Pilot-scale Research of Novel Amendment Delivery for in-situ Sediment Remediation

Final Progress Report
Grant # 5R01ES16182
Submitted to NIEHS Superfund Research Program
Project end date: August 31, 2012

Upal Ghosh
Department of Chemical, Biochemical, and Environmental Engineering
University of Maryland Baltimore County, Baltimore, MD 21042

Charles A. Menzie
Exponent

1.0. Executive Summary

Sediment-bound persistent organic contaminants such as PCBs and DDT pose a public health risk through contamination of the food chain and through direct exposure. This field research evaluated the effectiveness of a novel approach to alter the binding capacity of sediments to reduce ecosystem and human exposure to such contaminants. While recent work has demonstrated the feasibility of reducing contaminant bioavailability in-situ through the amendment of strong sorbents like activated carbon, a major challenge in full-scale implementation of this approach is the difficulty in delivering low density amendment materials into sediments. A novel approach for delivery of amendments was recently developed through a USEPA funded project that formulated the amendments into engineered pellets named SediMite that could be easily deployed through a water column into sediments. The pellets are designed to withstand dispersal through the water column with minimal release of active ingredients followed by slow disintegration and mixing into the bioactive zone of sediments through natural sediment mixing processes such as bioturbation. This pilot-scale demonstration study evaluated the effectiveness of this engineering approach to achieve the desired delivery of amendments, effectiveness of mixing by bioturbation, and effectiveness of the amendments delivered in this form in reducing contaminant bioavailability.

The pilot-scale demonstration study was conducted at a USEPA Superfund site (Bailey Creek, Ft. Eustis, VA) in an estuarine wetland environment impacted with PCBs. A site-specific treatability study was first performed to demonstrate the effectiveness of activated carbon amendments to reduce PCB bioavailability to benthic invertebrates. This was followed by scale up of production of the pelletized carbon at an industrial facility to produce the required quantity of the product for a pilot-scale study. Pilot-scale control and treatment sites were 15meters by 15meters, half within the channel segment and half in the bordering marsh. Activated carbon in the form of SediMite was applied using a boat-mounted dispersion device similar to a commercial fertilizer/herbicide spreader. The treatment was deployed in the summer of 2009. Samples were collected and examined before treatment, two months, and 15 months after treatment. Black carbon measurement in sediment cores demonstrated that the applied activated carbon remained in sediment after application and was found in the top 5 cm of sediment. Bioaccumulation studies using the benthic organism *Leptocheirus plumulosus* as well as aqueous concentration measurement using a passive sampler showed reductions in PCB bioavailability at the treatment sites after deployment. Benthic community sampling after application demonstrated no significant impact of the application on native biota.

The development of this technology for contaminated sediment management offers the potential to protect human health and ecosystem while significantly reducing costs and negative impacts on ecosystems. The SediMite technology has been commercialized through a startup company and is currently being implemented at several contaminated sites impacted with PCBs, PAHs, and mercury.

Key performers:
UMBC: Upal Ghosh, Seokjoon Kwon, Piuly Paul, Chirayu Joshi, and Phil Gidley
Exponent: Charles A. Menzie, Ben Amos

Table of Contents

2.0. Introduction

Aquatic sediments form the ultimate repositories of past and ongoing discharges of hydrophobic organic compounds (HOCs) such as polychlorinated biphenyls (PCBs). These sediment-bound pollutants serve as long-term exposure sources to aquatic ecosystems. Traditional approaches for remediation of contaminated sediments include dredging, capping, and monitored natural recovery. While these different approaches have proven useful, it is also often the case that these actions fail to achieve necessary risk reductions. For example, dredging may lead to short-term increase in risk due to sediment disturbance and resuspension while capping may not be practicable in sensitive ecosystems and where there is concern with changing sediment bathymetry.

A novel strategy for addressing risks posed by hydrophobic organic contaminants like PCBs involves applying a sorptive amendment that alters the physicochemical properties of the sediment or soil to reduce chemical bioavailability (Ghosh et al., 2011). Critical barriers in the adoption of this in-situ remediation approach is the availability of efficient delivery methods for amendments to impacted sediments and understanding of physical and biological processes in field sites that control the effectiveness of the technology. Recent bench-scale research developed a novel, low-impact approach for the delivery of treatment amendments for contaminated sediments. Unlike available delivery systems that rely on injection or mechanical mixing of the sediment, delivery in the form of especially formulated pellets makes use of material engineering aided by natural mixing (bioturbation) processes to work treatment materials into the biologically-active zone. The technology is applicable in areas where the implementation of current in-situ treatment practices are problematic and expensive, such as in deep water, in vegetated areas, in sensitive wetlands, or over very large areas. The engineered materials can be designed to carry a number of remedial amendments to sediment, allowing for in-situ treatment of a variety of contaminants. The main aim of this research was to develop the insitu remediation technology through a pilot-scale demonstration aimed at addressing the critical barriers in the advancement of the technology.

2.1. Organization of this report

This report presents a summary of results from this research that involved the following key steps: 1) selection of a project demonstration site through consultation with site managers and regulators, 2) site-specific treatability studies to evaluate the effectiveness of the proposed technology for site sediments, 3) development of a technology demonstration plan, 4) field implementation of the technology at pilot-scale, and 5) evaluation of the effectiveness of the technology through a set of detailed monitoring over a period of 1.5 years post implementation. This report starts with an introduction, research background and specific aims, followed by a set of chapters that describe the results and interpretation from the key research steps described above. The last section of this report provides a summary of key conclusions and recommendations from this research.

3.0. Research Background

In aquatic environments that are impacted by contaminated sediments, risk management strategies focus on interrupting potential exposure pathways by which contaminants might pose an ecological or human health risk. The cleanup process of sediment sites is complex and creates a unique challenge due to expensive cleanup strategies, large and diverse sediment sites, and presence of ecologically valuable resources or legislatively protected species or habitats (USEPA, 2005). Removal options such as dredging and excavation have certain clear advantages, especially in situations where hot spots exist and there is a desire to reduce sources and risks quickly and permanently. However, the limitations and disadvantages of these methods have also become better understood. Dredging and disposal can be expensive and disruptive to existing ecosystems. Moreover, contaminants can be released into the water and air environments during sediment dredging, transportation, and storage (Valsaraj et al., 1999; USEPA, 1996). In addition, dredging operations can cause temporary high levels of contaminants in the water column and surficial sediments due to resuspension of buried sediments and release of pore water. Capping with clean sediments may not be practicable in sensitive ecosystems and at sites where there is concern with changing the sediment bathymetry. New developments in in-situ remediation approaches are needed that are less energy-intensive, less expensive, less disruptive of the environment, able to reduce human and ecosystem exposure, and defensible through well grounded scientific understanding of contaminant fate processes and bioavailability in field conditions.

