In-Situ PCB Bioavailability Reduction in Grasse River Sediments

Final Work Plan

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Grasse River Study Area Massena, New York
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SECTION 1
INTRODUCTION

1.1 GENERAL DESCRIPTION

This Work Plan describes a proposed pilot project to be conducted by Alcoa Inc. (Alcoa) that will evaluate a promising new technology for the remediation of polychlorinated biphenyl (PCB)-containing sediments in the lower Grasse River, Massena, New York (Figure 1-1). The lower Grasse River is currently under a fish consumption advisory from the New York State Department of Health due to elevated PCB levels found in fish, and results of site investigation work conducted to date indicate that the major source of PCBs to the fish is from sediments in the river which have been impacted by past discharges (Alcoa, April 2001). The technology proposed for this pilot study consists of the addition of activated carbon to the upper layer of the sediment bed. Recent studies by Ghosh, Luthy and others have demonstrated that this technology is effective in reducing PCB bioaccumulation in benthic organisms, PCB release into the water column, and PCB uptake by semi-permeable membrane devices (SPMDs). Based on these results, the addition of activated carbon to sediments in the lower Grasse River has the potential to greatly reduce PCB leaching and bioavailability in the treated in-situ sediments. This, in turn, is expected to result in the reduction of PCB levels in both water column and fish of the lower Grasse River.

1.2 RECENT STUDIES ON ACTIVATED CARBON

Several recent studies have demonstrated that the addition of activated carbon to in-situ sediments is effective at reducing the bioavailability of PCBs in sediments. Zimmerman et al. (2004) and Millward et al. (2005) found that amending activated carbon to marine sediments resulted in a greater than 80 percent (%) reduction in PCB bioavailability to benthic organisms. Laboratory work with sediment from the lower Grasse River has shown that adding 2.5% activated carbon (by weight) reduced PCB uptake in the freshwater clam Corbicula fluminea by 95% (Luthy, unpublished) and in the freshwater oligochaete Lumbriculus variegatus by 93%.
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(Sun and Ghosh, 2005). Zimmerman et al. (2004) have demonstrated that addition of activated carbon to sediments from San Francisco Bay reduced the bioaccumulation of PCBs in *Macoma* clams by 69%, *Leptocheirus* amphipods by 72%, and *Neanthes* worms by 83% after a one-month period (Millward et al., 2005). Zimmerman et al. (2005) found biouptake reductions in 56-day exposure tests of up to 90 to 92% for Hunters Point sediment depending on activated carbon particle size. Zimmerman et al. (2004) also found that sediment treated with activated carbon attains equilibrium PCB concentrations 85 and 92% lower than untreated sediment in one-month and six-month contact experiments, respectively. Tests using freshwater sediments from the Grasse River, New Bedford Harbor and the Hudson River have shown 90 to 99% reductions in equilibrium aqueous PCB concentrations after addition of activated carbon (Ghosh, unpublished).

In-situ bioavailability reduction using carbon amendment may be applicable at sites where bioaccumulation reduction can reduce exposure and consequent risk to acceptable levels. Stanford University and the University of Maryland Baltimore County (UMBC) are currently performing a demonstration of this novel risk-reduction approach in the field at Hunters Point in San Francisco Bay, California through funding from the Navy and the Department of Defense. This new approach to management of contaminated sediments is also being tested for freshwater sediments from four Areas of Concern in the Great Lakes in the laboratory-scale study by UMBC through a project funded by the Great Lakes National Program Office.

1.3 APPLICABILITY TO THE LOWER GRASSE RIVER

Alcoa has conducted extensive long-term data collection efforts of sediment, water and fish, as well as performed numerous field and laboratory studies, to more fully understand PCB fate and transport within the lower Grasse River system. Results of the investigative studies indicate that ongoing source control efforts by Alcoa have been successful in significantly reducing the level of PCBs discharged to the river, and that currently the major source of PCBs to the water and fish is from sediments in the river which have been impacted by past discharges (Alcoa, April 2001).
In addition to these investigative efforts, Alcoa has conducted several in-river studies to evaluate various remedial technologies aimed at reducing PCB levels in sediment, water, and fish. The in-river studies have included a dredging removal action, a large pilot-scale capping study, and most recently a larger-scale pilot study of dredging and various capping designs. Conducted in 1995, the dredging removal action addressed a 1-acre area of sediments with elevated PCB concentrations located directly off-shore from the plant’s main wastewater discharge at Outfall 001 (Blasland, Bouck & Lee, Inc. [BBL], December 1995). The Capping Pilot Study (CPS), conducted in 2001, evaluated different cap material types and placement techniques in a 7-acre area of the river (Alcoa, April 2002). Annual monitoring of the CPS area in May 2003 showed that a portion of the pilot cap and some underlying sediments had been disturbed by scouring during a significant ice jam in the river (Alcoa, April 2004). Based on these results, Alcoa has worked with the United States Environmental Protection Agency (USEPA) to develop a follow-up investigation plan that included further evaluation of the potential remediation options to be considered for the lower Grasse River. The Remedial Options Pilot Study (ROPS), which was completed in 2005, consisted of the removal of sediment that was primarily focused on a 4.1-acre area of the river, as well as the construction of post-dredge, thin-layer and armored caps in portions of the river.

The nature of the sediment PCB source to the lower Grasse River makes it an ideal candidate for the novel treatment approach of in-situ PCB binding using activated carbon technology. The widespread, diffusive flux from the surface sediments is the primary source of PCBs to the water column and, ultimately, the fish (Alcoa, April 2001). As demonstrated in several recent studies, application of this material to the biologically active layer of PCB-containing sediment can be an effective method for sequestering PCBs in the activated carbon matrix and reducing the bioavailability of PCBs in the treated sediments. This, in turn, is expected to reduce the PCB flux from the treated sediments into the overlying water column and lead to lower PCB levels in fish.

The activated carbon technology also offers the benefit of a minimally altered river bathymetry after treatment, since only a thin layer of activated carbon is required for treatment (relative to a traditional cap). The need for only a thin layer of activated carbon may be an
attractive feature for the remediation of shallow near shore areas, where the desire to maintain water depths exists, or on the steeper side slopes, where the construction of a traditional cap may be difficult to implement. This technology can also be applied to deeper portions of the channel where minimally altered water depths are desired.

The study proposed herein consists of a pilot remediation effort using activated carbon to sequester PCBs in sediments at the lower Grasse River site. This work will entail pilot scale testing in an approximate 0.5-acre site in the lower Grasse River using activated carbon amendment to sediments, followed by a two-year physicochemical and biological assessment to evaluate the effectiveness of the treatment. The decision to extend the physicochemical and biological assessments to a third year will be based upon the results of the monitoring conducted over the first two years. Ultimately, results of these studies can be incorporated into the modeling framework that exists for the lower Grasse River to evaluate potential system-wide reductions associated with a hypothetical larger-scale application of this technology to river sediments. The physicochemical evaluations will investigate desorption and equilibrium partitioning characteristics of PCBs in the amended sediment. Biological monitoring will include benthic community assessments (pre- and post-treatment), similar to those conducted in 2005 as part of the ROPS (Alcoa, February 2005), as well as field and laboratory measurements of PCB biouptake in benthic organisms.

Alcoa recognizes that approval of this pilot study by the Agencies does not indicate acceptance of this approach as the final remedy for the part of the river covered by the pilot study. Alcoa also recognizes that, if not selected as a component of the final remedy, it may be required to remove the materials placed during this pilot study and restore the area.

1.4 DOCUMENT ORGANIZATION

Section 1 of this Work Plan provides an introduction to this pilot study, as well as a brief background on activated carbon technology and its suitability for application to the lower Grasse River. Section 2 describes the objectives and design for this study, and summarizes the various components to be conducted during the study. Implementation of the field activities are
discussed in Section 3. Section 4 presents an overview of the monitoring program to be conducted prior to, during, and after the activated carbon application. The overall schedule for the project is provided in Section 5. Finally, several documents are included as appendices to this work plan. Appendix A contains published manuscripts detailing various applications and studies of the activated carbon technology. Appendix B contains the UMBC standard operating procedures for the analytical methods to be employed during the study. Appendix C contains the UMBC method description and standard operating procedures for the in-situ PCB biouptake studies, while those for the laboratory studies (i.e., PCB aqueous equilibrium studies, PCB desorption rate studies, and ex-situ PCB biouptake studies) are included in Appendix D.
SECTION 2
OBJECTIVES AND APPROACH

2.1 OBJECTIVES

The activated carbon pilot study has the following objectives:

1) Evaluate the ability to deliver activated carbon into in-place sediments and determine the extent to which PCBs and sediments are released to the river during application.

2) Measure the change in PCB bioavailability to deposit-feeding benthic organisms that results from activated carbon amendment.

3) Evaluate the changes in PCB desorption kinetics and equilibrium partitioning from sediments that results from activated carbon amendment.

4) Evaluate whether the erosion potential of the sediments is altered by activated carbon amendment.

5) Evaluate changes to the benthic community, if any, as a result of this in-situ treatment application.

A summary of the proposed pilot study is presented below. Additional details regarding the individual components of the study are presented in subsequent sections.

2.2 STUDY DESIGN

This study consists of two components: 1) off-site land-based testing of various application and mixing techniques; and 2) in-river application and mixing of activated carbon to sediments in an approximate 0.5-acre portion of the lower Grasse River using the most effective application and mixing technique or techniques, as determined during the land-based testing. A two-year post-treatment physicochemical and biological assessment will be performed to assess the effectiveness of the treatment in reducing the bioavailability of PCBs in the treated
sediments. The decision to extend the physicochemical and biological assessments to a third year will be based upon the results of the monitoring conducted over the first two years.

2.2.1 Site Selection

The original plan was to conduct the pilot study in a shallow near shore area of the river (i.e., between T17 and T19) with surface sediment PCB concentrations in the 25 to 50 parts per million (ppm) range. However, sediment sampling results from this and other near shore areas of the river indicated PCB levels in these areas are low and often below the detection limit. Therefore, an investigation into moving the pilot study into a deeper water area within the main channel of the river was conducted. Sediment sampling was conducted in four main channel areas in June and July 2006 to facilitate identification of a suitable location for the study. PCB results from these sampling events were shared with the Agencies. The data from these sampling efforts were used to select the proposed pilot study area location identified below.

The proposed location is an approximate 0.5-acre area (75 feet wide by 500 feet long) along the northern portion of the main channel of the river between sediment probing Transect T44 and T45, approximately 3.5 miles downstream of Outfall 001 (Figure 2-1). This area was selected over the other three candidate main channel areas for several reasons: 1) average surface sediment PCB concentrations in this area are similar to or higher than those in the other candidate areas; 2) the study area is situated within a contiguous fine sediment deposit, which will help to reduce the potential for encountering rocks, boulders, etc. that are often found close to the sediment surface in coarse sediment deposits; 3) the river is wider and shallower in the proposed study area relative to the other candidate areas, meaning less of the river cross-section will be closed off with silt curtains during the study; and 4) the river bottom at this location is more regular than that in other areas, which will simplify placement and mixing operations during the study.

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1 The Agencies consist of the U.S. Environmental Protection Agency (USEPA), its technical consultants, New York State Department of Environmental Conservation (NYSDEC), New York State Department of Health (NYSDOH), St. Regis Mohawk Tribe (SRMT), and National Oceanic and Atmospheric Administration (NOAA).
The proposed location is situated in about 15 to 17 feet of water and has a relatively flat river bottom. Sediments in this area are primarily composed of silt, fine sand, and trace organics. Probing measurements of sediment thickness from this area in 2006 indicate that about 1.2 to 4.4 feet of sediment are present.

Four of the 15 sediment samples collected from this reach of the river (as part of the June/July 2006 main channel candidate area sampling) fall within the proposed pilot study area: A4-1; A4-3; A4-5; and A4-7 (see Figure 2-1). The surface (i.e., top three inches) sediments in these cores contained 13.1, 5.7, 4.2 and 6.6 ppm dry weight PCBs, respectively. The other 11 samples collected in the vicinity of the proposed pilot study location in 2006 contained surface PCB concentrations of 2.5 to 8.1 ppm, while samples collected historically (1991 to 2004) from this general area contained surface PCB concentrations of 0.7 to 14.3 ppm. The physical and chemical properties of the surface sediments collected from this general area are presented in Table 2-1.

No remedial activities have been conducted at this location in the past. This area is not expected to be impacted during significant ice jams such as that observed in the river during 2003, as impacts associated with this event were primarily limited to the reach of the river situated further upstream (Alcoa, April 2004).

Further characterization of this site will be conducted as part of the baseline monitoring prior to carbon application (see Section 4).

2.2.2 Study Components

The proposed pilot study area is divided into three sub-areas: an approximate 75-ft by 150-ft mixed treatment area; an approximate 50-ft by 100-ft unmixed treatment area; and an approximate 50-ft by 100-ft initial testing area (Figure 2-2). These sub-areas are separated by 50-ft buffer zones (within which no activated carbon will be placed) to reduce the potential for confounding study results.
The pilot study will be conducted in two phases. The initial trial phase of the study will focus on testing various application and mixing techniques in a controlled upland (e.g., tank) setting at the contractor’s facility, followed by field-scale demonstrations in an approximate 50-ft by 100-ft area at the downstream extent of the pilot study area (Figure 2-2). Collectively, these initial trials will identify the most effective method for delivering the activated carbon to the target sediments. There is a significant benefit in the initial demonstration trials, as they will provide the next level of understanding before mobilizing equipment and placing activated carbon in the river, thus enhancing the value of this pilot demonstration. Application and mixing techniques that may be tested (either in bench-, land-, or field-scale trials) as part of this study are identified below.

1) Hydraulic slurry pumped through injection nozzles attached to tines that penetrate the sediment surface (with or without enclosing shroud). Figure 2-3 presents photographs of a partially fabricated “sled” containing two staggered rows of approximately 20 tines each, with activated carbon injection nozzles mounted on each tine. This unit would be continuously towed along the river bottom during application of the activated carbon. Each tine is able to rotate approximately 90 degrees in the direction of travel, independent of the other tines, so that the tines can pass over debris encountered within their path without affecting the performance of the other tines. Two additional rows of spring-loaded vertical tines without injection nozzles are positioned at the back end of the sled and will provide additional mixing of the activated carbon with the existing sediments. Various flexible and rigid enclosing shroud configurations may be tested during the land-based trials based on the degree of resuspension generated during operation.

2) Hydraulic slurry pumped or gravity fed into enclosing shroud with rotational mixer. Figure 2-4 presents conceptual drawings of the rotational mixing device and enclosing shroud. The shroud will be positioned on the river bottom and activated carbon will be applied within the shroud through a series of inlet ports. Following carbon addition, mixing with underlying sediment will be performed using a system of five staggered
rows (front to back within the shroud) of approximately rotating mixers constructed from heavy-duty wire rope attached to a rotating axle (Figure 2-4e). This unit would remain stationary throughout the activated carbon application and mixing cycle for a footprint on the river bottom. After application of the activated carbon and mixing with the underlying sediments, the unit would be repositioned to an adjacent footprint and the cycle of carbon application and mixing repeated.

