

SEDIMENT FIELD DEMONSTRATION WORK PLAN BAILEY CREEK, FT. EUSTIS

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Prepared by

**Upal Ghosh, UMBC
Ben Amos, and Charles A. Menzie, Exponent
Bruce Fiddler, Malcolm Pirnie**

1.0 Project background

This document outlines the plans for a field demonstration of the efficacy of in-situ treatment of polychlorinated biphenyls (PCBs) in the sediments of Bailey Creek. The creek is a small tributary to the James River and is located within Fort Eustis. The demonstration relates to the delivery system known as SediMite for introducing activated carbon to the contaminated sediments.

Sediment-bound contaminants such as PCBs pose a public health risk through contamination of the food chain and through direct exposure. This field research is evaluating the effectiveness of a novel approach to alter the binding capacity of sediments to reduce the release and human exposure of such contaminants. Emerging laboratory-scale research by our group and others has shown that contaminant transport pathways and bioavailability can be interrupted by modifying and enhancing the binding and contaminant assimilation capacity of natural sediments. This is achieved by adding amendments such as activated carbon for binding persistent organic pollutants and natural minerals such as apatite, zeolites, or bauxite for the binding of toxic metals in sediments. 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. Our 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, SediMite 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 is to develop the in-situ remediation technology through a pilot-scale demonstration aimed at addressing the critical barriers in the advancement of the technology.

1.1. Study funding.

This research is being supported by the National Institute of Environmental Health Sciences Superfund Basic Research Program through a research project awarded to Dr. Ghosh and Dr. Menzie. Malcolm Pirnie is collaborating and providing logistical support for the in-field studies through internal research funding.

1.2 Brief update of project status and achievements

A description of field sampling and laboratory studies conducted in the last one year is provided in the Treatability Study report in Appendix 1. In partnership with research collaborator Exponent, and Malcolm Pirnie, a site survey and field sampling was conducted in the summer of 2008. Field sampling was performed at two locations in Bailey Creek on June 10, 2008 that had PCB concentrations in the range of 0.5 – 2 ppm based on historic sampling data. 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 assessment.

Laboratory treatability test were conducted in 2008 and the results indicate activated carbon amendment to Bailey Creek sediment reduces PCB biouptake in a benthic organism (*Leptocheirus plumulosus*) by 74% for adult organisms after a 14-day exposure, and by 82% for juvenile organisms allowed to grow in sediment for 60 days. 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 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 at Bailey Creek 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 is to perform a pilot-scale trial to evaluate the technology under field conditions. This work plan describes the proposed field demonstration testing of SediMite application at Bailey Creek.

1.4 Proposed location of SediMite demonstration

The proposed rectangular treatment (A) and control (B) areas are shown in white letters in Figure 1. Each of the two areas will be ~15m long along the river and ~15m wide, with half the width in the channel and the other half on the adjoining marsh. These dimensions may be modified in the field as needed to represent the desired types of environments. These proposed areas were selected based on historical sediment PCB concentration measurement in the range of 1 ppm, inclusion of both channel segment and adjoining marsh area, and lower likelihood of impact from planned site remedial activities. These are areas where we have sampled sediment from during summer of 2008 and appear to be an area that will be suitable for a field demonstration.

