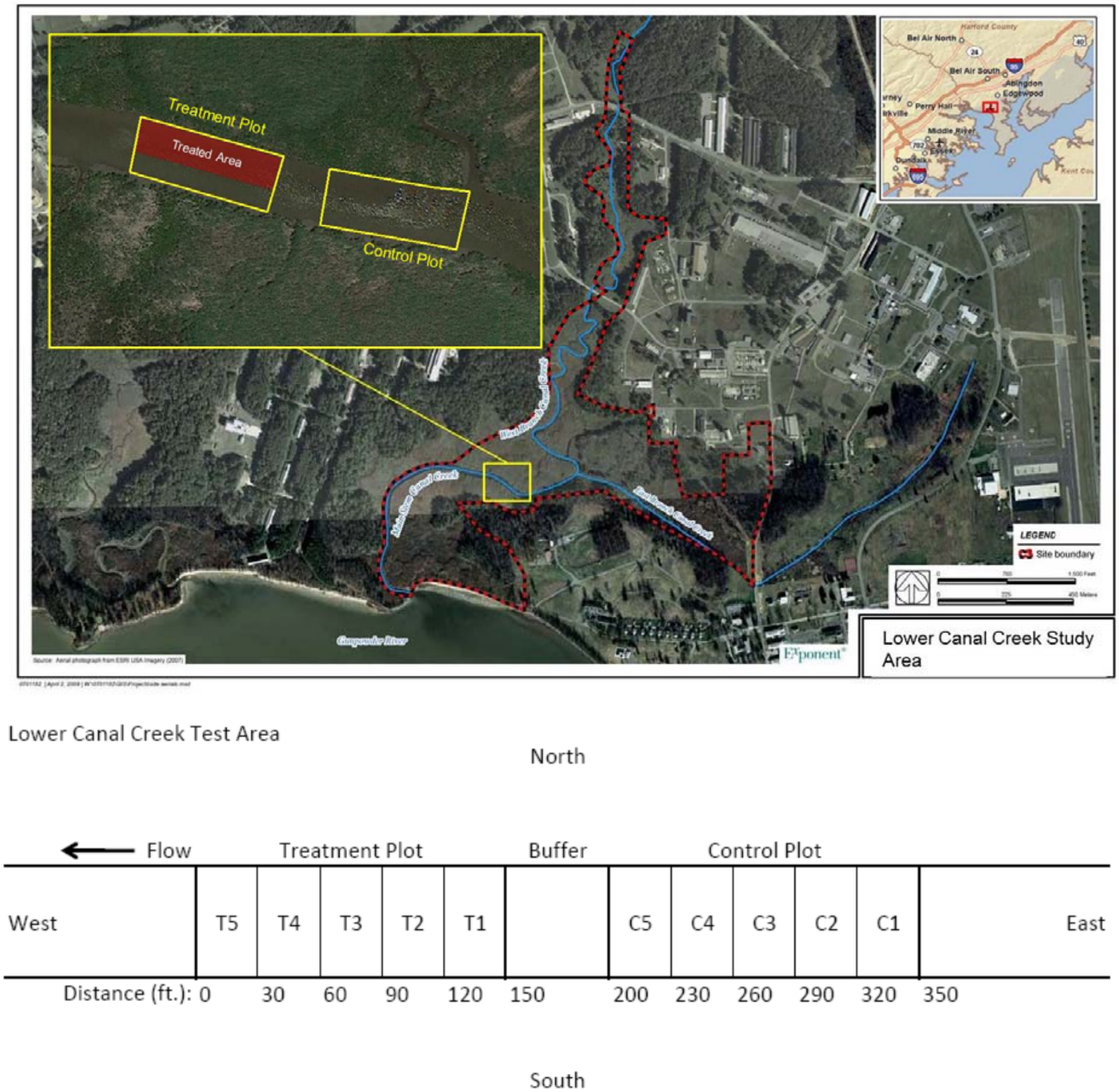


Figure 14. **LCC study area with depictions of the control and treatment plots. Each plot was divided into five sub-plots which provided the units for sampling (5 per control and treatment).**

5.5.3 Design for Bailey Creek

The Bailey Creek design involved two side-by-side plots (treated and untreated) in the creek covering an area of approximately 225 square meters. Each of the plots was subdivided into eight sub-plots for sampling. The plots extended into the *Spartina* salt marsh, including subtidal areas. The final report for the Bailey Creek study is included as Appendix D.

5.5.4 Design and Sampling for Berry's Creek

With permission of The Dow Company, we include results from the Berry's Creek site where SediMite® was applied to a plot in a *Phragmites* marsh. Comparisons were made over time between this plot and a control plot.

5.6 Sampling Methods for Canal and Bailey Creeks

The sampling methods used during the studies for UCC, LCC, and Bailey Creek are described in this section. Sediment samples were collected as discrete sediment grabs, bulk sediment composites, and sediment cores that were either sectioned by depth or analyzed intact. Table 4 details the type of samples collected during each stage of the study at APG, including the sample depth, sample volume, and the analyses performed. Table 5 details the type of samples collected during each stage of the study at Bailey Creek, including the sample depth, sample volume, and the analyses performed.

5.6.1 Grab and Composite Sediment Sampling Methods

Discrete sediment grabs were collected in areas with overlying water using a pre-cleaned petite Ponar dredge. The dredge was deployed by hand over the side of a work boat and lowered to the sediment surface while keeping tension on the deployment line. Upon contact with the sediment surface, the line tension was relieved allowing a spring-loaded tension pin to eject from the dredge's arms. The deployment line was then retrieved causing the dredge arms to pivot and close the dredge jaws, which collected the discrete grab sample. The dredge was brought to the work boat gunnel, and the overlying water was poured off from the dredge. The dredge was then opened by hand over a pre-cleaned stainless-steel bowl which caught the sediment grab sample. Once sufficient volume had been evenly collected over the targeted area, the sediment was thoroughly mixed until it reached a consistent color and texture. The composite sample was then transferred to the appropriate sample containers.

In the case of the benthic community samples collected from LCC, the contents of a single discrete grab were used as a sample. The material collected by that single grab was sieved through a 500-micron sieve, and the retained contents were collected in a sample jar, preserved with formalin, and shipped to a laboratory for taxonomy and enumeration.

Bulk sediment composite samples were collected from areas without overlying water using pre-cleaned spoons, trowels, or shovels. The tools were used to excavate surficial sediment from one or more locations in a targeted area and at a targeted depth as well as to transfer the sediment into a pre-cleaned stainless-steel bowl. Once sufficient volume had been evenly collected over the targeted area, the sediment was thoroughly mixed until it reached a consistent color and texture. The composite sample was then transferred to the appropriate sample containers.

Table 4. Samples Collected for the Canal Creek Pilot Studies

Study Component	Study Area	Samples Collected	Number of Samples Collected	Sample Depth	Sample Volume	Analyses
Treatability Study	Kings Creek	Bulk sediment composites	16	0–4 inches	2 liters	Not analyzed
	Upper Canal Creek	Bulk sediment composites	12	0–4 inches	2 liters	PCBs, DDx in sediment; PCBs, DDx, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*, AC dosing microcosms
	Lower Canal Creek	Bulk sediment composites	18	0–4 inches	2 liters	Total mercury, methyl mercury, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*
Pre-application Sampling	Upper Canal Creek treatment and control plots	Bulk sediment composites	1 sample per plot	0–4 inches	2 liters	PCBs, DDx in sediment; PCBs, DDx, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*
		Sediment core (2-in. OD)	2 samples per plot	Sectioned: 0–2 cm, 2–5 cm, 5–10 cm, 10–20 cm	4 oz.	TOC, black carbon
		Sediment core (4-in. OD)	1 sample per plot	Intact Core of 0–10 in. sediment depth		Laboratory PCBs, DDx in POM samplers
	Lower Canal Creek treatment and control plots	Sediment core (2-in. OD)	15 samples per plot	Intact core of 0–6 in. sediment depth		Total mercury, methyl mercury, bulk density, LOI, AVS/CRS, cations/anions/metals, anions, DOM, sulfide, pH, NH_3 in sediment and sediment-generated porewater
		Sediment core (2-in. OD)	1 sample per plot	Five composites of 0–2 cm, one each for 2–5 cm and 5–10 cm over treatment area	4 oz.	TOC, black carbon
		Discrete sediment grabs	2 samples per plot	0–4 in.	1 discrete grab, sieved (500 µm)	Benthic community
		Bulk sediment composites	1 sample per plot	0–4 in.	4 liters	Total mercury, methyl mercury, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*
Six-Month Post-Application Sampling	Upper Canal Creek treatment and control plots	Bulk sediment composites	1 sample per plot	Treatment zone (0–2 in.)	2 liters	PCBs, DDx in sediment; PCBs, DDx, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*

Study Component	Study Area	Samples Collected	Number of Samples Collected	Sample Depth	Sample Volume	Analyses
		Sediment core (2-in. OD)	2 samples per plot	Sectioned: 0–2 cm, 2–5 cm, 5–10 cm, 10–20 cm	4 oz.	TOC, black carbon
		Sediment core (4-in. OD)	1 sample per plot	Intact Core of 0–10 in. sediment depth		Laboratory PCBs, DDx in POM samplers
	Lower Canal Creek treatment and control plots	Sediment core (2-in. OD)	15 samples per plot	Intact core of 0–6 in. sediment depth		Total mercury, methyl mercury, bulk density, LOI, AVS/CRS, cations/anions/metals, anions, DOM, sulfide, pH, NH_3 in sediment and sediment-generated porewater
		Sediment core (2-in. OD)	1 sample per plot	Five composites of 0–2 cm, one each for 2–5 cm and 5–10 cm over treatment area	4 oz.	TOC, black carbon
		Sediment core (4-in. OD)	1 sample per plot	0–4 in.	4 liters	Total mercury, methyl mercury, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*
Sediment Re-Colonization Study	DeCoursey Cove, Wye River	Sediment colonization tray contents	24 trays	0–4 in.	1 sediment colonization tray, contents sieved (500 µm)	Benthic community
		Sediment colonization tray aliquot	24 samples	0–4 in.	4 oz.	TOC, black carbon
10-Month Post-Application Sampling	Upper Canal Creek treatment and control plots	Bulk sediment composites	1 sample per plot	Treatment zone	2 liters	PCBs, DDx in sediment; PCBs, DDx, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*
		Sediment core (2-in. OD)	2 samples per plot	Sectioned: 0–2 cm, 2–5 cm, 5–10 cm, 10–20 cm	4 oz.	TOC, black carbon
		Sediment core (4-in. OD)	1 sample per plot	Intact core of 0–10 in. sediment depth		Laboratory PCBs, DDx in POM samplers
	Lower Canal Creek treatment and control plots	Sediment core (2-in. OD)	15 samples per plot	Intact core of 0–6 in. sediment depth		Total mercury, methyl mercury, bulk density, LOI, AVS/CRS, cations/anions/metals, anions, DOM, sulfide, pH, NH_3 in sediment and sediment-generated porewater
		Sediment core (2-in. OD)	1 sample per plot	Five composites of 0–2 cm, one each for 2–5 cm and 5–10 cm over treatment area	4 oz.	TOC, black carbon
		Discrete sediment grabs	2 samples per plot	0-4 inches	1 discrete grab, sieved (500um)	Benthic community

Study Component	Study Area	Samples Collected	Number of Samples Collected	Sample Depth	Sample Volume	Analyses
		Sediment core (4 in. OD)	1 sample per plot	0–4 in.	4 liters	Total mercury, methyl mercury, lipids in tissue following 28-day laboratory bioaccumulation using *L. variegatus*

Table 5. Samples Collected for the Bailey Creek Study

Study Component	Study Area	Samples Collected	Number of Samples Collected	Sample Depth	Sample Volume	Analyses
Treatability Study	Bailey Creek	Bulk sediment composites	2	0–4 in.	4 liters	PCBs, TOC/BC content in sediment; PCBs, lipids in tissue of native organisms, PCBs, lipids following 28-day laboratory bioaccumulation using *L. plumulosus.*
		Discrete sediment grabs	6	0–4 in.	1 discrete grab, sieved (500 µm)	Benthic community
Pre-Application	Bailey Creek treatment and control plots	Sediment core (2-in. OD)	2 samples per plot	Sectioned: 0–5 cm, 5–10 cm, 10–15 cm, 15–20 cm	4 oz.	TOC, black carbon
		Bulk sediment composites	1 sample per plot	0–4 in.	4 liters	PCBs in sediment; PCBs, lipids following 28-day laboratory bioaccumulation using *L. plumulosus.*
		Discrete sediment grabs	1 sample per plot	0–4 in.	1 discrete grab, sieved (500 µm)	Benthic community
Two-Month Post-Application Sampling	Bailey Creek treatment and control plots	Sediment core (2-in. OD)	2 samples per plot	Sectioned: 0–5 cm, 5–10 cm, 10–15 cm, 15–20 cm	4 oz.	TOC, black carbon
		In-situ POM passive sampler installation	10 deployed	Sectioned: 0–5 cm, 5–10 cm, 10–15 cm, 15–20 cm	POM strip	PCBs in porewater following 13-month exposure
		Bulk sediment composites	1 sample per plot	0–4 in.	4 liters	PCBs in sediment; PCBs, lipids following 28-day laboratory bioaccumulation using *L. plumulosus.*
		Discrete sediment grabs	1 sample per plot	0–4 in.	1 discrete grab, sieved (500 µm)	Benthic community
15-Month Post-Application Sampling	Bailey Creek treatment and control plots	Sediment core (2-in. OD)	2 samples per plot	Sectioned: 0–5 cm, 5–10 cm, 10–15 cm, 15–20 cm	4 oz.	TOC, black carbon
		In-situ POM passive sampler retrieval	7 recovered	Sectioned: 0–5 cm, 5–10 cm, 10–15 cm, 15–20 cm	POM strip	PCBs in porewater following 13-month exposure
		Bulk sediment composites	1 sample per plot	0–4 in.	4 liters	PCBs in sediment; PCBs, lipids following 28-day laboratory bioaccumulation using *L. plumulosus.*
		Discrete sediment grabs	1 sample per plot	0–4 in.	1 discrete grab, sieved (500 µm)	Benthic community

The UCC treatment and control plots were sub-divided into four quadrants to accommodate the two rounds of post-application sampling, where samples were collected in opposing quadrants relative to center in event one and then the previously unsampled opposing quadrants in event two. This method ensured that areas of the marsh surface that were disturbed by sampling activities in event one would not be used for the collection of samples in event two.

Bulk sediment samples were collected from a “treatment zone” during the two post-application sampling events in the UCC study area. The treatment zone was the area of wetland soil in which AC could be visually defined during sampling and was determined to be the upper 2 inches of sediment during the post-application sampling events in June and October 2011. The sediment composite from the UCC control plots (Plots 12 and 15 in Figure 13) was collected from the same horizon of sediment determined to be the treatment zone in treated plots (i.e., 0–5 cm) during both post-application sampling events.

The treatment zone collection approach was used, as it was apparent that vertical mixing was slower in the wetland soils than for aquatic sediments, and ensured that the physical collection of samples was not inadvertently mixing treated wetland soils with deeper untreated soils. As discussed elsewhere in this report, this consideration was very important, because the concentrations of PCBs in UCC wetland soils increase with depth into the soil. Thus, mixing untreated deeper soils that have higher levels of PCBs with treated soils that have lower levels of PCBs would confound the interpretation of treatability performance.

5.6.2 Sediment Core Sampling Methods

Sediment cores were collected from areas with overlying water using one of two sediment core heads: an Ogeechee sand corer for the collection of intact samples for porewater and sediment analyses and a custom-built corer for the collection of intact samples for laboratory bioaccumulation studies.

The Ogeechee sand corer is a stainless-steel cylinder with a 2-inch inner diameter. A 2-inch outer diameter plastic core liner is loaded into the cylinder bottom and a stainless-steel nosepiece is threaded onto the cylinder to keep the core liner in place. A valve fitting is threaded onto the top of the cylinder and extension rods are threaded into the fitting. The Ogeechee sand corer is deployed by hand from the side of a work boat using the extension rods, lowered to the sediment surface, and then driven vertically into the sediment to the desired depth. The valve fitting is then closed by hand using a line, which causes suction within the cylinder to keep the sediment inside the core liner during retrieval. After removing the nosepiece, the bottom of the core liner is capped and extracted from the cylinder. The top of the core liner is then capped for use as an intact core sample (i.e., for LCC Hg/MeHg samples) or for later sectioning by sediment depth (i.e., for TOC/BC samples).

The custom-built corer uses the same principle of the Ogeechee sand corer by using a valve fitting to create suction in a core liner to maintain a subsurface sediment core sample during retrieval to a work boat. The custom core head was constructed of 4-inch inner diameter PVC pipe sections to fit a 4-inch outer diameter core liner. A steel valve fitting was threaded into the top of the PVC core head using a pipe flange, and steel extension handles were threaded into the valve fitting. The custom core head was deployed and retrieved by the same method as the Ogeechee sand corer. The 4-inch core liners were capped and used intact for *ex-situ* bioaccumulation assays for measuring bioaccumulation of Hg and MeHg from the LCC study area.

Sediment cores were collected from areas without overlying water by driving a core liner directly into the sediment to the desired depth. The top of the core liner would then be capped to create suction, and the sediment core would be directly withdrawn. If the suction was not sufficient to retain the sediment within the core liner, the bottom of the core liner would be capped with a gloved hand and withdrawn from the sediment. In either case, the bottom of the core liner would be capped after extraction. Depending on the analysis, samples were collected from the wetland soils using both 2- and 4-inch diameter core liners.

5.6.3 Decontamination

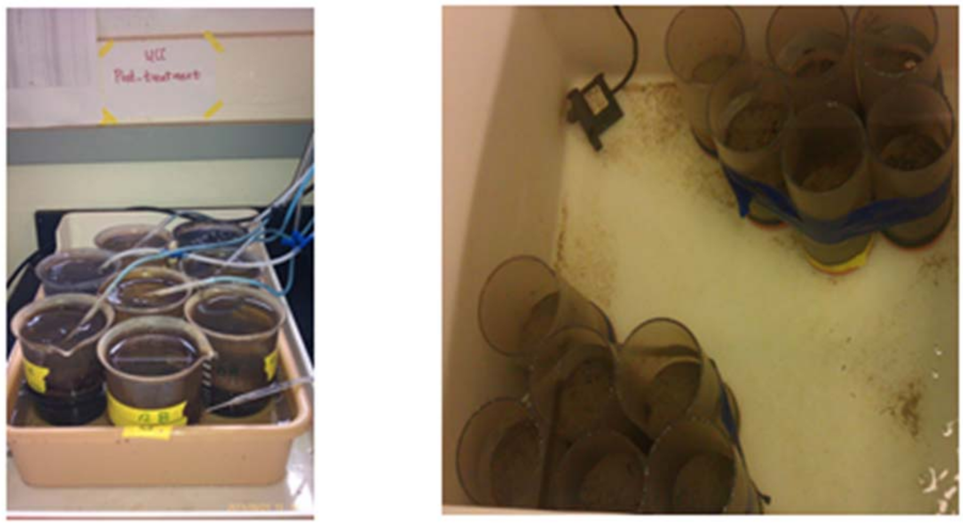
All re-useable sampling equipment used to collect samples for chemical analysis (i.e., spoons, trowels, shovels, bowls, petite Ponar) was decontaminated between sample stations. The equipment was first washed with site water and a scrub brush to remove the visible sediment. The equipment was then washed with a separate scrub brush using a distilled water and Alconox soap mixture. The equipment was then rinsed with distilled water to complete the decontamination process and wrapped in aluminum foil if it was not to be deployed immediately.

Re-useable sampling equipment that was used to collect samples for biological analysis (i.e., petite Ponar for benthic community samples) or that would not come into contact with the sample (i.e., core heads that used single-use core liners) were washed between deployments using site water and a scrub brush to remove visible sediment.

5.7 Analytical Methods

5.7.1 28-Day Laboratory Bioaccumulation Assays

As a metric of field treatment performance, laboratory bioaccumulation tests with the freshwater oligochaete *Lumbriculus variegatus* were used with field-collected sediments from LCC and wetland soils from UCC (Figure 15). The test method was based on the EPA *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates* (U.S. EPA 2000).



Bioaccumulation test set-up for exposure of *Lumbriculus* to wetland soils from UCC

Bioaccumulation test set-up for exposure of *Lumbriculus* to intact Sediment cores from LCC

Figure 15. Test set-ups for laboratory bioaccumulation studies with wetland soils from UCC and intact sediment cores from LCC.

Laboratory bioaccumulation tests were conducted for the field-collected sediments from control and treatment plots, before and after SediMite® application. The pre-application samples from both UCC and LCC that were used in the bioaccumulation assays were composited from the upper four inches of sediment from control and treatment plots in those study areas. The post-application samples from UCC treatment and control plots were composited from the upper two inches of sediment, as defined by the observations of treatment zone in the treated UCC plots. The post-application samples from LCC that were used for bioaccumulation tests were collected and analyzed as intact 4-inch sediment cores. Approximately 1 gram of wet *L. variegatus* was introduced to either 500 mL of wet sediment in 1-L glass beakers, as in the case of bulk sediment composite samples from the UCC study area, or directly into the intact 4-inch sediment core samples from the LCC study area. The intact cores were used as bioaccumulation chambers for LCC post-application measures. This limited the disturbance to the sediment column and its associated MeHg production and subsequent fate. Water from a freshwater stream was filtered and added to each beaker, and the temperature was maintained at a constant by partially immersing vessels in a large container of water. The overlying water in each vessel was renewed daily and aerated throughout the experiment. Water quality parameters (e.g., pH, temperature, dissolved oxygen, hardness, alkalinity, ammonia, nitrate) were measured throughout the experiment. After 28 days of exposure, the worms were collected and allowed to depurate for six hours prior to analysis.