3) Hydraulic slurry pumped or gravity fed into enclosing shroud without mixing device. Within the unmixed treatment area (see Figure 2-2), the activated carbon may be pumped or fed by gravity into a rigid or flexible enclosing shroud without any internal mixing. In this application, the activated carbon would be allowed to settle on top of the existing sediment surface without mechanical mixing. A shroud similar to that described above and shown in Figure 2-4a will be used for this application.

4) Rake and other similar mechanical mixing systems. Depending on the condition of the river bottom following carbon application and mixing using one of the devices described above, it may be necessary to perform additional mixing and/or leveling/smoothing using a rake or other similar device. Figure 2-5 presents conceptual drawings of such a device that would be towed over the treatment area following application of the activated carbon.

Note the application and mixing techniques listed above are initial candidates for the land-based testing that have been identified at this time. Additional techniques identified subsequent to the submission of this work plan may also be considered during this initial land-based testing. In the event that the land-based testing indicates difficulty in achieving or verifying the desired placement results, clean sand may be mixed with the activated carbon prior to the application to the river sediments. In this instance, a local borrow site for the sand will be identified, sand samples will be collected, and the sand will be physically and chemically characterized consistent with the cap material testing employed during the ROPS to ensure the
sand is suitable for placement in the river. The identified source of the sand and the results of the pre-placement testing will be reviewed with the Agencies prior to use in the field.

The treatment application and mixing technique that proves most successful during the initial trials will then be carried forward into the full-scale program. The full-scale pilot program will consist of four components:

1) Application of activated carbon to the target sediments located in the mixed and unmixed treatment areas (see Figure 2-2).

2) Mechanical mixing of the activated carbon into the surficial sediments\(^2\) located in the approximate 75-ft by 150-ft area at the upstream extent of the pilot study area (mixed treatment area; see Figure 2-2). The activated carbon will not be mixed into the sediments within the approximate 50-ft by 100-ft area in the middle of the pilot study area (unmixed treatment area; see Figure 2-2); this portion of the study area will be used to evaluate the incorporation of this material into the native sediments through natural processes (e.g., biological mixing).

3) In-field monitoring prior to, during, and after application.

4) Laboratory studies using sediment collected before and after activated carbon treatment.

A brief description of each study component is provided below.

\(^2\) The goal is to mix the applied activated carbon into the surface sediments (i.e., the top three inches of the sediment). However, given the vertical control tolerances of the proposed methods, mixing may extend to a depth of up to six inches below the sediment-water interface. For this reason, a target activated carbon dose concentration of 2.5% by weight when mixed into the top six inches of sediment will be applied during the study.
Following initial baseline surveys of the pilot study area, activated carbon will be applied to the surface of the existing sediment in the mixed treatment area by delivering activated carbon (or a mixture of activated carbon and sand, if needed) using one of the placement techniques described above (to be determined during the initial trials, as outlined above). Rotational equipment, rake systems, or other mechanical devices may be used to mix the activated carbon into the surface sediments. Additional details pertaining to implementation of the pilot study are provided in Section 3.

Following completion of the application of activated carbon within the mixed treatment area, activated carbon will be applied above the existing sediment surface in the unmixed treatment area. The activated carbon will not be mixed into the existing sediments in this area; this portion of the study area will be used to evaluate the incorporation of activated carbon into the native sediments through natural processes (e.g., biological mixing). Note that an approximately 50-ft buffer zone will be maintained between the mixed and unmixed treatment areas within which no activated carbon will be placed.

Field monitoring will be conducted prior to, during, and after activated carbon application. Monitoring will include water column sampling (during), sediment sampling (pre, during, post), benthic community and aquatic habitat assessments (pre, post), field PCB biouptake studies (pre, post), and testing of sediment erosion potential (pre, post). Laboratory studies will be conducted by UMBC using both treated and untreated sediments to determine PCB desorption rates, aqueous equilibrium, and PCB uptake rates by benthic worms. Details on the field and laboratory studies are presented in Section 4.
SECTION 3
IMPLEMENTATION

3.1 GENERAL

As identified in Section 2.1, this pilot study will evaluate the ability to apply (and mechanically mix, in certain areas of the study area) activated carbon to the target sediments in the field. This section describes the logistics of the implementation portion of the pilot study.

3.2 APPLICATION AND MIXING METHODS

The activated carbon to be applied during this study will be Calgon Carbsorb 50x200 granular activated carbon (75 to 300 microns), derived from bituminous coal. It will be purchased and likely delivered to the site in bags on pallets via flat bed trailer. It is anticipated that, due to the limited volume of materials necessary for this pilot study, all materials will be staged at the ROPS staging area in the vicinity of Outfall 001.

Activated carbon will be applied from floating marine equipment. The activated carbon will be first saturated (“wetted”) with water overnight before application. The wetted carbon will then be delivered to the target area using either hydraulic injection equipment (e.g., injection tines) or mechanical mixing equipment (e.g., roto-tiller) as discussed in Section 2.2.2, depending on the results of initial trials performed by the contractor and the portion of the study area (mixed or unmixed treatment area). As noted above, the activated carbon will be applied directly to the surface of the existing sediment and will not be mixed into the sediments within the unmixed treatment area; this portion of the study area will be used to evaluate the incorporation of the activated carbon into the native sediments through natural processes (e.g., biological mixing).

The horizontal and vertical coordinates of the placement and mixing device(s) relative to the sediment surface within the study area will be constantly tracked using Windows Offshore
Positioning Software (WINOPS) or equivalent during mixing to ensure precise and effective mixing of the activated carbon into the sediment.

The quantity of the activated carbon placed within a given area will depend on the target dose application concentration (2.5% by weight when mixed into the top 6 inches of existing sediment) and the method of delivery, as determined during the land-based testing. This target placement quantity will be verified during and immediately following application through a combination of placement rate tracking, visual observations, and laboratory tests to determine the percentage of carbon within or above the target sediments. In-situ samples of the carbon/sediment will be collected using sediment core sampling and other procedures (i.e., specific to the delivery method), as appropriate and described in Section 4.2.

It is anticipated that a silt curtain system similar to that used in the ROPS armored capping operations will be used to enclose the target area to the extent practicable to minimize potential water quality impacts associated with the mixing process.

3.3 RIVER ACCESS

In-river activities associated with this proposed pilot study will be conducted from small floating marine equipment. Equipment, materials and manpower resources used for preparation (i.e., silt curtain deployment, see below) and implementation activities will be transported to the pilot study location via over-land trucks. Floating equipment (barges or other floating platforms, work boats, etc.) will be launched into the Grasse River via crane from Alcoa’s facility. Mixing/application equipment and activated carbon will be housed on the barge/floating platform. It is anticipated that the staging area located near Outfall 001, which was originally established for the Non-Time-Critical Removal Action (NTCRA) work in 1995 and used during the 2001 CPS and the 2005 ROPS, will serve as the access point to the river. Since the staging area already has an access road, utilities, and river access, it is not anticipated that additional work will be required for this pilot project.
3.4 CONTAINMENT SYSTEMS

The pilot study area will be isolated using a silt curtain containment system to minimize the release of any fine sediment and/or activated carbon into the river channel during the mixing process. It is proposed that a single L-shaped silt curtain similar to that used during the armored capping activities conducted as part of the ROPS be used to maximize containment of any material that may be resuspended during application and mixing of the activated carbon with the in-situ surface sediment. This silt curtain design required significantly less maintenance than the design used for the ROPS main channel dredging component. An approximate 150-ft length of curtain will be situated about 100 ft downstream of the initial test area (perpendicular from shore) and then extend approximately 600 ft upstream (parallel to river flow and about 50 ft upstream of the mixed treatment area). The silt curtain will be floated at the water surface and extend down to about 1 to 2 feet above the river bottom. Consistent with the CPS and ROPS studies, these curtains will remain in place until such time that the work activities are complete and conditions within the curtain have returned to normal as indicated by turbidity readings.

3.5 SURVEY CONTROLS

All construction activities will be conducted using vertical and horizontal control that will be monitored through the use of a global positioning system (GPS) or differential GPS (DGPS) (i.e., WINOPS or equivalent). The GPS system will be used to locate the barge and associated equipment during the activated carbon application.
SECTION 4
MONITORING PROGRAM

4.1 OVERVIEW

Monitoring activities associated with the pilot study were designed to achieve the objectives presented in Section 2, and will include one baseline survey, one during application survey, and two post-treatment surveys. The decision to conduct a third post-treatment survey will be based on the results of the first two post-treatment surveys. Baseline monitoring will be conducted to establish pre-treatment conditions for comparison to future monitoring results to assess the achievement of the project objectives. Monitoring to be performed during the baseline survey includes the physical and chemical characterization of target sediments, a benthic community assessment, qualitative aquatic habitat survey, in-situ PCB biouptake study, and erosion potential testing. During-application monitoring will consist of water column monitoring to provide information pertaining to potential water quality effects associated with the treatment process, as well as sediment core sampling to verify the target thickness of the applied activated carbon has been achieved. Post-treatment monitoring will be performed approximately 12 and 24 months after activated carbon application to assess the effectiveness of the application/mixing process, the erosion potential of the treated sediments, recolonization of the pilot study area by benthic organisms, re-emergence of vegetation (if noted), and reduction in PCB bioaccumulation in benthic worms. Sediment cores to be used in the laboratory aqueous equilibrium and PCB uptake experiments will also be collected during these surveys. The proposed monitoring schedule is as follows:

- July – August 2006: baseline monitoring; trial runs for caged worms
- September – October 2006: in-situ application; during-construction monitoring
- Approximately 12-months post-treatment [July – August 2007]: post-treatment monitoring
- Approximately 24-months post-treatment [July – August 2008]: post-treatment monitoring
Since the proposed monitoring is identical for the baseline and post-treatment (i.e., 12- and 24-month) surveys, details pertaining to the monitoring activities are presented by monitoring component below.

4.2 FIELD INVESTIGATION

Field monitoring will include PCB, TOC and microscopy analysis in sediment cores to evaluate the uniformity of carbon delivery and mixing in the target surface sediments; water column monitoring during the application process to evaluate potential impacts on water quality associated with the application/mixing process; sediment core collection and visual observation to verify the target thickness of the applied activated carbon has been achieved; erosion potential measurements in sediment cores to evaluate the erosion properties of the sediment before and after carbon treatment; benthic surveys to measure changes in the benthic community due to carbon application; qualitative vegetation survey to document the types of vegetation present in the study area; and in-situ PCB bioaccumulation studies to monitor reductions in PCB uptake in benthic worms. A summary of the various monitoring components of the study are provided in Table 4-1. Each of these components is discussed in more detail below.

4.2.1 Sediment Sampling (Physical and Chemical Characterization)

Sediment cores will be collected for physical and chemical characterization during the baseline and two post-treatment surveys. During these three sampling events, sediment cores will be collected as follows (see Figure 4-1 for sample locations):

1) One sediment core\(^3\) will be collected (to refusal) from each of 9 evenly spaced locations within the pilot study area; six from the mixed treatment area (M1 to M6) and three from the unmixed treatment area (U1 to U3). These nine cores collected during the baseline (pre-treatment) survey will be used to characterize TOC and PCB levels in the top 12 inches of the treated and untreated sediments. Microscopy

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\(^3\) The size of the sediment coring apparatus to be used during the sediment sampling has not been determined at this time, but will selected based on the sample volume requirements necessary to complete the planned analyses.
examinations will also be performed on these cores to assess the extent of mixing of the activated carbon with the native sediments. Sediment core samples obtained during the two post-treatment surveys will be analyzed for TOC and subject to microscopy examinations.

2) One six liter (L) bulk sample of the top 3 inches of sediment will be collected from each of the six locations in the mixed treatment area (M1 to M6) using a box corer or similar device. Sediment samples from each locations will be used in the laboratory studies (i.e., aqueous equilibrium, PCB desorption, and PCB uptake studies).

The sediment cores described in #1 above will be segmented into six intervals: 0 to 1.5 inches; 1.5 to 3 inches; 3 to 4.5 inches; 4.5 to 6 inches; 6 to 9 inches; and 9 to 12 inches. All sample intervals will be submitted to UMBC for TOC analysis, microscopic examination, and PCB congener quantification. A description of each analysis is provided below. Details regarding the use of sediment samples in the aqueous equilibrium, PCB desorption, and PCB uptake studies are provided in Section 4.3.

**TOC Analysis**

Each of the sediment core sample intervals (as described above) will be analyzed for TOC by UMBC to assess the uniformity in the mixing of the carbon into the sediment. Since the natural TOC in the native sediments is in the range of 1.7 to 7.2%, it may be difficult to measure the bulk TOC increase caused by the addition of activated carbon to sediment. Therefore, to improve the ability to delineate the added activated carbon, two pre-treatments will be tried: 1) sieving to obtain the size fraction matching the size fraction of activated carbon added to the sediments; and 2) use of a low temperature pre-combustion method to separate natural organic carbon from the added activated carbon. Both pre-treatment methods will be evaluated for the site sediments before application during the monitoring studies.

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 milliliter (mL) of concentrated hydrochloric acid to each sample in the boats. After 1 hour of reaction and evolution of carbon dioxide, the boats will be placed in an oven at 105 degrees Celsius (°C) for 10 hours to remove the remaining hydrochloric acid before TOC measurement. Carbon in the sample is combusted to form carbon dioxide, which is detected by a non-dispersive infrared gas analyzer.

Quality assurance (QA)/quality control (QC) samples will include one blind duplicate per 20 sediment samples collected.

Microscopic Examination of Sediment Core Sections

Sub-samples of the sediment core sections used for TOC analysis will be examined by UMBC under an optical microscope to evaluate the abundance of activated carbon particles and corroborate the findings from the TOC analysis of the core sections. For example, if a high TOC value is obtained in a sample, microscopy analysis can confirm if the increase appears to be caused by abundance of activated carbon particles or from high levels of other natural organic particles such as wood or detritus. Microscopy analysis will be performed in visible light using a Leica MZ16 stereo microscope with an attached Canon EOS 10D digital camera. Sample images of river sediment versus activated carbon are shown in Figure 4-2.

PCB Analysis

Each of the individual sediment core sample intervals (as described above) will be analyzed for PCBs by UMBC to assess concentrations in the sediment prior to and after activated carbon application. Sediment PCBs will be extracted following the USEPA Method 3550B, and cleaned using USEPA Method 3630C (silica gel cleanup), Method 3665A (sulfuric acid cleanup), and Method 3660B (sulfur removal with copper). An Agilent gas chromatograph (Model 6890) with a fused silica capillary column (HP-5, 60 m x 0.25 mm ID, 0.25 µm film
thickness) and a micro electron capture will be used for analysis. The PCB calibration method is based on the original PCB congener method developed by USEPA (Mullin, 1994). This method is identical to the one being used as part of a USEPA GLNPO project quality assurance project plan entitled Assessment of AOC Sediments for Activated Carbon Treatment (Ghosh, 2004); details regarding the PCB extraction, cleanup, and analysis are provided in Appendix B.