In our recent work with PCB-contaminated sediments we have tested the use of activated carbon for in-situ bioavailability control. We have demonstrated that addition of activated carbon to PCB-contaminated sediments greatly reduces PCB bioavailability (Ghosh et al. 2011). Thus, application of activated carbon to the biologically active layer of PCB-contaminated sediment may be an effective in-situ stabilization method to reduce contaminant bioavailability to sediment organisms at the base of the aquatic food web. In-situ bioavailability reduction using carbon amendment may be applicable at sites where bioaccumulation reduction can reduce exposures and consequent risks to acceptable levels. In-situ treatment of sediments can help address the presence of residual contamination and, as proposed here, can be targeted at the surficial sediment layer of interest and implemented in a way that minimizes impact on native benthic and associated fish and wildlife communities. This alternative can be used by itself or in combination with other methods.

Many facilities across the country are challenged with management of sediments contaminated with persistent organic contaminants such as PCBs, PAHs, and DDT. This research addresses the need for cost effective, in-situ remediation technologies for persistent organic contaminants in sediments. In situ management does not involve dredging and habitat destruction. For large and sensitive sites, this technology may be more appropriate and acceptable to local communities than processes that rely on removal and disposal, and ex situ treatment such as incineration. The successful development of this technology for contaminated sediment management offers the potential to significantly reduce expenditures on environmental restoration, as well as gain acceptance by regulators and affected communities.

4.0. Specific Aims

Critical barriers in the adoption of in-situ remediation with sorbent addition are the availability of efficient delivery methods for amendments to impacted sediments and understanding of physical and biological processes at field sites that control the effectiveness of the technology. The main aim of this research is to develop the in-situ remediation technology through a pilot-scale research initiative aimed at addressing the critical barriers in the advancement of the technology. The specific objectives of this research were to:

1) Perform laboratory-scale testing to evaluate the dose of amendment required for the chosen sediment sites where pathways to humans exist (through direct contact and fishing) and where habitat protection is desired. The potential sites were selected through consultation with the U.S. Environmental Protection Agency and the National Oceanic and Atmospheric Administration in Philadelphia (USEPA Region 3).

2) Produce bulk quantities of engineered amendment pellets required for this pilot-scale demonstration at a large scale production facility.

3) Test physical delivery of engineered pellets in pilot treatment areas at a PCB impacted field site.

4) Evaluate the uniform delivery of amendment materials to the target zone immediately after application and after different periods of natural mixing processes such as bioturbation.

5) Evaluate effectiveness of the amendment technology through biological and physicochemical tests. These tests are designed to evaluate the potential reduction in human exposures through measures of bioavailability.

6) Evaluate the human health benefit through exposure modeling supported by field measurements.

5.0. Site selection and characterization

Based on deliberations with regulators and responsible parties from several potential project sites, two locations were evaluated:

1. U.S. Army transportation-training center at Ft. Eustis. This site was added to the National Priorities list by the EPA in 1994 (USEPA 2006). The specific location within this site that this project is focusing on, Bailey Creek, is contaminated with polychlorinated biphenyls (PCBs), lead, and pesticides. In partnership with research collaborator Exponent, and site contractor, Malcolm Pirnie, a site survey and field sampling was conducted in the summer of 2008. Sediments collected from this site was characterized for contaminant concentrations and geochemical characteristics.

2. Frankford inlet in Philadelphia, PA. Historic chemical manufacturing in the vicinity of this site resulted in contamination of the sediments with toxic chemicals including DDT and its derivatives. RCRA Corrective Action activities at this facility are being conducted under the direction of EPA Region 3 with assistance from the State. In partnership with research collaborator Exponent, and local industry at the site, Rohm and Haas, site survey and sediment sampling was conducted in the summer of 2008.

Based on the results from the site sampling and in consultation with site managers, it was decided to perform the pilot-scale demonstration in Bailey Creek at the Ft. Eustis site. The primary drivers for selecting the Ft. Eustis site was that it is a NPL site and the fact that the site was still undergoing deliberations for the selection of a final remedy.

Field sampling was performed at two locations in Bailey's Creek on June 10 that had PCB concentrations in the range of 0.5 – 2 ppm based on historic sampling data (Figure 1). The two sites sampled were B-4 and B-7. Approximately 1 gallon sediment was collected from each location and transported in a cooler to the UMBC laboratory. Additional samples were collected and screened on site for benthic community analysis. Initial PCB analysis of the sediment samples revealed PCB concentrations of 1.4 and 0.4 ug/g in samples B-4 and B-7 respectively (Figure 1). These concentrations are in the range of past measurements performed at this site. As shown in Table 1, total organic carbon in the sediment ranged from 4-6% and black carbon ranged from 0.6 – 0.9%. The PCB homolog distribution shown in Figure 2 indicate an aroclor 1260 type profile with penta, hexa, and heptachlorobiphenyls being the dominant homologs.

To evaluate the feasibility of performing PCB analysis on benthic organisms that can be grown in the sediment, two live polychaetes (Figure 2) found near the top of the B-7 sediment container and were removed for PCB analysis. The two polychaetes were allowed to depurate in 15 ppt artificial seawater for 12 hours before extraction and PCB analysis. The PCB homolog profile (Figure 2) in the polychaete reflects the PCB distribution in sediments and was high enough for quantitative analysis.

Figure 1. Sediment sampling at Bailey's Creek, June 10, 2008.

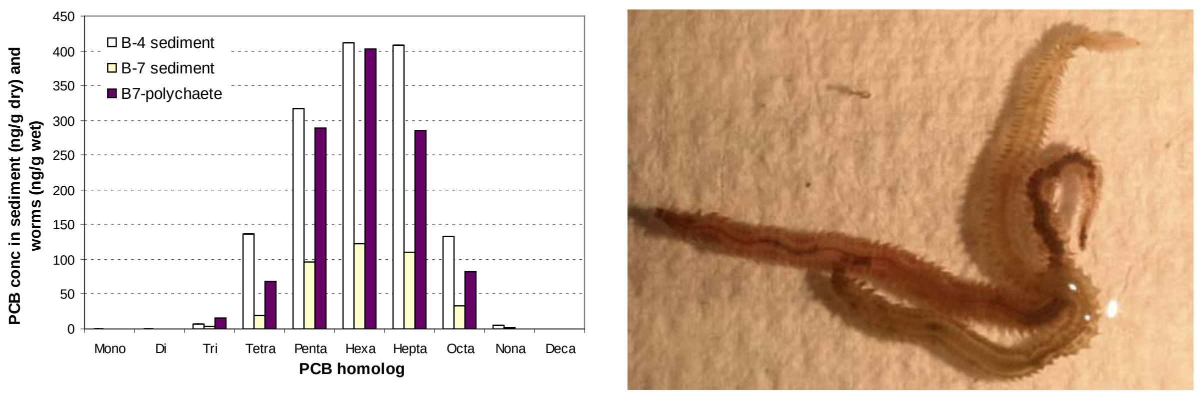

Figure 2. PCB homolog distribution in sediment and polychaete. Penta hexa, and hepta are the dominant PCB homologs in sediment and polychaete. Picture on the right shows two polychaetes picked from B-7 sediment sample and used for PCB measurement.