5.7.2 PCB Aqueous Equilibrium Tests

Equilibrium studies were performed to evaluate the change in PCB equilibrium partitioning from field-collected sediments at various intervals after application of SediMite®. The PCB aqueous partitioning measurements were carried out in the laboratory using field-collected whole sediment. Bulk sediments (500 mL) collected from each plot and stream water were placed in 1-L jars. About 1 gram of POM sampler (77 µm thick) was cut into strips and added to the overlying water in each jar. The samples were slowly mixed on a shaker for 30 days. The gentle mixing helped with minimizing sediment resuspension and avoided further mixing of the carbon into the sediments while mixing the water phase. Sodium azide was added to the water as a biocide, and photodehalogenation was suppressed by keeping the samples under dark conditions. After mixing and equilibrating for 30 days, passive samplers were retrieved, rinsed with deionized water, and wiped dry with a Kimwipe to remove fine particles and sediment residue.

5.7.3 Porewater PCB Analysis in Intact Sediment Cores

PCB porewater profiles were determined in the laboratory using intact 4-inch cores collected from the field. The sediment surfaces of the intact cores were kept submerged in about four inches of water in a large bucket. The POM passive samplers (77 µm thick) were cut into long strips and fixed into metal frames and inserted into the core sediment samples. The set-up is shown in Figure 16. After six months of exposure, samplers were retrieved, rinsed with deionized water, and wiped dry. The passive samplers were sectioned into the following lengths: 0–2 cm above sediment (overlying water) and 0–2 cm, 2–5 cm, 5–10 cm, and 10–20 cm below sediment surface.

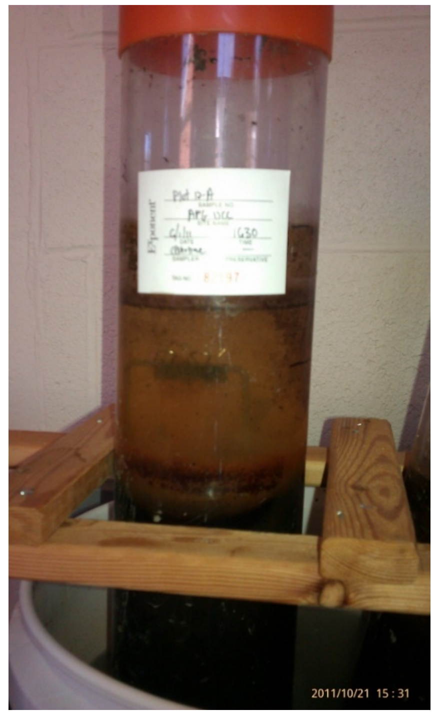


Figure 16. Laboratory set-up for intact cores from UCC. Strips of POM are used to assess the vertical gradient in resultant porewater concentrations.

5.7.4 PCB Analytical Method

PCBs were measured at the University of Maryland Baltimore Country (UMBC). Sediment and tissue samples were weighed and mixed with anhydrous sodium sulfate to form a free-flowing powder. Surrogate PCB #14 and 65 were used for assessing the process efficiency. A hexane/acetone mixture (1:1, v/v) was used as the solvent for ultrasonic extraction. The slurry was sonicated for nine minutes. PCB cleanup was based on EPA SW846 Methods 3660B (activated copper cleanup) and 3665A (sulfuric acid cleanup). Extracts from each sample were solvent exchanged to hexane and cleaned using deactivated silica gel (for PCB) or activated florisil (for DDx) columns. Eluates from the florisil columns were solvent exchanged to hexane and concentrated using a nitrogen blowdown apparatus before analysis. Samples were analyzed using a gas chromatograph with an electron capture detector. PCB BZ#30 and 204 were used as internal standards.

PCB congener-specific analysis was performed using modified EPA Method 8082. An Agilent gas chromatograph (Model 6890) with a fused silica capillary column (HP-5, 60 m x 0.25 mm inner diameter) and an electron capture detector were used for analysis. PCB standards for calibration were obtained from EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, Michigan, and also from Ultra Scientific. A four-level PCB calibration table was prepared using a known PCB mixture containing 250 µg/L of Aroclor® 1232, 180 µg/L of Aroclor® 1248, and 180 µg/L of Aroclor® 1262 yielding a total PCB concentration of 610 µg/L. Concentrations of individual PCB congeners in the mixture were obtained from Mullin (1994). Two internal standards were used: PCB 30 (2,4,6-trichlorobiphenyl) and PCB 204 (2,2',3,4,4',5,6,6'-octachloro biphenyl), which are not present in commercial Aroclor® mixtures. Using this protocol, 92 PCB congeners or congener groups can be identified and quantified. Where coeluting PCB peaks occur in the analysis, they are calibrated as a sum of congeners. Details of the PCB extraction, cleanup, analysis, calibration, and the quality assurance and quality control (QA/QC) plan are available in the UMBC standard operating procedure for PCB analysis.

POM strips were extracted for PCBs and pesticides using a mixture of hexane and acetone (1:1, v/v). Samples were solvent switched to hexane and cleaned up following the same procedure.

5.7.5 Activated Carbon/Black Carbon Analysis

AC content of sediments was measured at UMBC by wet chemical oxidation as described in Grossmann and Ghosh (2009). This method entails oxidation of natural organic matter with sulfuric acid and potassium dichromate, followed by thermal oxidation of the black carbon remaining in the sample by a Shimadzu TOC analyzer. The value of black carbon content measured by this instrument was corrected for carbon content of the AC to determine AC dose in the sediment sample.

5.7.6 Porewater Extraction for Mercury and Supporting Geochemistry

Porewater was extracted from core sections, as described in Mitchell and Gilmour (2008), within 36 hours of collection. Core sections were sequentially filtered inside an anaerobic glove box through 0.7-mm glass fiber filters and then 0.22-mm polycarbonate membrane filter units. The filter units were acid-cleaned, flushed with deionized water, and held in the anaerobic chamber for several hours prior to use.

5.7.7 Total Hg and MeHg Analysis

Total Hg analysis was performed at the Smithsonian Environmental Research Center (SERC) following digestion, reduction, and gold-trapping (EPA Method 1631). MeHg analysis was done by distillation, ethylation, and gas chromatographic separation (EPA Method 1630).

For the analysis of both ambient and enriched isotopic MeHg, samples of all matrices were distilled (Horvat et al. 1993) and then derivatized using sodium tetraethylborate. After distillation and ethylation, volatile Hg species are purged and concentrated onto traps filled with Tenax®, thermally desorbed, separated on an OV 3/Chromasorb column, and directly introduced on a stream of argon into an inductively coupled plasma-mass spectrometry (Perkin-Elmer Elan DRC II) for detection. For quantification, SERC used isotope dilution techniques (Hintelmann and Evans 1997; Hintelmann and Ogrinc 2003), in which trace amounts of enriched methyl^{199} Hg are added to each sample as an internal standard.

For each batch of total Hg or MeHg samples, a suite of QA/QC measures was run and reported. This included the analysis of blanks, analytical duplicates, and certified reference materials where available and appropriate. Typical detection limits for total Hg are <1 ng/L for porewaters, <0.5 ng/L for surface waters, and 0.1 ng/g for sediments, soils, and tissue. Typical detection limits for MeHg are <0.5 ng/L for porewaters, <0.25 ng/L for surface waters, and <0.1 ng/g for sediments, soils, and tissue. Details of SERC methods and quality assurance can be found in recent publications (Mitchell and Gilmour 2008; Hollweg et al. 2009).

5.7.8 Additional Analyses

SERC analyzed several additional parameters that impact Hg methylation and bioavailability in sediments from the LCC study area.

Soil moisture content/porosity and bulk density were determined using standard gravimetric methods. Organic matter content was determined by percent loss-on-ignition of dried soil samples in a muffle furnace at 550 °C for four hours.

Porewater concentrations of iron, manganese, sodium, calcium, magnesium, potassium, and phosphorus were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Perkin-Elmer Optima 3000DV ICP-OES. Solid phase crustal metals were measured by ICP-OES after digestion.

Anions were analyzed by ion chromatography using standard methods and a Dione ion chromatography system.

Extractable iron (Fe[II]/[III]) in sediments was measured by light digestion of soil samples with 0.5 M Hall, centrifugation, and analysis of aliquots using Ferrozine-Hepes and UV spectrophotometry at 562 nm (Stookey1970; Lovley and Phillips 1986). 0.5 M HCl-extractable Fe(III) is determined as the difference between extractable total iron and extractable iron (Fe[II]). Total extractable iron is obtained by reducing all Fe(III) using hydroxylamine hydrochloride (NH2OH HCl) prior to colorimetric analysis.

The character of dissolved organic matter (DOM) in porewater was assessed using proxy measures related to the UV spectrophotometric analysis of chromophoric DOM. These parameters include specific UV absorbance at 280 nm (SUVA280) and the absorbance slope ratio, defined by Helms et al. (2008). To characterize DOM, UV absorbance is measured at wavelengths between 270 and 750 nm using clean 1-cm quartz cells on a Cary 4E UV visible spectrophotometer. SUVA280 is calculated by dividing the UV absorbance measured at 280 nm by the concentration of DOC in the sample (units of $L \cdot mg^{-1} \cdot m^{-1}$). Slope ratio is calculated by dividing the fitted UV-absorbance slope between 275 and 295 nm by that between 350 and 400 nm (Helms et al. 2008). Both measures can be used as a first approximation of the molecular weight of DOM in the range of approximately 500–4,000 (Chin et al. 1994, Helms et al. 2008). SUVA280 is also related to percent aromaticity (Chin et al. 1994). Porewater sulfide is measured using an ion-specific electrode on samples preserved in sulfide anti-oxidant buffer (SAOB, Brouwer and Murphy 1994) and calibrated with lead-titrated standards.

Acid-volatile sulfide and chromium reducible sulfur were analyzed via distillation under N_2, according to Fossing and Jorgensen (1989). Sulfides were trapped in SAOB (Brouwer and Murphy 1994) and analyzed using an ion-specific electrode. Standard calibration curves were performed daily.

Ammonia was analyzed with a Hach Color Wheel Test kit, which has an analytical range of 0.1–2.5 mg/L.

6.0 SAMPLING RESULTS

6.1 Activated Carbon in Sediments

6.1.1 Upper Canal Creek Study Area

The core samples revealed that the highest concentration of AC in UCC wetland soils was found in the surface (0–2 cm depth) (Figure 17) with levels declining sharply below this. For the June 2011 samples (6 months post-application), the elevated AC levels measured at all depth intervals were statistically significant (at 95% CI) compared to the control plots. For October 2011 samples (10 months post-application), the elevated levels were statistically significant (at 95% CI) for the 0–2, 2–5, and 5–10 cm depth intervals compared to the controls. AC appears to be only slightly elevated above those observed for controls at wetland soil depths deeper than 5 cm.

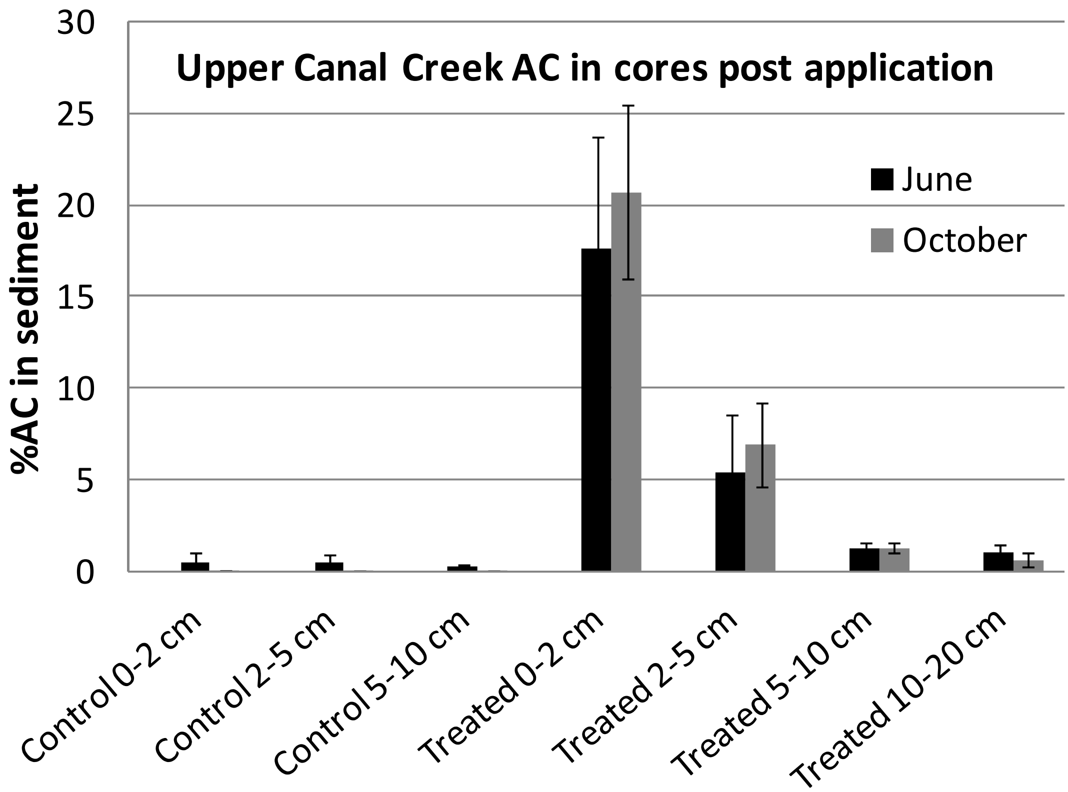


Figure 17. AC levels in cores taken from control and treated plots for UCC 6 and 10 months post-application in 2011.

Retention of AC in UCC plots was high. The calculated mass recovery of AC from the top 10 cm of sediment was 92% in the June 2011 sampling and 110% in October 2011 sampling (Appendix B). These results indicate that AC applied in the form of SediMite® persisted in the test plots for the 10-month period following application. It is important to note that Hurricane Irene and Tropical Storm Lee occurred during the observation period, and the AC was retained in UCC sediment despite the hurricane and record rainfall. Based on the two post-application monitoring rounds, about 60% of the recovered AC was found in the top 2 cm of sediment, while the remaining 40% penetrated below the top 2 cm and was found mostly in the 2- to 5-cm depths. It is expected that further incorporation of the AC into the deeper layers of sediment will occur slowly over time via natural mixing processes and deposition of new soil and organic matter.

It appears that for the UCC wetland system, applied SediMite® forms a thinner treatment layer as compared to applications to aquatic systems such as Bailey Creek, which is discussed later. High AC retention and an initially thick treatment layer were also observed for the *Phragmites* marsh plot treated with SediMite® at Berry Creek in New Jersey (Sanders et al., 2015). After two years, AC had mixed downward by ~5 cm at the Berry's Creek site and had been largely retained despite diurnal tidal flooding and the occurrence of Superstorm Sandy in October 2012.

AC was measured in the bulk field-collected wetland soil samples from the UCC study area that were used for assessing field treatment over time using laboratory bioaccumulation studies. These bulk samples were collected from the treatment zone or from surficial soils of comparable depth in the control plots. This was typically in the upper 2 cm of wetland soils. Although the average AC content in the bulk soil is high, there is large variability among plots (Appendix B). Bulk samples from treated plots 17 and 19 had high AC content (up to 37%), while bulk samples from treated plots 16 and 18 had AC content in the top 10 cm of soil closer to the target dose of 5.7% AC (Appendix B). Three of the control plots (12A, 12B, and 15B) showed elevated AC in the range of 0.6–1.0% in the June 2011 samples as compared to what had been observed during the pretreatment studies (~0.2%). In the October 2011 samples, the AC levels in the control plots were lower and were considered more indicative of background levels as revealed in the pretreatment studies. As noted earlier, the AC in the control plot in June 2011 could have been caused by movement of AC from one of the slurry carbon treatments that were applied as part of a separate but contemporaneous project (ER-200825).

6.1.2 Lower Canal Creek Study Area

A detectable but small amount (~1.2% in upper 2 cm) of delivered AC was present in the first post-treatment monitoring in June 2011 (Figure 18). While this is more than twice as high as the control sediments, the level is less than the intended 3–7% AC dose. Within the treatment plot, the AC declined with depth. The lower than expected AC levels could reflect one or more of the following scenarios: 1) much of the applied AC was washed out of the system and what was retained was mixed downward, 2) vertical mixing of AC into the sediment was much greater than anticipated, and/or 3) there is a large lateral influx of sediment and dispersion of AC that dilutes the AC signal. Unfortunately, sufficient information to discriminate among these possibilities is not available. However, the observation underscores the importance of having sufficient information on sediment processes. Reconnaissance observations indicated that Canal Creek had soft substrate and was depositional, but it was not known whether the system might be flashy, nor was information available on the actual rates of deposition and lateral/vertical mixing. Estimates or measure of these processes would help inform the design of SediMite® and other *in situ* remediation applications.

The October 2011 sampling in LCC revealed that AC levels were only slightly elevated relative to the control (Figure 18). LCC experienced two major storm events between June and October

2011: Hurricane Irene on August 27, 2011, and Tropical Storm Lee on September 4, 2011. These storms could have either washed out the AC in LCC sediments or delivered new sediment material that was deposited on top of the treatment area. The concentration of AC in the treatment plot for LCC in October 2011 was barely above the AC levels seen in the control plots (~0.3%). Because of the low recovery of AC in the LCC 10-month samples, further bioaccumulation studies were not conducted using these samples from the LCC study area.

Additional sediment core samples were collected at locations 5 feet and 10 feet downstream of the application area in October 2011. These samples (average of top 20 cm core sections) showed a small elevation of AC compared to the control plots but were lower than the carbon measured in the treated plots. The result indicates that lateral distribution is occurring in LCC.

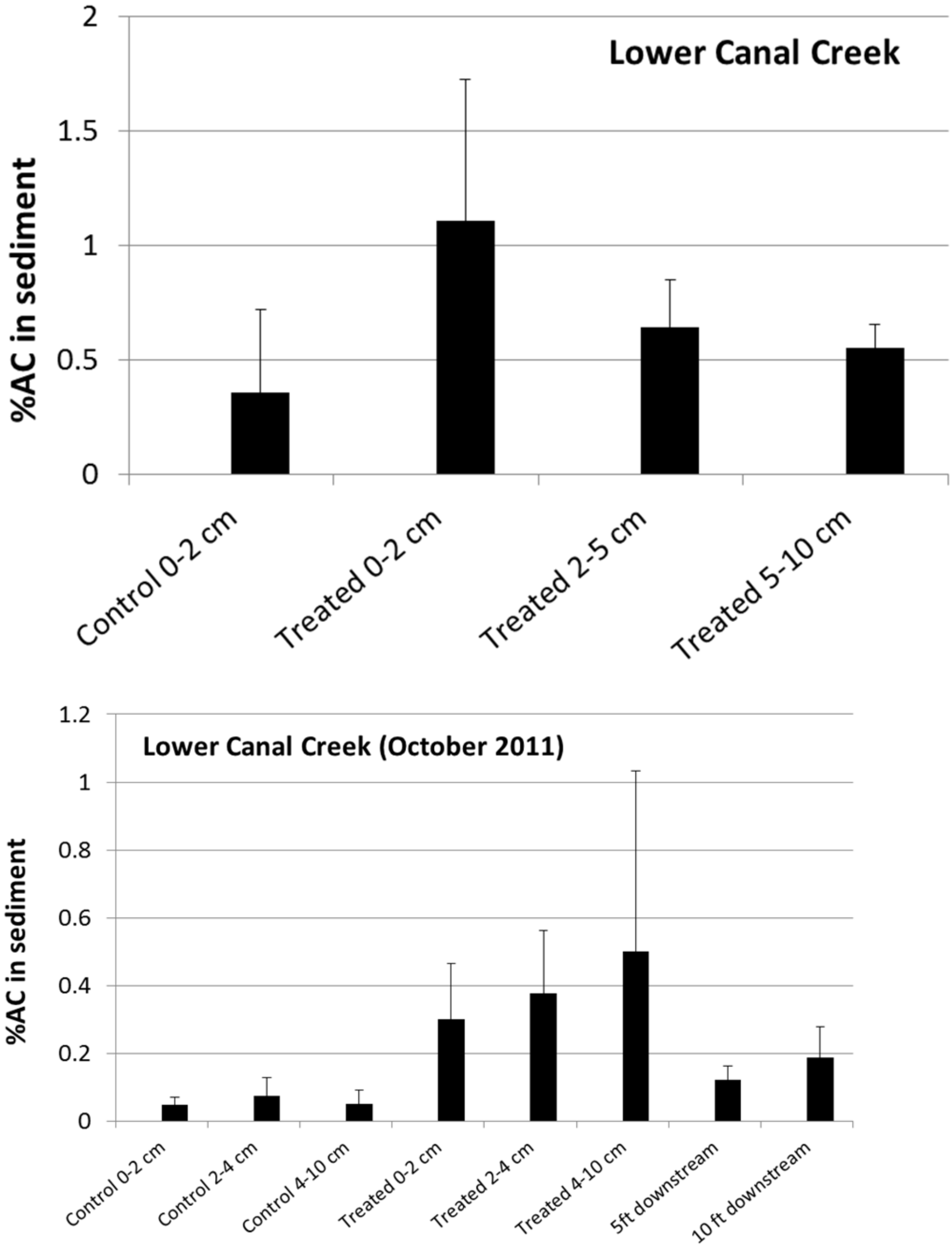


Figure 18. AC (black carbon) in LCC plots in June and October 2011.