QA/QC samples will include one blind duplicate and one matrix spike (MS)/matrix spike duplicate (MSD) sample per 20 sediment samples collected. The blind duplicate and MS/MSD will be analyzed for PCB (congener). If sampling is conducted with non-disposable equipment, rinse blank samples are to be collected before and after sampling and analyzed for PCB (congener).

4.2.2 **Water Column Monitoring**

The water column will be monitored daily during activated carbon application at four locations (one upstream of, one adjacent to, and two downstream of the pilot area) during-application to assess the immediate affects of construction on water quality (see Figure 4-2). The upstream monitoring location will be situated at T43, approximately 500 feet upstream of the pilot study area, and will serve as the “background” location for the study. One station situated adjacent to the pilot area and another immediately downstream of the pilot study area will serve as the local monitoring stations, and will be used to identify any potential near-field releases of PCBs and/or TSS during the study. The downstream station will be situated at T46, approximately 500 feet downstream of the pilot area, and will serve as the far-field monitoring location for the study.

Consistent with the transect monitoring performed during the 2005 ROPS, the total water column depth will be measured using a depth finder, and grab samples will be collected from three depths (0.2, 0.5, and 0.8 times the total water column depth) at each of three equally-spaced locations across the upstream (T43) and downstream (T46) transects, resulting in a total of nine grab samples. For the two local monitoring stations, grab samples will be collected from the three depths (0.2, 0.5, and 0.8 times the total water column depth) at each discrete monitoring
location (for a total of three grab samples per location). Samples will be collected using a Kemmerer stainless steel sampler, composited by location, and submitted to the Alcoa ChemLab for PCB (Aroclor, unfiltered) and total suspended solids (TSS) analyses. If stratification is observed at any of the sampling locations, as determined by comparison of water temperature and specific conductivity measurements in the surface and deep sample locations (i.e., 0.2 and 0.8 times the total water depth, respectively), samples will be composited accordingly to reflect the two water masses (e.g., if the water column is stratified between the 0.5 and 0.8 sampling depths, the 0.2 and 0.5 grab samples will be composited and analyzed and the 0.8 grab sample will be analyzed separately). Water temperature, dissolved oxygen (DO), specific conductivity, pH and turbidity measurements will also be collected at each sampling depth at all locations.

QA/QC samples will include rinse blank samples before and after sampling, one blind duplicate and MS/MSD sample per 20 water column samples. The blind duplicate will be analyzed for PCB (Aroclor, unfiltered) and TSS; the MS/MSD samples and rinse blanks will be analyzed for PCB (Aroclor).

Consistent with previous site work, a maximum turbidity level of 25 nephelometric turbidity units (NTUs) over background (i.e., as measured at T43) will be imposed at the downstream sampling location (i.e., T46). Exceedances of this level will result in implementation of corrective action measures to reduce turbidity. Results from the locations immediately adjacent to the silt curtain (also monitored for turbidity) will be used as an early warning indicator to proactively adjust construction activities to mitigate the potential for downstream exceedances.

As indicated in Section 3.4, turbidity will be monitored within the silt curtained area after application of the activated carbon is complete to evaluate conditions prior to removal of the silt curtains.
4.2.3 Sediment Sampling (for Verification of Target Thickness and Adequate Mixing)

Sediment cores will be collected, as needed, throughout the pilot study area during and immediately after: 1) placement of the activated carbon (to verify that the minimum target placement thickness has been achieved); and 2) mixing of the activated carbon with the in-situ sediments (to verify complete mixing). Sediment push cores will be collected using Lexan tubing such that the top 6 to 12 inches of sediment are obtained. Verification of the target thickness (after placement) and mixed depth (after mixing) will be accomplished through the visual inspection of the sediment cores.

4.2.4 Erosion Potential Testing

Sediment cores will be collected during the baseline and two post-treatment surveys for testing of sediment stability before and after treatment with activated carbon. Duplicate sediment cores (of at least six inches in depth) will be collected at each of five locations within the proposed pilot area; three locations (or six cores; M7 to M9) from the mixed treatment area and two locations (or four cores; U4 and U5) from the unmixed treatment area (see Figure 4-3). Erosion potential will be determined for each core using a shaker apparatus, following the same methodology that was used during previous testing conducted on lower Grasse River sediment in 1998, 2000, and 2002 (Alcoa, April 2001; Alcoa, September 2003). Data generated using this method will be comparable to the results from testing of native lower Grasse River sediment from 1998 and 2000 and on cap material placed during the CPS in 2001.

Two cores will be collected at each location, placed in the shaker apparatus, and subjected to various shear stresses (3, 5, and 9 dynes/square centimeter [cm²]) applied approximately one inch above the sediment-water interface. Each shear stress application will last ten minutes. Prior to the initial test and following each shear stress test, samples of the overlying water column will be collected and submitted to the Alcoa ChemLab for TSS analysis. TSS results will then be used, along with an empirical formulation, to determine the erosion potential for the treated and untreated sediments.
QA/QC samples will include one blind duplicate per 20 water samples collected. The blind duplicate will be analyzed for TSS.

### 4.2.5 Benthic Invertebrate Community Studies

Benthic invertebrate community studies will be conducted during the baseline and two post-treatment surveys (conducted within the same timeframe each year). Alcoa will review the results of the two years of post-monitoring with USEPA and jointly determine whether or not to extend the post-treatment monitoring for an additional year. Each survey will be conducted using modified USEPA Rapid Bioassessment Protocols (RBP; USEPA, 1999) in the area targeted for activated carbon application. This study will assist in evaluating any changes to the benthic community as a result of the in-situ treatment application.

Sediment samples will be collected from the 10 locations in the proposed pilot area for benthic invertebrate community studies (see Figure 4-1). This includes: one at an upstream background location; six from the mixed treatment area (M1 to M6); and three from the unmixed treatment area (U1 to U3). The upstream background location will be determined in the field and will be selected in an area with comparable substrate type and benthic habitat as the pilot study area (based on visual observation). Samples will be collected using a petite Ponar dredge (as used during the ROPS). Samples will be sieved and preserved in the field and will be sent to Chadwick & Associates, Inc. for sorting, identification and enumeration, including taxonomic identification to the lowest practical level, to provide standard measures of density, abundance, and diversity (i.e., quantitative measurements). RBP metrics to be evaluated will include measures of taxa richness, composition, tolerance, feeding, and habitat. Sediments from a colocated grab sample will be collected concurrently with each benthic sample and submitted for TOC and grain size analysis.

### 4.2.6 Qualitative Aquatic Habitat Survey

It is not anticipated based on previous observations of deeper water Grasse River areas that aquatic vegetation will be present in the pilot study area. This supposition will be confirmed.
by visual observation via boat using an underwater video camera. In the instance that aquatic vegetation is observed, a qualitative aquatic habitat survey will be performed for the pilot study area where feasible. The aquatic habitat survey will be performed using a modified RBP approach (USEPA, 1999). As possible, the survey will consist of a visual estimation of the presence and percent cover of different habitat types (primarily aquatic vegetation and different substrate types) observed along transects in the pilot study area. Observation will be performed via boat using an underwater video camera; no physical collection of aquatic vegetation will be performed. This evaluation will be supplemented by TOC and grain size data to be collected in association with the benthic community assessment, as described above. In addition, information regarding water depth and water quality (i.e., velocity, temperature, pH, conductivity, turbidity, and DO) will be collected.

The aquatic habitat surveys will be performed concurrent with the benthic community assessments described in Section 4.2.5.

4.2.7 In-Situ PCB Uptake Studies

PCB uptake in the freshwater oligochaete *Lumbriculus variegatus* will be measured in-situ to assess the change in PCB bioavailability to benthic organisms after amending sediments with activated carbon. This organism was selected for these tests based on the USEPA method for testing bioaccumulation in freshwater sediments (USEPA, 2000), as well as previous studies by Burton et al. (2005) and Sibley et al. (1999), which have demonstrated the use of this organism for in-situ bioaccumulation measurements in freshwater sediments. Bioaccumulation tests will be conducted before treatment, and during the 12-month and 24-month post-treatment surveys. Results from the before treatment in-situ studies will serve as the baseline conditions for comparison of the effects of activated carbon addition to the sediments. During these surveys, *L. variegatus* will be deployed in screened cages or bioassay chambers at six sampling locations (M1 to M6; see Figure 4-1) and at one upstream location (to be determined in the field) for an exposure period of 14 days, following the draft ASTM method described in the *Draft Standard Guide for Assessing Freshwater Ecosystem Impairment Using Caged Fish or Invertebrates* (Burton et al., 2002). In support of this in-situ approach, trial field deployments
will be performed in summer 2006 (prior to the baseline studies) to evaluate the logistics associated with deploying and retrieving the caged worms in the river and the survival of the worms in field conditions.

The in-situ deployment will follow the “surficial sediment and pore water exposure” method outlined in Burton et al. (2002). This in-situ testing method is designed to achieve organism exposure to surficial sediment and sediment pore water at the site. In-situ exposure chamber design will follow Burton et al. (2002) as shown in Figure 4-4. The chambers are constructed of cellulose acetate butyrate tubes 12.7 cm in length and 7 cm outside diameter in which two 4x8 cm openings are constructed and covered with a nylon mesh. At each sampling location, five replicate chambers will be deployed mounted together on a rack for ease of retrieval. One set of five test chambers will also be deployed at each sampling time at the chosen upstream location. To initiate the caged exposure, surficial sediment will be collected from the location and split for use in the in-situ and ex-situ bioaccumulation tests. Sediment will be placed in each chamber, filled with site water, and allowed to equilibrate and settle for 15 minutes before introduction of the worms. Due to the water depth of the pilot study area, the worms will not be flushed down an inlet tube as suggested in the ASTM draft method. The amounts of sediment and worms placed in each in-situ bioassay chamber will be similar to the amounts used for the ex-situ bioaccumulation studies for ease of comparison. The bioassay chambers will remain in the river for 14 days. After the exposure duration, the cages will be located and retrieved, and the worms separated from the sediment. The worms will be counted and placed in depuration chambers (for a 6-hour depuration period) before being frozen and shipped to the laboratory for PCB extraction and analysis. Congener level PCB analysis will be conducted on worms retrieved from each exposure chamber separately.

Total lipid content of the worms will be determined by spectrophotometric analysis, based on the original work performed by Van Handel (1985) and used by Landrum et al. (2004). For this analysis, the worms will be placed in an Econo-grind homogenizer (Radnoti Glass Technology Inc., Monrovia, CA) and crushed. A 2 mL solution of 1:1 chloroform:methanol will be used to extract the lipids from the worm tissue. The extract will then be transferred to a clean tube and reduced to dryness by heating at 100°C in a water bath (GCA Corp., Chicago, IL).
Then 0.3 mL concentrated sulfuric acid (95-98%) will be added to the tube and the sample will be heated again at 100°C 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 nanometers against the standards of 50, 100, 200 and 400 microliters per liter made from soybean oil (Fisher Scientific).

Additional details regarding the in-situ PCB biouptake studies are provided in Appendix C.

4.3 LABORATORY STUDIES

Laboratory activities will include a suite of physicochemical and biological tests conducted before and after the application of activated carbon to sediments to monitor the effectiveness of the field treatment in reducing PCB flux from sediments and uptake by epibenthic animals. Studies will include examination of aqueous equilibrium, PCB desorption rates, and measurement of PCB uptake in worms. These studies will follow methodologies previously employed by UMBC in other studies involving application of activated carbon to sediment. Details regarding each of the experimental studies are provided below.

4.3.1 PCB Aqueous Equilibrium

Measurement of PCB aqueous partitioning will be performed to evaluate the change in PCB equilibrium partitioning from sediments after amendment with activated carbon in the field. Using 1L of sediments collected from each of the six sampling locations within the mixed treatment area (M1 to M6), 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 sediments will not be mixed into a slurry to avoid additional mixing of the carbon into the sediments beyond what was achieved in the field. These tests will therefore be carried out in the dark (to prevent excessive growth of algae during the experiment), in one liter glass bottles containing a layer of 100 grams (g) of sediment in the bottom and one liter of water on the top.
The bottles will be placed on a slowly rotating table to produce some mixing in the water phase without any disturbance to the sediments. Sodium azide (1000 milligrams per liter [mg/L]) will be added to the water to minimize biological activity. For the untreated sediments, the approach to an apparent equilibrium will be monitored 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, a 0.5L water sample will be removed and analyzed for dissolved and suspended PCBs. The water will be transferred into a sample bottle and the suspended particulates will be removed by flocculating with alum based on previously published methods (Ghosh et al., 2000). The aqueous phase with dissolved PCBs will be extracted with hexane and analyzed. Additional details regarding the PCB aqueous equilibrium studies are provided in Appendix D.

### 4.3.2 PCB Desorption Rate

Measurement of PCB desorption rate will be done to evaluate the change in PCB desorption kinetics in sediments after amending with activated carbon in the field. PCB desorption kinetic studies will be conducted by UMBC using whole sediments collected via box cores at each of the six sampling locations within the mixed treatment area (M1 to M6) and will follow previously used procedures (Ghosh et al., 2003). Tenax beads (0.2 g, 40-60 mesh, Suppelco, Pennsylvania) and sediment sample (1.0 g) will be added to a 12 mL glass vial containing 10 mL of water and continuously mixed in a rotator. Sodium azide (1000 mg/L) will be added to the mixture to prevent biological growth. At each sampling time (2 hours, 6 hours, 1 day, 2 days, 5 days, 10 days, 30 days, and 60 days), the Tenax beads will be harvested by allowing the sediment to settle and the Tenax beads to float up. The Tenax beads containing the desorbed PCB will be scooped out of the test tube and fresh Tenax will be added. These studies will be conducted in duplicate. PCBs will be extracted from the Tenax beads by agitating the beads in 10 mL of hexane and acetone (50:50 mixture) for 12 hours and repeating two more times. The extracts will be combined and concentrated, cleaned using silica gel chromatography, and analyzed by gas chromatography-electron capture detection (GC-ECD). Additional details regarding the PCB desorption rate studies are provided in Appendix D.
4.3.3 Ex-Situ PCB Uptake in Biota

PCB uptake in oligochaetes (*L. variegatus*) will be measured to assess the change in PCB bioavailability to benthic organisms after amending sediments with activated carbon. The test method will be based on the USEPA *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates* (USEPA, 2000). Bioaccumulation tests will be conducted for the before treatment, 12-month and 24-month treated sediments from sampling locations M1 to M6 (see Figure 4-1). *L. variegatus* will be obtained from Aquatic Research Organisms, Hampton, New Hampshire. Worms will be exposed to the sediments in 400 mL glass beakers (150 mL sediment and 0.5 g worms per beaker; 4 replicates per sample) for 14 days and maintained at 23 ± 1 °C in a water bath with a 16 hour light:8 hour dark photoperiod. At the termination of the experiment, worms will be removed from the sediments and allowed to depurate for 6 hours in a clean beaker containing water. The depurated worms are then homogenized with excess sodium sulfate and extracted with a 50:50 mixture of hexane and acetone under sonication. Additional details regarding the ex-situ PCB biouptake studies are provided in Appendix D.