6.0. Treatability study results

A treatability study was conducted to evaluate the potential of using activated carbon as an amendment for in-situ remediation of PCB contaminated sediments at Bailey Creek in Ft. Eustis, VA. Sediment samples collected from the site in June 2008 were characterized for PCB congener concentrations, total organic carbon (TOC) content and black carbon (BC) content. These measurements were followed by laboratory mesocosm experiments that exposed a marine benthic amphipod (*Leptocheirus plumulosus*) to untreated sediment and sediment treated with activated carbon amendment. PCB bioaccumulation in the amphipod was measured after an exposure period of 14 days in the laboratory. Treated and untreated sediments were also exposed to passive samplers to measure changes in sediment porewater PCB concentration.

6.1. Bioaccumulation of PCBs in Leptocheirus plumulosus

Laboratory bioaccumulation tests were conducted to evaluate the impact of activated carbon sorbent amendments in reducing PCB biouptake by benthic organisms that form the base of the aquatic food chain. *L. plumulosus* is a burrow-building infaunal amphipod found in subtidal portions of Atlantic Coast brackish estuaries. It is common in protected embayments, but has also been collected in channels of estuarine rivers at water depths up to13 m. A 14-day bioaccumulation study was performed using sediment collected from Bailey Creek and *L. plumulosus* as the test organism. Six beakers of volume 1 L each were set-up as follows - 3 controls (without any amendment) and 3 treatments (5 % activated carbon by dry weight, Calgon TOG of mesh size 80 x 325). The 5% activated carbon dose was selected to match the sediment total organic carbon. Sediment slurry was filled to the 150 ml mark in all 6 beakers and artificial sea water (20ppt) was added to a final volume of 750 ml. The beakers were allowed to aerate for a week to remove any ammonia that might be toxic to the *Leptocheirus*. After a week of aeration, 10 adult *Leptocheirus* of average size 13 mm were added to each beaker. Overlying water was replaced thrice a week to maintain optimum concentration of oxygen and also to reduce ammonia levels. The organisms were fed Tetramin-fish powder thrice a week 1mg/*Leptocheirus*). After 14 days of exposure to sediment, the test organisms were retrieved by sieving the sediment using three sieves of mesh size 1 mm, 0.6 mm and 0.25 mm. The average adult organism recovery for the control sediment was 77% and for the treated sediment was 90%. The organisms were allowed to depurate for four hours in clean artificial sea water. They were then weighed and frozen until further analysis.

Prior to PCB analysis, the organisms were ground with anhydrous sodium sulfate and extracted by sonication using three volumes of 30 ml each of hexane-acetone mixture (1:1) according to EPA SW846 method 3550B. Sample cleanup was performed based on EPA SW846 methods 3660B (activated copper cleanup), 3665A (sulfuric acid cleanup), and 3630C (silica gel cleanup). PCB analysis was done using an Agilent 6890 gas chromatograph with a micro electron capture detector.

Results of tissue PCB concentrations are shown in Figure 5. *L. plumulosus* exposed to Bailey creek sediment accumulated a total of 40 ug/g wet tissue PCB concentration. The distribution of PCB homologs in tissue was similar to that of the sediment. Amendment of sediment with 5% activated carbon by dry weight reduced PCB bioaccumulation in *L. plumulosus* to 12 ug/g (74%

reduction in bioaccumulation). As shown in Figure 3, generally, the percent reduction was higher for the lower chlorinated PCB homologs.

The *L. plumulosus* were found to actively reproduce in the control and AC-treated sediments during the exposure study. The second generation of organisms was allowed to grow in the untreated and AC-treated sediment for 60 days following which the organisms were harvested, weighed, and analyzed for tissue PCB concentrations. Average tissue recovery from the AC-treated sediment (0.4 ± 0.07 g) was not statistically different from the untreated sediment (0.44 ± 0.08 g). Tissue PCB concentration in the second generation organisms after 60 days exposure is shown in Figure 3. For the second generation, there was an overall 82% reduction in total PCBs in the AC-treated sediment exposure compared to the untreated sediment.

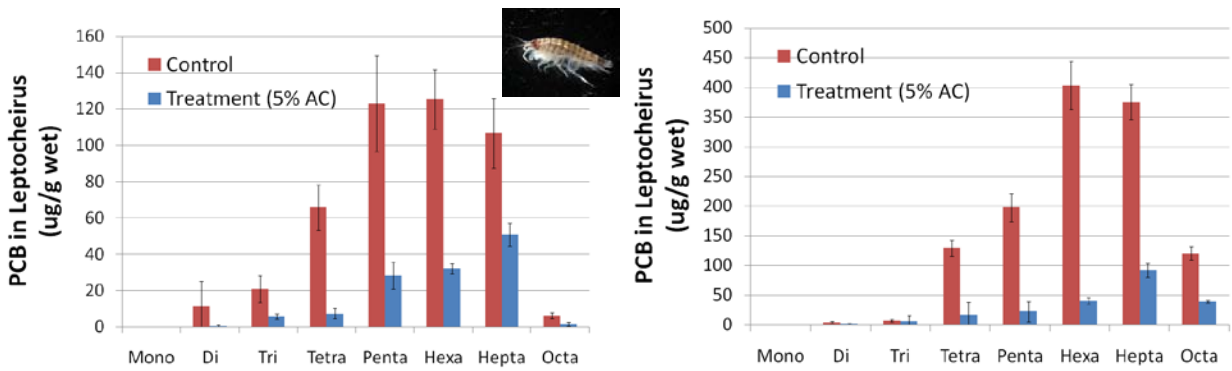

Figure 3. PCB bioaccumulation in *L. plumulosus* after 14 days of exposure in Bailey Creek sediment with or without 5% activated carbon by dry weight (left) and PCB bioaccumulation in second generation *L. plumulosus* after 60 days of exposure in in Bailey Creek sediment with or without 5% activated carbon by dry weight (right).