6.1.3 Bailey Creek

For Bailey Creek, AC was within the target range for treatment two months after application (Appendix B). Mass balance calculations indicate that 70% of the applied AC was present within the treatment plots at this time. After 15 months, the concentration of AC was ~2.5% in the upper 5 cm and 50% of the applied AC was estimated to be present within the plots. It is believed that lateral mixing with untreated sediments (i.e., edge effects) reduced AC levels within the plots while the rest was transported laterally into areas outside the plots. While this mixing process was much slower than what might have occurred in Canal Creek, these processes are aspects of design that should be considered. Edge effects would, however, diminish as the scale of the treatment area is increased. Thus, for full-scale design purposes, it would be useful to be able to have estimates of mixing and transport at the scale of the relevant project site.

6.2 Bioaccumulation

6.2.1 PCBs and DDx in Upper Canal Creek Wetland Soils

Concentrations of PCBs in wetland soils from UCC showed considerable spatial and vertical variability (Figures 19–21). The PCB concentration in wetland soils in the proposed control and treatment plots showed 1–2 orders of magnitude in spatial variability and ranged from 0.8–26 µg/g. PCB concentrations in wetland soils post-application in the plots actually used are lower and show much less variability in samples taken in June and October 2011 (mostly ranging from 0.5–3 µg/g). The tri- and tetra-chlorinated PCBs are the most dominant, contributing to 60–80% of the total followed by di- and penta-chlorobiphenyls. These four homolog groups constitute 85–95% of the total PCBs in sediment. It is important to note that PCB extraction efficiency from sediment is greatly reduced in the presence of activated carbon. Previous work has demonstrated that at 5–10% activated carbon dose, the extraction efficiency of PCBs from sediment can be lower by 40% (Beckingham et al. 2011). Thus, the measurements of PCBs in sediments from the SediMite-treated plots could be underestimated. When tissue samples are normalized by these underestimated soil concentrations, the reductions in bioaccumulation appear lower.

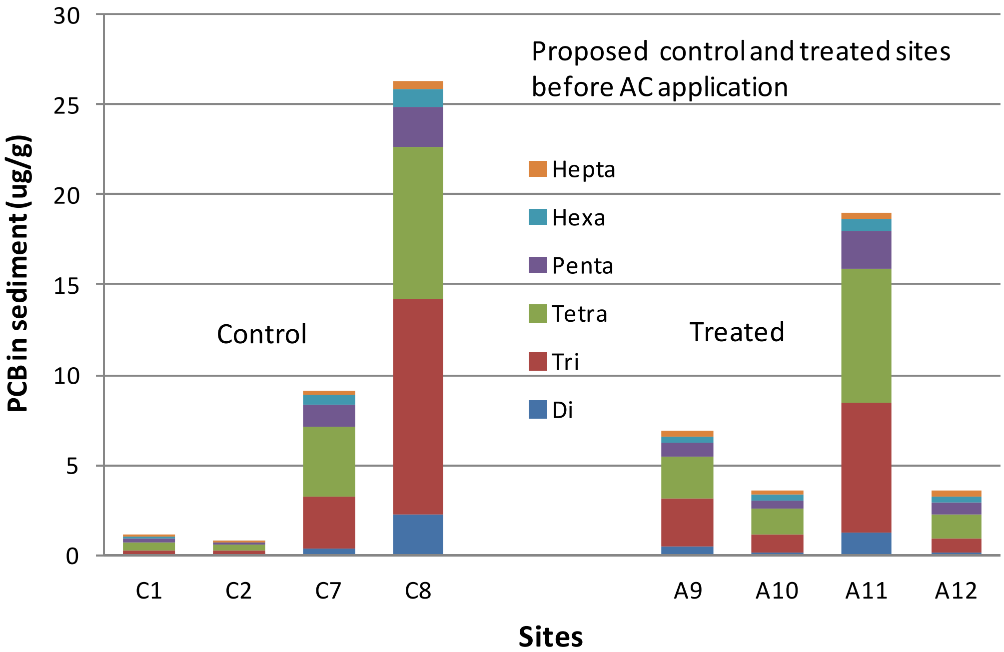


Figure 19. PCB concentration in sediment from plots originally designed as control and treatment plots. Samples were collected in October 2009.

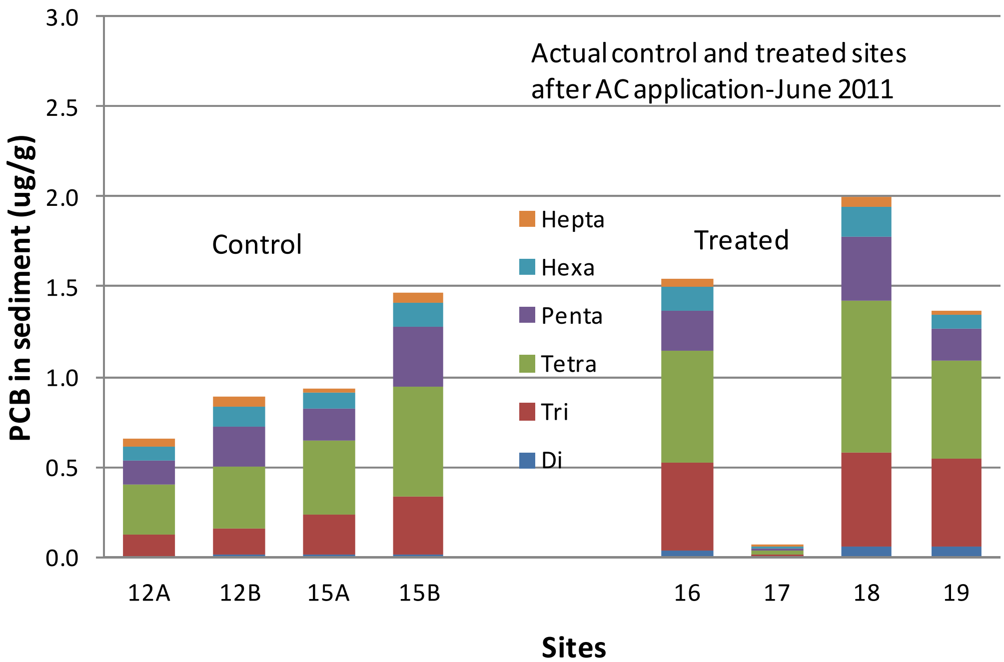


Figure 20. PCB concentration in sediment after SediMite® application from control and treatment plots. Samples were collected in June 2011.

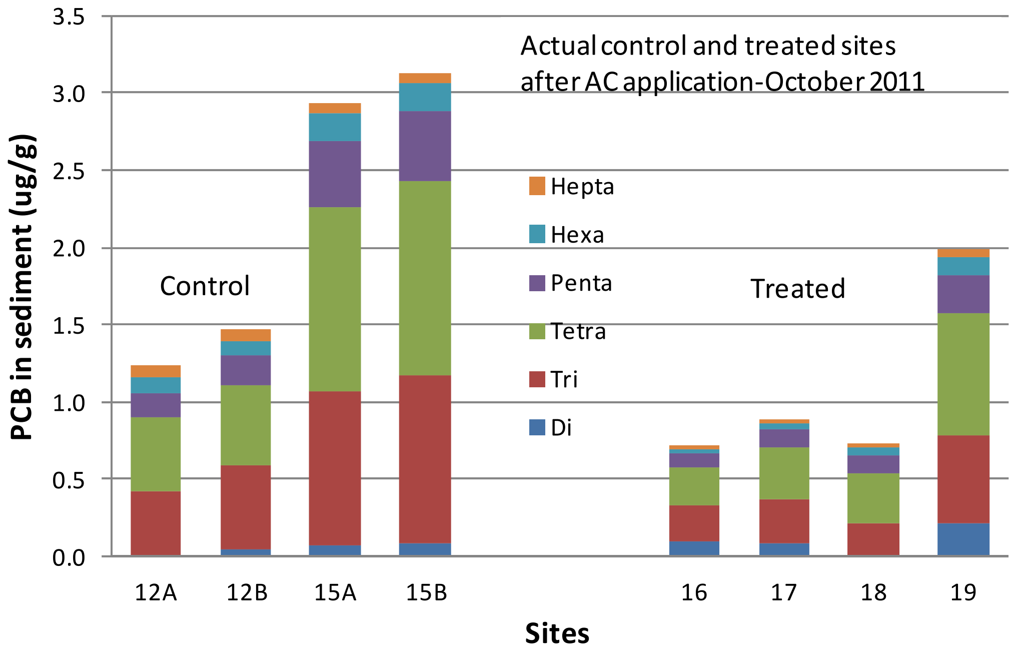


Figure 21. PCB concentration in sediment after SediMite® application from control and treatment plots. Samples were collected in October 2011.

DDx in wetland soils also exhibited variability (Figure 22). In general the control soil samples exhibited higher bulk concentrations than did the treatment samples. Some of this systematic difference between controls and treatment samples may reflect the observation by Beckingham et al. (2011) that extraction efficiency for PCBs from soils can be lower in the presence of 5% AC; the amount of PCBs in bulk soils are underestimated. Perhaps other chlorinated organic chemicals such as DDx are influenced in the same way by the presence of AC.

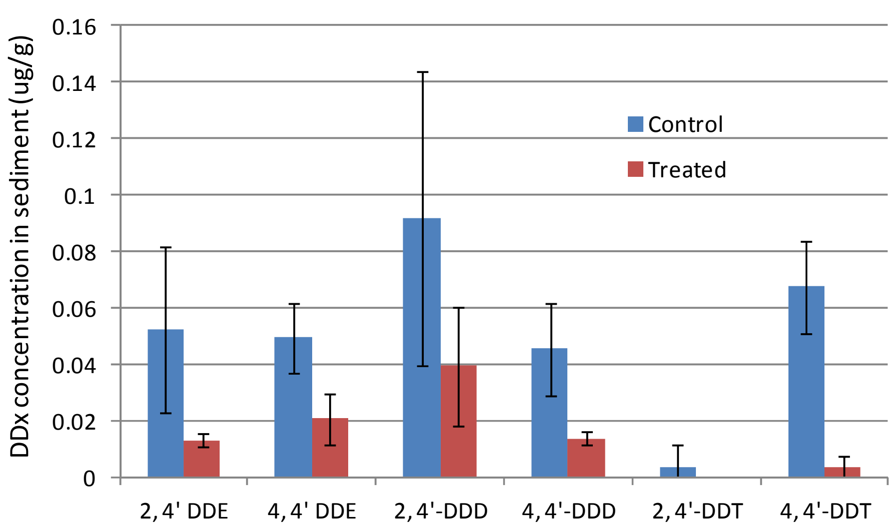


Figure 22. DDx compounds in wetland soils of UCC at 10 months post-treatment.

6.2.2 PCBs and DDx in Worm Tissues

Tabulated results of laboratory bioaccumulation studies on field-treated sediments from UCC are presented in Appendix B. Worm mass recovery was more than 100% in most sediment samples except for the samples with levels of activated carbon greater than 10% (samples 17 and 19 in June 2011, and samples 16, 17, 18, and 19 in October 2011 samples). For these high AC content samples worm mass recoveries were low at 30–60% but were sufficient for conducting PCB analysis.

Pretreatment baseline samples. PCB bioaccumulation in worms for the pretreatment baseline samples are shown in Figure 23. For the baseline samples, bioaccumulation generally follows PCB levels in wetland soils with plot C8 showing the highest level of bioaccumulation corresponding to the highest level of PCB found in soil at this plot (26 μg/g). Site C2 shows the lowest PCB bioaccumulation also corresponding to the lowest PCB level in soil (0.4 μg/g). PCB homolog concentrations distribution in worms also reflected the distribution in wetland soil with tri- and tetrachlorobiphenyls being the dominant homologs.

Post-treatment samples from June 2011 (six months after). In the post-treatment samples, PCB bioaccumulation in the control plots generally followed PCB levels in wetland soils, where plot 12A showed the least accumulation, and plot 15B showed the highest PCB bioaccumulation (see Figure 24). Post-treatment samples from June 2011 show reductions in PCB uptake in worms in the SediMite® treated areas. The reductions are the highest in the plots receiving high levels of AC (17 and 19). Treated plot 18 showed PCB bioaccumulation close to the control plots likely due to the highest level of PCB in sediment at this plot (higher than all the control plot sediments) and also due to the fact that this plot received less than the target dose of AC at 3.2%. After six months, the reduction in total PCBs in tissues of worms from treated as compared to control plots was 57%; this reduction was not statistically significant as evaluated by comparisons of means using a one-tail t-test ($p < 0.05$).

Post-treatment samples from October 2011 (10 months after). In the post-treatment samples, PCB bioaccumulation in the control plots generally followed PCB levels in wetland soils for plots 12B, 15A, and 15B, but showed higher than expected bioaccumulation in plot 12A (see Figure 25). All SediMite® treated plots showed reduced bioaccumulation of PCBs in worms for the October 2011 samples. The reduction in tissue levels for treated plots was 92% relative to the control plots; this reduction was statistically significant as evaluated by comparisons of means using a one-tail t-test ($p < 0.05$). The lower bioaccumulation in the treated plots from October 2011 was likely due to lower variability in AC contents of the bulk samples and generally high levels of AC above the target dose at each of the treated plots.

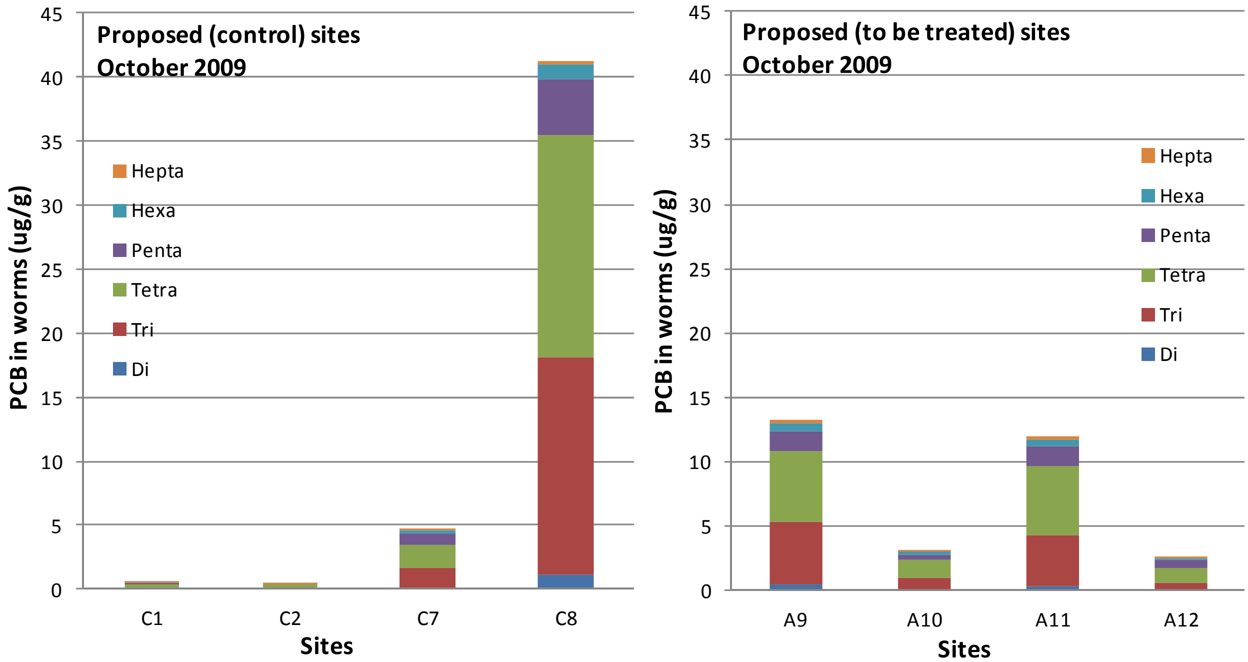


Figure 23. PCB bioaccumulation in worms (μg/g) in pretreatment baseline samples collected in October 2009.

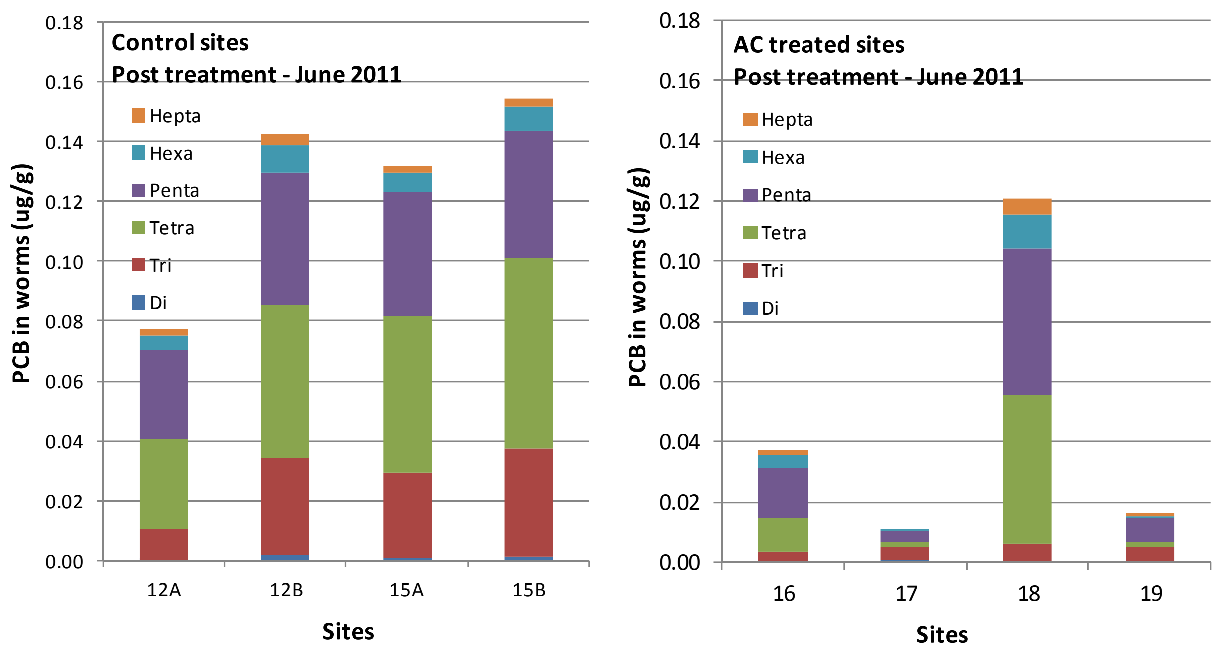


Figure 24. PCB bioaccumulation in worms (μg/g) in post-treatment samples collected in June 2011. Reduction in total PCBs was not statistically significant at 57%.

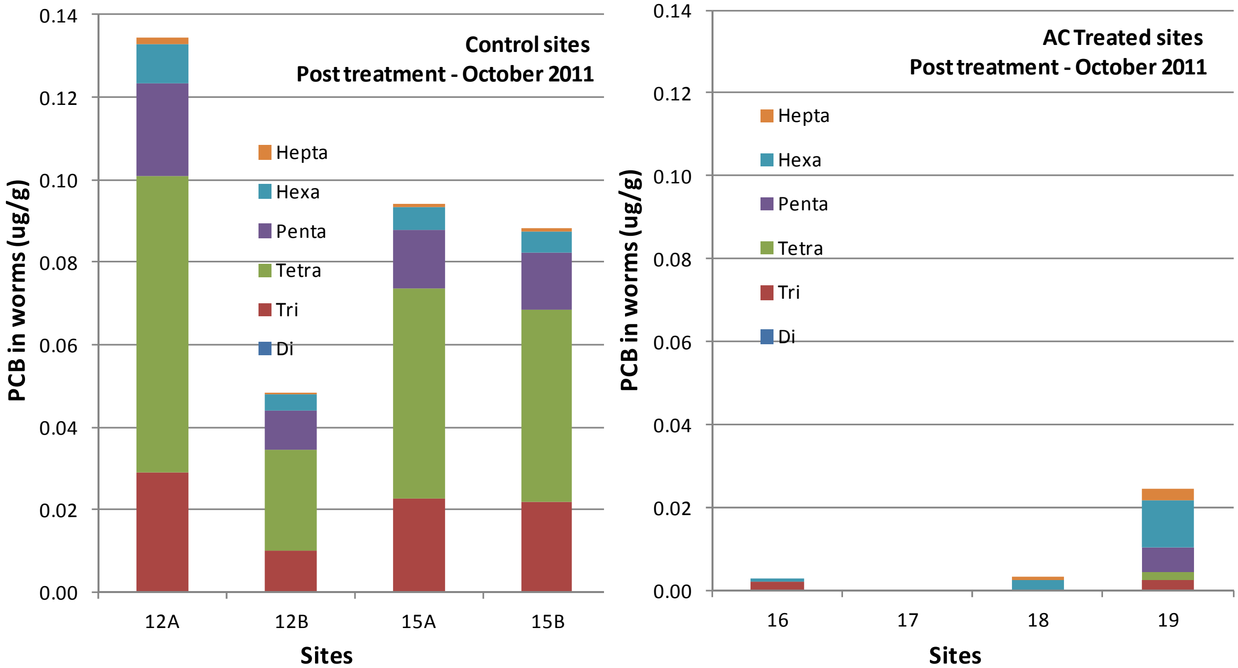


Figure 25. PCB bioaccumulation in worms (µg/g) in post-treatment sediment samples collected in October 2011. Reduction in total PCBs was statistically significant at 92%.