4.4 STATISTICAL DESIGN AND INTERPRETATION FOR THE FIELD INVESTIGATION

Statistical testing will be conducted using data collected during the pilot study to aid in the interpretation and evaluation of: 1) the feasibility of applying activated carbon on river sediments using large-scale equipment; and 2) the effectiveness of activated carbon in reducing PCB bioavailability.

The statistical design for testing the feasibility of activated carbon application involves two main factors or treatments:

1) placement of activated carbon as a thin layer on the sediment surface without further mixing; and
2) placement and mixing of activated carbon into the surface sediments.

The primary performance criteria used to evaluate the feasibility of activated carbon application involves pre- and post-treatment measurement of the applied carbon in the treatment plots through TOC analysis (in duplicate) of sediment core sections obtained from within each treatment plot (i.e., mixed and unmixed treatment areas). The pre-treatment analysis of sediment core sections will provide an assessment of background levels of carbon measured in the treatment plots. A principal question addressed in the pre-treatment TOC analysis of sediment cores is whether sediment TOCs 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. Highly variable native TOC concentrations could confound the assessment of the added activated carbon after treatment. Therefore, the TOC analysis planned will focus on the sediment particle-size range of the added activated carbon and may also use a low temperature pre-combustion method to separate natural organic carbon from the added activated carbon as outlined in Section 4.2.1. The 12- and 24–month post-treatment monitoring will sample sediments from the same locations in each treatment area and the data analysis will involve evaluation of the treatment effect of activated carbon addition through placement as a layer and placement with mixing. Since 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: the addition and mixing of activated carbon into the surface sediments. The primary performance criteria that will be used to evaluate the effectiveness of activated carbon in reducing PCB bioavailability are:

1) in-situ biouptake in L. variegatus;

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4 The unmixed treatment area is being used to evaluate the incorporation of activated carbon into the in-situ sediments through natural processes (e.g., biological mixing). Since the proposed methods for PCB bioavailability monitoring (i.e., in-situ and ex-situ biological testing and physicochemical testing) involve sample handling that would introduce mixing of the collected sediments and, thus, eliminate any deployment differences between the mixed and unmixed treatment areas. Therefore, PCB bioavailability monitoring has not been proposed for the unmixed treatment area and sediment sampling being performed to support these tests is only being conducted in the mixed treatment area.
2) ex-situ laboratory biouptake in *L. variegatus*;
3) PCB aqueous equilibrium measurements; and
4) PCB desorption kinetics measurements.

Each of these performance measures will be carried out at six equally-spaced locations within the mixed treatment area and at one upstream location. The in-situ and ex-situ biouptake measurements for each location will be performed in quadruplicate, as suggested in the standard method being followed. The aqueous equilibrium and desorption rate studies will be conducted in duplicate for each location. Paired difference t-tests will be performed to evaluate how a PCB bioavailability measure is affected by treatment for any sampling location. In addition, statistical testing following the method described in Ratkowsky (1983) will be evaluated for use in the analysis and interpretation of the desorption kinetics data.

The existing surface sediment PCB concentrations measured in the proposed pilot study area in July 2006 are variable, ranging from 4.2 to 13.1 ppm. However, the pre-treatment and 12- and 24–month post-treatment monitoring will be performed at the same locations within the mixed treatment area, which is likely to reduce variability of PCB concentrations of sediments obtained from each location over the 24-month period. 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. variegatus* will be expressed as biota-sediment accumulation factors which are obtained by dividing the PCB concentration in the organism by the 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 (*K*d) and the desorption kinetics data will be expressed as fraction desorbed as a function of desorption time.
SECTION 5
SCHEDULE

The proposed pilot study is scheduled to take place from summer 2006 through spring 2009, including baseline (pre-construction) monitoring, field application of the activated carbon, post-construction monitoring, laboratory studies and a summary report.

A detailed schedule for each of the study components is summarized below.

- July – August 2006: land-based testing of application and mixing techniques; baseline monitoring; field testing and baseline testing of caged *L. variegatus*
- September - October 2006: in-situ application of activated carbon; during application monitoring
- Spring 2007: development of interim summary report
- July – August 2007: approximate 12-month post-treatment monitoring; initiate 12-month laboratory studies
- Spring 2008: development of interim summary report
- July – August 2008: approximate 24-month post-treatment monitoring; initiate 24-month laboratory studies
- Spring 2009: development of final summary report
SECTION 6
REFERENCES


Table 2-1
Physical and Chemical Properties of Surface Sediments in Vicinity of Proposed Pilot Study Area

In-Situ PCB Bioavailability Reduction in Grasse River Sediments – Final Work Plan
Grasse River Study Area, Massena, New York

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<th>Collection Year</th>
<th>Sample ID</th>
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<td>A4-15</td>
<td>5.33</td>
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</tbody>
</table>

Notes:
1. Surface sediments defined as top 3 inches of sediment column.
2. Values represent average of top 8 centimeters of sediment column.
   - PCB = polychlorinated biphenyl
   - ppm = parts per million
   - % = percent
   - g/cm³ = grams per cubic centimeter
   - --- = not measured
<table>
<thead>
<tr>
<th>Matrix</th>
<th>Location</th>
<th>Sample Type/Number</th>
<th>Sampling Interval</th>
<th>Analyses</th>
<th>Objective</th>
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<tr>
<td><strong>Baseline Monitoring Program (July-August 2006)</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td><strong>Sediment (Figure 4-1)</strong></td>
<td>Pilot study area</td>
<td>9 cores (6 from mixed treatment area, 3 from unmixed treatment area)</td>
<td>Every 1.5 inches in top 6 inches of sediment, and every 3 inches in next 6 inches of sediment (0-1.5, 1.5-3, 3-4.5, 4.5-6, 6-9 and 9-12 inches)</td>
<td>PCB (congener), TOC (on sieved sediment fraction) and microscopy examination</td>
<td>Characterize sediment in pilot study area prior to activated carbon treatment</td>
</tr>
<tr>
<td></td>
<td>Pilot study area</td>
<td>6 box cores (mixed treatment area only)</td>
<td>Top three inches of sediment</td>
<td>---</td>
<td>Provide untreated sediments for use as control in aqueous equilibrium and desorption studies, and biouptake studies (worms)</td>
</tr>
<tr>
<td></td>
<td>Pilot study area</td>
<td>10 cores (duplicates cores at each of 3 mixed treatment area and 2 unmixed treatment area locations)</td>
<td>---</td>
<td>TSS analysis of sediment shaker samples</td>
<td>Evaluate stability of sediment in pilot study area prior to activated carbon treatment</td>
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<tr>
<td><strong>Benthic Community /Aquatic Habitat Study (Figure 4-1)</strong></td>
<td>Pilot study area; reference location (if necessary)</td>
<td>10 petite ponar dredge samples (6 from mixed treatment area, 3 from unmixed treatment area, 1 from background location)</td>
<td>Top four inches of sediment</td>
<td>Sediment type, organism density, abundance and diversity, and habitat type</td>
<td>Characterize benthic community in pilot study area prior to activated carbon treatment</td>
</tr>
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<td><strong>During-Application Monitoring Program (September-October 2006)</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Treated Sediments</strong></td>
<td>Initial test area</td>
<td>Cores (as needed)</td>
<td>---</td>
<td>Visual observation</td>
<td>Evaluate ability of various application and mixing techniques in delivering activated carbon mixture to in-situ sediments</td>
</tr>
<tr>
<td></td>
<td>Pilot study area</td>
<td>Cores (as needed)</td>
<td>---</td>
<td>Visual observation</td>
<td>Verify thickness of applied activated carbon mixture to in-situ sediments</td>
</tr>
</tbody>
</table>
### Table 4-1
**Monitoring Program Summary**
In-Situ PCB Bioavailability Reduction in Grasse River Sediments – Final Work Plan  
Grasse River Study Area, Massena, New York

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Location</th>
<th>Sample Type/Number</th>
<th>Sampling Interval</th>
<th>Analyses</th>
<th>Objective</th>
</tr>
</thead>
</table>
| **Water Column**  
(Figure 4-1) | 2 transect monitoring locations (T43 and T46) | 1 composite per location of grab samples unless stratification is present | Grab samples at 3 depths (0.2, 0.5, and 0.8 times the total water column depth) at 3 locations and composited (except water quality parameters) | PCB (Aroclor), TSS, turbidity, DO, temperature, pH, and conductivity | Assess potential water column effects associated with application and mixing of activated carbon to in-situ sediments |
| | 2 local monitoring locations (adjacent to and downstream of silt curtain) | 1 composite per location of grab samples unless stratification is present | Grab samples at 3 depths (0.2, 0.5, and 0.8 times the total water column depth) and composited (except water quality parameters) | PCB (Aroclor), TSS, turbidity, DO, temperature, pH, and conductivity | Assess potential water column effects associated with application and mixing of activated carbon to in-situ sediments |

<table>
<thead>
<tr>
<th><strong>Post-Treatment Monitoring Program (July-August 2007 and July-August 2008)</strong></th>
</tr>
</thead>
</table>
| **Sediment**  
(Figure 4-1) | Pilot study area; reference location (if necessary) | 9 cores (6 from mixed treatment area, 3 from unmixed treatment area) | Every 1.5 inches in top 6 inches of sediment, and every 3 inches in next 6 inches of sediment (0-1.5, 1.5-3, 3-4.5, 4.5-6, 6-9 and 9-12 inches) | PCB (congener), TOC (on sieved sediment fraction) and microscopy examination | Characterize sediment in pilot study area after activated carbon treatment; Evaluate uniformity in mixing of activated carbon to in-situ sediment |
| | Pilot study area | 6 box cores (mixed treatment area only) | Top three inches of sediment | --- | Provide treated sediments for use in aqueous equilibrium and desorption studies, and biosorption studies (worms) |
| | Pilot study area | 10 cores (duplicates cores at each of 3 mixed treatment area and 2 unmixed treatment area locations) | --- | TSS analysis of sediment shaker samples | Evaluate stability of sediment in pilot study area after treatment with activated carbon |
| **Benthic Community/Aquatic Habitat Study**  
(Figure 4-1) | Pilot study area; reference location (if necessary) | 3 petite ponar dredge samples (6 from mixed treatment area, 3 from unmixed treatment area, 1 from background location) | Top four inches of sediment | Sediment type, organism density, abundance and diversity, and habitat type | Characterize benthic community in pilot study area after treatment with activated carbon |
Notes:
1. Quality Assurance/Quality Control (QA/QC) samples are not included in the number of samples presented.
2. If stratification is present, the sampling protocol will be altered such that grab samples from above and below the demarcation of stratification will be composited (i.e., for a total of 2 samples) separately and analyzed.
   
   DO = dissolved oxygen
   PCB = polychlorinated biphenyl
   TOC = total organic carbon
   TSS = total suspended solids
   --- = not applicable
Figure 2-1. Proposed Area for Activated Carbon Pilot Study

LEGEND

- ▲ July 2006 Surface PCBs (ppm)
- Target Area
- Historical Surface Sediment PCBs (ppm)
  - ○ < 10.0
  - ▲ 10.0 - 25.0
  - ● > 25.0
- Near Shore Area
- Grasse River Shoreline
- Sediment Probing Transects

GRASSE RIVER STUDY AREA
MASSENA, NEW YORK

July 2006 Surface PCBs (ppm)
Figure 2-2. Proposed Layout for the Activated Carbon Pilot Study

LEGEND

Mixed Treatment Area
Unmixed Treatment Area
Initial Testing Area

Locator Map

GRASSE RIVER STUDY AREA
MASSENA, NEW YORK

Proposed Work Areas
- Initial Testing Area
- Mixed Treatment Area
- Unmixed Treatment Area
- Near Shore Area

- Grasse River Shoreline
- Sediment Probing Transects

GRAPHIC SCALE

0
75
150
300

Feet

July 2006
Note: Photographs show partially fabricated equipment. Tine system may be enclosed within shroud. Final equipment may vary from that shown.
A. ISOMETRIC VIEW
NOT TO SCALE

B. CROSS SECTION VIEW
NOT TO SCALE

C. CROSS SECTION VIEW
NOT TO SCALE

D. TILLER BLADE DETAIL
SCALE 1"=10'

E. TILLER BLADE PHOTO

Notes:
1. Drawing prepared by electronic file provided by J. F. Brennan Co., Inc.
2. Photographs show partially fabricated equipment. Final equipment may vary from that shown.
Notes:
1. Drawing prepared from electronic file provided by J.F. Brennan Co. Inc.
2. Tine system may be enclosed within shroud. Final equipment may vary from that shown.
Figure 4-1. Sampling Locations for Sediment, Water Column, and Benthic Community Monitoring

LEGEND

- Proposed Sediment Locs
- Water Column Sampling Locs
- Water Column Transects
- Proposed Work Areas
  - Initial Testing Area
  - Mixed Treatment Area
  - Unmixed Treatment Area
  - Approximate Silt Curtain Loc
- Near Shore Area
- Grasse River Shoreline
- Sediment Probing Transects

GRAVINE RIVER STUDY AREA
MASSENA, NEW YORK

July 2006

ALCOA
Figure 4-2. Light microscopy pictures of 63-250 micron size sediment particles (left) and 75-300 micron size activated carbon particles (right).
Figure 4-3. Sampling Locations for Erosion Potential Testing
Figure 4-4. Design of surficial sediment and pore water exposure chamber from Burton et al. (2002) shown on the left and deployment of five replicate chambers on a rack illustrated in the figure on the right.
APPENDIX A

Journal Publications Pertaining to Activated Carbon Technology
Relationship between PCB Desorption Equilibrium, Kinetics, and Availability during Land Biotreatment

Upal Ghosh,* A. Scott Weber,† James N. Jensen,* and John R. Smith*†
Department of Civil, Structural, and Environmental Engineering, State University of New York at Buffalo, Buffalo, New York 14260, and Environmental Science & Technology Development, Alcoa Inc., Alcoa Center, Pennsylvania 15069

The purpose of this research was to study the changes in polychlorinated biphenyl (PCB) availability as measured by desorption equilibrium and kinetics from industrial lagoon sediments collected at different times during a 24-month period of pilot-scale land biotreatment. During biotreatment, reductions of the lower chlorinated PCB congeners in the industrial lagoon sediments were observed. On the basis of past work on soils and sediments, it was originally hypothesized that these reductions in PCB concentration would result in reduced PCB availability. To evaluate this hypothesis, equilibrium partitioning studies and sorption kinetic studies were conducted with the industrial lagoon sediments (containing 0.91% oil and grease) as a function of biotreatment duration. Contrary to initial expectations, equilibrium aqueous total PCB concentrations increased with PCB loss during land biotreatment. This behavior was attributed to the association of PCBs with a waste oil phase in the lagoon sediment and an oil phase loss rate greater than the PCB loss rate during the bioremediation study. Maximum PCB desorption rates for the lagoon sediments also changed with biotreatment. A two-phase sorption behavior characterized by fast and slow desorbing fractions were observed. The estimated fast pool fraction for each PCB homologue decreased with biotreatment time, suggesting preferential removal of the PCBs from the fast pool during the bioremediation process. Although PCB availability based on estimated fast pool fraction decreased with biotreatment, availability based on aqueous equilibrium measurements increased with biotreatment over the 24 months of study.