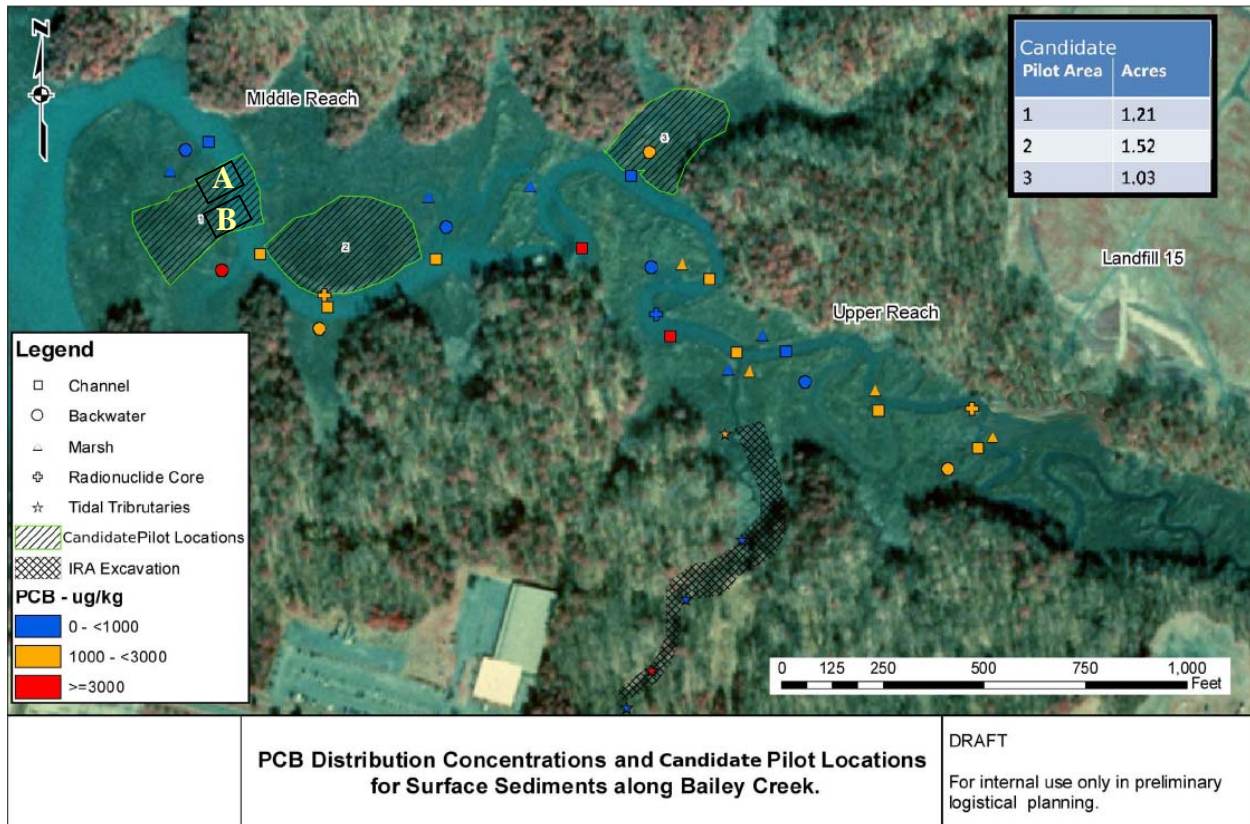


Figure 1. Proposed area (A & B) of SediMite field demonstration at Bailey Creek, Ft. Eustis.

2.0 Demonstration plan description.

The pilot-scale trials will involve two side-by side plots (treated and untreated) in the creek covering an area of approximately 225 square meters each. The SediMite pellets containing activated carbon will be applied using a boat/barge-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. We have successfully tested the application of the Vortex Systems air blowing system for the delivery of treatment pellets. Baseline monitoring will be performed at the site to evaluate PCB concentrations in sediment, porewater, and benthic organisms before application of activated carbon in the treatment plot. It is anticipated that the baseline monitoring and activated carbon application will be performed in the summer of 2009. The first post application sampling will be performed in Fall 2009, 2 months after the application of activated carbon in the field. This will be followed by a field sampling in the summer of 2010 to assess bioavailability changes after one year of carbon application.

2.1 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 Bailey Creek, the dose of SediMite would be 5% of the sediment dry weight in carbon equivalents. SediMite will contain 60% by weight of activated carbon. For the study sediment we anticipate 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 will be about 773 kg or about 1,700 lb of SediMite. At a expected application rate of 10 kg/min the application is expected to take less than two hours. The application will result in an initial SediMite layer of 1 cm. As this layer breaks down (falls apart) the AC is incorporated into the sediment by the organisms that live on or in the sediments. This is a natural bioturbation process and we have demonstrated that this occurs in laboratory mesocosms.

Table 1. Calculation of SediMite application rate at Bailey Creek Demonstration site.

Loading rate of SediMite in Bailey Creek 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. (measured 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

2.2 SediMite application

The Bailey Creek test plot will be treated using the Vortex TR Aquatic system that will be mounted on a shallow-draft boat. A staging area will be established at the boat launch site. Two boats will be launched from this location and proceed up the Bailey Creek to the demonstration site. One boat will contain the deployment crew of two people (the boat operator and the Vortex

operator), the Vortex machine, and any amount of SediMite bags that can be safely stored on board without exceeding the boat's weight limit. The second boat will contain the boat operator and any amount of SediMite bags that can be safely stored on board without exceeding the boat's weight limit. Additional craft may be launched to accommodate observers. All boating operations will be performed according to Exponent's Safety During Aquatic Operations SOP HS-04, which is included in Appendix A.

The application will involve staking out the treatment area with markers positioned at pre-determined GPS coordinates. The ~15x~15m areas (or a modified plot based on field observations) will be subdivided into five 3m wide strips perpendicular to the creek also marked by stakes. Application will start by positioning the shallow draft boat at the edge of the first strip to be treated. Application rate of SediMite will be calibrated in advance and also monitored during application. The spreader nozzle will be directed over the strip and directed side to side to obtain an even application of SediMite over the 3x15m strip. SediMite applied will be monitored and if necessary application will be continued till the required dose for the 3x15m strip is achieved. The application will be partly in the creek and partly over the adjacent marsh area as illustrated in Figure 2. As noted, some in-field adjustments to the application areas may be needed to meet this objective.