To account for the differences in PCB concentrations in wetland soil, the worm PCB concentrations were normalized to the PCB concentrations in soils for the three most dominant homologs in sediment: trichlorobiphenyls, tetachlorobiphenyls, and pentachlorobiphenyls (Figure 26). The normalized values were equivalent to biota-soil/sediment accumulation factors (BSAFs). In this case, the BSAF is obtained by dividing PCBs in tissues on a wet weight basis by PCBs in wetland soils on a dry weight basis. The ratio of PCBs in worms to PCBs in wetland soils ranged from 0.5–2 before application of SediMite®. After SediMite® application, the same ratio decreased to 0.00–0.07 in the treated plots. The control plots also showed some reduction in uptake in worms compared to pretreatment results but less so than the treated plots. After 10 months, BSAFs were significantly reduced ($p > 0.05$) compared to control plots (normalized to soil PCB concentration) with reductions ranging from 60% for the pentachlorobiphenyls to more than 90% for trichlorobiphenyls (Figure 27). When compared to pretreatment conditions, the reductions in PCB uptake were much higher. It is important to recall two confounding factors that would reduce the apparent efficiency of the SediMite® treatment: 1) the control plots also ended up receiving some AC from nearby slurry treatment plots, and 2) PCB bulk measurements in soils may be underestimated due to the presence of high levels of AC, which reduces extraction efficiencies (Beckingham et al. 2011).

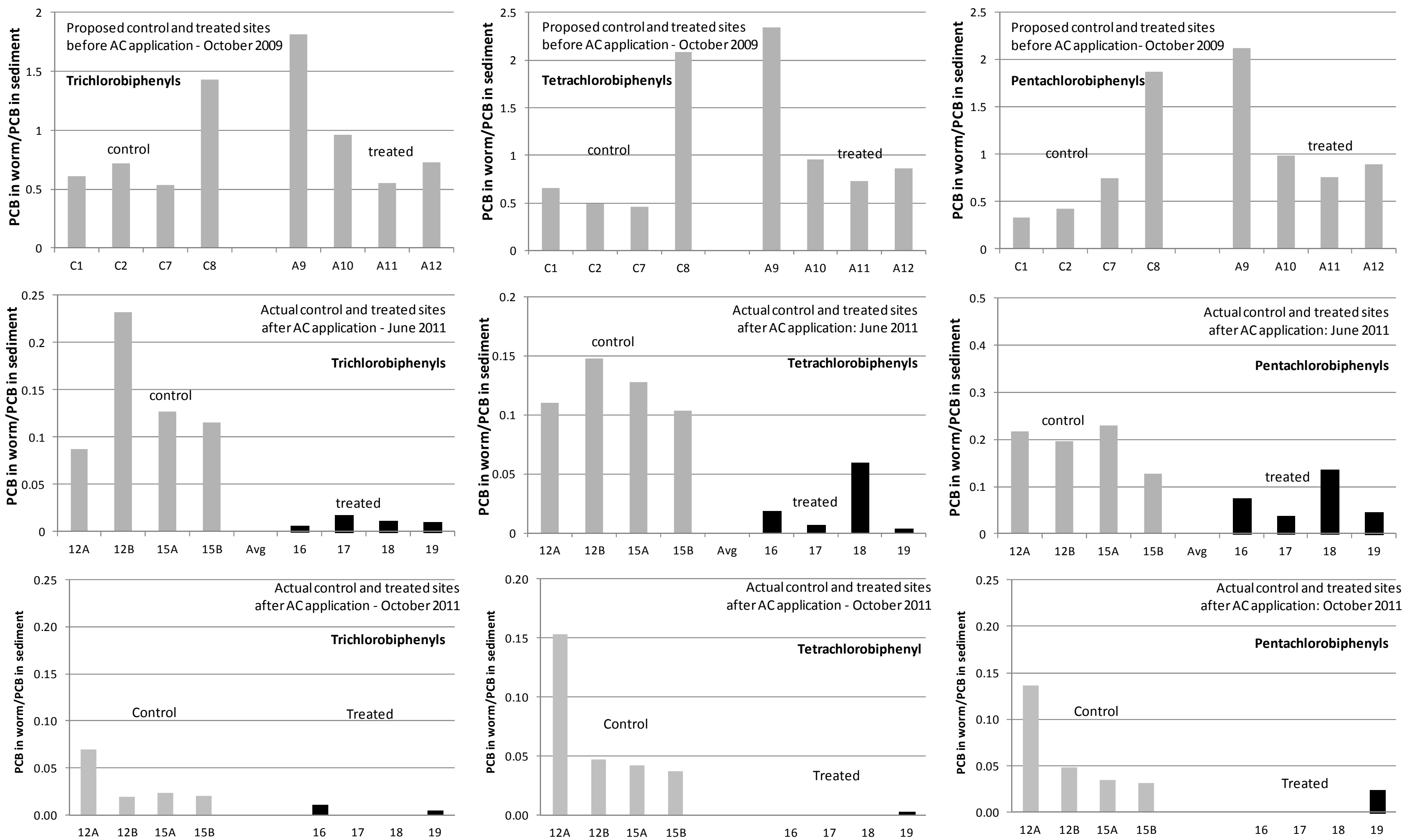


Figure 26. PCB bioaccumulation in worms in control and treated wetland soils, normalized to soil PCB concentration.

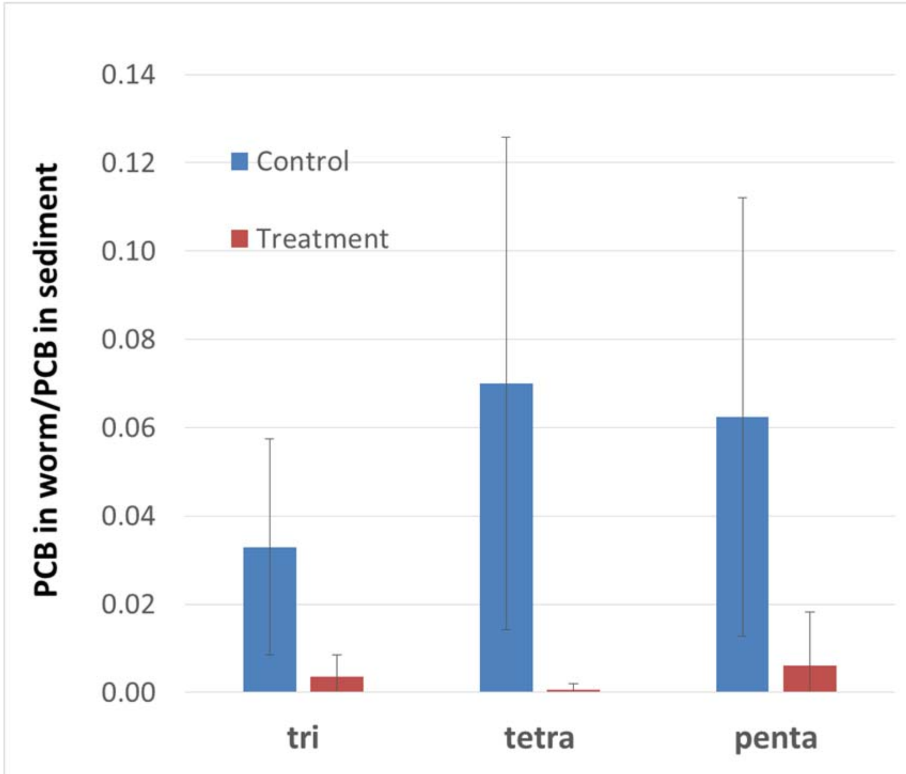


Figure 27. Average BSAF values (PCBs in tissue normalized to PCBs in wetland soils) for treated and control plots for post-application conditions after 10 months for three predominant homologues. Reductions are statistically significant.

A comparison of measurements made after 6 and 10 months for raw measurements in worm tissues as well as for BSAF values suggests there was an increase in treatment effectiveness of AC with time. An increase in apparent effectiveness was also observed for the Grasse River site in upstate New York (Beckingham and Ghosh 2011). It is believed that the increase in effectiveness with time reflects continued mixing of AC with wetland soils allowing for more complete contact between contaminants and the applied AC. Analysis of AC (measured as black carbon) showed that distribution became more uniform within the wetland soils between the two post-application monitoring events (see Appendix B).

Following 10 months of treatment, the bioaccumulation of DDx in worms exposed to surface wetland soils (0–5 cm) from SediMite®-treated plots was 80% lower than worms exposed to wetland soils from controls (Figure 28 and Appendix B). Because of the variability in soil concentrations described earlier, worm tissue values were also normalized by concentrations in wetland soils. When normalized, the reduction in bioavailability appeared smaller at 33%. As noted earlier, this could be an underestimate if AC is reducing the extractability of DDx from the soils.

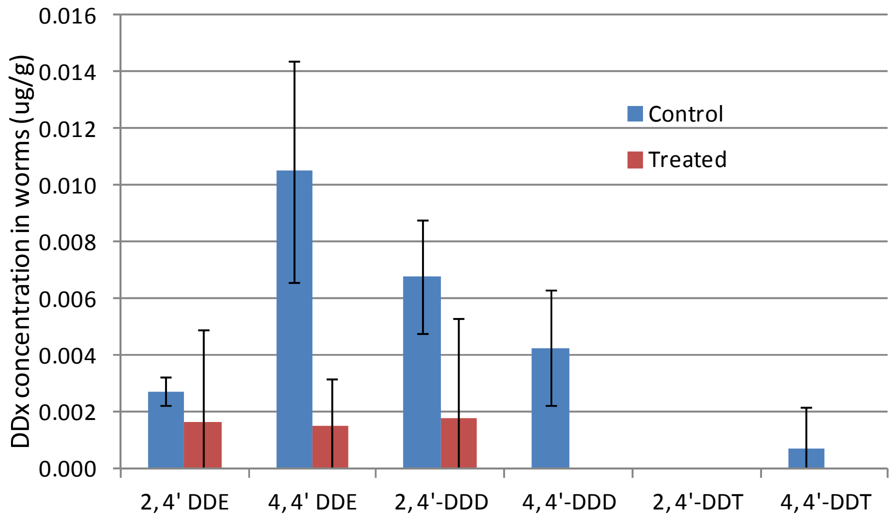


Figure 28. DDx concentrations in worm tissue for animals exposed in the laboratory to field-collected wetland soils from SediMite®-treated and untreated plots after 10 months in UCC.

6.2.3 Lower Canal Creek (MeHg)

Results for LCC are provided in Appendix C. The bioaccumulation of MeHg from LCC sediment into worm tissue was evaluated for one post-application monitoring event in June 2011, six months after the application of SediMite®. For this sampling event the MeHg concentrations in worm tissue were significantly lower for sediments from the treatment plot as compared to the control plot (Figure 29). For this performance metric, testing the statistical significance was based on a test of mean concentrations using a t-test ($p < 0.05$). The average reduction was slightly greater than 50%, which was the performance criterion.

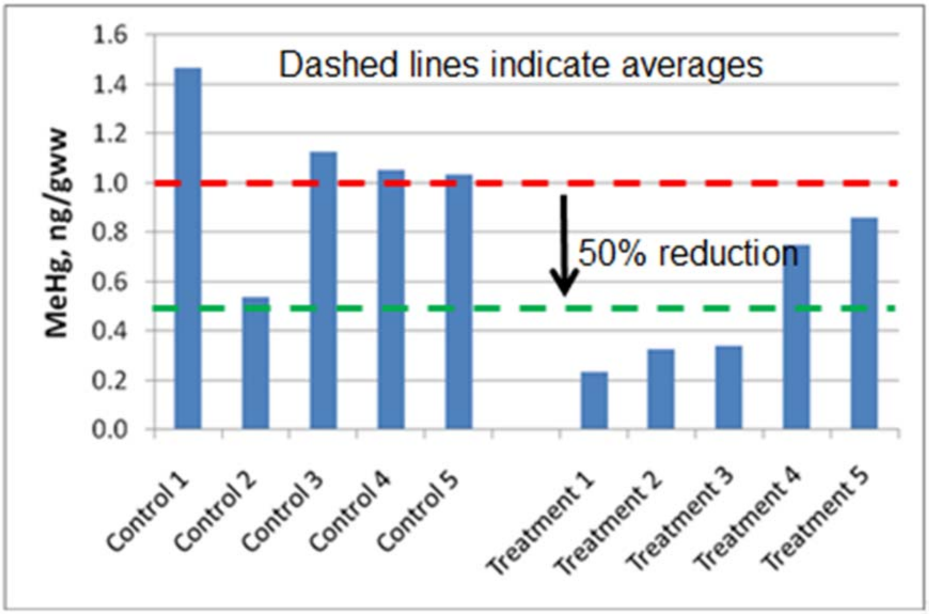


Figure 29. Tissue levels of MeHg in worms exposed to control and SediMite®-treated sediments from LCC. The reduction in mean concentrations is statistically significant.

When results for tissue concentrations are normalized for sediment concentrations (i.e., calculated BSAFs) the reduction was greater (Figure 30). The field-collected treatment results were comparable to what was observed in the laboratory treatability studies. However, as noted earlier, AC decreased in concentration during the course of the project. Therefore, while the results show that AC applied via SediMite® can reduce bioaccumulation of MeHg in field applications, additional information on sediment dynamics and long-term performance of AC are needed to plan a full-scale remediation. The results suggest that AC applications may reduce bioaccumulation of MeHg in field applications, but additional work is needed before AC applications as a remedial method for mercury can be recommended without considering site-specific factors. Ongoing work is showing that AC mitigates exposure to mercury, but, again, variations occur among sites such that site-specific factors must be viewed as an important influence on treatment efficacy by AC (Gilmour et al. 2013).

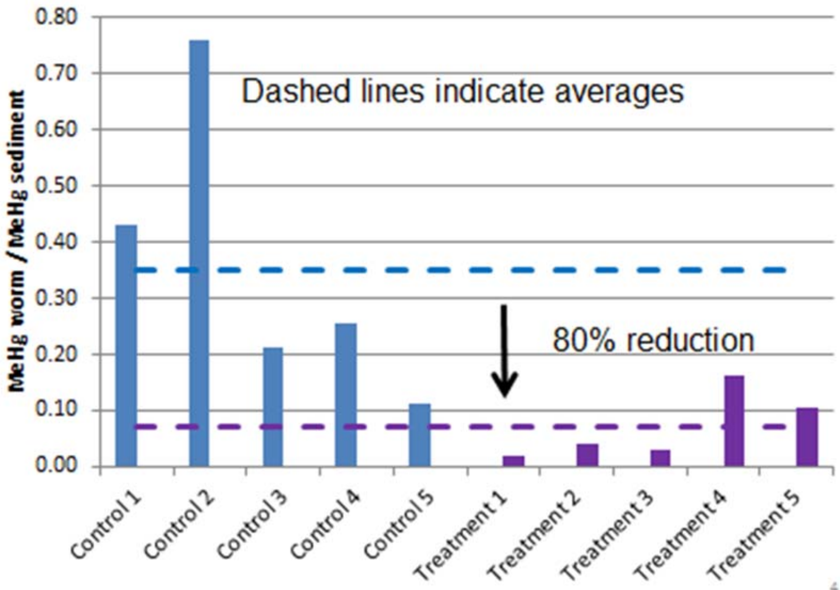


Figure 30. **Biota (wet wt.) to sediment (dry wt.) accumulation factors (BSAFs) for MeHg in worms exposed to control and SediMite®-treated sediments from LCC six months following application. The reduction in BSAF values is statistically significant (t-test of means at $p < 0.05$).**

6.2.4 Bailey Creek (PCBs)

The results for the Bailey Creek application of SediMite® are provided in Appendix D. The results from bioaccumulation studies with the amphipod *Leptocheirus plumulosus* are shown in Figure 31.

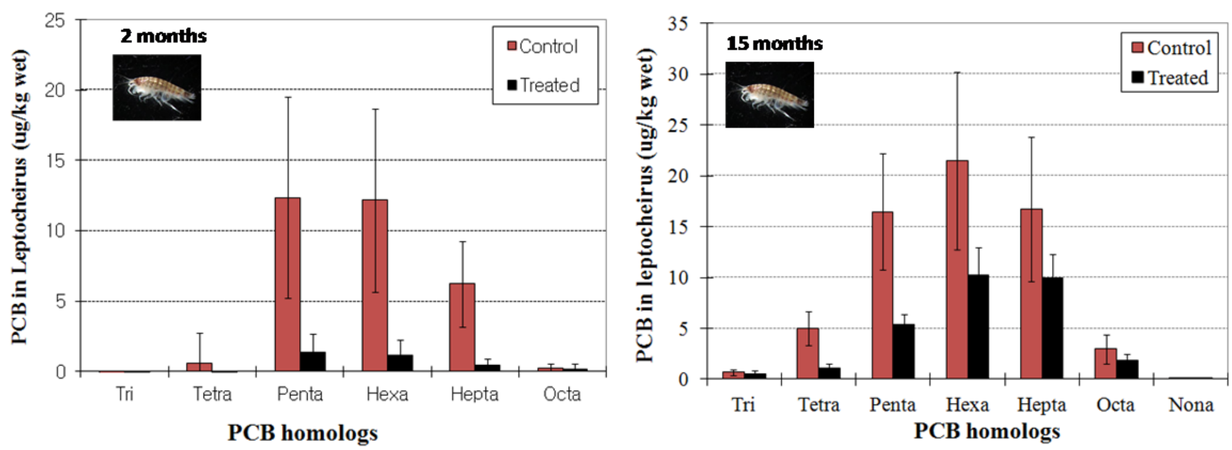


Figure 31. **Comparisons of tissue levels for PCBs in tissues of the amphipod *L. plumulosus* exposed to Bailey Creek sediment from control and SediMite® treatment plots at 2 and 15 months following application.**

Statistically significant reductions ($p < 0.05$) in bioaccumulation of PCBs were observed at 2 and 15 months following treatment. PCBs in tissues were reduced by 90% after 2 months. Reductions were ~50% after 15 months, likely due to reduction in AC levels and influx of new PCBs from surrounding untreated sediments. The results suggest that there may have been an influx of new PCBs to the area between 2 and 15 months. This is indicated by the higher tissue concentrations in the controls and the appearance of octa-chlorinated biphenyls at 15 months as compared to their absence at 2 months. The control and treatment plots are located within a much larger area that is scheduled for remediation. The area chosen for the demonstration has sediment concentrations that are somewhat lower than the surrounding area. Thus, it is conceivable that sediment transport from these areas has brought PCB-contaminated sediments into the study area over the duration of the project. This is considered to be a reflection of edge effects and a limitation on longer-term pilot studies that involve treatment areas that are small in size relative to the surrounding source area. Such edge effects would diminish as the scale of treatment increases relative to the zone of contamination that serves as an adjacent source of contamination. In light of these results, information on sediment transport and mixing at the scale of the area scheduled for remediation is considered especially important for the design of full-scale *in situ* remedial options. In the case of Bailey Creek, this would require an assessment of sediments over a broad reach of the tidal creek.

6.2.5 Berry's Creek *Phragmites* Marsh

Data on bioaccumulation studies for PCBs at Berry's Creek (Sanders et al. 1915) are referenced herein, as they provide additional insight into treatment efficacy for wetland systems. That study included measures for field-collected native amphipods (*Orchestia*), caged *in situ* exposures of an amphipod species (*Leptochierus*), and laboratory exposures of *Leptochierus* to field-collected wetland soils. Relative to the control plot, PCB concentrations in the biota exposed to wetland soils from the SediMite® treated plot were lower by 78% for native animals, 98% for caged animals (*in situ* exposures), and 84% for amphipods exposed *ex situ* to field-collected soils in the laboratory.

6.3 Performance as Judged by Reduced Porewater Concentrations or Increased K_d

The influence of AC delivered via SediMite® on porewater was evaluated by examining resultant porewater concentrations, equilibrium partitioning, and through the derivation of K_d values that reflect partitioning between solid and porewater phases. The confounding factors already discussed for PCBs are also present when evaluating porewater. Thus, a few different comparisons have been made.

6.3.1 Upper Canal Creek

Tabulated results for UCC are provided in Appendix B. Equilibrium porewater concentration in bulk sediment samples used in bioaccumulation experiments was measured using POM passive samplers.

<u>Pretreatment baseline samples</u>. PCB in the equilibrium aqueous phase for the pretreatment baseline samples are shown in Figure 32. For the baseline samples, porewater PCB

concentrations followed PCB levels in sediment with plot C8 showing the highest level of bioaccumulation corresponding to the highest level of PCB found in sediment at this plot. Plots C1 and C2 showed the lowest porewater PCBs also corresponding to the lowest PCB level in sediment. PCB homolog concentrations distribution in porewater was shifted toward the lower chlorinated congeners compared to the distribution in sediment. In the porewater samples of untreated sediments, di-, tri-, and tetrachlorobiphenyls dominate.

Post-treatment samples from June 2011 (six months after). In the six-month post-treatment samples, porewater PCBs in the control plots (Figure 33) were high but do not necessarily follow total PCB levels in sediment. Some of the discrepancy could have been caused by the higher-than-background levels of AC found in some of the control plots after treatment applications in neighboring plots. Post-treatment samples from June 2011 showed reductions in porewater PCBs in the SediMite®-treated areas. The reductions were the highest in the plots receiving high levels of AC (17 and 19). Treated plot 18 showed the highest porewater PCB levels likely due to the highest level of PCB in sediment at this plot (higher than all the control plot sediments) and also due to the fact that this plot received only 3.2% AC—less than the target dose. The results for the slowly mixed samples showed that six months after application, average porewater concentrations in the SediMite®-treated surface (0–2 in.) wetland soils were 65% lower than the control soils, but this difference was not statistically significant.