Introduction

The primary objective of bioremediation is contaminant reduction leading to reductions in contaminant availability for toxicity and migration. Historically, predictions of contaminant leaching from sediment have assumed equilibrium partitioning between dissolved and sorbed contaminants. The simplest equilibrium model is based on a linear partitioning of contaminant between the sediment organic matter and the aqueous environment (1). In some situations, nonlinearity is observed in the equilibrium behavior and is described by a limited-surface Langmuir isotherm or the empirical Freundlich isotherm (2). Heterogeneity in soil/sediment sorption properties can lead to more complicated formulations of sorption equilibrium behavior (3).

While an equilibrium approach has been used historically to establish cleanup guidelines, this approach may not be valid for hydrophobic organic compounds (HOCs) such as PCBs where sorption kinetics may limit the contaminant flux to the dissolved phase (4). Desorption of HOCs from soils and sediments have often been observed to take place in two stages: a rapid stage followed by a stage of much slower release (5–7). The fraction that is rapidly released has often been considered available for biodegradation and toxic response (4, 8–12). Previous work suggests that biotreatment reduces this available fraction and thereby reduces the availability and toxicity of the contaminant sequestered in soil or sediment (4, 11–15). Contaminants such as PCBs sorbed on degradable organic matter (OM) may behave differently if the amount and nature of the OM is altered during biotreatment. Thus, an understanding of the changes in the amount and nature of OM in sediment is necessary for predicting changes in availability with biotreatment.

In sediments where the organic carbon is comprised primarily of stable osified remains of biological origin, little change in organic carbon content of the sediment is expected during typical time frames of bioremediation. However, fresh natural material from plants or animal origin or oils originating from industrial sources may be present in the sediment as biodegradable organic matter. For example, Avnimelech et al. (16) studied decomposition rates of organic matter in (>6 in. deep) sediments from 64 lakes, reservoirs, and estuaries in the United States and estimated average first-order degradation rates of 0.024 yr⁻¹ (half-life of 30 yr). In contrast, degradation rates for fresh organic matter in surface sediments derived from algal blooms have been reported at 0.6 yr⁻¹ (half-life of 1 yr) (16). Reductions of an oily OM or nonaqueous-phase liquid have been reported in several studies during bioremediation (17, 18) and with water flushing (19). Salanitro et al. (17) observed that for soils contaminated with crude oil hydrocarbons, 3–4 months of bioremediation resulted in 70–90% removal of carbon number species in the range of C₁₁–C₂₂, 40–60% for C₃₃–C₃₄, and 35–60% for C₃₅–C₄₄. In comparison to oil degradation, biodegradation of certain HOCs like higher chlorinated PCBs may be much slower (20).

Although several studies to date have investigated bioremediation of PCB-contaminated soils and sediments, none have examined the resulting changes in OM and the influence on PCB equilibrium and kinetics during bioremediation. Therefore, the purpose of this study was to investigate how availability of PCB congeners as determined by desorption equilibrium and kinetics was altered as a function of land biotreatment for an industrial lagoon sediment containing an appreciable amount of oily OM. Batch equilibrium and desorption rate tests were conducted to measure PCB equilibrium partitioning and desorption kinetics, respectively, from field contaminated sediments during a pilot-scale land biotreatment. Changes in oily OM were monitored during the bioremediation process.

Materials and Methods

Description of Sediment Source and Land Biotreatment.

Industrial lagoon sediments containing PCBs employed in these studies were obtained from a pilot-scale biological land treatment unit operated by Alcoa in Massena, NY. The PCB-
impacted sediments originated primarily from two industrial lagoons in the site, which had been in operation for several years until the early 1980s and contained a significant oil and grease content. These lagoons received varied waste ranging from waste oils and wastewater from industry operations containing PCBs and were historically used as settling/treatment units. Approximately 1500 kg (dry weight) of sediment from these lagoons were mixed with 1500 kg of clean sand (medium to fine grade) to produce the sediment mixture that was easy to handle and was added to the land treatment unit. The land treatment unit consisted of a lined trench in the ground in which the amended lagoon sediment was placed in a layer 6–24 in. deep. The active biotreatment process entailed periodic tilling to enhance aeration, addition of growth nutrients, and irrigation to regulate moisture content. Lagoon sediment/sand samples (henceforth called lagoon sediments) were collected before bioremediation, after 3 months of active bioremediation, and after 21 months of subsequent passive treatment (total of 24 months) during which no tilling or nutrient addition was performed.

**Particle Size Distribution.** The mixed lagoon sediment that went into the land treatment units was analyzed for particle size. A total of 15% of the dry sediment consisted of gravel (> 2.0 mm), and 66% consisted of medium to coarse sand (2.0–0.15 mm). The remaining fines (19%) that passed through a 100 mesh sieve (nominal diameter = 150 μm) were analyzed for particle size distribution using Malvern Mastersizer/E particle size analyzer. The particle size distribution of the fines based on a mass distribution ranged between 1 and 100 μm with a peak at about 7 μm. Further details of particle analysis are provided in Ghosh et al. (21).

**PCB Extraction and Analysis.** Congener-level PCB analysis was performed in this study. Samples were extracted in an acetone–hexane mixture by sonication (EPA Method 3555B), passed through a silica gel cleanup procedure (EPA Method 3630C), and analyzed using a gas chromatograph equipped with an electron capture detector (EPA Method 8082). The sample preparation, cleanup, and PCB analysis procedures are described in detail in Appendix 1 in the Supporting Information.

**Organic Matter Measurements.** Four organic matter measurements were performed on the lagoon sediment samples.

- **Total Extractable Organics (TEO).** A 6-h Soxhlet extraction using dichloromethane was used to extract the oil phase in the sediment as outlined by Rutherford et al. (22). The mass of extractable organic matter was determined gravimetrically after dichloromethane was removed by evaporation.

- **Total Organic Carbon (TOC).** TOC measurements were performed by an outside analytical laboratory using EPA Method 9060 based on oxidation of the organic carbon and measurement of the CO₂ evolved. The TOC value of the 24-month treated lagoon sediment was measured on a composite sample. However, the TOC value for the untreated lagoon sediment had to be estimated based on the measured TOC values of the constituents of the sediment mixture.

- **Oil and Grease.** Oil and grease measurements were performed by an outside laboratory based on Freon extraction following EPA Method 9071A.

**Volatile Matter.** Volatile matter was measured based on ASTM Method D2974C, which involves measurement of loss of weight of the sample by heating at 550 °C. This includes both organic and inorganic volatiles.

**Batch Equilibrium Tests.** Sediment–water equilibrium tests were conducted in 50-mL glass centrifuge tubes with Teflon-lined caps. To initiate the equilibrium testing, centrifuge tubes were filled with measured quantities of sediment and water in the weight ratio of 1:10. The tubes were then tumbled end-over-end at 3–4 rpm at 25 ± 2 °C in darkness. At each sampling time, replicate tubes were removed from the tumbler, and the solid and aqueous phases were separated.

Because of the high partitioning of PCBs on particulates, special care was taken to ensure proper solid/liquid separation. To remove colloidal particulates from solution without sacrificing aqueous PCB composition integrity, tube contents were centrifuged for 10 min at 2000g to settle the coarse particles. This step was followed by the addition of 0.001 M alum solution and adjustment of pH back to neutral with NaOH solution. The supernatant water was mixed carefully using a glass pipet for 2 min to mix and flocculate the alum without disturbing the settled particles. Sweep floc was formed in less than 1 min, which was subjected to centrifugation for 40 min at 2000g. A very clear supernatant was formed after centrifugation of the sweep floc. The supernatant then was transferred carefully to an extraction vessel using a glass pipet and extracted with three fresh volumes of hexane. The extracted hexane was collected together, dried using anhydrous sodium sulfate, concentrated to 1 mL, and cleaned by a silica gel cleanup method, and the final clean eluate was concentrated to 1.5 mL for GC analysis.

A possible concern in the use of alum was the extent of adsorption of PCBs on the alum floc during particle separation. Control runs were performed to test for adsorption of PCBs on alum floc using aqueous PCB solutions. The total PCB loss during alum treatment was measured at 1.3% and was therefore considered negligible for the rest of the study. There was no observable bias in the loss across PCB homologue groups. A possible reason for the low adsorption of PCBs on alum floc is that aluminum hydroxide solid at neutral pH is hydrophilic and, therefore, not amenable to the adsorption of highly hydrophobic PCB molecules.

**Desorption Rate Experiments.** Batch desorption experiments were conducted in 12-mL glass vials with Teflon-lined caps as described in detail in ref 21. Multiple tubes were filled with 1 g of lagoon sediment (wet weight), 1 g of XAD-4 resin, and 10 mL of water and placed in a tumbler. XAD-4 resin is a strong adsorbent of PCBs and provided a maximum driving force for PCB desorption from sediment by reducing the aqueous concentration to near zero. At each sampling time, four vials were removed and sacrificially sampled. PCB analysis was performed on each of the three phases present in the batch desorption vials which were the sediment, the XAD resin, and the aqueous phase. Average sediment PCB concentration for each sample was calculated by averaging the four replicates. There were no losses of PCBs by biodegradation during these tests as indicated by mass balance shown in Appendix II in the Supporting Information. A phenomenological two-compartment model as presented in eq 1 that describes both fast and slow desorbing PCB concentration in sediment decreased during land
biodeterioration. PCB concentrations in the lagoon sediment before biotreatment, after 3 months of active biotreatment, and after 21 months of subsequent passive biotreatment are shown along with the 95% confidence intervals in Figure 1. Dichlorobiphenyls were completely removed in the first 3 months. Significant reductions in tri- and tetrachlorobiphenyls were observed in the first 3 months of active biotreatment and also in the following passive phase till 24 months. Small but significant reductions were observed in the concentrations of penta- and hexachlorobiphenyls during the 24-month biotreatment period. Changes in the concentrations of hepta-, octa-, and nonachlorobiphenyls were not significant at the 95% confidence level. The greater removal of the lower chlorinated PCB homologues is attributed to their higher biodegradability, faster desorption rates, higher solubility in the aqueous phase, and/or higher volatility. Several researchers have reported faster rates of biodegradation with decreasing level of chlorination of PCB congeners (25, 26).

Effect of Ortho-Chlorination on Extent of Removal by Land Biotreatment. To investigate the effect of ortho-chlorination on removal during land biotreatment, congeners-level PCB data were analyzed. As discussed earlier, all the dichlorobiphenyl congeners were removed after 3 months of active biotreatment. Among the tri- and tetrachlorobiphenyls, which were partially removed, there appears to be varying degrees of removal for different ortho-chlorinations as shown in Figure 2. The trichlorobiphenyl congeners were grouped into two categories: coplanar (i.e., congeners with a single chlorine substituent in the ortho position—235, 234, 245, 244, 233, 234, 2256, and 234) and noncoplanar (i.e., congeners with two or three ortho chlorines—226, 225, 224, 236, 236, 223, and 246). Congener 2256 was included in the coplanar group because it coeluted with 233 and 234 and was a minor component of the peak. After 24-month biotreatment, the percentage remaining of coplanar trichlorobiphenyl congeners was 19% as compared to 53% for the noncoplanar congeners. Therefore, greater removal of the coplanar trichlorobiphenyl congeners was achieved as compared to the noncoplanar congeners. Tetrachlorobiphenyls showed a similar trend of greater removal of coplanar PCBs as compared to the noncoplanar PCBs. Two coplanar congeners (2345 and 2345) showed equally slow removal as the other noncoplanar congeners within the homologue group. For the rest of the coplanar tetrachlorobiphenyls (2345, 2345, 2344, and 2334), the fraction of total congeners remaining after 24-month biotreatment was 40% as compared to 73% of the other noncoplanar tetrachlorobiphenyl congeners. The extent of removal of the penta and higher chlorinated congeners was small, and relative differences between chlorine positions were not clear.

These observations agree with refs. 27 and 28, who reported that PCB congeners containing two chlorines in ortho positions either on one or each ring were more resistant to biodegradation. In an earlier study (21), it was reported that the more hydrophobic coplanar trichlorobiphenyls desorbed more slowly than the less hydrophobic noncoplanar trichlorobiphenyls in batch desorption tests with the same sediment. Had the overall process been mass transfer rate limited, we would have seen slower removal of the coplanar congeners. The faster biodegradation rate of the coplanar congeners appears to dominate the overall rate shift. For a mass transfer limited process, a higher biodegradation rate should not significantly change the overall rate. This indicates that desorption rate is not the limiting process for the slow degradation of the noncoplanar PCBs. It also is evident from the observation of greater removal of coplanar PCBs that biodegradation might have played a more significant role than leaching and/or volatilization in the removal of PCBs in the land treatment units.

An important implication to the fate and transport of PCBs is evident from the above observation. The noncoplanar PCB congeners, which are more leachable due to their lower hydrophobicity, are less degraded during biotreatment. Therefore, these noncoplanar PCB congeners are expected to be more labile during biotreatment. This is supported by aqueous equilibrium measurements later.

Aqueous Equilibrium Concentration as a Function of Land Biotreatment. Lagoon sediment–water equilibrium tests were conducted to evaluate the aqueous availability of PCBs before and after biotreatment. PCB congeners contributing to di through hexachlorobiphenyl homologue groups were measured in the aqueous solution almost immediately, signifying fast approach to batch equilibrium. There was very little change in aqueous phase concentrations of each homologue beyond 5 days of equilibrium up to 40 days (Appendix III in the Supporting Information). Tri- and tetrachlorobiphenyls were the most abundant homologue groups present in the aqueous solution. To compare the change in PCB equilibrium concentration with treatment, the aqueous PCB concentrations during the steady-state period (between 5 and 40 days) were averaged for each treatment time and plotted in Figure 3. With biotreatment, equilibrium aqueous phase concentrations of dichlorobiphenyls decreased from approximately 0.5 μg/L with no treatment to near zero with treatment for 24 months. Trichlorobiphenyls increased from 2.2 to 2.5 μg/L during the first 3 months, followed by little change up to 24 months. Tetrachlorobiphenyls increased with treatment from about 1.2 μg/L for the untreated sediment to 2.6 μg/L for the 24-month treated sediment. The penta- and hexachlorobiphenyls present in small concentrations also showed increased aqueous equilibrium concentration with treatment. The observed increase in equilibrium aqueous PCB concentration with biotreatment was contrary to expectations based on reductions in sediment PCB concentrations.