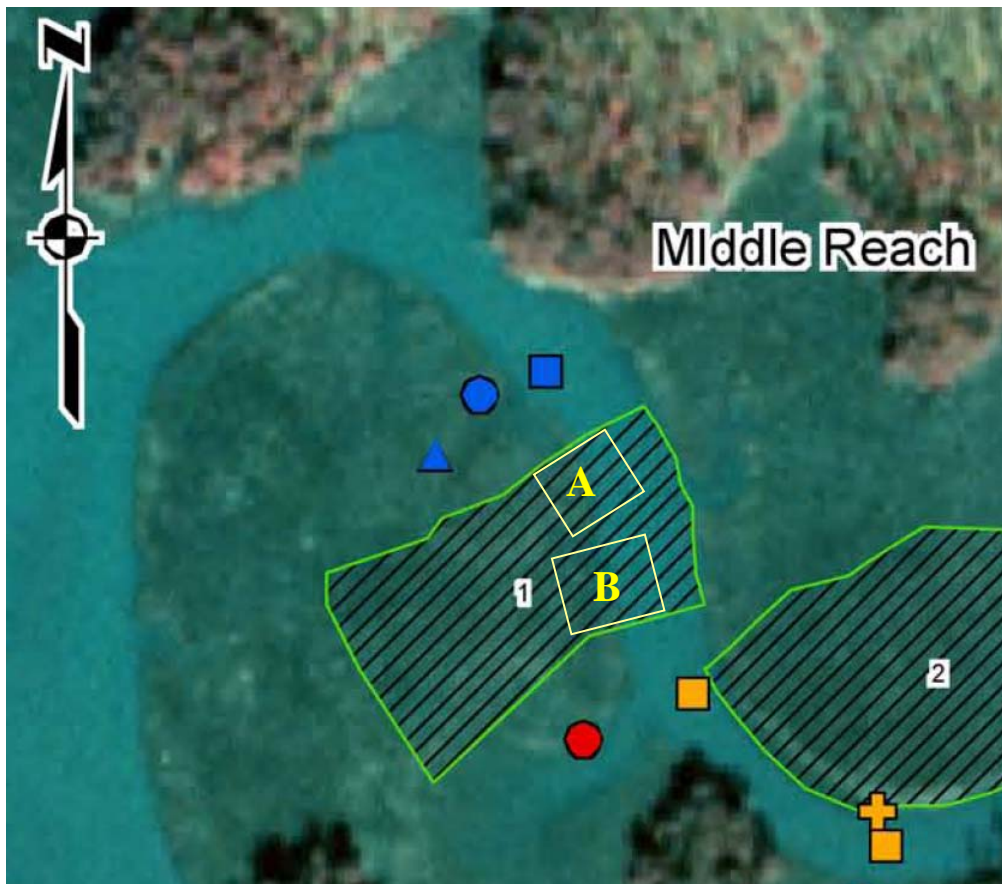


Figure 2. Closeup of proposed treatment areas aligned along the edge of Bailey Creek. The two areas will each be 15m in length along the shore and 15m wide and will include both the creek and upland marsh areas.

2.3 Description of TR Vortex system to be used for application.

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 3 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 3 has been purchased at UMBC and tested for the successful application of SediMite on land.



Figure 3. TR Vortex system to be used for SediMite application

2.4 Safety concerns during application:

The primary human health safety concerns during the demonstration related to operating from boats. All project personnel will follow Exponent's Safety During Aquatic Operations SOP HS-04. At a minimum, flotation devices will be worn at all times by personnel near (within 10 ft) or on water. Boat weight limits will be strictly followed. Each boat pilot will carry a 2-way radio and will be able to contact or be reached by the harbormaster. Operations will 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. All care will be taken to minimize airborne dust generation. Trial application on land performed at UMBC found minimal generation of airborne dust. Personnel will be positioned upwind of application as much as possible. Where necessary, project personnel will wear dust masks during activity.

Activated carbon is flammable under high temperature. During application and handling open fires of any kind will not be allowed in the vicinity.

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

3.0 Monitoring Program.

A major component of this project is 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 will be conducted before and after the application of activated carbon to sediments to evaluate technology performance. The ultimate goals of remedial activities are 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 we propose that the metrics of success will be 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.

Baseline monitoring will be performed at the site to evaluate PCB concentrations in sediment, porewater, and benthic organisms before application of activated carbon in the treatment plot. It is anticipated that the baseline monitoring and activated carbon application will be performed in the summer of 2009 immediately before the application of SediMite. The first post application sampling will be performed in Fall 2009, 2 months after the application of activated carbon in the field. This will be followed by a field sampling in the summer of 2010 to assess bioavailability changes after one year of carbon application. The list of measurements and time of performance is presented in Table 2.