6.2. Uptake of PCBs in polyoxymethylene solid phase passive sampler.

Passive samplers have been used to probe concentrations of sparingly soluble hydrophobic chemicals in sediment porewater. Bailey Creek sediment treated with different doses of activated carbon was exposed to polyoxymethylene (POM) passive samplers in 100 ml vials and placed in a roller for 14 days. After the exposure period, the POM samplers were retrieved, and analyzed for PCB congeners. Results of the experiment are shown in Figure 4. Amendment of sediment with activated carbon reduced passive PCB uptake in POM by 59% at a dose of 1% by dry weight and by 96% at a dose of 3% by dry weight. These reductions in the passive samplers reflect reductions in sediment porewater PCBs after amendment of the sediment with activated carbon. At steady state, porewater PCBs reflect the activity of the chemical in the sediment phase. Reduction in porewater PCBs indicate reduced bioavailability of the contaminants in sediment and is expected to reduce the dermal uptake pathway for contaminant bioaccumulation in benthic organisms.

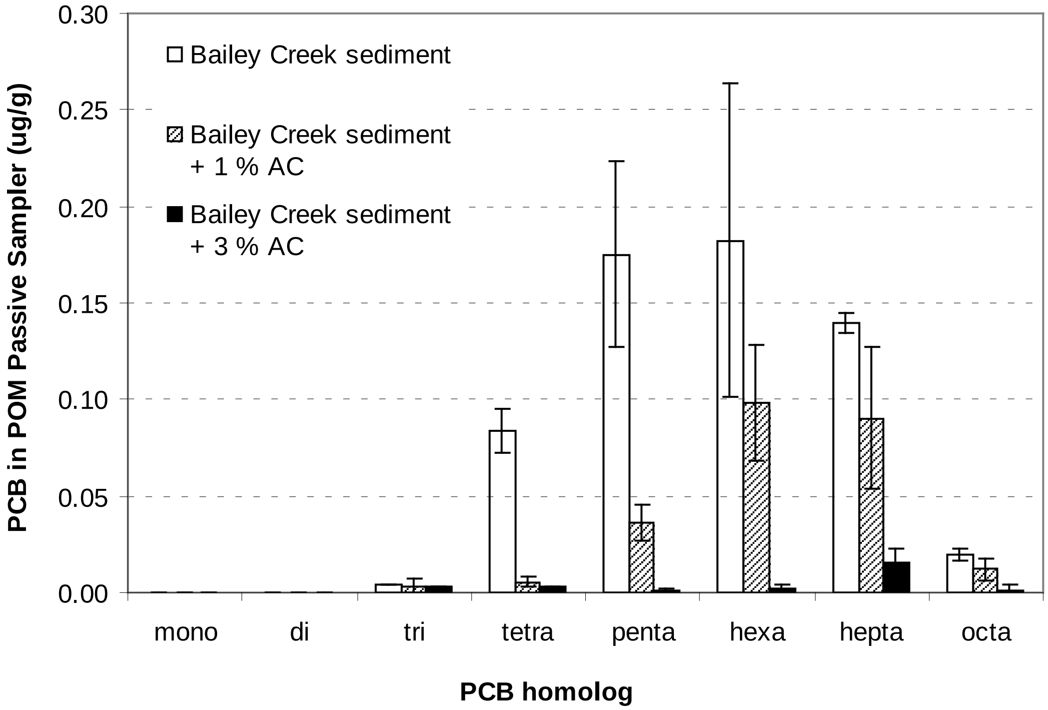

Figure 4. PCB concentration in polyoxymethylene passive samplers after exposure to Bailey Creek sediment treated with different doses of activated carbon.

The laboratory treatability test results indicate activated carbon amendment to Bailey Creek sediment reduces PCB biouptake in a benthic organism by 74%. Additionally, passive sampler results indicate that sediment porewater PCB concentration is reduced drastically by 96% when 3% by weight of activated carbon is added. Based on these results it appears that the impacted sediments at Bailey Creek are amenable for PCB bioavailability reduction through the amendment with activated carbon sorbent. Both uptake of PCBs in the food chain, and potential diffusive release of PCBs from sediment into overlying water, are reduced after amendment of sediment with activated carbon. Additional information from the site visit indicates that the area under consideration is amenable for in-situ treatment because the site while being tidally influenced, is generally a low-energy site and is not impacted by strong currents. Also, the PCB concentrations in the sediment are low to moderate and can benefit from reductions in PCB bioavailability. Questions remain on the effectiveness of activated carbon in reducing PCB bioavailability under field conditions. Thus the next logical step in this investigation was to perform a pilot-scale trial to evaluate the technology under field conditions.

7.0. Pilot study design and application

7.1. Demonstration plan description.

The pilot-scale trials involved two side-by side plots (treated and untreated) in the creek covering an area of approximately 225 square meters each as illustrated in Figure 5. The SediMite pellets containing activated carbon was applied using a boat-mounted dispersion device similar to a commercial fertilizer/herbicide spreader (Vortex Systems). Such devices have been used in the past in agricultural and weed removal applications. The Vortex granular application system uses a flow of air to draw in the pelletized application material into an air stream and ejects the material to a distance up to 40 ft. The rate of application and distance of throw can be controlled by the operator. The Vortex TR™ system shown in Figure 5 is manufactured by Vortex Granular Systems LLC and is a proven granular application system in the landscape, pest control and maintenance industry. The applicator is primarily designed to apply fertilizers, pre-emergent herbicides, ice melt products, granular growth regulators, aquatic herbicides and most granular or pelletized products used in an outdoor setting. The unit is lightweight for use in small watercraft and equipped with a vibration system to insure continuous flow. The unit shown in Figure 5 was purchased and first tested on ground for the application of SediMite in the field.

7.2. SediMite dose

Based on the treatability test result and past experience with carbon dose at pilot test sites, AC amendment is effective in reducing the availability of PCBs in sediment at a dose close to the native TOC of sediment. For the study Creek, the dose of SediMite chosen was 5% of the sediment dry weight in carbon equivalents. SediMite contained 60% by weight of activated carbon. For the study sediment we anticipated the top 10 cm of sediment to be most bioactive. Shown below in Table 1 are calculations of SediMite dose per square meter and for a total treatment area of 225 square meters when the treatment layer thickness is the surficial sediment depth of 10 cm (4”). The calculations shown below include a 25% safety factor to result in a dosing rate of 3.4 kg SediMite/square meter. The total mass of SediMite required to treat 225 square meter area was 773 kg or about 1,700 lb. At an expected application rate of 10 kg/min the application was expected to take less than two hours.