Organic Matter Changes with Land Biotreatment. To explain the observed increase in aqueous PCB concentrations with biotreatment, it was hypothesized that PCBs were associated with an OM phase that was degraded during biotreatment. Four methods used to measure organic matter in the lagoon sediments were TEO, TOC, oil and grease, and volatile matter. Results of these analyses for the sediment samples are shown in Table 1. All four measures of organic matter showed reductions during biotreatment. Nearly half of the TOC at any time appears to be contributed by a waste oil phase as measured by TEO and oil and grease. It has been shown by Rutherford et al. (22) and Sun and Boyd (29) that, in the presence of equivalent mass fractions of oil versus other organic matter, the oil compartment dominates the sorption process of a hydrophobic organic compound.
Therefore, waste oil from historical industrial operations as described before was assumed to be the primary constituent responsible for PCB sorption in the lagoon sediments. Waste oil in the sediment was reduced to less than half of the initial amount during the biotreatment process and could have resulted in increased relative amounts of PCBs in the oil phase and thereby in aqueous equilibrium concentrations.

In an earlier work using pure PCB mixtures, we observed increased leaching with time of the higher chlorinated PCB homologues from a generator column due to initial removal of more soluble components (30). A similar phenomenon of increased leaching of benzo[a]pyrene due to compositional changes in a complex mixture during remediation has been predicted by model simulation (31).

To further confirm the role of waste oil in determining PCB partitioning behavior, equilibrium studies were conducted using the extracted oil from the untreated lagoon sediment. The dichloromethane-extracted oil from 40 g of sediment was contacted with 400 mL of Nanopure water to test equilibrium partitioning between the oil and aqueous phases. The extracted oil was found to be viscous, heavier than water, and adhered to the glass surface. After the equilibration period, the aqueous phase was centrifuged and subjected to alum flocculation to remove any particulate or organic phases and extracted to measure PCBs by congener. The results of

**TABLE 1. Lagoon Sediment Physical/Chemical Characterization**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Moisture (%)</th>
<th>pH</th>
<th>Volatile Matter (%)</th>
<th>Total Extractable Organics (TEO) (%)</th>
<th>Oil and Grease (O&amp;G) (%)</th>
<th>Total Organic Carbon (TOC) (%)</th>
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</thead>
<tbody>
<tr>
<td>Initial</td>
<td>5.5</td>
<td>6.5</td>
<td>2.4</td>
<td>0.73</td>
<td>0.91</td>
<td>1.8</td>
</tr>
<tr>
<td>3 month</td>
<td>12.2</td>
<td>7.2</td>
<td>2.3</td>
<td>0.48</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td>24 month</td>
<td>7.8</td>
<td>6.1</td>
<td>1.8</td>
<td>0.34</td>
<td>0.31</td>
<td>0.67</td>
</tr>
</tbody>
</table>

*a* nm, not measured.

**TABLE 2. Equilibrium Partition Coefficients**

<table>
<thead>
<tr>
<th>Homologue Group</th>
<th>lagoon sediment–water partition (log Kow)</th>
<th>oil phase partition (log Koil)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log Kow (ref 30)</td>
<td>0 month</td>
</tr>
<tr>
<td>di</td>
<td>4.9–5.3</td>
<td>4.1</td>
</tr>
<tr>
<td>tri</td>
<td>5.5–5.9</td>
<td>4.2</td>
</tr>
<tr>
<td>tetra</td>
<td>5.6–6.5</td>
<td>4.7</td>
</tr>
<tr>
<td>penta</td>
<td>6.2–6.5</td>
<td>5.2</td>
</tr>
<tr>
<td>hexa</td>
<td>6.7–7.3</td>
<td>5.9</td>
</tr>
</tbody>
</table>
11-day equilibrium measurement of the oil phase matched closely to the average equilibrium concentration of the untreated lagoon sediment as shown in Figure 4. This observation supports the hypothesis that partitioning of PCBs between the lagoon sediment and the aqueous phases was controlled by desorption from the waste oil phase present. The effects of changing oil phase amount and PCB composition on equilibrium concentrations are elaborated further in Appendix IV in the Supporting Information.

**FIGURE 5. Change in PCB desorption during land biotreatment.** Standard deviation values shown in parentheses.

To quantify the relationship between aqueous and lagoon sediment PCB concentrations at equilibrium, partition coefficients based on total sediment ($\log K_{d}$) and based on oil ($\log K_{oil}$) were calculated and are reported in Table 2 along with desorption time and concentration data for tetrachlorobiphenyls, pentachlorobiphenyls, and hexachlorobiphenyls.
with the published range of log $K_{ow}$ values. The values of log $K_{ow}$ for the 24-month treated lagoon sediment were close to the range of reported values of log $K_{ow}$. However, the values of log $K_{ow}$ for the untreated lagoon sediment were slightly higher. Thus, the aqueous partitioning of PCBs from the sediment oil phase is not very different from that of octanol. Calculated values of log $K_{ow}$ decreased with land biotreatment corresponding to increased aqueous equilibrium concentrations. Values of $K_{ow}$ also decreased with land biotreatment but to a lesser extent. While most of the increase in aqueous phase PCB concentration observed with treatment time may be explained by the reduction in the oil phase, there appear to be other contributing factors as well. One possible explanation for decreasing $K_{ow}$ with biotreatment is that changes in the oil phase composition may lead to changing PCB partitioning. For example, preferential removal of the lower molecular weight fractions of oil with bioremediation has been observed in other studies (17, 22). Rutherford et al. (22) found an increase in average molar weight of the total extractable OM from 248 to 338 during soil bioremediation. Increasing average molecular weights of an oil mixture can lead to increased mole fraction of PCBs present leading to increased aqueous concentrations (30, 31, 33). Additionally, chemical changes in the oil constituents during biotreatment may alter activity coefficients. Therefore, it is not unreasonable to assume that reduction in oil mass and composition in oil constitution could together lead to increased partitioning of the PCBs into the aqueous phase with biotreatment.

**Effect of Ortho-Chlorination on Changes in Equilibrium Concentration.** PCB congeners within a homologue group vary in physical/chemical properties and toxicity. Therefore, the influence of chlorine position on partitioning behavior was evaluated. A greater increase in leachability of the noncoplanar congeners as compared to the coplanar congeners of tri- and tetrachlorobiphenyls was observed. The sum of coplanar trichlorobiphenyl congeners decreased by 12% in the aqueous equilibrium concentration in 24 months of treatment as compared to an increase of 52% of the sum of non-coplanar trichlorobiphenyl congeners. For the tetrachlorobiphenyls, both groups of congeners increased in aqueous equilibrium concentration with biotreatment. However, the increase in aqueous equilibrium concentration of the non-coplanar congeners was higher (190%) than that of the coplanar congeners (118%). It should be remembered that concentration of all tri- and tetrachlorobiphenyl congeners in the lagoon sediment decreased during land biotreatment. The non-coplanar tri- and tetrachlorobiphenyls, which are less hydrophobic and more labile, are also less biodegradable. Therefore, a greater partitioning of non-coplanar congeners into the aqueous phase during equilibrium tests is expected as compared to the coplanar congeners.

Thus, during biotreatment, attention must be paid to the less biodegradable non-coplanar PCB congeners that may show increased leachability during biotreatment. Increased leaching of the non-coplanar congeners however may not affect leachate toxicity significantly because non-coplanar congeners are non-dioxin-like and less toxic (34, 35).

**Comparisons of PCB Desorption Rates and Fast and Slow Pool Speciation.** PCB desorption experiments were carried out to investigate how maximum desorption kinetics were affected by land biotreatment. Desorption profiles of the coplanar, tri-, tetra-, penta-, and hexachlorobiphenyl homologue groups for the untreated, 3-month treated, and 24-month treated lagoon sediments are plotted in Figure 5a–d, respectively. Dichlorobiphenyls were completely removed during the first 3 months of treatment and thus are not plotted. For each homologue group, there is a decrease in initial PCB concentration, and the period of fast desorption appears to decrease with increased treatment time.

To estimate desorption rate constants, a dual desorption rate model as presented in eq 1 was fitted to the PCB homologue desorption data for the three sediment treatments. The three parameters fitted to each PCB congener desorption data were the fast and slow desorption rate constants and the fraction of congener in the fast pool and are presented along with the graphs in Figure 5.

A possible mechanistic interpretation of the slow and fast pool speciation of PCBs in the lagoon sediments is the association of PCBs with an oil phase (fast) and a biologically stable sediment OM phase (slow). There is a small increase in the fast pool rate constants after 24 months of biotreatment, which is possibly caused by changes in the nature of the residual oil phase after biotreatment. The estimated fast desorbing fraction for each congener decreased with biotreatment time, which suggests preferential removal of the PCBs from the fast pool during the biotreatment process. Similar decrease in the fast desorbing fraction of PAHs with biotreatment has been reported (12, 15). Smaller fast desorbing pool or available fraction of a contaminant has typically been associated with lower toxicity and environmental risk (4, 11, 12, 15). In soil/sediment containing little or no oily OM, previous work has demonstrated continued reduction of PCB/PAH availability with biotreatment (11, 14, 15, 36). However, in the case of the study lagoon sediments, the equilibrium aqueous PCB concentrations increased with biotreatment. Therefore, in the presence of an oil phase, reductions in total PCBs or fast pool PCBs may not lead to reductions in aqueous PCB availability. Changes in aqueous partitioning behavior caused by alterations in the oil phase during biotreatment may play a more significant role in determining short-term aqueous availability than reductions in total PCBs alone. Therefore, in the short term, PCB availability may increase due to fast reduction in the oil phase. In the long term, PCB availability may be reduced once the oil phase degradation stops or is modified into a different form. It is therefore extremely important to understand the type of contaminant association in soils and sediments and the changes in the nature of organic matter to reasonably anticipate the effect of a treatment process on aqueous availability and leaching. Knowledge gained from this work allows better anticipation of changes in contaminant availability and possible leaching potential during biotreatment of field sediments. Continued monitoring of these study lagoon sediments is ongoing to evaluate very long-term effects (~2 yr) of land biotreatment on PCB and PAH aqueous availability.

**Acknowledgments**

This study was sponsored by the U.S. Department of Energy, the Office of Biological and Environmental Research (BER) through the Environmental Technology Partnerships (ETP) Program (Contract DE-FG02-96ER62279). The authors would also like to acknowledge Alcoa Inc. (Pittsburgh, PA) for their financial and technical support in this research.

**Supporting Information Available**

The following additional information is available: 1) PCB extraction and analysis details, 2) PCB mass balance of desorption studies, 3) time to reach equilibrium, 4) Raoult’s Law prediction of changes in equilibrium partitioning with treatment. (6 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

**Literature Cited**

PCB and PAH Speciation among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability

UPAL GHOSH,*, J JOHN R. ZIMMERMAN, AND RICHARD G. LUTHY
Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020

This research provides particle-scale understanding of PCB and PAH distribution in sediments obtained from three urban locations in the United States: Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY. The sediments comprised mineral grains (primarily sand, silt, and clays) and carbonaceous particles (primarily coal, coke, charcoal, pitch, cenospheres, and wood). The carbonaceous fractions were separated from the mineral fractions based on their lower density and were identified by petrographic analysis. In all three sediments, carbonaceous particles contributed 5–7% of the total mass and 60–90% of the PCBs and PAHs. The production of carbonaceous particles is not known to be associated with PCB contamination, and it is very unlikely that these particles can be the source of PCBs in the environment. Thus, it appears that carbonaceous particles preferentially accumulate PCBs acting as sorbents in the aqueous environment if PCBs are released directly to the sediment or if deposited as airborne soot particles. Aerobic biofiltration treatment resulted in negligible PAH loss from the carbonaceous coal-derived material in Milwaukee Harbor sediment but resulted in 80% of the PAHs being removed from carbonaceous particles in Harbor Point sediment. Microscale PAH extraction and analysis revealed that PAHs in Harbor Point sediment were associated mainly with coal tar pitch residue. PAHs present in semisoloid coal tar pitch are more bioavailable than PAHs sorbed on carbonaceous particles such as coal, coke, charcoal, and cenosphere. Results of this study illustrate the importance of understanding particle-scale association of hydrophobic organic contaminants for explaining bioavailability differences among sediments.

Introduction

The management of sediments and the control of sediment contaminants are among the most challenging and complex problems faced by environmental engineers and scientists. Because of the strong binding of hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), sediments serve as a long-term source of the contaminants to water bodies and biota, even long after the original source of contamination has been removed. While recent advances in analytical techniques make it possible to quantify even the smallest amount of anthropogenic contaminants present in sediment, our ability to relate sediment concentrations to water quality, biological availability, and toxicological effects is hindered by inadequate understanding of the binding and release of the contaminants in the sediment. This is due to the inherent heterogeneity of sediment material that defies organic geochemical generalizations based on bulk sediment physicochemical parameters such as total organic carbon content, surface area, and particle size distribution.

PCBs and PAHs sorb to the organic carbon fraction of sediment, and thus organic carbon fraction is taken as a measure of the sorption capacity for regulatory purposes. This enables normalization of the aqueous equilibrium relationship for sediments containing different amounts of organic carbon (1). However, a major problem with this approach is that organic carbon in sediment comes in different forms that may have very different sorption capacities for HOCs. For example, in addition to natural materials such as vegetative debris, decayed remains of plants and animals, and humic matter, sediment organic carbon also comprises particles such as coal, coke, charcoal, and soot that are known to have extremely high sorption capacities (2–6). Figure 1 shows a comparison of reported organic carbon-normalized phenanthrene partition coefficients (Koc) for different sorbents (5, 7–12). The Koc values for different organic carbon forms span several orders of magnitude. On the basis of the partition coefficients presented in Figure 1, it is clear that HOCs associated with soot- or coal-type carbon may be orders of magnitude less available in the aqueous phase than HOCs associated with natural organic matter in soils and sediment. Thus, HOCs that end up in the sediment as contaminants may be of more or less concern depending on how weakly or strongly they are sorbed to the sediment organic matter.

Past work indicates the possible importance of soot carbon in sorption processes in sediment (2, 6, 13, 14). These studies measured soot carbon in sediment using partial thermal treatment to remove non-soot organic carbon followed by treatment with acid to remove inorganic carbon and analysis of the remaining carbon. The soot carbon material isolated by partial thermal oxidation does not retain sorbed chemicals for further analysis. However, Gustafsson et al. (2) and Bucheli and Gustafsson (13) showed that elevated PAH partitioning in sediment samples could be explained on the basis of the soot carbon content and known high PAH sorption capacity of soot. They concluded that sorption of PAHs on a soot-like phase in sediments may impact in situ bioavailability of PAHs. Accardi-Dey and Gschwend (6) performed PAH sorption studies with the isolated soot carbon and demonstrated that a modified, soot-partitioning inclusive, distribution model can better predict the observed PAH partitioning from sediment. Karapanagioti et al. (5) showed that sediments containing coaly particulates exhibited high Koc values and nonlinear isotherms for phenanthrene sorption. Recently Aalloum et al. (12) studied the sorption of phenanthrene on several aliphatic natural organic matter types (algae, cellulose, collagen, cuticle, lignin, kerogen, and humic acid) and concluded that aliphatic organic matter domains in soils and sediment may also play a significant role in the sorption of HOCs. However, none of these studies directly measured the levels of PAHs on natural organic matter particles, soot, or coal particles in field sediment, and as such, the conclusions are based on inference from equilibrium partitioning...
and not on direct evidence of PAH association. Thus, from these studies it is not clear whether natural organic matter or black carbon in sediments comprise the predominant repository of hydrophobic contaminants such as PCBs and PAHs. In our earlier work, we demonstrated the predominant association of PAHs with coal-derived particles in Milwaukee Harbor sediments (4). We found from direct analysis of separated fractions and particle-scale microanalysis that the majority of PAHs in the sediment was associated with coal-derived particles and that these PAHs were strongly bound, not easily desorbable, unavailable for biological treatment, and unavailable for uptake in earthworms (4, 15, 16).