Table 2. List of monitoring methods and schedule of performance

Monitoring Test	Before application	During application	2 months after	1 year after
1) Water quality measurement downstream of application area	X	X	X	
2) Sediment cores for AC/TOC measurement	X		X	X
3) Sediment cores for PCB measurement	X		X	X
4) Surficial 10 cm sediment for laboratory bioaccumulation studies	X		X	X
5) In-situ passive samplers			X	X
6) Benthic community analysis	X		X	X
7) PCB aqueous equilibrium measurement	X		X	X

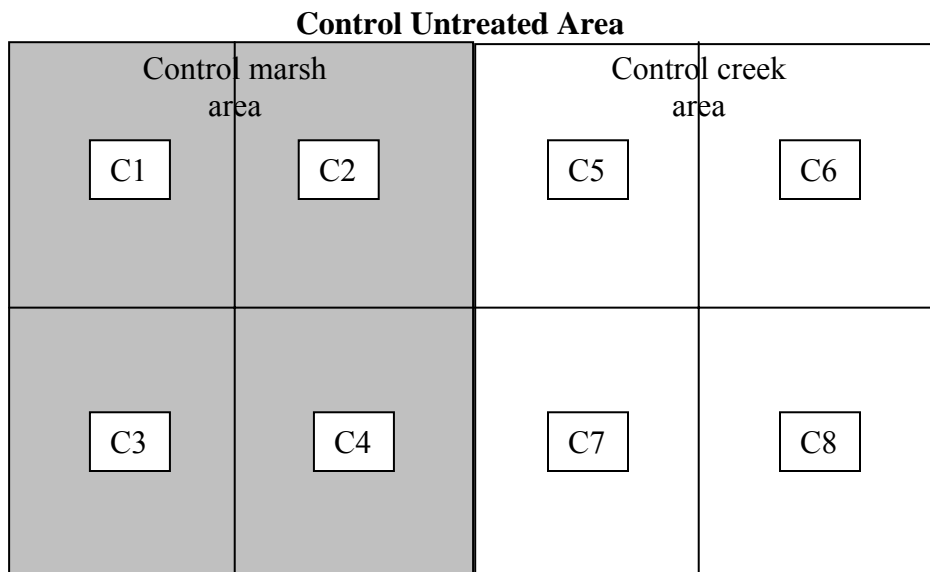
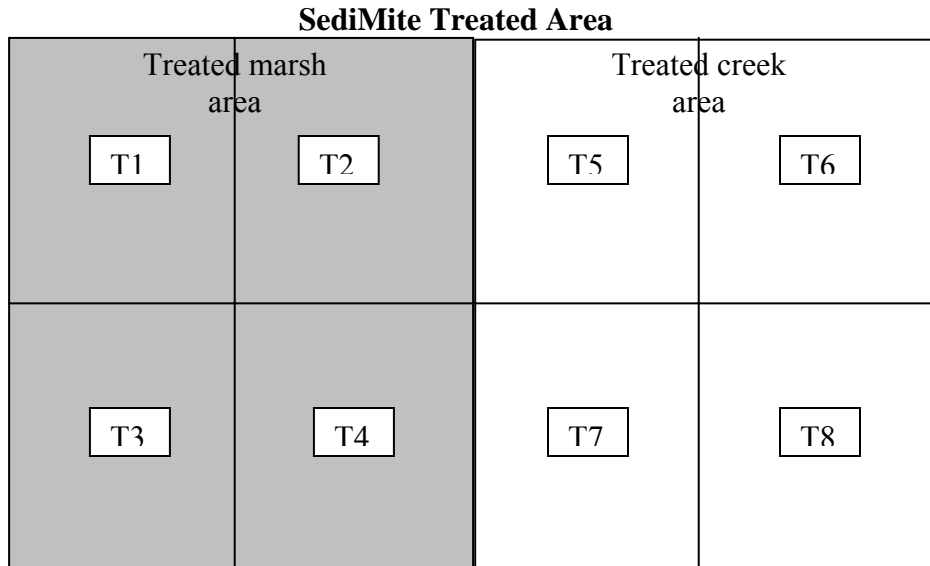


Figure 3. Sampling locations in the treated (T1-T8) and untreated control (C1-C8) areas.

3.1 Description of monitoring tests

3.1.1 Water quality measurement downstream of application area

Water quality measurements will be conducted before, during, and after the SediMite application area to monitor for any changes during application. The measurements will be conducted at 30 minute intervals starting one hour before application and will continue for an hour after

application. The water quality parameters measured will include temperature, turbidity, conductivity, and dissolved oxygen. These measurements will all be made using electronic probes.