Table 1. Calculation of SediMite application rate at the demonstration site.

Loading rate of SediMite for top 10cm and 25% safety factor	Value	Units
Volume of sediment treated per square meter (1 sq. m. x 0.1m)	0.1	cu m
Dry mass of sed to be treated/sq. m. (dry density of sed = 0.33 kg/L)	33	kg
Mass of native carbon/ sq m (at 5% by dry weight)	1.65	kg
Weight of SediMite per square m (60% AC in SediMite)	2.75	kg
Mass of SediMite/sq m plus 25% safety factor	3.44	kg
SediMite required for treatment area (225 sq. m)	773	kg
Time to apply (rate of application = 10 kg/min)	1.29	h

7.3. SediMite application

The test plot in the creek was treated using the Vortex TR Aquatic system mounted on a shallow-draft boat rented from the Virginia Institute of Marine Sciences. A staging area was established at a nearby boat launch site. Two boats were launched from this location and proceed up the Creek to the demonstration site. One boat contained the deployment crew of two people (the boat operator and the Vortex operator), the Vortex machine, and SediMite buckets that could be safely stored on board without exceeding the boat's weight limit. The second boat contained the boat operator, additional observers, and remaining amount of SediMite buckets that could be safely stored on board without exceeding the boat's weight limit. All boating operations were performed according to Exponent's Safety During Aquatic Operations SOP HS-04. The application involved staking out the treatment area with markers positioned at pre-determined GPS coordinates. The ~15x~15m treatment area were subdivided into five 3m wide strips perpendicular to the creek also marked by stakes. Application started by positioning the shallow draft boat at the edge of the first strip to be treated. Application rate of SediMite was calibrated in advance and also monitored during application. The spreader nozzle was positioned over the strip and directed side to side to obtain an even application of SediMite over the 3x15m strip. SediMite applied was monitored and application continued till the required dose for the 3x15m strip was achieved. The application performed was partly in the creek and partly over the adjacent marsh area as illustrated in Figure 5.

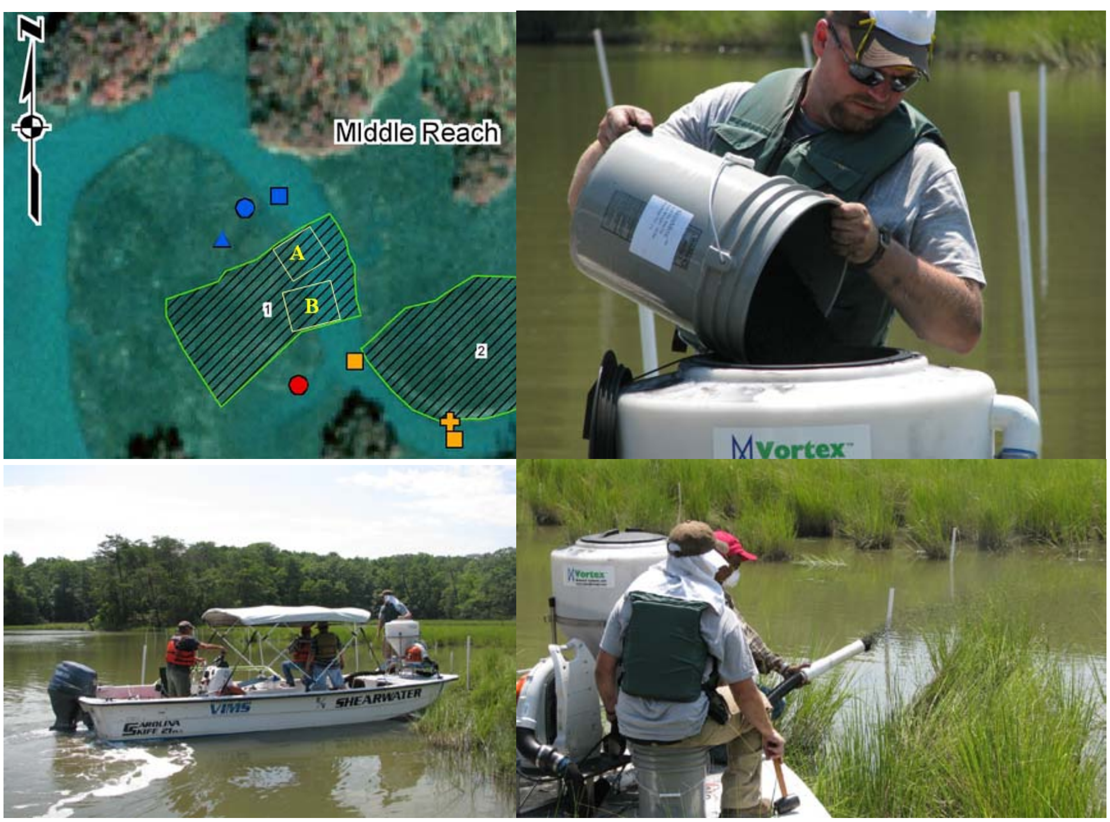

Figure 5. Top left: position of treatment areas aligned along the edge of the Creek. Remaining pictures show deployment on a boat and application using the Vortex device for application of SediMite in the estuarine wetland at Ft. Eustis.

7.4. Safety concerns during application:

The primary human health safety concerns during the demonstration related to operating from boats. All project personnel followed Exponent's Safety During Aquatic Operations SOP HS-04. Flotation devices were worn at all times by personnel near (within 10 ft) or on water. Boat weight limits were strictly followed. Each boat pilot carried a 2-way radio and was able to contact or be reached by the harbormaster. Operations were to be shut down in the event of storm-related emergencies or potential hazards such as lightening or excessive wind.

Secondary human health concern can arise from inhalation of dust associated with SediMite application. Care was taken to minimize airborne dust generation. Personnel were positioned upwind of application as much as possible. Where necessary, project personnel close to the application wore dust masks during activity. Activated carbon dust is flammable under high temperature. During application and handling open fires of any kind was not allowed in the vicinity.

Operations in open water during the summer can cause heat stress. Adequate skin protection from UV radiation was maintained by personnel and each boat had adequate supply of drinking water. Depending on cloud cover, hats were worn to limit direct exposures. The crews were periodically checked and rest stops were taken on a periodic basis.