The objective of this research is to extend particle-scale understanding of PCB and PAH distributions in sediment by comparing sediments from three different geographical locations and to illustrate the effect of PAH association with particle types on bioslurry treatment. We use three different aged, harbor sediment samples to investigate the importance of carbonaceous particles in the sequestration of PCBs and PAHs. The particulate organic carbon components in the sediments were separated by a density technique that preserves the physical and chemical integrity of the particles. Two of the sediments containing high levels of PAHs were subjected to aerobic bioslurry treatment to investigate PAH bioavailability to microorganisms. Microscale extraction and analysis were carried out to illustrate differences in PAH levels among carbonaceous particle types in sediment and to explain differences in PAH bioavailability.

Materials and Methods

Contaminated sediments often occur near harbors and old industrial establishments. Therefore, we selected three harbor/industrial locations across the country to study the extent distribution of PCBs and PAHs among particle classes. Three sediments used in this study were obtained from the following locations. All sediment samples were stored at 4 °C until used.

(i) Hunters Point, San Francisco Bay, CA. Sediment samples were collected from the intertidal zone in South Basin near the southern edge of the Hunters Point Naval Shipyard in January 2001 and screened through a 4 mm screen. Sampling took place during low tide along approximately 150 yards of shoreline within the intertidal zone. Historic shipyard and industrial activities in the adjacent region discharged PCBs, PAHs, and heavy metals into the soil and sediment. Operations at the site included a former transformer storage yard, industrial landfills, fuel lines, a scrapyard, and an oil reclamation area. Between 1954 and 1974, nearly 250 gal of PCBs was estimated to have been released in the scrapyard parcel adjoining South Basin (17). Other PCB releases may have occurred as well. The Hunters Point South Basin Area is designated as a PCB hotspot in San Francisco Bay (18).

(ii) Milwaukee Harbor Confined Disposal Facility (CDF). Sediments in the CDF originated from Milwaukee Harbor during dredging operations to maintain waterway navigability. This acre facility is operated by the Milwaukee Harbor Port Authority. Concerns have been raised about the potential for release of contaminants from such CDF sites and about closure requirements, as discussed by Bowman (19). Samples for this work were collected in fall 1996 at a depth of 4 m in the CDF. The sediment was sieved through a 3/4 in. screen in the field.

(iii) Harbor Point Sediment, NY. This sediment sample was collected in 1999 from a freshwater harbor site located near a former manufactured gas plant in Utica, NY. The sediment was collected using 1–2 ft cores and sieved through 3/8 in. mesh and composited on site. High levels of PAHs in the sediments are thought to have originated from a historic gas manufacturing facility in the vicinity.

Size and Density Separation. Wet sieving was performed to separate the sediment into four size fractions (<63, 63–250, 250–1000, and >1000 μm). The larger size fractions (>63 μm) were composed primarily of sandy grains, carbonaceous particles, and woody material. The lighter carbonaceous particles were washed off from the heavier sand particles by swirling with water in a beaker and draining off the entrained lighter particles, giving two separate fractions that we define as “light” and “heavy”. As a final step, a saturated cesium chloride solution with a specific gravity of 1.8 was used to remove the remaining lighter density particles. Materials in the fine fraction (<63 μm) were density-separated using the cesium chloride solution. Five grams of wet sediment and 40 mL of cesium chloride solution were mixed and centrifuged at 2000g for 10 min in 50 mL glass centrifuge tubes. Separated particles were washed with water to remove cesium chloride (4).

Coal Petrography Analysis. Coal petrography analysis of sediment particles was performed according to ASTM standard methods for coal analysis: D2797 (Preparing Coal Samples for Microscopic Analysis by Reflected Light), D2798 (Microscopic Determination of the Reflectance of Vitrinite in a Polished Specimen of Coal), and D2979 (Microscopic Determination of Volume Percent of Physical Components of Coal).

PCB/PAH Analysis. Soil PCBs and PAHs were extracted following U.S. EPA Method 3550B using 3 volumes of 40 mL each of an acetone—hexane mixture (1:1) and sonicated the slurry for 6 min (pulsing for 15 s on and 15 s off). Pesticide-grade hexane and acetone were used for all extractions. EPA Method 3630C was followed for sample cleanup where the and concentrated extracts are passed through a deactivated silica gel column to remove organic interferences and to separate the PCBs and PAHs. PCB congenic-specific analysis was performed using a modified EPA Method 8082. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m × 0.25 mm i.d.) and an electron capture detector was used for analysis. PCB standards for calibration were purchased as hexane solutions from Ultra Scientific (North Kingstown, RI) and also obtained from the U.S. EPA’s National Health and Environmental Effects Research Laboratory in Grosse Ile, MI. A multi-level calibration table was prepared using a 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.

![FIGURE 1. Organic carbon-normalized partition coefficient for phenanthrene for different types of organic carbon. Data sources: activated carbon (7); root carbon (8); particulate coal, particulate charcoal, and amorphous organic matter (9); heavy fuel oil (10); several soils and sediments showing average and range (10, 11); Pula kerogen, collagen, humic acid, degraded algae, Green River kerogen, oxidized humic acid, cuticle, algae, lignin, and cellulose (12); coal tar (23).](image-url)
of 610 μg/L. Tenax beads were harvested by allowing the sediment to settle and the Tenax beads to float up. The Tenax beads were scooped out of the test tube, and fresh Tenax was added. PAHs were extracted from the Tenax beads and analyzed by GC-FID.

Results and Discussion

Sediment Particle Characterization. Sediments from the three locations were separated into four size classes: < 63, 63–250, 250–1000, and > 1000 μm. Light microscopy illustrates the diversity of particles and identifies prominent particle classes in the sediment samples. As shown in the microscopic image of sediments from the three locations in Figure 2, the 250–1000 μm size sediments comprise mineral grains (primarily sand) and organic particles of various kinds such as wood, charcoal, coal, coke, pitch, and cenosphere. An exact identification of the nature of organic particles was performed through petrographic analysis. Petrographic analysis involves preparation of a polished particle surface followed by visualization under a microscope using normal or polarized light. This technique has been used historically to identify coal maceral structures, rank coals, identify different stages of coal pyrolysis and coke formation, determine coal tar and pitch quality, and identify chars and cenospheres (21). Karapanagioti et al. (5) used petrographic techniques to identify types of organic matter including coals in different size fractions of aquifer material. In our earlier work, we used similar techniques to identify coal-derived particles in Milwaukee Harbor sediment (4).

The various kinds of organic particles identified in the three sediments in this study by petrographic analysis are shown in Figure 3. A striking common feature in the analysis of the three sediments is the abundance of coal and coal-derived particles in all three sediments. Possible sources of coals in these sediments are coal transportation activities in harbors near the sampling locations, historic coal use in the local area, and coal gas manufacturing facilities in the vicinity. All three sediments showed the presence of wood particles. Hunters Point and Harbor Point sediment showed significant presence of lignite and cenospheres. Cenospheres are more or less spherical, porous semicoke or coked particles formed during the rapid heating of unconfined coal (21). These particles appear as hollow carbon spheres often broken into pieces in the sediment. A special feature of the Harbor Point sediment was the presence of pitch, a likely residue and waste product from former manufactured gas operations. The Milwaukee Harbor sediment was unique in showing a preponderance of coal-derived particles. The Hunters Point sediment showed significant presence of charcoal, which was not observed in abundance in the other sediment samples. Oil-soot particles were not seen abundantly in the two size fractions that were studied in detail: 63–250 and 250–1000 μm. Oil-soot particles are typically nanometer sized globules, often in grape-like clusters several microns in size. On the basis of the size of oil-soot particles, these may be present in the study sediments in the < 63 μm lighter density fraction. In our petrographic analysis for Hunters Point sediment, we found an oil-soot cluster in the 63–250 μm size range among more prevalent black carbonaceous particle types described above. Although there were differences in carbonaceous particle types found in the three sediment samples, a common characteristic is the abundance of highly sorbing carbon substrates in all three sediments.

PCB and PAH Concentrations in Sediment. PCB homologue and PAH concentrations in the three sediments are shown in Figures S3 and S4, respectively, in the Supporting Information. Among the three sediments, Hunters Point showed significant sorbing carbon substrates in all three sediments.
the highest levels of PCBs at 9.9 ± 0.9 mg/kg with predominately higher chlorinated congeners and resembling Aroclor 1260 in congener distribution. The most abundant PCB homologues were hexa- and heptachlorobiphenyls. The PCB concentrations at this site are approximately 3 orders of magnitude higher than background PCB levels (25 µg/kg) in the sediment in San Francisco Bay (18). Total PCB concentration in Milwaukee Harbor sediment was 1 mg/kg with tetra- and pentachlorobiphenyls being the most abundant homologues. Although PCBs were detected in Harbor Point sediment, a detailed study of the PCB distribution in this sediment was not conducted as part of this investigation. Research with Harbor Point sediments focused on PAHs, which were the primary contaminant of concern at this site at 262 ± 25 mg/kg total PAHs. This sediment also appears to be the least weathered based on the relatively higher levels of lower molecular weight PAHs such as phenanthrene. Total PAH concentration in Milwaukee Harbor sediment was 90 ± 7 mg/kg. Hunters Point sediment had the lowest levels of PAHs at 8 mg/kg.

It is well-known that hydrophobic organic compounds such as PCBs and PAHs partition into organic carbon on soils and sediments. However, this partitioning process may vary greatly if the organic carbon present in soils and sediments comprises various forms such as humic matter particles, humic matter sorbed on mineral surfaces, animal and vegetative debris, and products of coal and wood use and combustion. Our earlier work with Milwaukee Harbor sediment showed the importance of coal-derived particles in sorption of PAHs. The following compares the distribution of PCBs and PAHs among particle sizes and density classes for three different sediments.

**Sediment Mass Distribution among Particle Classes.** The carbonaceous sediment fraction comprising coal, coke, charcoal, pitch, cenospheres, and wood are separable from the mineral fraction based on their lower density. The three sediments were separated into size and density fractions and analyzed for PCBs and PAHs in each fraction. Results of sediment mass distribution by size and density shown in Figure 4 reveal for each size fraction that the lighter density fraction has much smaller mass as compared to the heavier mineral fraction. For all three sediments 5–7% of the total sediment mass is contributed by the lighter density carbonaceous particles. The two freshwater sediment samples, Milwaukee Harbor and Harbor Point, have clay/silt (≤ 63 µm heavy) as the predominant sediment component. The Hunters Point sediment is coarser in grain size with fine and coarse sands comprising the majority of the sediment.

**Sediment PCB and PAH Distribution among Particle Classes.** PCB and PAH analyses of the lighter and heavier density fractions reveal that the majority of the contaminants are associated with the small quantity of lighter density carbonaceous particles. As shown in Figure 5, the fraction of total PAHs associated with the lighter density carbonaceous particles in Hunters Point, Milwaukee Harbor, and Harbor Point sediments are 89%, 68%, and 62%, respectively. We find that the fraction of total PCBs associated with lighter density carbonaceous particles in Hunters Point and Milwaukee Harbor sediments are 68% and 58%, respectively (Figure 6). Thus, for all three sediments, PAHs and PCBs are predominantly associated with the carbonaceous particles. Earlier work by us for Milwaukee Harbor sediment (4) and recent work by Rockne et al. (22) for NY/NJ harbor sediments has shown that PAHs can be found predominantly in the lighter density fraction of sediments. As with PAHs, our data for two sediments are the first reporting of the distribution of PCBs among sediment particle density classes.

PAH and PCB analyses by size and density fractions shown in Figures 5 and 6 reveal that except for the fine grained (< 63 µm) sediment fraction, for every size fraction, the lighter density material contributes to the majority of PAHs and PCBs in the sediment. For the fine size fraction (< 63 µm), in all three sediments the heavier density particles contributed more PCBs and PAHs than the lighter density particles. Possible reasons for the difference with the finest size fraction are the much larger surface area of the finer size fraction and the comparatively larger overall mass of heavy particles in this size fraction. For example, in the case of Harbor Point
sediment, only 1% by mass in the <63 μm size fraction comprises light particles.

**Implications of PCB Speciation in Carbonaceous Particles.** Since combustion and pyrolysis processes are associated with the production of PAHs as a byproduct, there is a possibility that the coal- and combustion-derived particles reach the sediment with PAHs already sorbed to the particles. In our current work, we analyzed PCB distribution in two of the sediments. Results of PCB analysis by sediment density fractions reveal a strikingly similar story wherein the majority of the PCBs are associated with the lighter density carbonaceous particles. Since the production of coal, coke, charcoal, and cenosphere is in no way associated with PCB use, it is unlikely that these particles can be the source of PCBs in the environment. For the <63 μm size light fraction, if airborne soot particles are present, those may have picked up some...
of the PCBs from the atmosphere before depositing in the sediment. For the larger sized particles such as coal, coke, and charcoal, it appears that over a long period of time, PCBs in the sediment tend to preferentially accumulate in these carbonaceous particles where they may be strongly bound. Such migration of PCBs and possibly PAHs into a more strongly sorbing matrix has significant implications for assessment of sediment quality criteria and for possible in situ stabilization approaches. For example, addition of sorbent carbonaceous material like activated carbon to the sediment may enhance the sequestration of these hydrophobic compounds in the sediment, making them less available for biological uptake and release into the overlying water.

**Effect of PAH Association with Particle Types on Bioavailability.** Aerobic bioslurry experiments were carried out using the two sediments that had high levels of PAHs: Milwaukee Harbor (90 mg/kg) and Harbor Point (262 mg/kg). We reported in an earlier study for Milwaukee Harbor sediment that PAH biodegradation was achieved mainly within the <63 μm heavy fraction comprising the clays and silt, for which there was 75% reduction in PAHs (16). The coal-derived material from Milwaukee Harbor sediment showed no significant reduction in PAH concentrations during the biotreatment process. Thus PAHs associated with the lighter density fraction of Milwaukee Harbor sediment, which was primarily coal-derived particles, appear to be strongly bound and not available for biological degradation.