3.1.2 Sediment cores for AC measurement

Eight sediment core samples will be collected from the treatment area and the control area during each sampling event. The core samples will be collected using lexan core tubes and will be sampled down to 30 cm of sediment. The core tubes will be capped and brought to the shore for splitting and sectioning. The cores will be sectioned at 5 cm intervals. This involves the use of a core extruder.

3.1.3 Sediment cores for PCB measurement

Sediment core sample sections obtained for AC measurement will be subsampled for PCB measurement. Congener specific PCB analysis will be performed as described in the UMBC PCB analytical procedure.

3.1.4 Surficial 10 cm sediment for laboratory bioaccumulation studies

Bulk sediment from the top 10 cm of sediment bed (the primary bioactive zone) will be collected using an Eckman grab sampler. The sampling locations are shown in Figure 3. Laboratory bioaccumulation tests will be 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. *Leptocheirus 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 to 13 m. A 14-day bioaccumulation study will be performed using sediment collected from Bailey Creek and *L. plumulosus* as the test organism. One beaker of volume 1 L each will set-up for each of the eight test site locations for the treated and control plots. Sediment slurry will be filled to the 150 ml mark in all beakers and artificial sea water (20ppt) will be added to a final volume of 750 ml. The beakers will be 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 will be added to each beaker. Overlying water will be replaced thrice a week to maintain optimum concentration of oxygen and also to reduce ammonia levels. The organisms will be fed Tetra-min fish powder thrice a week (1mg/*Leptocheirus*). After 14 days of exposure to sediment, the test organisms will be 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 target for the control and treated sediment is 70%. The organisms will be allowed to depurate for four hours in clean artificial sea water before being weighed and frozen until further analysis.

Organism lipid will be determined by spectrophotometric analysis (Van Handel, 1985). The worms are placed in a Econo-grind homogenizer (Radnoti Glass Technology Inc., Monrovia, CA) and crushed. A 2 ml solution of 1:1 chloroform : methanol is used to extract the lipids from the worm tissue. The extract is transferred to a clean tube and reduced to dryness by heating at 100 oC in a water bath (GCA Corp. Chicago, IL). Then 0.3 ml concentrated sulfuric acid (95-98%) is added to the tube and the sample is heated again at 100 oC for 10 minutes. After cooling, the color is developed by pouring vanillin phosphoric acid reagent to the 5 ml mark of the tube. After 5 minutes of color development, the samples are read on a Genesys 10 spectrophotometer

(Thermo electron corp. Waltham, MA) at 525 nm against the standard of 50, 100, 200 and 400 $\mu\text{l/l}$ made from soybean oil (Fisher Scientific.).

3.1.5 In-situ passive samplers

PCBs in sediment porewater are accessible to benthic organisms through dermal uptake and also drive the flux of PCBs into the water column. Polyoxymethylene-solid phase extraction (POM-SPE) method has been used to measure low aqueous concentrations of PAHs and PCBs in sorption isotherm studies with strong sorbents. Work at UMBC has extended the calibration of the POM samplers for a larger range of PCB congeners. We propose use POM passive samplers to measure low levels of porewater PCB concentrations that may be difficult to achieve using the alternate water extraction method. At the Ft. Eustis site, the total PCB concentration in sediment is about 1 mg/kg. Our initial laboratory treatability studies indicated that direct measurement of dissolved PCBs in sediment porewater is difficult due to extremely low concentrations.

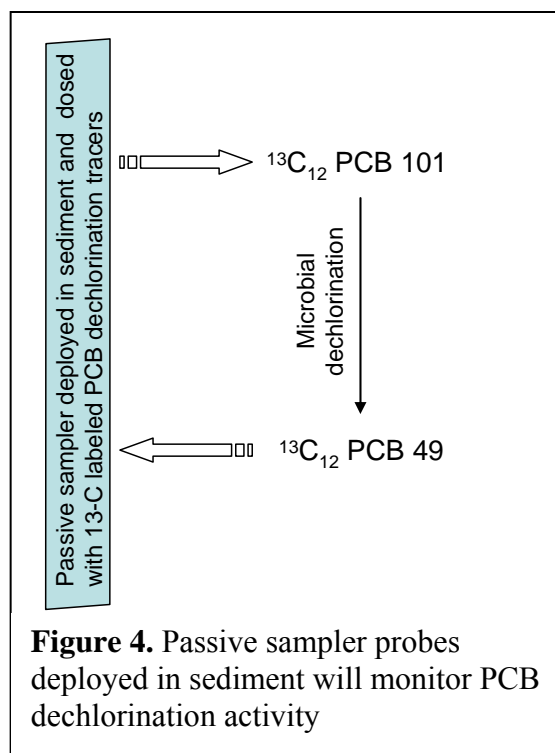


Figure 4. Passive sampler probes deployed in sediment will monitor PCB dechlorination activity