7.5. Monitoring Program.

A major component of this project was to monitor the effectiveness of the field treatment in reducing PCB flux from sediments and uptake by benthic animals. A suite of physicochemical and biological tests were conducted before and after the application of activated carbon to sediments to evaluate technology performance. The ultimate goals of remedial activities were to reduce the concentration of PCBs in the native fish and to reduce the flux of PCBs into the overlying water. However, it may be nearly impossible to perform these endpoint measurements directly following pilot-scale testing of a treatment technology that treats only a small footprint of the contaminated sediment. Field monitoring for treatment performance can be confounded by influences from adjacent untreated areas, especially when the treatment area is small compared to the total impacted area. In this work the metrics of success were a demonstration of reductions in the PCB uptake exposure pathways to fish from the field-treated sediment. Specifically, this involves demonstrating a reduction of PCBs in pore water and in benthic organisms that serve as food for fish. Benthic community analysis was also performed to evaluate potential negative impacts of activated carbon amendments.

Baseline monitoring was performed at the site to evaluate PCB concentrations in sediment, porewater, and benthic organisms before application of activated carbon in the treatment plot. The baseline monitoring was performed in the summer of 2009 immediately before the application of SediMite. The first post application sampling was performed in Fall 2009, 2 months after the application of activated carbon in the field. This was followed by a field sampling in the late Fall of 2010 to assess bioavailability changes 15 months after carbon application.

8.0. Results from pilot study

The results of this research project have been presented at several conferences and are being written into a journal manuscript. The key findings are summarized here.

8.1. Activated carbon in sediments.

Activated carbon was measured in sediment cores collected from the treatment and control plots by sectioning the sediment cores at different depths: 0-2cm, 2-4cm, 4-6, 6-10cm layers. Each core section was dried, homogenized, and then processed for activated carbon determination based on method developed by Grossman et al. (2009). As shown in Figure 6, the highest levels of AC were found in the top 2 cm of sediment. The background black carbon levels in sediment is close to 0.3%. The surface application of activated carbon was found down to the depth of 6 cm below surface 15 months after treatment. This observation suggests vertical mixing of the applied dose of activated carbon through natural processes such as bioturbation, sediment resuspension and settling, and deposition of new sediment over time. The percent recovery of activated carbon from the actual treated area after 2 months was 70% based on analysis of cores and 88% based on analysis of bulk samples collected using ponar grabs.   After 15 months, the percent recovery of activated carbon from the actual treated area was 50% based on cores as well as based on bulk samples collected using ponar grabs. There was evidence of a greater lateral dispersion of AC in the creek treatment area compared to marsh. More activated carbon was recovered from the sediment in the marsh area compared to the creek areas. There was evidence of AC in sediment cores collected 5' upstream and downstream of the treated creek area. Thus, there was likely some lateral mixing of sediment possibly from tidal action in the creek. Overall these results indicate that activated carbon delivered as SediMite largely persisted in sediment with penetration down to 6" depth over a year and a potential lateral mixing due to tidal flow in the creek.

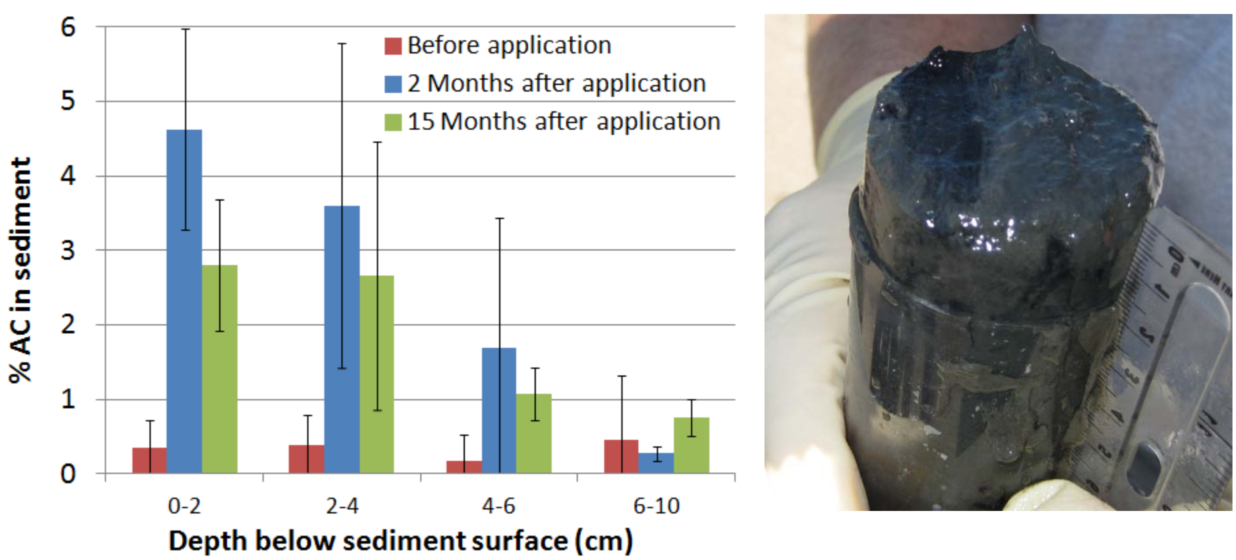

Figure 6. Activated carbon measured in different depth sections of sediment cores collected from the SediMite treated site. Picture on the right shows sediment cores being extruded for sectioning and analysis.

8.2. PCB bioaccumulation in an estuarine amphipod.

The average total PCB concentration in sediment was 0.5 mg/kg in the treated and control sites and there was considerable variability among the replicate sampling locations as shown in Figure 7. PCB bioaccumulation in the estuarine amphipod *L. plumulosus* was reduced in the treated plot compared to the untreated control plot. The percent reduction in total PCB bioaccumulation after 2 months of treatment in the field was close to 90% which reduced to 50% after 15 months. Results shown in Figure 8 represent an average of 8 samples collected from each plot which included locations within the marsh as well as the creek. Generally, in the marsh sites more activated carbon was retained in the sediments and bioaccumulation reductions were better compared to the creek. The lower bioaccumulation reduction seen in 15 months compared to 2 month is likely due to the ongoing influence of contaminated sediment movement and deposition within the large contaminated area of which the treatment plot was a very small fraction. Thus, small pilot plots that are influenced by ongoing deposition of contaminated sediments from large untreated surrounding areas can have a limited time-span over which treatment effectiveness can be effectively monitored.