Post-treatment samples from October 2011 (10 months after). In the 10-month post-treatment samples, porewater PCBs in the control plots generally followed PCB levels in sediment (Figure 34). All SediMite®-treated plots showed greatly reduced porewater PCBs for the October 2011 samples. The consistently lower porewater PCBs in the treated samples from October 2011 was likely due to lower variability in AC contents of the bulk samples and generally high levels of AC above the target dose at each of the treated plots. At 10 months after application, the treated surface soils exhibited porewater concentrations that were 92% lower than the control soils, and this difference was statistically significant.

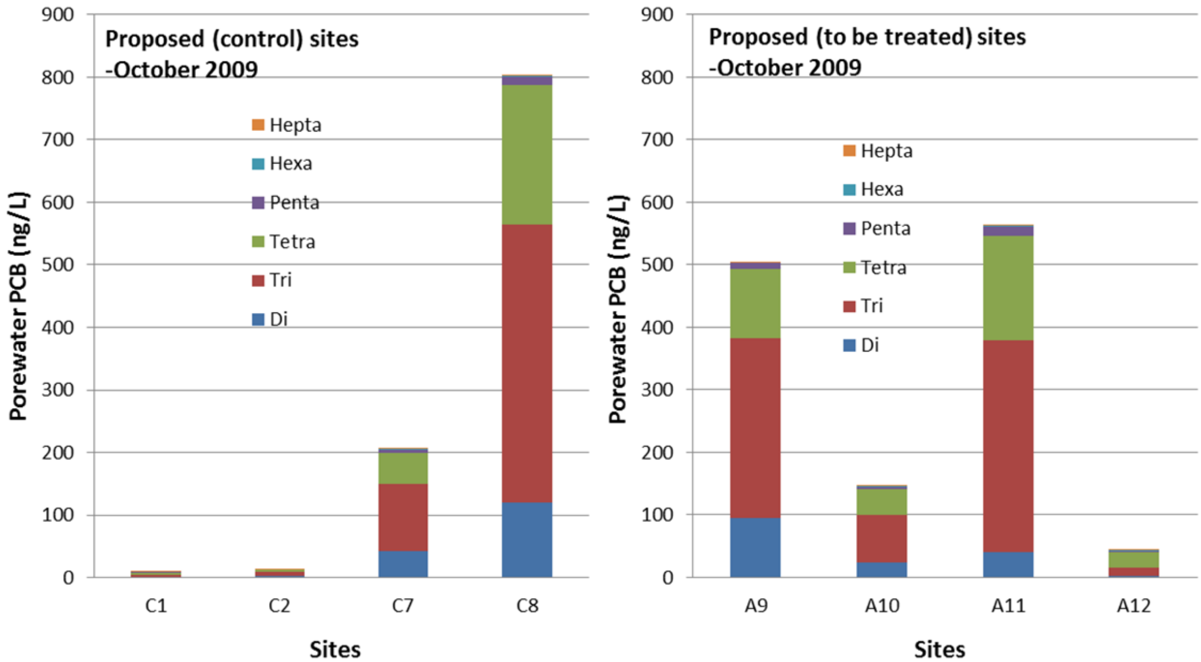


Figure 32. Equilibrium porewater PCB concentration in sediment collected before application of SediMite® (October 2009).

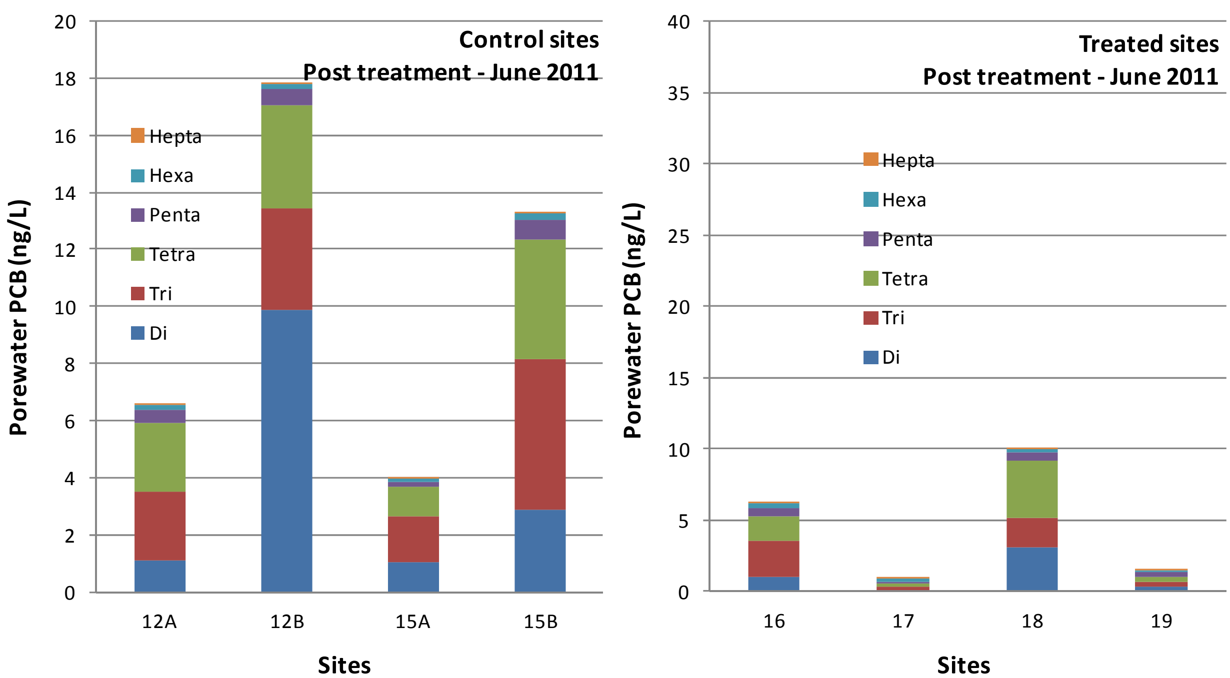


Figure 33. Equilibrium porewater PCB concentration in sediment collected after application of SediMite® (June 2011).

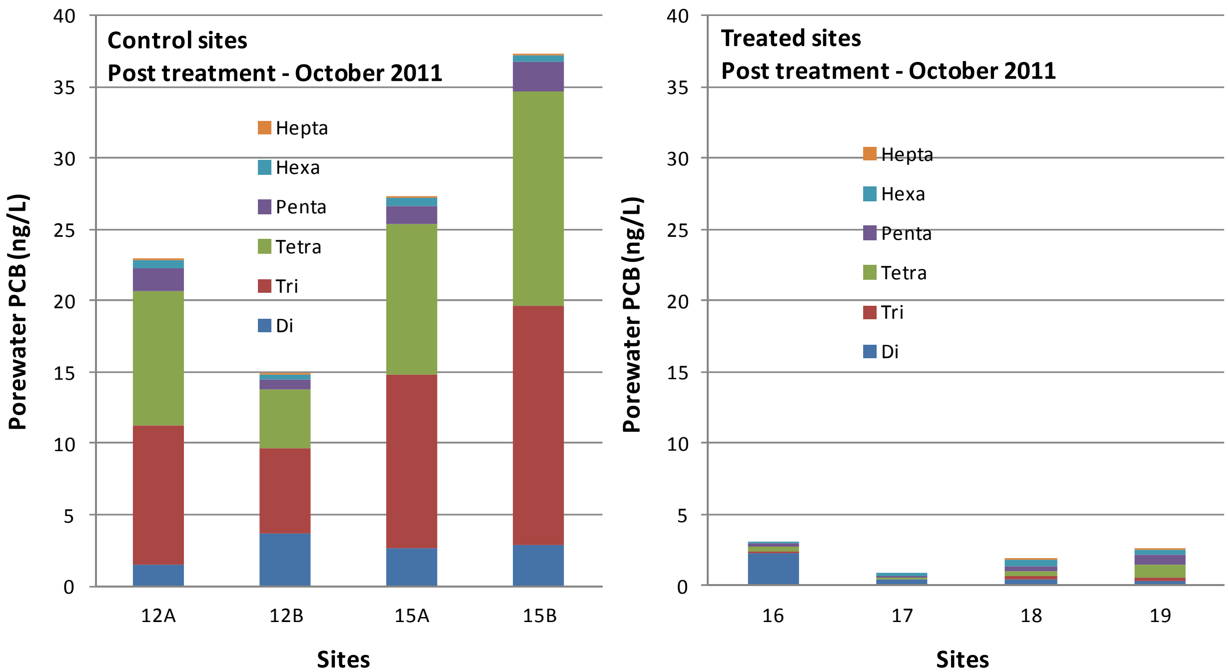


Figure 34. Equilibrium porewater PCB concentration in wetland soil collected after application of SediMite® (October 2011).

To account for the differences in PCB concentration in sediment, the porewater PCB concentrations were normalized to wetland soil PCB concentrations. The normalized porewater PCB concentrations are plotted for the three most dominant homologs in soil: di-, tri-, and tetrachlorobiphenyls (Figure 35). After normalization with soil PCB concentration, the porewater PCB concentration showed less variability across the plots (within an order of magnitude) compared to data presented in Figure 32 for the pretreatment samples. The post-application treated plot samples showed a much-reduced porewater PCB concentration compared to the untreated control plots for all three dominant homolog groups.

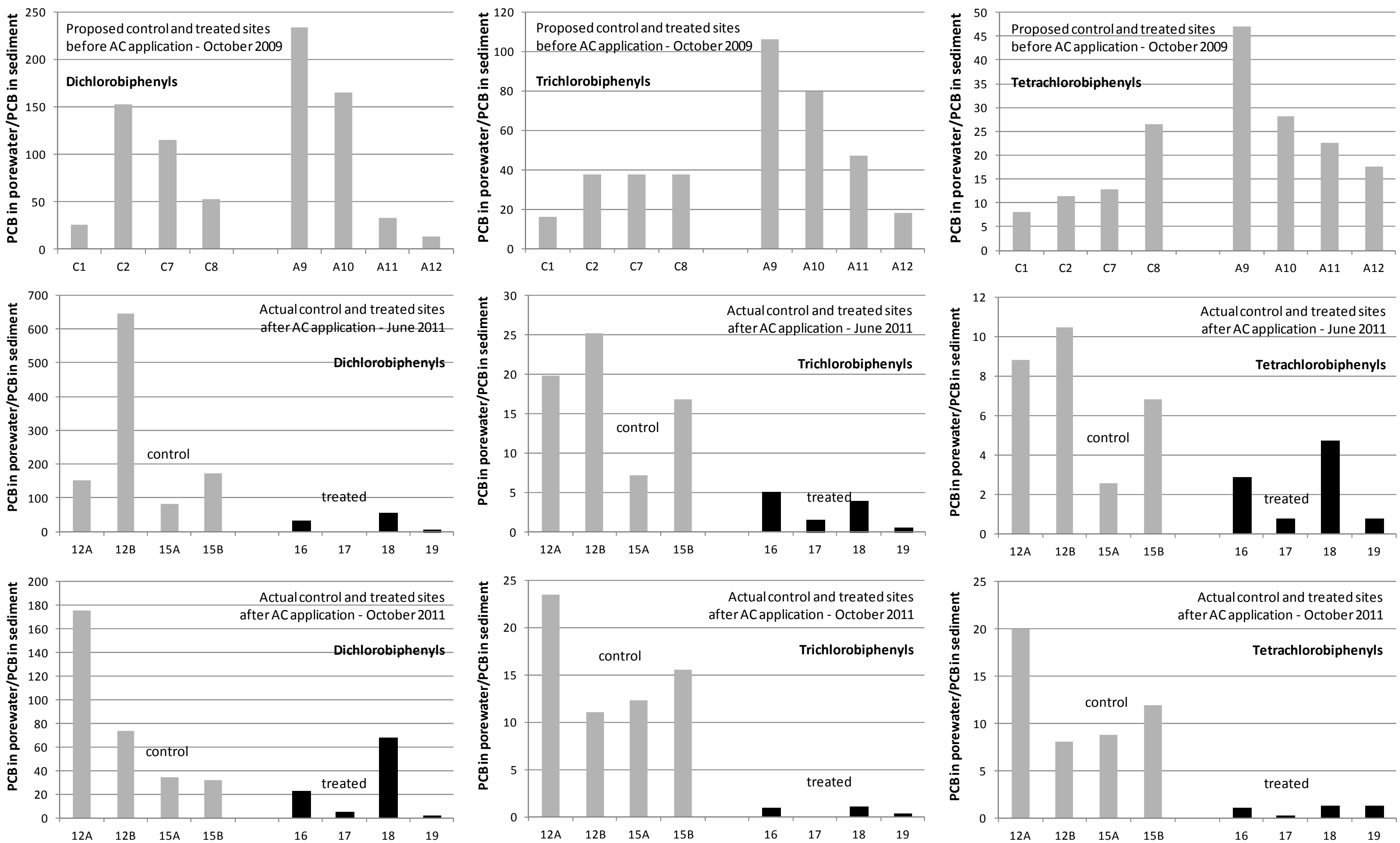


Figure 35. PCB concentrations in the equilibrium aqueous phase in control and treated plot sediments, normalized to sediment PCB concentration. The units in the y-axis are (ng/L)/(mg/Kg) or (Kg/L)x10^{-6}

6.4 Porewater PCB Concentration Profiles in Intact Cores of Wetland Soils

Sediment porewater PCB concentrations were measured in intact cores collected from the control and treated plots 6 and 10 months after SediMite® application. The results showed increasing porewater PCB concentrations with depth in wetland soil possibly reflecting increasing PCB concentrations in the deeper soils. Porewater PCB concentrations in the surface soils (0–2 cm and 2–5 cm) show lower values in the treated plots compared to the control plots. The depth-weighted average PCB porewater concentration in the 0–5-cm zone was lower by 50% in the treated plot compared to the control plot in June 2011 samples. The 0–5-cm depth zone was where most of the AC was found as described earlier. This reduction in porewater PCB concentration in the intact core studies were similar to the 55% reduction in porewater PCBs observed in the bulk equilibrium porewater concentrations in June 2011 samples.

Porewater PCB concentrations for the October 2011 samples were extremely variable from plot to plot, especially in the treated locations (Figure 38). Location 19 was especially high at 10–20-cm depth showing PCB porewater concentrations that were nearly three orders of magnitude higher compared to the concentrations seen in most of the remaining cores at that depth. Due to the large variability in concentrations between replicates within plots (See Figure 38) it was difficult to interpret the results and develop comparisons between treatment and control plots. Ignoring the variability, the average porewater PCB concentrations in the surface layer (0–2 cm) of wetland soil in treated plots were lower than control plots by 54%. For deeper layers, average porewater PCB concentration was much higher than in the controls, which was largely driven by the extremely high concentrations measured in treated plot 19. If treated plot 19 is removed as an outlier, the average PCB porewater concentrations were lower in the treated plots by 67% in the 0–2-cm depth and by 55% in the 2–5-cm depth. Total PCB concentration measured in porewater at the 10–20-cm depth interval in plot 19 was 106,000 ng/L (Figure 38). This concentration was extremely high and within a factor of two of saturated aqueous PCB concentrations reported in Ghosh et al (1998) when Aroclor 1242 is equilibrated with water. Thus, it is likely that treated plot 19 had free phase PCB oil present at 10–20 cm depth.

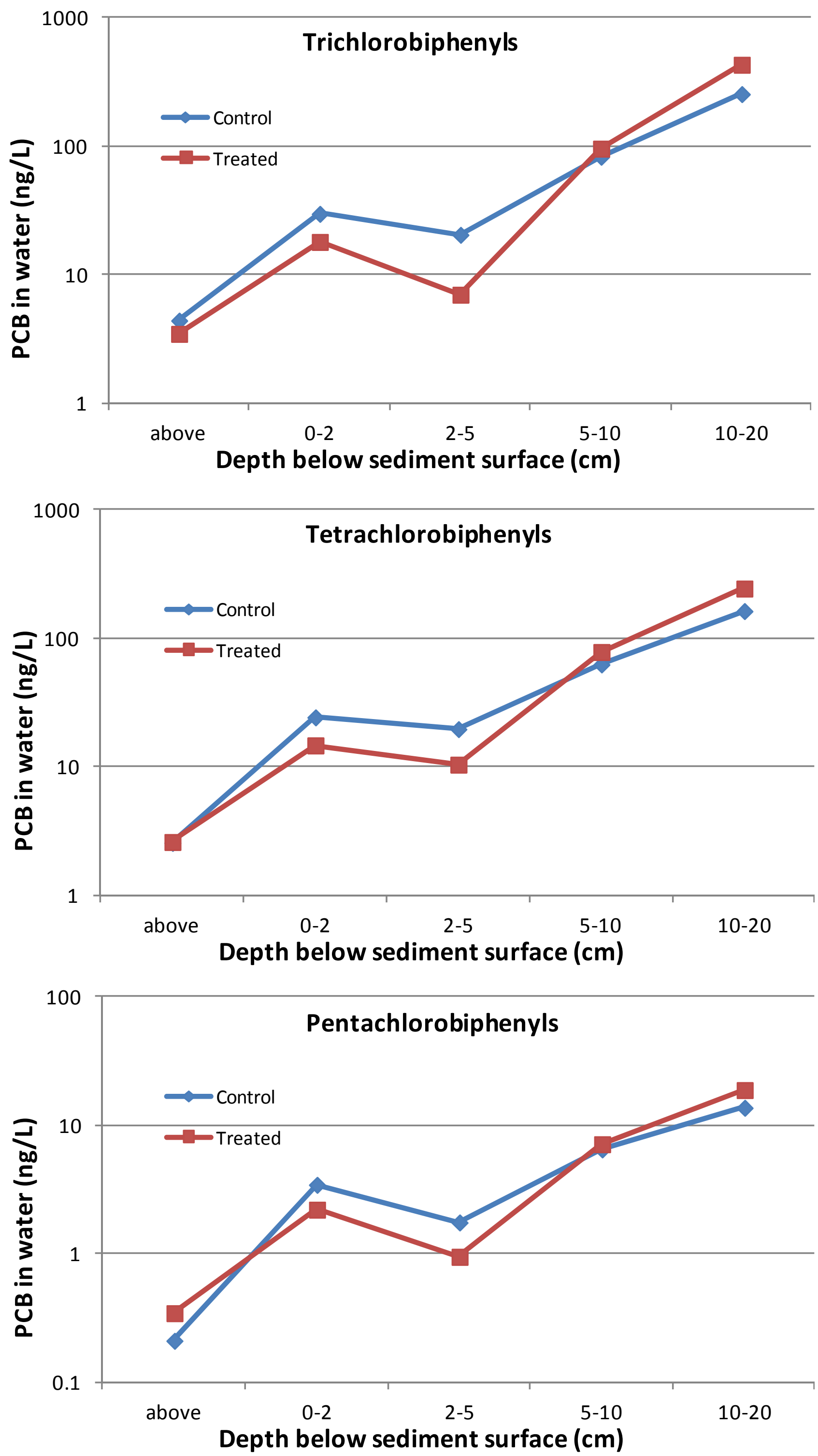


Figure 36. porewater PCB concentration measured in intact cores of wetland soils collected on June 2011 six months after SediMite® application in the field. Values represent average of four replicate cores taken from the control and treatment plots each.

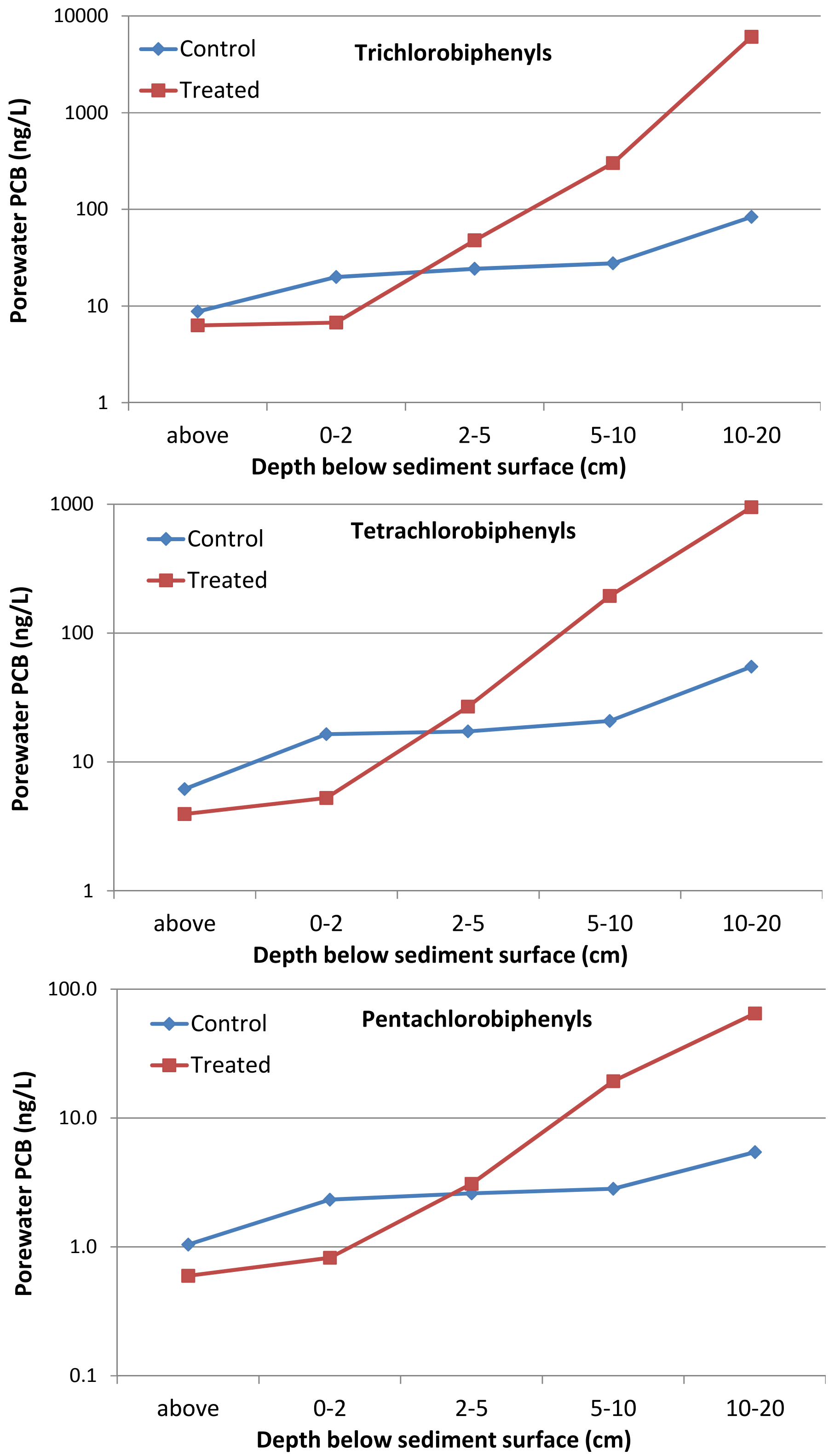


Figure 37. Porewater PCB concentration measured in intact wetland soils cores collected on October 2011 ten months after SediMite® application in the field. Values represent an average of four replicate cores each taken from the control and treatment plots.