The passive sampler probe is described in Figure 4. The passive sampler is dosed with a low concentration (mimicking native PCB concentrations at the site) of C-13 labeled PCB congeners that are known to dechlorinate and then inserted into the sediment to a depth of up to 2 feet. The probe is allowed to equilibrate for a period of 2-6 months and then retrieved. After retrieval, the passive sampler in the probe is sectioned and analyzed for native PCBs that have sorbed on the sampler, and also any of the parent or byproducts of the C-13 labeled compounds. If successful, this modified passive sampling technique can not only inform us on the existing porewater PCB concentrations in the field, but also allow us to interpret ongoing microbial dechlorination activity in the field. We will use this tool to assess if and how microbial dechlorination processes continue to attenuate PCB concentrations below an actively treated layer of sediment.

The rationale of the experimental set-up is that $^{13}\text{C}_{12}$ labeled PCB congeners sorbed to the POM would diffuse out into the sediment pore water in order to reach equilibrium conditions. Similarly, some of the products formed from dechlorination of the stable isotope labeled congeners will adsorb back to the POM. The three different stable isotopes of PCB that will be used are PCB 28 (2, 4, 4'-triCB), PCB 101 (2,2',4,5,5'-pentaCB) and PCB153 (2,2',4,4',5,5'-hexaCB). Previous laboratory research has shown that PCB 101 is reductively dechlorinated to PCB 49 (2,2',4,5'-tetraCB) and no further dechlorination occurred after 250 days of incubation [2]. PCB 153 has been reported to undergo reductive dechlorination to form PCB 99 (2,2',4,4',5-pentaCB) which can undergo further dechlorination to form PCB 47 (2,2',4,4' tetra-CB) [3]. Bedard et al. has shown that PCB 28 underwent > 80% degradation by different strains of

bacteria isolated from PCB contaminated sites [4]. PCB 28 has an open 2,3 position which makes it susceptible to attack by 2,3-dioxygenase. The degradation of biphenyl by microorganisms has been shown to be initiated mostly by a biphenyl 2,3-dioxygenase [5]. Another route of PCB degradation is the 3, 4-dioxygenase pathway [6] which requires an open 3,4 position. PCB 101 has an open 3,4 site making it susceptible to attack by a 3,4-dioxygenase. PCB 153 has both 2,3 and 3,4 sites blocked making it inaccessible for degradation aerobically by the known dioxygenases.

There currently exists a lot of debate in the scientific community about the best methods to assess in-situ PCB dechlorination activity. We think that passive sampler probes can be used to directly assess transformation activity in-situ without having to bring sediment samples back to the laboratory for simulated incubations. presence of these organisms on the biofilm recovered from the deployed passive samplers. The hypothesis is that if there is ongoing microbial activity in the sediment that produces a stable isotope byproduct signature on the passive sampler, we should be able to detect known dechlorinating organisms in the biofilm.

3.1.6 Bioaccumulation into native benthic species and benthic community analysis. A predominant group of deposit-feeding benthic organisms (either polychaetes or bivalves) will be collected for PCB tissue analyses at 2 and 12 month intervals following application of SediMite. The goal is to collect enough tissue biomass to form three composites for each plot. This will involve a randomized collection from the treatment and control plots. Animals will be held overnight in clean site water to allow for depuration of sediment material in the digestive system. The animals will then be transferred to the UMBC laboratory for analyses.

To help evaluate possible adverse effects of SediMite application on the benthic community, the benthic community will be assessed using indices of abundance and community structure. Measures of abundance by taxa provide an indication of the reproductive success of the organisms and of the ability of organisms to maintain population numbers. Measures of community structure (diversity, species richness, evenness, dominance) all give insight into the ability of sediments to support benthic invertebrates. Samples will be collected from treatment and control plots at the end of the exposure period (test period). Three Eckman or ponar grabs will be collected from each treatment plot. These will be sieved in the field and the benthic invertebrates will be preserved in ethanol and taken to a laboratory for identification. Comparisons between treatment and control plots will involve a randomized stratified design and will employ parametric and non-parametric tests as appropriate for the data and the statistic.