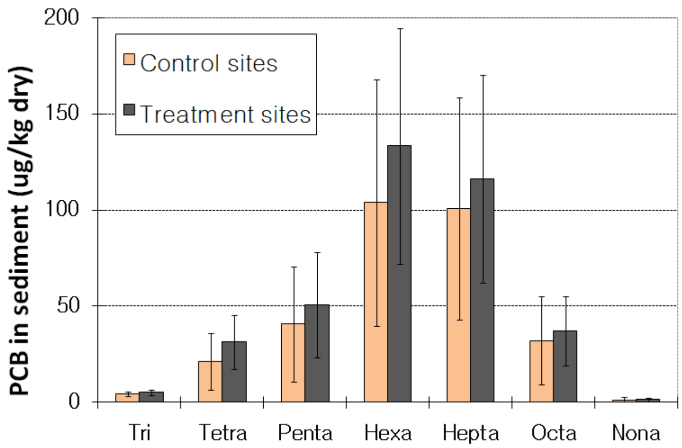

Figure 7. PCB homolog concentration in sediment from control and treatment site locations.

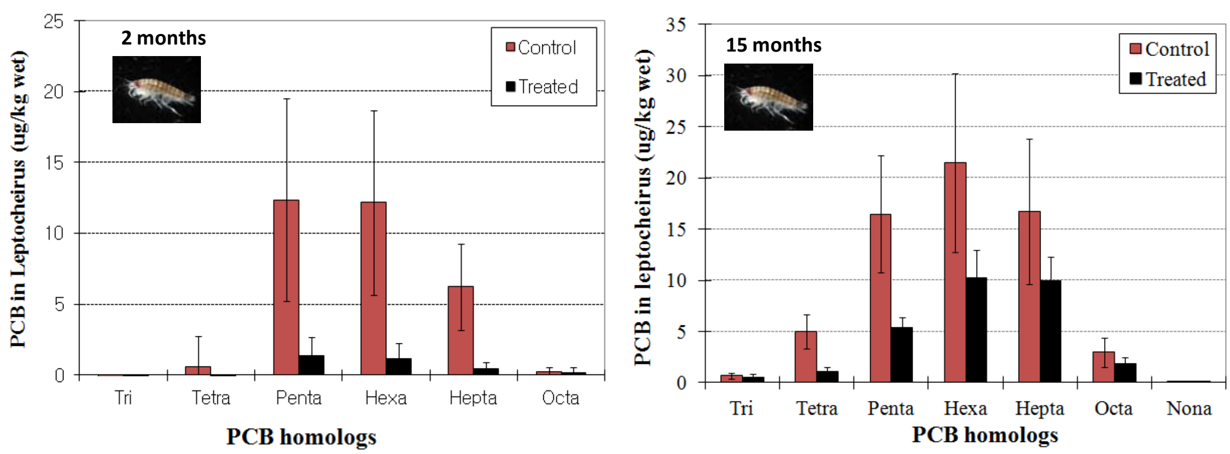

Figure 8. PCB bioaccumulation in *L. plumulosus* in treated versus untreated sediments 2 and 15 months after application of SediMite in the field.

8.3. Impact of SediMite application on native benthic community in sediments

Sediment samples for benthic community analyses were collected before and after treatment application. As shown in Figure 9, little change was observed in benthic community diversity and abundance after treatment. There were small differences observed over the period of monitoring but these changes were similar in the control and treatment plots. A major implication of this observation is that the application of activated carbon to sediment at a dose <5% by dry weight did not significantly impact the native benthic community.

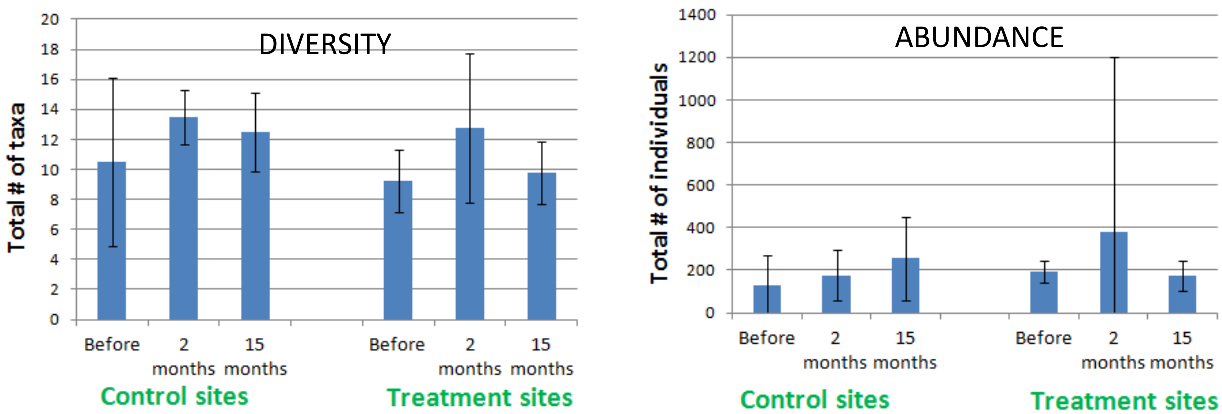

Figure 9. Diversity and abundance of benthic community in sediments collected from control and treatment plots before and after application of SediMite in the field.

8.4. Key conclusions and recommendations

The major conclusions and recommendations based on this pilot-scale demonstration study are:

1. Activated carbon in the form of SediMite pellets can be applied to sediment in a large scale
2. Activated carbon remains in place 15 months after placement but a greater lateral dispersion of the carbon is observed in the creek compared to the marsh possibly due to tidal action.
3. Significant reductions were observed in PCB levels in benthic organism tissue after activated carbon amendment to sediment.
4. There was no significant impact on benthic community as a result of activated carbon amendment into sediments in the estuarine marsh.
5. Results from this study indicate that amendment with activated carbon will be most effective at sites that are depositional in nature, less prone to sediment erosion, and where ongoing contribution from off-site sources have been controlled.
6. AC amendment provides several advantages over traditional remediation methods such as less disruption to benthic habitats in sensitive systems, amenability to shallow or constricted locations, potential for lower cost, and less concern about mobilizing buried contaminants.
7. Full-scale application and long-term testing is recommended as the next steps to evaluate effectiveness of in-situ treatment with activated carbon in reducing pollutant accumulation in human health risk drivers such as fish.

8.5. Disclosure statement

Upal Ghosh is a co-inventor of two patents related to the technology described in this paper for which he is entitled to receive royalties. One invention was issued to Stanford University (US Patent # 7,101,115 B2), and the other to the University of Maryland Baltimore County (UMBC) (U.S. Patent No. 7,824,129). In addition, UG is a partner in a startup company (Sediment Solutions) that has licensed the technology from Stanford and UMBC and is transitioning the technology in the field.