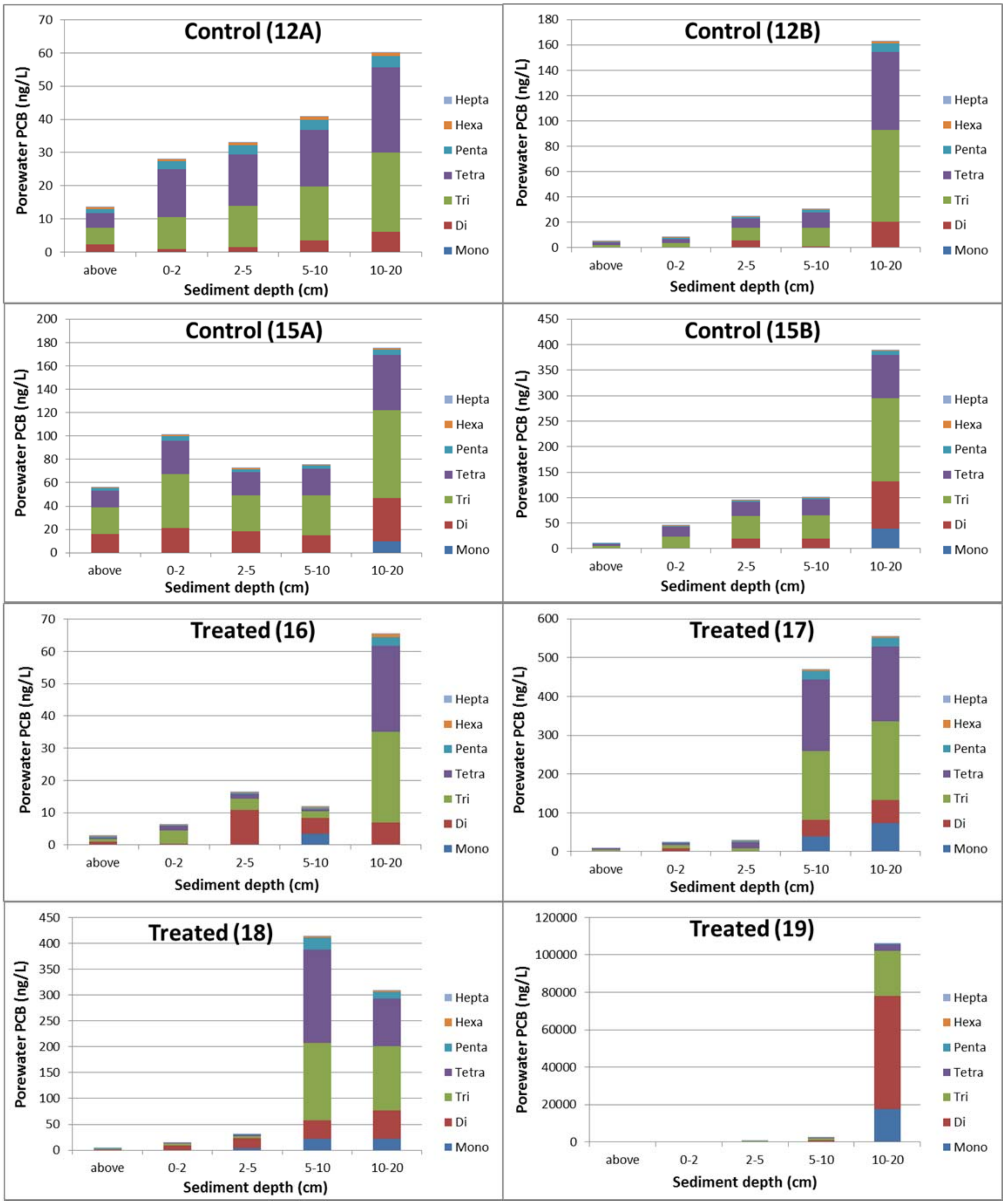


Figure 38. Porewater PCB concentration measured in individual intact cores of wetland soils collected on October 2011 ten months after SediMite® application in the field.

The data represent individual measurements made in each sediment core. All wetland soil porewater concentration profiles decreased from bottom to the surface of soil; the decreases appeared to be much steeper for the treated plots, especially for October samples, compared to the control plots. This steep decrease in porewater concentrations approaching the soil surface could have been caused by the presence of activated carbon in the top layer; alternatively, the steep decrease could have also been due to existing gradients in sediment PCB profiles. To address this large variability in PCB porewater concentrations among replicates observed, additional measurements were performed on PCB in wetland soil in samples collected from each depth of the intact cores used for porewater profile measurements.

PCB concentrations in the intact cores are presented as a function of depth in Figure 39. In most plots, there was an apparent increase in PCB concentrations with depth. At the control locations, the PCB concentrations were generally less than 2 mg/kg in surface soil (0–2 cm) and increased to up to 17 mg/kg by the deepest depth in October 2011 samples. However, at the treated locations, the PCB concentrations in October 2011 range from 1–11 mg/kg in the surface (0–2 cm) and increased to 730 mg/kg in plot 19. These greatly elevated PCB concentrations at depth partly explain the high porewater concentrations observed with depth.

PCB partition coefficients (K_d values) between wetland soil and water were compared among treatment and control plots examined as an additional means to investigate treatment effects in light of the high spatial variability of PCB concentrations in wetland soils. Partition coefficients for two representative congeners (tri and tetra) are plotted as a function of depth in Figure 40. Although PCB concentrations in soil changed by nearly an order of magnitude at the control plot with depth, the calculated K_d value for each congener remained relatively constant with depth as shown in Figure 40. However, in the treated plot, there was a marked increase in K_d by about an order of magnitude in the surface sediments compared to the deepest sediment layer. The high K_d value observed in the 5–10-cm sediment depth is difficult to explain given that AC measurements shown in Figure 2 indicated that the amendment did not reach this depth. It is possible that insertion of the passive sampler frame into the intact core resulted in vertically downward migration of some AC in the vicinity of the sampler. Nonetheless, results shown in Figure 40 indicated that presence of AC in the surface soil had a strong influence in increasing *in situ* partition constants of PCBs.

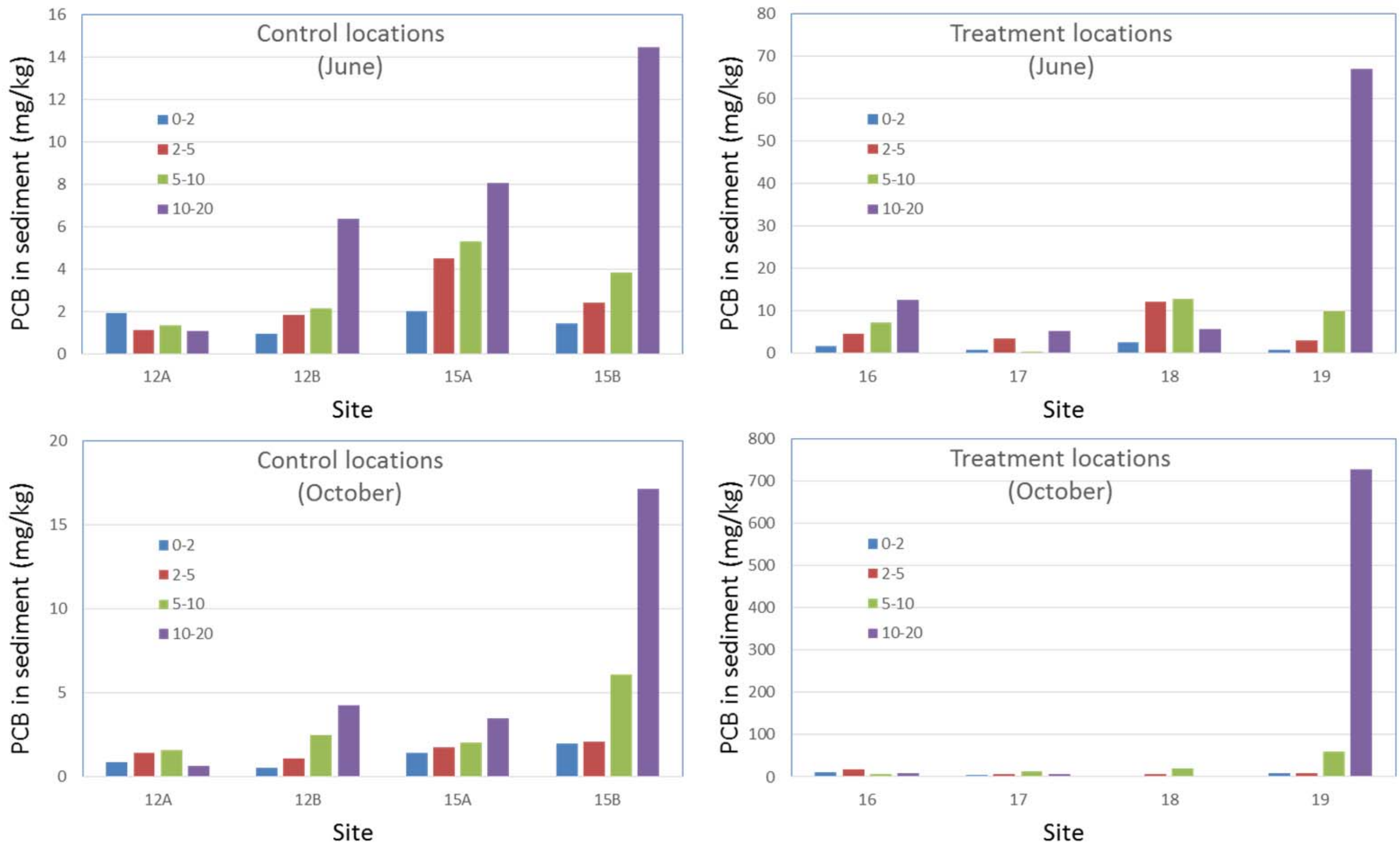


Figure 39. PCB concentrations in core sections taken from intact cores used for porewater gradient measurements in the laboratory.

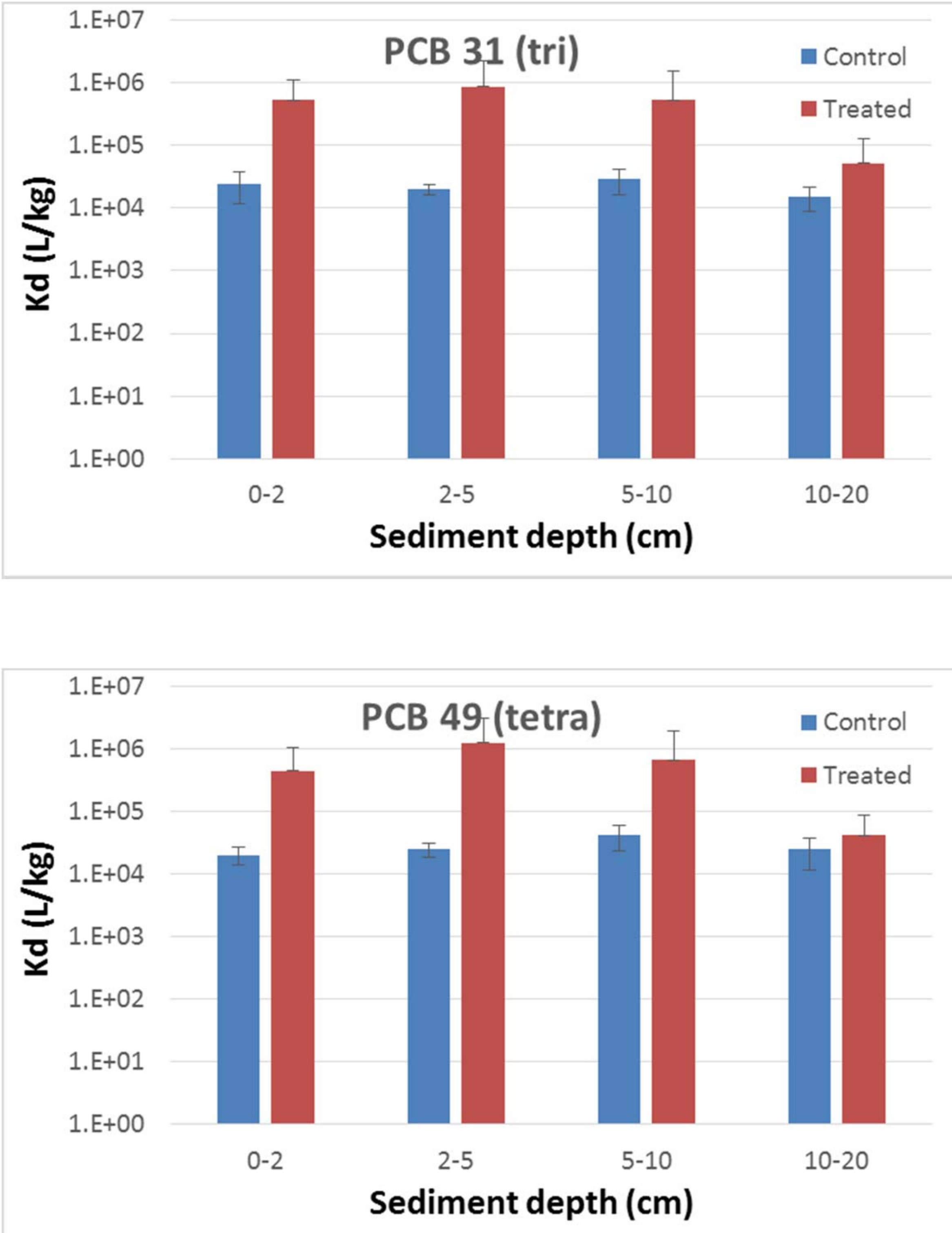


Figure 40. *In situ* partition constants of two dominant PCB congeners in intact cores as a function of depth. The results indicate higher partitioning in surface sediments in treated plots.

6.4.1 Lower Canal Creek

There was no statistically significant difference in MeHg porewater concentrations between the treatment and control plot for the June 2011 post-application monitoring event based on a t-test ($p < 0.05$). There was a slight and statistically significant increase in the K_d between the treatment and control plot (Figure 41). While the difference is statistically significant ($p < 0.1$), the variability was evident in the figure.

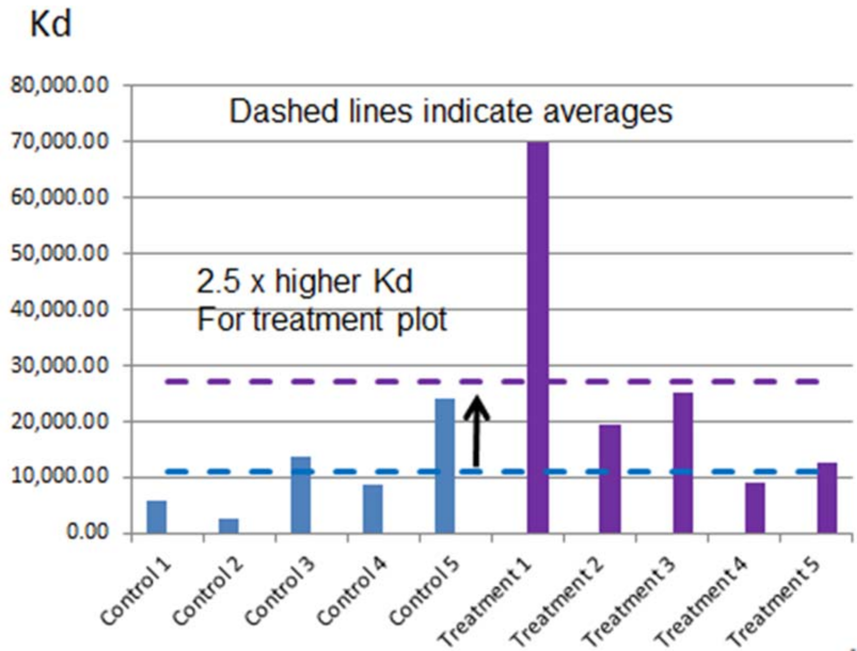


Figure 41. Calculated K_d values (sediment:porewater) for MeHg in LCC sediments for June 2011, six months after application of SediMite®.

Although the data indicate that the presence of AC may have increased the MeHg K_d value of the treatment plot relative to the control for the June 2011 post-application monitoring, there was no significant difference based on a t-test of means between the MeHg K_d values when pretreatment (measured in September 2009) was compared to the post-treatment conditions in June 2011 (Appendix C). (Note: The post-application mean K_d was higher, but the difference was not statistically significant.) These observations, together with the data on porewater concentrations, suggest that the effect of low levels of added AC (~1 %) on porewater concentrations and on partitioning for MeHg were small. While the laboratory treatability studies indicated that AC at levels comparable to TOC levels (i.e., ~7%) could reduce MeHg in porewater by 90%, these treatment levels for AC were not achieved in the field and treatment for MeHg in porewater was consequently much lower.

6.4.2 Berry's Creek

At Berry's Creek, the efficacy of SediMite® on reducing porewater concentrations of PCBs in the *Phragmites* wetland was evaluated *in situ* using passive samplers (Sanders et al. 2015). The results of comparing the treated and untreated (control) plot showed that after 21 months, porewater concentrations of PCBs in the SediMite®-treated plot (averages for depth intervals ranged between 0.5 to 2.7 ng/l) were substantially lower than the untreated plot (averages for depth intervals ranged between 9.6–10.9 ng/l through the upper 10 cm.

6.5 Evaluation of Biological Effects

The effects associated with SediMite® applications on benthic invertebrate communities were evaluated, and the growth of SAV in LCC was examined qualitatively. The results are presented below.

6.5.1 Effects on the Benthic Invertebrate Community of LCC

The results of benthic invertebrate studies for LCC are presented in Appendix E. The data set includes pretreatment samples collected in September 2009 and post-treatment samples collected in October 2011 for both the control and treatment plots. Ten samples were collected from each plot for each date. As noted earlier, the levels of AC in the post-treatment plot were low, with an average value of a little over 1% in June 2011 and <1% in October 2011. Thus, the results reflect conditions under low dose field exposures to AC over a 10-month period. The results indicated that these low-dose exposures to AC did not result in adverse effects on the benthic community in the treatment plot as judged by species richness (Figure 42), the general composition of the benthos, and abundance (Figure 43). The average numbers of species in LCC sediments were significantly higher for the control and treatment plots in 2011 as compared to the pretreatment conditions. Testing of statistical significance was based on a test of means using a t-test ($p < 0.05$). There also was no significant difference in species richness between the control and treatment plots at the end of the 10-month post-application period. As indicated in Appendix E, the benthic community was represented largely by tubificid oligochaetes, chironomid insect larvae, and crustaceans. There were some differences in species composition of the benthos for the September 2009 and October 2011 sampling dates. A review of these differences suggests that the fauna in 2009 was more representative of brackish conditions than was the fauna of 2011. The Chesapeake Bay area where Canal Creek is located can be subject to changes in salinity; salinity was higher in the 2009 sampling period as compared to 2011. With respect to the abundance of the fauna, there were no significant differences among any of the sets of samples.