3.1.7 Total Organic Carbon (TOC) and Activated Carbon measurement. TOC will be measured to assess the uniformity in the mixing of the carbon into the sediment. TOC measurement will be performed on sections of a sediment core taken from each of the locations. The sediment cores will be 2" in diameter and 1 ft deep from the sediment surface. We expect the bulk sediment TOC to be in the range of 1-5%. Thus, spatial variations in native sediment TOC may make it difficult to measure the bulk TOC increase caused by the addition to activated carbon to sediment. To improve our ability to delineate the added activated carbon a new method developed in our laboratory will be used to remove

interference with natural organic matter. We have developed a method based on a chemical oxidation technique to remove natural organic matter before subjecting the sediment sample to TOC measurement based on a high temperature oxidation. We have found that pre-treatment with chemical oxidation performs better than a low-temperature (375°C) oxidation step used by others to remove natural organic matter. The TOC analysis will be performed using a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). The sediment TOC analysis will follow an operating procedure recommended by the manufacturer. The sediment sample will first be homogenized in a clean ceramic mortar to a powder. One 0.5 gram sub-sample of the homogenized sediment from each core section will be placed in ceramic combustion boats. Inorganic carbon will be removed from the homogenized samples by adding 1 ml of concentrated hydrochloric acid to each sample in the boats. It is important to make sure that the entire sample is wetted by the acid. After 1 hr of reaction and evolution of carbon dioxide, the boats will be placed in an oven at 105 °C for 10 hours to remove the remaining hydrochloric acid before TOC measurement. Carbon in the sample is combusted to form CO₂ which is detected by a non-dispersive infrared gas analyzer.

3.1.8 PCB Aqueous Equilibrium measurement. Equilibrium studies will be performed to evaluate the change in PCB equilibrium partitioning from sediments after amendment with activated carbon in the field. The PCB aqueous partitioning measurements will be carried out in the UMBC laboratory with special attention to minimizing additional mixing of sediments during the test.

The equilibrium setup will consist of duplicate 1L glass bottles with Teflon-lined caps. Each bottle will be filled with 100g sediment and 900 ml of site water. The sediment will not be mixed into a slurry to avoid additional mixing of the carbon into the sediments beyond what was achieved in the field. The bottles will be placed on a slowly rotating shaker table (typically around 20 rpm) to produce mixing in the water phase without significant disturbance to the sediments. Sodium azide (1000 mg/L) will be added to the water to minimize biological activity. Equilibrium tests will be carried out for the untreated sediments to evaluate the approach to an apparent equilibrium by sampling the water phase for PCBs every two weeks for four months. Once the time required to reach an apparent equilibrium is determined, it will be used for all aqueous partitioning measurements. After reaching an apparent equilibrium, the bottles will be removed from the shaker table and allowed to settle. Settling of the colloidal particles will be aided by an alum flocculation method that has been demonstrated to remove colloids from the aqueous phase without altering the dissolved PCB concentrations (Ghosh et al., 2000). The alum flocculation is carried out by adding alum solution to the water to achieve 0.01M alum concentration and adjusting the pH to neutral with a solution of NaOH. The supernatant water is mixed with a glass rod slowly for 2 minutes taking care not to resuspend settled sediments. After alum addition and slow mixing, the bottles are allowed to settle for 24 hours in the dark. After colloidal particles have been settled from the water column, a 250 ml glass pipette is used to transfer the water sample into a glass separatory funnel. After transferring 750 ml of water, the glass pipette is rinsed with hexane and the rinsate is added to the separatory funnel. Surrogate PCB standards are spiked into the water sample in the separatory funnel. The water sample in the separatory funnel is then extracted with three 50 ml aliquots of hexane. The hexane extracts are dried over anhydrous sodium sulfate and concentrated for cleanup using silica gel.

3.1.9 Data analysis and statistical design/interpretation. The statistical design for testing the feasibility of activated carbon application involves one main factor or treatment:

1) Placement of activated carbon in the form of engineered pellets as a thin layer on the sediment followed by natural mixing into the bioactive zone.

The primary performance criteria used to evaluate the feasibility of activated carbon application involves pre and post-treatment measurement of the applied activated carbon in the treatment plots through TOC/AC analysis (in duplicate) of sediment core sections obtained from eight equally-spaced locations within each treatment plot. The pre-treatment analysis of sediment core sections will provide an assessment of background levels of TOC/AC measured in the treatment plots. A principal question addressed in the pre-treatment TOC/AC analysis of sediment cores is whether sediment TOC/ACs are homogeneous across the treatment plots. This will be accomplished using one-way analysis of variance (ANOVA) of the TOC data from each depth section. If the native TOC concentrations are highly variable, it could be a confounding factor for the assessment of the added activated carbon after treatment. Therefore, analysis planned will focus using a chemical oxidation pre-treatment step to separate natural organic carbon from the added activated carbon as outlined in the AC method description. The two post treatment monitoring events will sample sediments from the same locations in each treatment plot and the data analysis will involve evaluation of the treatment effect of activated carbon addition through placement as a layer. Because the sampling locations are fixed, paired difference t-tests will be performed to assess the significance of added activated carbon to each sediment cross section.