9.0 Publications and presentations

9.1. Publications

1. In-situ sorbent amendments: A new direction in contaminated sediment management. Upal Ghosh, Richard G. Luthy, Gerard Cornelissen, David Werner, Charles A. Menzie. ***Environ. Sci. Technol***. Feature Article, 45, 1163–1168. 2011.
2. Low-impact delivery of sorbent amendments into sediments. S. Kwon, P. Paul, B. Amos, C.A. Menzie, and U. Ghosh. Manuscript in preparation.
3. In-situ Measurements of PCB Pore Water Concentration Profiles Using Passive Samplers. Piuly Paul and Upal Ghosh. Manuscript in preparation

9.2. Presentations

1. Low-impact delivery of sorbent amendments to reduce contaminant bioavailability in sediments. U. Ghosh. ***NIEHS Annual Meeting***, Lexington, KY. Oct. 23-25, 2011.
2. Sorbent amendments to reduce contaminant bioavailability in sediments. U. Ghosh. ***CH2M Hill Internal Webinar***, Sep 15, 2011.
3. Alternative Methods of Sediment Remediation using Carbon Amendments. U. Ghosh. ***Manhattan College, 56th Institute in Water Pollution Control***, June 13-16, 2011.
4. New Advances in Contaminated Sediment Remediation in US and Europe. ***Indian Institute of Technology, Chennai, Department of Chemical Engineering***, August 10, 2011.
5. Sorbent amendments to reduce contaminant bioavailability in sediments. ***The Superfund Research Program, Risk e-Learning Web Seminar Series: Contaminated Sediments: New Tools and Approaches for in situ Remediation.*** December 8, 2010
6. Low-impact delivery of sorbent amendments to reduce contaminant bioavailability in sediments. U. Ghosh. ***Superfund Research Program Annual Conference***, R01 Session, November 10, 2010, Portland, OR.

7. Field Evaluation of sorbent deployment methods for in-situ sediment remediation. U. Ghosh, Invited talk. ***International Network of Sediment Research***, University of Newcastle, July 6, 2010.
8. New Approaches for the Remediation of Contaminated Sediments. U. Ghosh. ***Hong Kong University of Science and Technology***, June 10, 2010.
9. Application of activated carbon in the remediation of PCB contaminated sediment. U. Ghosh. ***SETAC Asia Pacific***, Guangzhou, China, June 4-7, 2010.
10. Application of activated carbon in the remediation of PCB contaminated sediment. U. Ghosh. ***International PCB workshop***, Visby, Sweden, June 1, 2010
11. In-situ Sorbent Amendments: It's Not Just Pixie Dust. U. Ghosh. EPA National Association of Remediation Project Managers Annual Training Conference. Contaminated Sediments: New Tools And Approaches For In-Situ Remediation Using Amendments May 24-27, Washington, DC, 2010.
12. In Situ Remediation with Activated Carbon:Pilot-Scale Demonstrations at Superfund Sites. U. Ghosh. ***U.S. EPA/U.S. ACE/SMWG Joint Sediment Conference***, April 13-14, 2010.
13. Field Demonstration of Activated Carbon Amendment to Sediment in a River. U. Ghosh. ***Partners in Environmental Technology Technical Symposium and Workshop, DoD.*** Nov 30-Dec 2, 2009.
14. Low-impact delivery system for in situ treatment of sediments contaminated with methylmercury. ***Department of Energy Mercury Summit***, October 22-23, 2009. Vanderbilt University.
15. Novel Application of Activated Carbon in the Remediation of PCB and DDT contaminated Sediments. ***International Activated Carbon Conference***, October 5-6, 2009, Pittsburgh, PA.
16. Transitioning Technologies to the Field: A Case Study of In-Situ Sediment Remediation, ***Department of Geography and Environmental Engineering Seminar, The Johns Hopkins University***, October 1, 2009.
17. Emerging technologies for protecting coastal waters from pollutants delivered through storm water runoff and flux from bedded sediments. ***Keynote talk at the World Water Week, session on Protecting Coastal Waters.*** Stockholm, August 2009.
18. Emerging technologies for protecting coastal waters from pollutants delivered through storm water runoff and flux from bedded sediments. ***Center for Marine Biotechnology Seminar***, August 2009.
19. New advances in sediment remediation: Reducing Contaminant Bioavailability. U. Ghosh. ***ERM's Problem Site Series: Contaminated Sediment Strategies.*** October 30, 2008, Princeton, New Jersey
20. In-situ Remediation Update: PCB Bioavailability Reduction in Sediments Using Activated Carbon Amendment. Upal Ghosh. ***Sediment Management Workgroup Annual Meeting***, New Orleans, Jan 8-9, 2008.

10.0. ARRA Supplement to Parent Grant

The ARRA supplemental request was aimed at accelerating the pace of research in assessing the performance of the treatment technology in the field. This was achieved through the hiring of additional research personnel and the purchase of a sample evaporator for rapid processing of solvent extracts before analysis. The supplemental effort allowed us to explore the use of passive samplers in-situ to measure porewater concentrations of PCBs in the treated and control plots. Additionally, the supplemental research also explored the use of passive samplers dosed with stable isotope labeled PCBs as a probe to evaluate in-situ microbial activity of PCB dechlorination. A progress report of the ARRA supplemental effort is being submitted separately.

11.0. References

Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A., 2011. In-situ sorbent amendments: A new direction in contaminated sediment management. *Environ. Sci. Technol*. 45, 1163–1168.

Grossman, A.; Ghosh, U. Measurement of activated carbon and other black carbons in sediments. *Chemosphere* 2009, 75, 469–475.

US EPA. Contaminated sediment remediation guidance for hazardous waste sites. EPA-540-R-05-012, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency. Washington, DC, 2005.

US EPA. Fort Eustis (US Army) current site information. U.S. Environmental Protection Agency Mid-Atlantic Superfund website, http://www.epa.gov/reg3hwmd/npl/VA6210020321.htm, 2006.

Valsaraj, K.T.; Ravikrishna, R.; Choy, B.; Reible, D.D.; Thibodeaux, L.J.; Price, C.B.; Yodt, S.; Brannon, J.M.; Myers, T.E. Air emissions from exposed contaminated sediments and dredged material. Environ. Sci. Technol. 1999, 33, 142-149.

US EPA. Estimating contaminant losses from components of remediation alternatives for contaminated sediments. EPA 905-R96-001, Great Lakes National Program Office, U.S. Environmental Protection Agency, Chicago, IL, 1996.