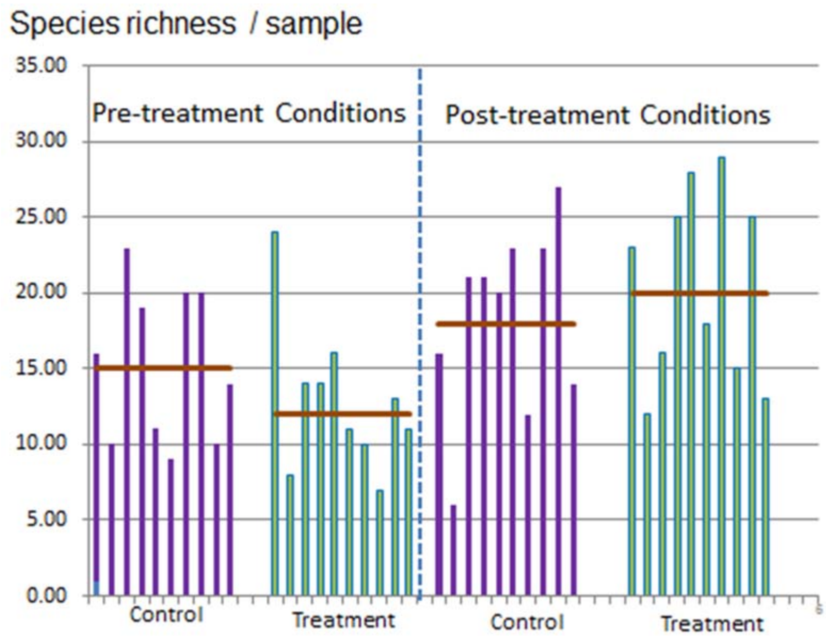


Figure 41. Species richness for benthic invertebrate communities in control and treatment plots of LCC prior to treatment (September 2009) and 10 months post-treatment (October 2011). Averages are indicated by horizontal bars.

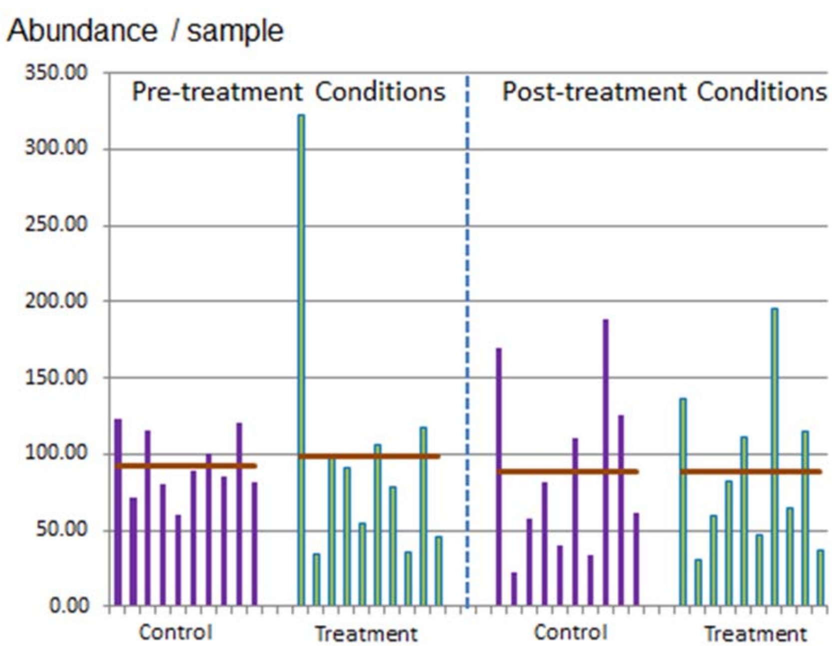


Figure 42. Abundance of benthic invertebrates in control and treatment plots of LCC prior to treatment (September 2009) and 10 months post-treatment (October 2011). Averages are indicated by horizontal bars.

6.5.2 Effects on the Benthic Invertebrate Community of Bailey Creek

The benthic invertebrate data for Bailey Creek is provided in Appendix E. Sampling was conducted prior to treatment (August 2009), at 2 months following treatment (October, 2009), and at 15 months following treatment (November, 2010). A benthic grab sample was collected from each of four control and four treatment plots on each of these dates. The average AC levels in the treatment plots was ~4.5% in the upper few centimeters after 2 months and ~2.8% after 15 months.

Species richness and abundance values are shown in Figures 43 and 44, respectively. Control and treatment plots were not significantly different prior to treatment or two months after treatment. Testing of statistical significance was based on a test of means using a t-test ($p < 0.05$). However, there was a difference ($p < 0.1$) at 15 months, with a lower mean value in the treatment plot (9.75) as compared to the control (12.5). However, for the treatment plot, there was neither a significant difference between the pre- and post-treatment conditions after 15 months nor between the control plots for these sampling events. The benthic community composition was typical of brackish waters with a mix of polychaetes, tubificid oligochaetes, bivalves, and chironomid insect larvae. The fauna at 15 months appeared to include more marine species than freshwater species.

The abundance of benthic invertebrates was not significantly different between the control and treatment plots prior to treatment or for either of the post-application monitoring events. There was no significant difference between the control plots prior to treatment and at 15 months after application; there was also no difference for the treatment plots. Overall, with the possibility that there might be slightly lower species richness in the treatment plots at 15 months, the studies indicate that the presence of AC in the range of 2.8–4.5% in the upper few centimeters does not adversely affect the benthic community.

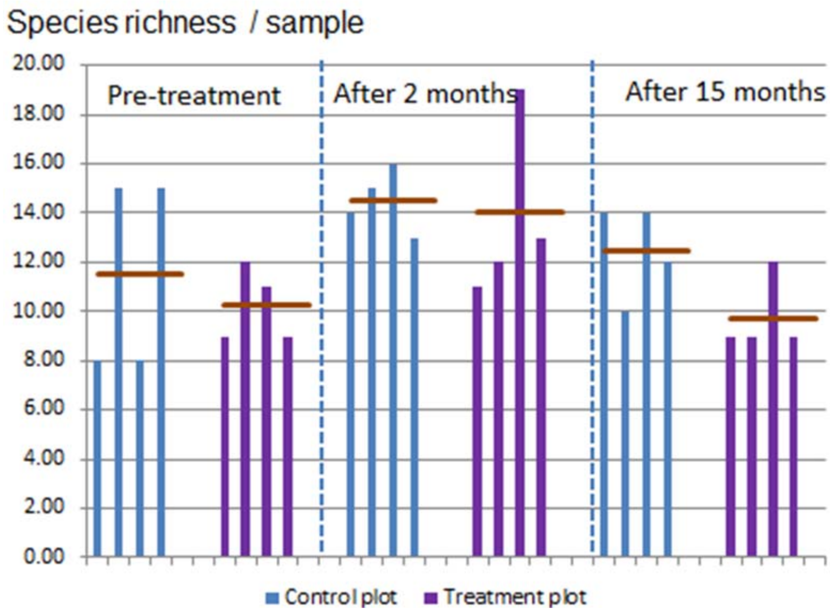


Figure 43. Species richness for benthic invertebrate communities in control and treatment plots of Bailey Creek prior to treatment (August 2009) and at 2 months (October 2009) and 15 months (November 2010) post-treatment. Horizontal bars indicate averages.

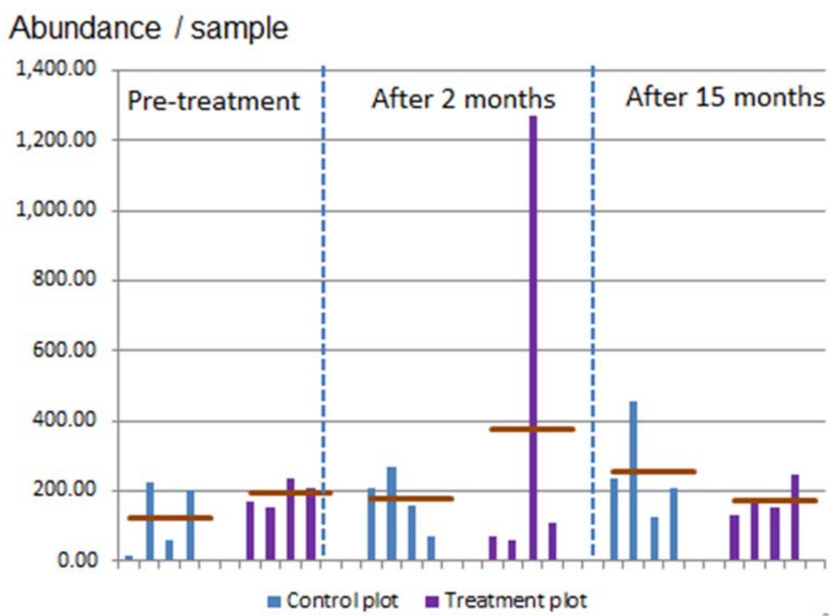


Figure 44. Abundance of benthic invertebrate communities in control and treatment plots of Bailey Creek prior to treatment (August 2009) and at 2 months (October 2009) and 15 months (November 2010) post-treatment. Averages are indicated by horizontal bars.

6.5.3 Benthic Colonization Studies

The benthic colonization studies involved amending native but azoic sediment with four dose levels of AC from SediMite® and then placing these sediments in trays in the Wye River, a tributary of the Chesapeake Bay. The Wye River was chosen as a source of sediments and as a location for this study, because the sediments are relatively clean of contaminants, and there is a wide range of benthic invertebrates. Therefore, the study design permitted an examination of colonization for a broader range of estuarine invertebrates than is found in Canal Creek. The AC doses by weight were 2.5% (T1), 5% (T2), 10% (T3), and 20% (T4). However, over the course of the experiment the amounts of AC were reduced by resuspension of sediment within the trays and by introduction of sediment with low levels of black carbon. Thus, after the 17-month deployment (March 2010–August 2011), the AC levels were present but low. A few of the species that colonized the trays are long lived, and the collection of larger individuals of these species reflects colonization that occurred during 2010, while other species would have colonized throughout 2010 and 2011. The experiment may be used to indicate whether sediments amended by SediMite® can be colonized by a broad range of organisms comparable to what occurs for unamended sediments but may not be used to determine a threshold concentration of AC above which colonization is measurable as adversely effected.

The study examined colonization of macrobenthic invertebrates and meiobenthic invertebrates. These groups are distinguished by size. Macrobenthic invertebrates in estuaries are typically composed of polychaete worms, amphipod crustaceans, and mollusks; meiobenthic invertebrates typically include nematode worms, harpacticoid copepods, and juveniles of macroinvertebrates. All data are provided in Appendix E.

The species richness and abundance of benthic macroinvertebrates that colonized the trays are shown in Figures 45 and 46. Species richness and abundance of macroinvertebrates were not significantly different between control and treatments amended with SediMite®. Testing of statistical significance was based on a test of means using a t-test ($p < 0.05$).

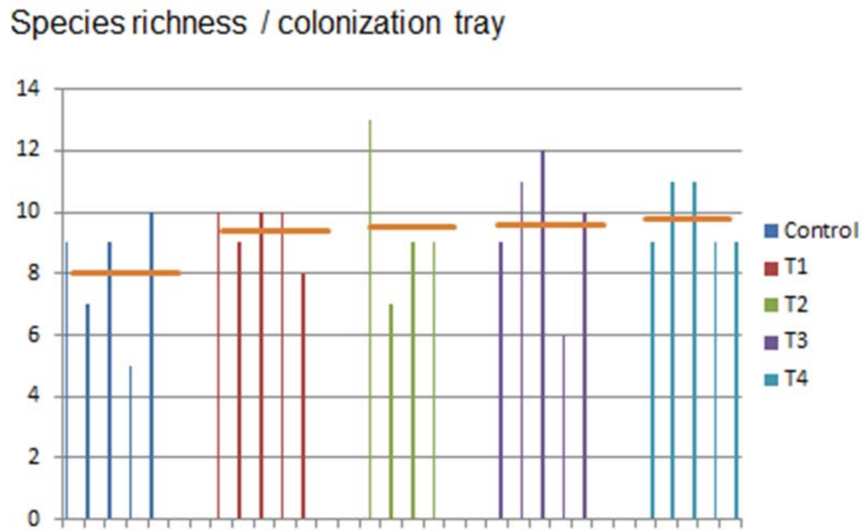


Figure 45. Species richness for benthic macroinvertebrate communities that colonized control sediment and sediment amended with SediMite® at four dose levels (T1 through T4). AC decreased from levels as high as 20% in T4 at the beginning of the 17-month experiment to low levels by the end of the experiment. Thus, the exact exposure levels for T1 through T4 are not known. Averages are indicated by horizontal bars.

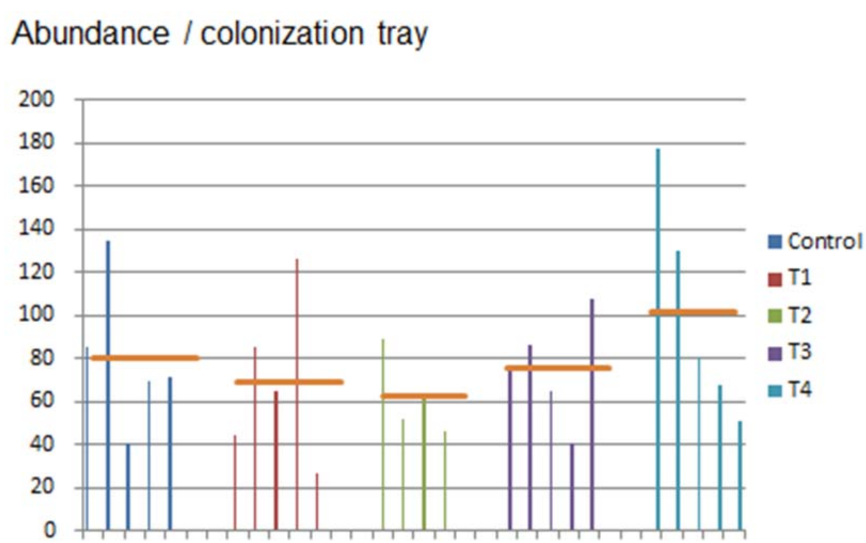


Figure 46. Abundance of the benthic macroinvertebrate communities that colonized control sediment and sediment amended with SediMite® at four dose levels (T1 through T4). AC decreased from levels as high as 20% in T4 at the beginning of the 17-month experiment to low levels by the end of the experiment. Thus, the exact exposure levels for T1 through T4 are not known other than that the AC was present to varying degrees. Averages are indicated by horizontal bars.

It is not possible to determine when most macroinvertebrates colonized the trays. Many species pass through a lifecycle that is shorter than the 17-month duration of the colonization study. However, in the case of the clams, some insight may be gained from the sizes of the animals. Two of the more noticeable clams in the colonization trays are *Macoma balthica* and *Tagelus plebeius* (Figure 47). The sizes of these individuals indicate that clams of this size would have colonized the trays in 2010 rather than 2011. The individual of *M. balthica* is ~15–20 mm and estimated to have settled in a colonization tray in 2010, within a few months of the placement of the trays into the Wye River. This estimate of settlement time was based on growth rate information provided in Gilbert (1973). Christopher Long, who has studied *Macoma* in the Chesapeake Bay, also agreed that the animals settled in 2010 (personal communication to C. Menzie in August 2013). The individual of *T. plebeius* shown in Figure 31 is 55 mm in length. If the size with age data from Grussendorf (1979) is used as a gauge, an animal of this size collected in August 2011 would have settled in the spring or early summer of 2010. Rochelle Seitz of VIMS agreed with this conclusion. Therefore for these clams, settlement occurred within a few months of when the colonization trays were placed in the Wye River (March 2010). Three individual *T. plebeius* were recovered from the colonization trays that had initial AC concentrations of up to 5%. *M. balthica* was the most numerous clam species found in the trays. For this species, the abundance of clams was significantly greater, based on a t-test ($p < 0.05$), in trays with initial AC concentrations of 10 to 20% as compared to trays with ~0 and 2.5%. To the extent that the abundance of these clams was influenced positively by the addition of AC, this may be a due to a physical modification of the sediment. The AC may have resulted in increased silt-size particles, which may have accommodated settlement and easier burrowing.

Figure 47. Two clam species from the colonization trays. *Macoma balthica* is on the left and *Tagelus plebeius* is on the right.

The colonization trays were also examined for the presence of meiofauna. This work was performed by Dr. Jeffrey G. Baguley of the Department of Biology, University of Nevada, Reno, and Dr. Baguley's report is provided in Appendix E. The analysis included detailed characterization of the abundance and species composition of the fauna based on an analysis of core samples (2.9-cm inner diameter) taken from each of the colonization trays (one core per tray). No significant differences were found among the treatments for species composition, taxa richness, or abundance. Testing of statistical significance was based on a test of means using a t-test ($p < 0.05$). The work indicated that at the end of the 17-month exposure period, the colonizing meiofaunal communities were the same across the treatments. The meiofaunal community tends to have a high turnover rate, and there may have been several generations of organisms over the 17-month exposure period. Because AC decreased in the trays over the 17-month period and because turnover of the community is high, it is not possible to establish the exact exposure levels of AC experienced by the meiofaunal community that was present when the trays were retrieved.

7.0 PERFORMANCE ASSESSMENT

The results presented above support the following conclusions related to the performance of SediMite® as a delivery mechanism for AC and the performance of the delivered AC as a means of reducing exposures of animals to contaminants present in wetland soils and sediments:

1. Trial and field applications showed that SediMite® can be effectively delivered to wetland soils and aqueous sediments using either blower systems such as Vortex or spreader systems such as TurfTiger. The appropriateness of an application method would depend on the nature of the area. For smaller areas and areas that are difficult to access, smaller delivery systems make sense, while for large areas where access can be achieved via water or overland vehicles, larger spreader systems can be used. The application to UCC involved direct spreading on an exposed soil surface; the applications to LCC and Bailey Creek involved applications to water environments that were < 3 m in depth.

2. The fate of the delivered AC varied among systems. For the UCC wetland soils, the AC was retained but mixing into the soils was slower than had been observed for aqueous sediments. As a result, AC was concentrated in surficial soils of the upper 5 cm. This created a surface "treatment zone" or layer for these wetlands. The creation of a treatment layer has since been observed at Berry's Creek marsh in New Jersey. These observations indicate that AC application to a wetland could provide a layer that may serve as an exposure barrier in two ways: 1) a reduction in the bioavailability of contaminants present within the treatment zone and thus a reduction in exposures to surface dwelling animals and animals that forage upon them and 2) sorption of contaminants that may migrate via porewater from deeper layers.

3. For aqueous sediments in LCC and Bailey Creek, AC retention varied. Retention within LCC diminished more quickly than in Bailey Creek, possibly due to several factors including flushing associated with storms, deeper than anticipated mixing, and deposition associated with solids carried into Canal Creek via runoff. The low retention of AC in LCC indicates the need for more complete information on sediment stability and dynamics as part of designing applications for SediMite®.

4. AC retention for Bailey Creek was high over the first 2 months following application but had diminished to about 50% after 15 months. It is believed this diminishment over time for the plots in the pilot study was due to edge effects that involved lateral mixing with sediments that had not been treated by AC. These effects would decrease if the size of the treated area were increased. Because the scales of lateral and vertical mixing are important elements of design, they should be characterized as part of planning full-scale applications.

5. Exposures of invertebrates to PCBs in laboratory test systems were reduced for the SediMite®-treated wetland soils at UCC and for the SediMite®-treated sediments of Bailey Creek. These reductions met stated performance objectives with respect to the relative change in bioavailability and bioaccumulation based on comparisons of treated and untreated field wetland soils and/or sediments. Reductions in bioavailability persisted at UCC over the 10-month observation period. Reduction in bioavailability for Bailey

Creek was high at 2 months after treatment but was lower at 15 months; this is likely a reflection of edge mixing effects with untreated sediment as AC also diminished over the 15-month period.

6. The effect of treatment on porewater for mercury in LCC was considered to be low, which was likely due to the low levels of retained AC as opposed to the inability of applied AC to treat MeHg. Despite the low retention of AC in LCC, exposure to MeHg in treated sediment was reduced to levels that met performance objectives related to bioaccumulation into benthic invertebrates as evaluated using laboratory tests on field-collected intact cores. Laboratory studies with LCC sediments showed that if levels of AC are equivalent to ambient TOC, then MeHg in porewater can be effectively reduced.

7. Surficial applications of AC via SediMite® appear to have negligible adverse effects upon native benthic invertebrate communities at target AC dosages by weight in sediments (on the order of several percent). The 2-month post-application data from Bailey Creek support the conclusion that the communities of benthic invertebrates present when SediMite® was applied continue to be sustained. The 15-month Bailey Creek data, the 10-month LCC data, and the colonization studies are consistent with the conclusion that benthic invertebrates can continue to colonize areas where treatment has occurred.

8.0 COST ASSESSMENT

This section provides information that could be used to develop a cost estimate for the use of SediMite® for *in situ* remediation.

8.1 Cost Model

Table 6 presents a cost model for deploying SediMite® at a site. It is assumed that the site has been thoroughly characterized in terms of chemical concentration and distribution, as would be expected for sites where remediation alternatives for the site are being considered. Therefore, many of the characterization activities performed in this study, which were designed to determine the efficacy of *in situ* treatment with SediMite®, would not be required.

8.1.1 Treatability and Baseline Characterization

As noted above, the cost model assumes that the site to be treated would be characterized as is typical of a project at the stage where remediation alternatives are being chosen. Therefore, additional sampling at the site would likely be limited to the collection of bulk sediments for use in a treatability study and to characterize the native TOC/BC content. The treatability study would incorporate elements of the ones used for this study, such as comparative analysis of sediment, porewater, and exposed tissue concentrations among sediments amended with varying levels of SediMite®, in order to ascertain the optimal dose of AC to treat the site sediments. The number of samples would be determined by the historical data for the site and would likely be between 5–10 samples per acre. The collection of these samples would require the typical logistics of a sediment sampling event and would take one day to accomplish.