The statistical design for evaluating the effectiveness of activated carbon in reducing PCB bioavailability involves one main factor or treatment:

1) Addition and natural mixing of activated carbon into the top layer of sediment.

The primary performance criteria that will be used to evaluate the effectiveness of activated carbon in reducing PCB bioavailability are:

- i. ex-situ laboratory bipuptake in *L. plumulosus*
- ii. ex-situ PCB aqueous equilibrium measurement
- iii. in-situ porewater PCB measurement using POM passive samplers
- iv. tissue levels of PCBs in native species (polychaetes or bivalves) at 2 and 12 months

Each of these performance measures will be carried out at eight equally spaced locations within the treatment and control plots. Paired difference t-tests will be performed to evaluate how a PCB bioavailability measure is affected by treatment for any site.

We expect to find a heterogeneous distribution of existing PCB concentration in the top layer of sediments at the test site. However, the pre-treatment and the two post treatment monitoring will be performed at the same eight equally-spaced locations within the treatment and control plots, which is likely to reduce variability of PCB concentration of sediments obtained from each

location over the period of 2 years. Also, each of the measures of PCB bioavailability listed above will be normalized to PCB concentration in sediment measured at each sampling time. For example, the biouptake in *L. plumulosus* will be expressed as biota-sediment accumulation factors which are obtained by dividing the PCB concentration in organism by PCB concentration in the sediment at that location. Thus small differences in sediment PCB concentrations that may be observed over time at any one location will have little effect on the PCB bioavailability assessment. The PCB aqueous equilibrium measurement will be expressed as compound partition coefficient (Kd).

3.2 Tentative project timetable. The proposed research will be carried out in a three year period with the following timetable:

ACTIVITY	END DATE
1. Production of required quantity of SediMite and shipping to site	6/x/2009
2. Baseline sampling and marking of test plots in the field	7/x/2009
3. Application of SediMite in marked treatment areas in the field	7/x+1/2009
4. 2-month post application monitoring	9/x//2009
5. 1-year post application monitoring	7/x/2010

4.0 Performance Assessment

4.1. Performance Criteria

Table 4.1. List of performance criteria and descriptions

Performance Criteria	DESCRIPTION	Primary or Secondary
1) Ease of use	Based on field demonstration experience, the application technologies will be assessed in terms of its a) mobilization to a sediment plot, b) movement to another plot, c) delivery of SediMite to plot, and d) demobilization from sediment plots.	Primary
2) Distribution of AC in sediment	AC will be measured in sediment composite core sections to evaluate the dose and evenness of the distribution	Primary
3) PCB bioaccumulation in <i>L. plumulosus</i>	Biouptake in the marine amphipod <i>L. plumulosus</i> will be measured to assess the change in PCB bioavailability to benthic organisms after amending sediments with SediMite.	Primary
4) Aqueous equilibrium	Equilibrium studies will be performed to	Primary

measurement of Hg/Me-Hg/PCB/DDT	evaluate the change in PCB/DDT equilibrium partitioning from sediments after amendment with SediMite in the field.	
5) In-situ porewater assessment of PCBs	Passive samplers will be used to evaluate how surficial sediment porewater PCB concentrations in-situ and PCB dechlorination are impacted by SediMite treatment.	Secondary
6) Effect of SediMite on tissue levels of PCBs in native species and changes in benthic community	Native species will be collected at 2 and 12 month intervals for measurement of PCBs in tissues; three composites per plot are planned for each event. Benthic organisms will be sieved from quadrats taken in all five plots once before and twice after treatments. The benthic community structures that exist in each quadrat will be compared to evaluate effects of AC on benthic recolonization, community structure and organism growth.	Primary/Secondary
7) Scale up potential to full scale	Actual application rate of SediMite in the field will be monitored to assess the potential of scaling up of the technology to full scale. Bottlenecks of production rate will be identified.	Secondary

4.2. Performance confirmation methods

The effectiveness of the demonstration will be evaluated through the four primary performance criteria: Ease of Use, homogeneity of AC application, PCB bioaccumulation in test organisms, and aqueous equilibrium measurements. A successful demonstration would result if the following performance metrics are achieved:

- 1) The SediMite application devices are able to apply AC in the plots safely and with ease (qualitative)
- 2) SediMite is applied at the desired dose and the applied carbon remains in place after 1-year of deployment. (quantitative)
- 3) Significantly lower PCB concentrations are measured in test *organisms* in treated plots when compared to controls; (quantitative)
- 4) significantly lower PCB equilibrium concentrations are measured in treated plots when compared to controls; (quantitative)

APPENDIX 1: Bailey Creek Activated Carbon Treatability Study Report

APPENDIX 2: UMBC Laboratory Test Methods

APPENDIX 3: Health and Safety Plan