Table 6. Cost Model for SediMite® Application

Cost Element	Data Tracked during the Demonstration	Costs	
Treatability Study and Baseline Characterization	• Personnel and Labor • Materials • Analytical laboratory costs	Field technicians, 80 h Project manager, 15 h Sampling materials Analytical laboratory	$4,000 $1,500 $5,000 $130,000
Cost for SediMite®	Unit: $ per ton for SediMite® Data requirements: • Initial amount of material required based on treatability and baseline characterizations • Area to be treated	• Current cost is $3,730 per ton for SediMite® containing 50% AC by weight (bituminous coal based) • Loading rate is 10 lbs SediMite® per square meter based on typical native TOC/BC content • One ton of SediMite® would treat approximately 0.05 acres • Cost per acre is $74,600	
Application Cost: Mobilization and Demobilization of Equipment for Spreading	• These are presumed to be fixed charges for acquiring equipment, mobilization, and demobilization	• Preparation and mobilization of equipment and supplies including labor is estimated at $23,000, and this is presumed to be constant over a range of 1–10 acres	
Application Cost: Set up and Incremental Cost for Field Work involving a Spreader such as a TurfTiger	• Time it takes to apply SediMite® to an area using a spreader	For 1 acre = $57,000 (includes set up and breakdown and one day for application); this is composed of $47,000 of set-up and staging and travel and a daily operational cost of $10,000 Sites up to 10 acres are presumed to have same fixed costs plus operational costs of $10,000/day over application duration	

8.1.2 Material Cost

The SediMite® manufacturing process involves purchasing and processing several raw materials, the most expensive of which is the treatment amendment. As with any manufactured material, the raw material and manufacturing costs are affected by market conditions. The amount of SediMite® needed to treat sediment with AC will vary depending on the TOC levels of the sediments and the mixing depth. As noted earlier in the report, for wetlands where vertical mixing is slower than for aquatic sediments, it may make sense to apply small amounts of SediMite® over a long period of time. However, a typical value of 10 lbs of SediMite® per square meter is used for the cost comparisons based on several rules-of-thumb:

- The target post-application AC sediment content is 4–7%
- The typical native TOC content is 6.5%
- The biologically active zone of sediment is 0–10 cm.

The actual loading rate would be calculated based on TOC/BC analytical results, and the total cost would then be a function of the true loading rate and the total area to be treated. Shipping, storage, and staging costs would be based on site-specific logistics.

8.1.3 Application Costs

The costs associated with application depend on factors of the individual sites as this dictates the equipment that can be used for application as well as the methods for moving the equipment, SediMite®, and other materials in and around the site. Application is the primary cost driver for using SediMite® for smaller sites but diminishes in relative contribution as the size of the site increases.

8.1.4 Long-term Monitoring

The long-term efficacy of *in situ* sediment remediation has been identified as a critical research need by SERDP-ESTCP (2012) in a recent workshop. As such, long-term monitoring of the efficacy of AC delivered as SediMite® to a site would be recommended to ensure the reductions in exposure, as seen in this study, are maintained. The monitoring events would include measuring AC in sediment profiles, chemical analysis in bulk sediment and porewater, and tissue analysis using bioaccumulation assays. The estimated cost for a single round of monitoring is based on a one-acre site with typical access and logistical considerations and would take approximately two days of collection. The results of the monitoring would be used to determine if the remedy is effective over the long term or if re-application or another remediation alternative is appropriate.

8.2 Cost Drivers

The cost drivers associated with the use of SediMite® for *in situ* remediation at a site are discussed in this section.

The costs for SediMite® itself are based on material costs, production, shipping, and storage as well as site-specific conditions. For the conditions outlined in Table 5, the per acre cost of SediMite® is $74,600. There are several categories for application costs, some of which are fixed and others of which are variable. The greatest variance in application costs for a particular application involves site-specific characteristics affecting application logistics. Examples of site characteristics that will influence the application costs include the following:

- **Site Setting:** Open water, submergent wetland, emergent wetland, or intertidal wetland sites will restrict the equipment that may be used for application
- **Water Depth and Tidal Fluctuation:** In all site settings, the water depth and tidal fluctuation will restrict the equipment that may be used for application as well as the work hours the equipment may be used. Site access will also be restricted.

- **Vegetation:** The type of vegetation at the site will heavily influence the application for a broad spectrum of reasons. A *Phragmites*-dominated marsh will restrict the movement of most heavy and light equipment that may be used for application. Additionally, application in areas of sensitive environmentally-beneficial vegetation would restrict the use of heavy application equipment.
- **Site Infrastructure:** A site that is remote from major roadways for equipment and material delivery will require additional time and logistics for receiving, staging, and transporting equipment and material. A site without access from an established boat launch would require additional logistics if application were to be done by boat or barge.

For example, the estimated application times that drive the costs given in Table 6 assume that both large- and small-scale equipment (i.e., turf spreader and Vortex, respectively) could be used in conjunction with minimal logistical challenges. However, if that acre site were entirely intertidal *Phragmites* marsh, the turf spreader and most other heavy equipment would be impractical, and application time would therefore increase, because smaller equipment might be used. There may be a tradeoff between crew size and equipment cost between large and small projects. The latter could be performed by a smaller crew with smaller equipment and associated costs, but the time may be longer per unit area.

However, none of the factors affecting application costs are specific to the use of SediMite®. These factors would affect the application of any other *in situ* treatment material, sediment cap, or reactive barrier. The ability to use small-scale applicators such as the Vortex allow for application of SediMite® to areas where other technologies would be impractical. For example, SediMite® has been demonstrated, when applied from the Vortex to the crown of a *Phragmites* stand, to fall through the vegetation directly to the sediment surface allowing for application to a *Phragmites*-dominated wetland without necessitating the need of removing the vegetation. This would not be possible with other AC delivery methods, such as below a sand cap or as a slurry.

8.3 Cost Analysis

This section presents estimates of the costs of implementing SediMite® for remediating contaminants *in situ* at hypothetical sites of 1, 5, and 10 acres and compares this cost with the traditional remediation technique of dredging and disposal.

The assumptions behind the cost analysis for the three different sized sites include the following:

- The sites have been thoroughly characterized for chemical concentration and gradient through sediments as would be typical with a site in the phase of selecting remediation alternatives.
- The sites are open, navigable waters.
- The sites are operable units of a larger terrestrial site that includes logistical support such as roadways and paved staging areas close to the water body.
- The sediments of the sites are contaminated with low- to moderate-levels of PCBs, pesticides, and Hg.

The cost of applying SediMite® to the LCC test plot are used for this analysis, as the techniques used for this application are readily scalable to a large, open water site. Costs of the analysis include the labor and equipment for application at LCC.

Mobilization and demobilization for the LCC application was approximately $23,000. For LCC, the onsite mobilization and demobilization was completed in three days, and included several UXO-avoidance activities that would not be applicable to all sites. It is anticipated that mobilization and demobilization for each of the 1-, 5-, and 10-acre sites could be accomplished in seven days. A cost of $47,000 is estimated to cover the types of onsite staging of equipment and materials that may be required for DoD sites as well as travel, which is arrived at by backing out actual time for application.

The delivery time is estimated using the experience gained during the application of SediMite® to LCC via a spreader mounted on a barge. The application of SediMite® to LCC took approximately four hours, including the launching and coupling of the barge, setting the spreader and generator onto the barge, launching the push boats, loading the SediMite®, moving to the application area, applying the SediMite®, and returning to the staging area. Many of these tasks would have been completed during one of the mobilization days, but the application took place in extremely cold temperatures, and the equipment could not be left in the creek or exposed overnight. The actual application of SediMite®, where approximately 4,500 square feet of the creek was treated, took approximately 30 minutes. Using this application rate, the estimated time to apply SediMite® to a 1-, 5-, and 10-acre site would be 5, 25, and 50 hours, respectively. However, this would only represent the time of active application and would not include loading or onsite travel time. The estimated number of days for application of SediMite® to a 1-, 5-, and 10-acre site would be 1, 4, and 8 days, respectively.

Realized application times can also be compared to the time it takes to lay down thin-layer sand caps. These vary in relative thickness and may be used as a basis for comparison. A layer of SediMite® is approximately ¼ to ½ inch in thickness which is considerably thinner than a sand cap of 2–6 inches. If the materials are being delivered by the same device, it would take much less time to complete the application for SediMite® as compared to the sand cap. Using the information from LCC, an estimated per diem daily application cost would be $10,000. This daily cost is added to the mobilization costs and to the travel and site staging costs.

Using these figures, the estimated costs for 1-, 5-, and 10-acre applications of SediMite® are provided in Table 7.

Table 7. Cost of *In Situ* Remediation with SediMite® for Sites 1, 5, and 10 Acres in Size.

Cost elements	Unit Costs			Site Size (acres)		
	Fixed per project	Cost per acre	Cost per application day	1	5	10
SediMite material cost		$74,600		$74,600	$373,000	$746,000
Mobilization/Demobilization	$23,000			$23,000	$23,000	$23,000
Application travel and staging	$47,000			$47,000	$47,000	$47,000
Per diem application			$10,000	$10,000	$40,000	$80,000
			Project cost =	$154,600	$483,000	$896,000
			Cost/acre =	$154,600	$96,600	$89,600

Note: costs do not include a feasibility study within which there would have been a $15,000 treatability study
costs also do not include monitoring

Project costs (excluding feasibility study and monitoring) would be as follows:

- Approximately $154,600 for a 1-acre site
- Approximately $483,000 for a 5-acre site
- Approximately $896,000 for a 10-acre site.

As the scale of the site increases, the fixed costs become spread over a larger number of acres, and some efficiency in operations would be expected. Thus the per-acre cost decreases as follows:

- $154,600/acre for a 1-acre site
- $96,600/acre for a 5-acre site
- $89,600/acre for a 10-acre site

8.4 Comparison to Dredging/Removal Costs

The rule-of-thumb costs for dredging increase when considered for sites with contaminated sediment that require not only dredging but de-watering and disposal. A review of Superfund contaminated sediment megasites, or sites at which sediment remediation activities cost at least $50 million, provided remediation costs of $145/CY, $260/CY, and $530/CY of contaminated sediment (NRC 2007). These figures included the costs of design, mobilization, marine demolition, and construction/EPA oversight, which would likely be included in any sediment remediation program.

Recent estimates for sediment remediation are also available for the Lower Duwamish Waterway Superfund Site, where remediation alternatives ranging from dredging to enhanced monitored natural recovery (EMNR) are being considered. The recently published proposed plan for the Lower Duwamish Waterway Superfund site (U.S. EPA 2013) details the remediation alternatives being considered for approximately 412 acres of contaminated sediments. Six remediation alternatives were considered, with the preferred alternative being a combination of dredging, capping with possible amendment with activated carbon and ENR, which also includes amendment with activated carbon. Under this scenario, 84 acres would be dredged, resulting in an estimated 790,000 CY of sediment being disposed in an upland landfill. Twenty-four acres would be capped, with possible amendment with activated carbon, and a further 48 acres would receive a thin-layer cap, possibly amended with activated carbon, for ENR. The estimated cost of this alternative is $305,000,000. Detailed cost estimates for this alternative are presented in the project Final Feasibility Study (AECOM 2012): the costs directly associated with dredging operations include direct dredging operations ($26,341,156), sediment handling and disposal ($76,016,104), and sediment capping/dredging residuals/dredge backfill ($21,243,378). The sum of these values, $123,600,638, accounts for a total dredging volume of 790,000 CY (U.S. EPA 2013), resulting in a cost of approximately $156/CY. From this estimate, the calculated per acre cost for the dredging component of this alternative is ($156/CY·790,000 CY)/84 acres or $1,467,142/acre. U.S. EPA (2013) also presented a removal alternative involving 274 acres and 3,900,000 CY of dredged sediment at a cost of $810,000,000. A dredging cost of approximately $3,000,000/acre at a cost of approximately $208/CY is derived using those values. This range of values calculated for the Lower Duwamish ($156–$208/CY) falls within the range ($145–$530/CY) reported by the NRC (2007) but are nearer the lower range.

Because dredging involves a volume to be removed as compared to alternatives that treat surface sediments, costs for environmental dredging projects are very sensitive to the depth of the dredging and need for backfill. Therefore, another way to compare costs is to consider alternative dredge depths. To dredge sediment to a depth of 1 yard would deliver approximately 4,840 CY of sediment; a depth of 0.5 yard would yield approximately 2,420 CY. Using the value for remedial dredging cost of $156/CY for the Lower Duwamish yields costs of $755,040/acre and $377,520 for environmental dredging projects of involving sediment depths of 1 and 0.5 yards, respectively.

8.5 Comparison to Thin-Layer Capping/EMNR Costs with and without AC Addition

The equipment and methods used to apply SediMite® to LCC were first designed for placement of thin-layer sand caps. Therefore, to compare the costs of SediMite® to thin-layer capping, the material cost, volume required, and time required to apply the material are the primary variants. Presumably, the feasibility studies and monitoring requirements would be similar. The following unit cost information was available from Merritt et al. (2009), ENVIRON et al. (2008), and Johnston et al. (undated):

1. The costs for sand capping material ranged between $4 and $18/CY. And thin-layer sand caps are typically around 6 inches (15 cm) in thickness.
2. The costs for sand amended with 4% AC was $161.48/CY; the method for accomplishing mixing would add cost on the application side.
3. The cost for AquaGate+PAC™ is ~$700/ton for the product and shipment. An application of 2–3 inches would require 280 tons; an application of 4 inches would likely require at least 50% more or 420 tons. Thus material costs for AquaGate+PAC™ are $147,000 per acre for a 2- to 3-inch layer and $294,000 per acre for a 4-inch layer.
4. Because of the larger volumes to be delivered per acre, the duration for delivery will be longer for sand caps, and AquaGate+PAC™ and staging will require more equipment and space.

For purposes of comparison, it is assumed that each type of application has the same mobilization and demobilization and other fixed costs as does the estimate for SediMite® (Table 6). However, for similar pieces of equipment, the duration needed to treat an acre will vary. For SediMite®, the treatment of the upper four inches of sediment with ~5% AC would involve placing about 0.25 inch of SediMite® as compared to a 15-inch thickness for a thin-layer sand cap and a four-inch thickness for a sand cap augmented with AC or an AquaGate+PAC™ cap. Thus, thicknesses may vary by 8 times higher than SediMite® for AC-based thin-layer caps to 12 times higher than SediMite® for a thin-layer sand cap without AC. The fastest application duration identified from the literature was a thin-layer sand cap over 27 acres that took approximately 30 days (ENVIRON et al. 2008). Table 6 details that it would take approximately 8 days to treat 10 acres or approximately 21 days to treat 27 acres. Thus, a factor of 1.42 is used to adjust delivery times. This factor seems an appropriate adjustment for the variable thicknesses, as it is less than a factor of two, while actual differences in thicknesses vary by 8–12. A value of $11/CY for sand is assumed, as this is the mid-point of the reported range. Table 8 provides the comparison of costs using these values.

Table 8. Comparative Costs among SediMite® and Thin-Layer Capping Alternatives.

Cost elements	Unit Costs: Fixed per project	Unit Costs: Cost per acre	Unit Costs: Cost per application day	Site Size (acres): 1	Site Size (acres): 5	Site Size (acres): 10
SediMite material cost		$74,600		$74,600	$373,000	$746,000
Sand cap without AC and assuming a 6" thickness		$8,873		$8,873	$44,365	$88,730
Sand cap with AC and assuming a 4" thickness		$86,840		$86,840	$434,200	$868,400
Aquagate + PAC and assuming a 4" thickness		$294,000		$294,000	$1,470,000	$2,940,000
Mobilization/Demobilization	$23,000			$23,000	$23,000	$23,000
Application travel and staging	$47,000			$47,000	$47,000	$47,000
Per diem application for SediMite			$10,000	$10,000	$40,000	$80,000
Per diem application for caps			$14,200	$14,200	$71,000	$142,000
			SediMite Project cost =	$154,600	$483,000	$896,000
			Sand cap without AC project cost	$93,073	$185,365	$300,730
			Sand cap with AC project cost	$171,040	$575,200	$1,080,400
			Aquagate + PAC project cost	$378,200	$1,611,000	$3,152,000
			SediMite cost/acre	$154,600	$96,600	$89,600
			Sand cap without AC cost/acre	$93,073	$37,073	$30,073
			Sand cap with AC cost/acre	$171,040	$115,040	$108,040
			Aquagate + PAC cost/acre	$378,200	$322,200	$315,200

Note: costs do not include a feasibility study within which there would have been a $15,000 treatability study
costs also do not include monitoring

Among the comparisons in Table 8, a thin-layer sand cap without AC is the least expensive alternative. Among the alternatives that include AC amendment, SediMite® is the least expensive. Figure 48 compares costs per acre of treatment for a 10-acre site. Approaches are arrayed from least expensive to most expensive. The *in situ* approach involving SediMite® and the thin-layer capping methods are obviously less expensive than dredging alternatives.

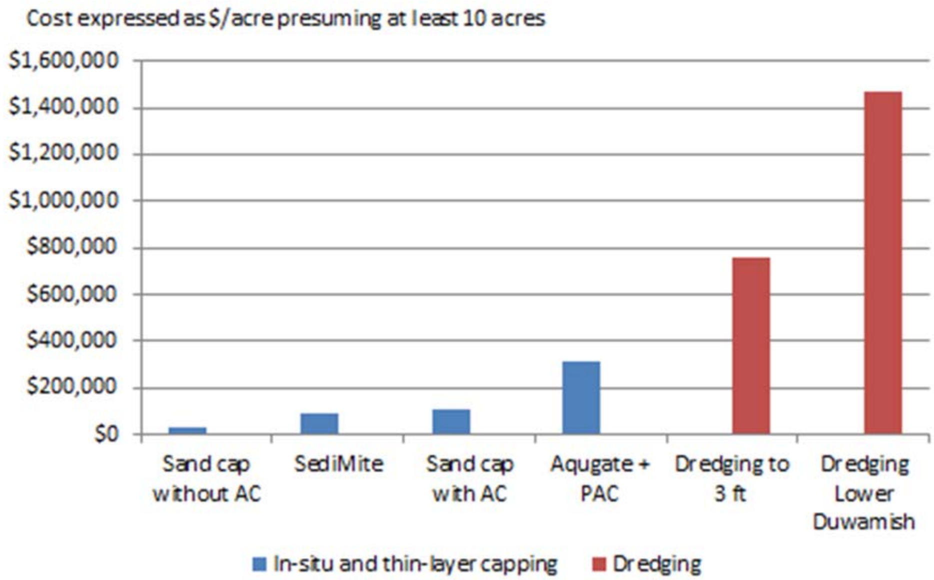


Figure 48. **Costs/acre for various remedial approaches for a 10-acre site. Approaches are arrayed from least to most costly. Costs do not include feasibility work or monitoring. The graphic also does not indicate value with respect to effectiveness of remedies.**

9.0 IMPLEMENTATION ISSUES

This section describes implementation issues that arose during the performance period of this research.

The project was severely delayed due to an unforeseen need for permitting outside of the APG's ability to authorize or oversee work as part of the ongoing CERCLA program. The permitting requirement was initiated by a review of the demonstration work plan by U.S. EPA stakeholders in the CCSA, who determined that the project should be reviewed by Maryland and federal agencies under whose authority the study may lie. Representatives of these agencies regularly meet to allow applicants the opportunity to present their projects and determine the agencies that would require a permit application. Exponent attended one of these meetings and presented the study's scope of work. It was determined that two agencies would require permits: the wetlands divisions within the Maryland Board of Public Works (BPW) as well as the U.S. Army Corps of Engineers (USACE). The BPW permit was required to ensure that the project complied with the provisions of Title 16, Environmental Article, Annotated Code of Maryland (1996 Replacement Volume and Supplement) titled *Wetland and Riparian Rights*. The primary concern expressed by BPW was whether the project would constitute filling an area of wetland. The USACE permit was required to ensure the project complied with Section 404 of the Clean Water Act. The specific concern expressed by the USACE was whether the project would constitute a discharge of fill material into a navigable waterway. The process of obtaining these permits took over a year.

It is believed that future applications will not have to undergo as extensive an examination to obtain or be exempt from permits, as this and other similar projects have familiarized many regulatory agencies with SediMite®. However, it is recommended to submit a work plan for review to the agencies to ensure project timelines are met.

Another implementation issue that arose at the LCC study area was the presence of an American bald eagle nest. The presence of the nest restricted the activities that could take place in the LCC study area between the time when eggs are typically laid (mid-February) until the time when any successful chicks had fledged (typically mid-June). APG allowed sampling to occur in the LCC study area during this time period but restricted the use powered equipment, such as the turf spreader and Vortex, during the nesting period. APG was specifically concerned that the use of powered equipment in the vicinity of the nest, which is in a restricted waterway and therefore not frequented by other disturbances, would cause stress upon the nesting eagles. This restriction led to the application of SediMite® in December 2010 in conditions that were not ideal.

This issue is not expected to affect future applications as the instances requiring restrictions were so specific to the demonstration area.

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ATTACHMENTS

Attachment 1: Points of Contact

POINT OF CONTACT Name	ORGANIZATION Name Address	Phone Fax E-mail	Role in Project
Charles Menzie	Exponent 1800 Diagonal Road Suite 500 Alexandria, VA 22314	571-214-3648 Fax: 571-227-7299 camenzie@exponent.com	Principal Investigator
Upal Ghosh	University of Maryland Baltimore County 1000 Hilltop Circle Baltimore, MD 21250	Phone: 410-455-8665; Fax: 410-455-6500 ughosh@umbc.edu	Co-Investigator
Cynthia Gilmour	Smithsonian Environmental Research Center 647 Contees Wharf Road Edgewater, MD 21037	443-482-2498 Fax:443-482-2380 gilmourc@si.edu	Co-Investigator