A similar aerobic bioslurry treatment study was conducted using Harbor Point sediment to compare with the finding from the Milwaukee Harbor study. As shown in Figure 7, nearly 75% reduction of total PAHs was achieved during 2 months of aerobic bioslurry treatment of Harbor Point sediment. Greater than 90% reduction was achieved for the low molecular weight PAHs (2–3 ring) and 20–50% reduction was achieved for the high molecular weight PAHs (5–6 rings). PAH analysis by particle size and density revealed that, although reductions of PAHs associated with the heavy sand/silt/clay fractions were high (69%), significant PAH reductions were also achieved for PAHs associated with the lighter density fractions comprising coal, charcoal, char, cenospheres, and coal tar pitch (80%). As shown in Figure 8, the four size classes of the lighter density fraction of Harbor Point sediment underwent significant losses of PAHs during the bioslurry treatment process.
PAH Desorption Kinetics. Abiotic desorption studies using Tenax resin were conducted with two size fractions (63–250 and 250–1000 μm) of the lighter density particles in Milwaukee Harbor and Harbor Point sediments. Results of these desorption studies are shown in Figure 9 where the fraction of PAHs released from the sediment particles after different times of desorption are plotted over a 8–10 day period. For the three most prominent PAHs that were degraded during biotreatment (phenanthrene, fluoranthene, and pyrene), 10–20% of the PAHs are desorbed in Milwaukee Harbor sediment as compared to 40–70% for Harbor Point sediment in the same time period. Thus, mass transfer of PAHs from the lighter density particles is much faster in Harbor Point sediment as compared to that in Milwaukee Harbor sediment. The striking difference in PAH desorption rates in the lighter density fraction of the two sediments explains the differences in extents of PAH biodegradation observed.

Microscale PAH Extraction from Organic Particle Types. Microscale extraction and analysis was performed on the different particle classes in Harbor Point and Milwaukee Harbor sediments to investigate further the association of PAHs with the lighter density carbonaceous particles in these two sediments. Individual particles of the lighter density fraction particles (250–1000 μm) were separated manually using a pair of fine-point tweezers under a microscope. The five types of carbonaceous particles separated out as shown in Figure S1 in the Supporting Information are coal tar pitch, charcoal, cenosphere, coal/cope, and wood (56%, 9%, 18%, 5%, and 12%, respectively, by weight). Coal petrography analysis performed on another set of particles confirmed the presence of these particle types (see Figure 3). Results of
that PAHs desorb much faster when associated with pitch softer coal tar pitch matrix and therefore more easily available particles; in the second case, PAHs are partitioned into a Harbor Point sediment) are largely bioavailable. In the first observation under a microscope revealed a similar nature of particles amount to the remaining 4% of the PAHs. Although the individual particle separation and microscale PAH analyses were not possible for the smaller size fractions, visual observation under a microscope revealed a similar nature of particle distribution across particle sizes in the lighter density fraction. Thus, for Harbor Point sediment, the predominance of PAHs in the lighter density particles is due to the presence of PAH containing coal tar pitch particles. The implications from these observations are as follows:

PAHs sorbed on coal-derived particles and aged for years in the field (as seen in Milwaukee Harbor sediment) are strongly bound and not available for biodegradation, whereas PAHs associated with semisolid, coal tar pitch (as seen in Harbor Point sediment) are largely bioavailable. In the first case, PAHs are sorbed on highly aromatic, hard, coal-derived particles; in the second case, PAHs are partitioned into a softer coal tar pitch matrix and therefore more easily available for desorption. Our results from abiotic desorption tests show that PAHs desorb much faster when associated with pitch particles as compared to coal/coke particles. Log $K_{oc}$ values for phenanthrene sorption on coals are reported to be 6.3–6.4 (5) as compared to a log $K_{oc}$ of 5 for phenanthrene partitioning from coal tars (23) (assuming carbon content of coal tar to be 95%). Thus, based on equilibrium partitioning, PAHs associated with coal tar are much more available in the aqueous phase than PAHs sorbed on coals. The semisolid matrix of coal tar pitch may inhibit mass transfer rates but not as much as polymer-like diffusion in coals. Work by Ortiz et al. (24) reports solid-phase diffusivities for phenanthrene through solid paraffin in the order of $10^{-10}$ cm$^2$/s, which is orders of magnitude higher than estimated diffusivities of PAHs in coal matrix reported by us of $10^{-17}$ cm$^2$/s (15) and those reported by Karapanagioti et al. (5) of $10^{-14}$ cm$^2$/s. On the basis of the large differences in equilibrium partitioning and desorption rates between hard coal versus the softer semisolid pitch matrix and the fact that during bioslurry treatment some of the soft coal tar pitch particles may also undergo breakdown, it is not surprising that we see significantly higher extent of biotreatment in Harbor Point sediment as compared to Milwaukee Harbor sediment.

Several recent studies suggest the predominant role of soot carbon or black carbon in the sequestration of PAHs in sediments (2, 3, 6, 8, 14). Most of these studies use two separate observations: high sorption capacity of soot carbon and identification of soot carbon in sediments to infer that PAHs in sediment are actually associated primarily with the soot carbon, as equilibrium conditions would dictate. Nonetheless, there is little direct evidence that soot carbon in sediment indeed contains a major fraction of PAHs. Results of this study illustrate the importance of direct measurements at the particle scale to understand the nature of PCB and PAH distribution in contaminated sediments. We show here that black carbon particles in aged, field sediments may accumulate PCBs. Furthermore, as shown in the case of Harbor Point sediment, even in the presence of black carbon (coal, coke, cenospheres, and charcoal), PAHs may remain primarily associated with original source materials such as coal tar pitch and may be available to microorganisms for biodegradation.

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Supporting Information Available

Additional light microscopy images of representative organic particle types in Harbor Point sediment and additional data on PCB and PAH distributions in the three sediments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulosus)

ROD N. MILLWARD,† TODD S. BRIDGES,§ JOHN R. ZIMMERMAN,∥ AND RICHARD G. LUTHY*,∥∥

Analytical Services Inc., Engineering Research and Development Center (ERDC), 3909 Halls Ferry Road, Vicksburg, Mississippi 39180, United States Army Corps of Engineers, Engineering Research and Development Center (ERDC), 3909 Halls Ferry Road, Vicksburg, Mississippi 39180, Department of Civil and Environmental Engineering, University of Maryland, Baltimore County, 100 Hilltop Circle, Baltimore, Maryland 21250, and Department of Civil and Environmental Engineering, Terman M52, Stanford University, Stanford, California 94305.

This work examines the effects of adding coke or activated carbon on the bioavailability of polychlorinated biphenyls (PCBs) in contaminated sediment from South Basin at Hunters Point, San Francisco Bay. We show with 28-day sediment exposure tests that PCB bioaccumulation in a polychaete (Neanthes arenaceodentata) is reduced by 62% following 1-month contact of sediment with activated carbon and by 87% following 6-months contact of sediment with activated carbon. PCB bioaccumulation in an amphipod (Leptocheirus plumulosus) is reduced by 70% following 1-month contact of sediment with activated carbon and by 75% after 6-months contact of sediment with activated carbon. Adding coke had a negligible effect on reducing PCB bioaccumulation, probably because of the low specific surface area and the slow kinetics of PCB diffusion into the solid coke particles. Reductions in congener bioaccumulation with activated carbon were inversely related to congener Kow, suggesting that the efficacy of activated carbon is controlled by the mass-transfer rate of PCBs from sediment and into activated carbon. We find that reductions in aqueous PCB concentrations in equilibrium with the sediment were similar to reductions in PCB bioaccumulation. While no lethality was observed following activated carbon addition, growth rates were reduced by activated carbon for the polychaete, but not for the amphipod, suggesting the need for further study of the potential impacts of activated carbon on exposed communities. The study suggests that treatment of the biologically active layer of contaminated sediments with activated carbon may be a promising in-situ technique for reducing the bioavailability of sediment-associated PCBs and other hydrophobic organic compounds.

Introduction

Persistent hydrophobic organic contaminants released into the aqueous environment eventually become associated with sediments, where the contaminants may reside for long periods of time because of the combination of strong sorption and slow degradation. Consequently, such contaminants, including polychlorinated biphenyls (PCBs), remain in riverine and coastal sediments of the United States despite bans or restrictions on their use (1). Currently, the most commonly used management options for PCB-contaminated sediments are removal by dredging or in-situ capping (2).

Recent work demonstrates the important role of lighter density, black carbonaceous particles in sediments such as soot carbon, coal, coke, and charcoal in reducing contaminant aqueous availability and bioavailability. For example, Jonker and Koelmans (3) found that soot and sootlike materials have very high affinities for polycyclic aromatic hydrocarbon (PAHs) and PCBs and that the presence of these materials can lower aqueous concentrations of the contaminants, implying a reduction in the potential uptake by aquatic organisms. Several other studies have similarly demonstrated the role of so-called black carbonaceous particles in reducing contaminant aqueous availability (4–8). In our earlier work (9, 10), we demonstrate that PAHs associated with coal-derived particles are much less available for biological uptake. These findings suggest that the presence of black carbonaceous particles in sediments naturally reduces contaminant availability. McLeod et al. (11) showed in clam particle feeding studies that the absorption efficiency for a tetrachloro-PCB was only 1–2% via ingestion if the PCB was sorbed to activated carbon, compared to about 90% for PCBs sorbed to diatoms.

Building on these recent findings, we propose a novel in-situ remediation technique to reduce PCB bioavailability by repartitioning PCBs onto black carbon sorbents that are mixed into the sediment’s biologically active layer to enhance the natural process of contaminant stabilization. Microporous black carbon particles have high affinities for hydrophobic organic contaminants (HOCs), as well as high sorption capacities and slow release rates (9, 12–14), making them promising candidates as sorbents for sediment remediation. Activated carbon is particularly suitable, given its sorption capacity for HOCs, accessible microporous structure, and high specific surface area, commonly about 1000 m²/g. The surface of activated carbon particles is characterized by sites with a variety of potential adsorptive interactions, and this heterogeneity in surface character, and the resulting diversity in potential interaction mechanisms, makes activated carbon suitable as a sorbent for a broad spectrum of HOCs (15, 16).

In related work, we demonstrated that adding activated carbon to PCB-contaminated sediment from Hunters Point Naval Shipyard, San Francisco, CA, decreased PAH and PCB aqueous equilibrium concentrations, PAH and PCB uptake by semipermeable membrane devices (SPMD), and diffusive flux of PCBs from sediment into overlying water (17). This paper addresses the effects of addition of either coke or activated carbon to sediment on PCB bioaccumulation by two benthic species, with different feeding strategies and hence different exposure characteristics: the particle-browsing amphipod Leptocheirus plumulosus and the bulk-sediment ingesting polychaete Neanthes arenaceodentata.
This study also addresses the effects of these sorbents on the survival, growth, and reproduction of *L. plumulosus* and the survival and growth of *N. arenaceodentata*.

**Experimental Methods**

**Sediment—Sorbent Contact.** Field sediment collection and handling are described in Zimmerman et al. (17). Briefly, intertidal sediment was collected from South Basin at Hunters Point, San Francisco Bay, CA, and sieved to remove particles >4 mm. Sediment was amended with either coke or activated carbon, and separate batches were mixed for either 1 or 6 months at approximately 3 rpm on a roller. Activated carbon was 75–300 μm type TOG (Calgon Corp., Pittsburgh, PA) dosed at 3.4% dry weight. Coke was obtained as coke breeze (Ispat Inland, East Chicago, IL) and dosed in two size ranges (fine, 63–105 μm, and coarse, 105–250 μm) and at two concentrations (3.4% or 8.5% dry weight). However, since neither the physicochemical tests (17) nor the bioaccumulation tests (present study) revealed significant differences in coke efficacy because of either dose, particle size, or contact time, only the results from the coarse 3.4% coke treatments are presented here. The same activated carbon- or coke-amended sediment, and nonamended sediment, were used in both physicochemical tests (17) and biological tests (this paper).

**PCB Bioaccumulation and Carbon Sorbent Toxicity.** Both bioaccumulation and biological effects of the adsorbent amendment were studied using modified 28-day sediment toxicity protocols for *N. arenaceodentata* (18, 19) and *L. plumulosus* (19, 20). Twenty-five 2-day-old *L. plumulosus* were placed in 1-L beakers containing sediment (100 g dry weight) and c. 725 mL of 20% artificial seawater (Forty Fathoms Crystal Sea, Marine Enterprises International, Baltimore, MD). Overlying water was aerated gently and exchanged three times each week. *Leptocheirus plumulosus* were fed Tetramin (Tetra Holdings, Blacksburg, VA, 12 mg per replicate) and *N. arenaceodentata* 10–2-week-old worms were placed in 1-L beakers containing sediment (100 g dry weight) and c. 725 mL of 30% artificial seawater (Instant Ocean, Aquarium Systems, Mentor, OH). *Neanthes arenaceodentata* were fed twice a week (12 mg per replicate) after each water exchange. After a 28-day exposure, *L. plumulosus* were removed from the sediment and allowed to clear gut contents for 2–4 h. *Neanthes arenaceodentata* were depurated for 12 h in 30% artificial seawater, after which any remaining ingested sediment was removed by applying gentle rearward pressure along the digestive tract. Tissues were stored at −80 °C prior to PCB measurement. Tissue PCB concentrations were normalized by lipid content to aid comparison of bioaccumulation by species. To address the effects of congener chlorination on activated carbon effectiveness, PCB congeners were summed by homologue group, and percentage reductions in bioaccumulation by homologue were investigated for each group, using average homologue *K*<sub>ow</sub> values from Erikson (21).

Potential effects of coke and activated carbon amendments on the organisms were assessed by comparison of the survival, growth rate, and lipid content of both *N. arenaceodentata* and *L. plumulosus*, and juvenile production in *L. plumulosus*, in untreated sediment and sediment with either 3.4% coke or 3.4% activated carbon additions after 1-month contact time. At the termination of the exposure, animals were removed from test sediments by gentle sieving and the survival and wet weight were recorded. *L. plumulosus* juvenile abundances were noted, and the tissues were analyzed for lipid content (see below).

**Digestive Fluid Extracts.** We assessed the ability of activated carbon to reduce PCB bioavailability from ingested sediment by measuring PCB concentrations extracted from amended and nonamended sediment by a polychaete digestive fluid, using methods based on those of ref 22. Digestive fluids were taken from the deposit-feeding polychaete Arenicola brasilienensis collected near San Francisco in May 2001 and stored at −80 °C until use. Whereas digestive fluids from *N. arenaceodentata* might have been preferable, the small size of this species and the large digestive fluid requirements precluded their use. Digestive fluid was mixed with either wet sediment or wet-activated carbon-amended sediment (1.2 mL digestive fluid to 0.6 g sediment on a dry weight basis) in precleaned screw-capped glass centrifuge tubes. Mixtures were vortexed for 30 s before placement in a culture-tube rotator for 3 h, with additional vortexing every hour. We used 3-h extractions as an estimate of gut passage time for the subadult *N. arenaceodentata* used in these experiments, interpolated from gut passage time data for juvenile (0.5–1 h) and adult (>5 h) *Neosuccinea* (23). After vortexing, tubes were then removed and centrifuged at 4000 rpm for 10 min. After centrifugation, 1 mL of supernatant was removed and frozen at −80 °C until analysis. Three replicates were analyzed per sediment, together with one method blank (digestive fluid with no sediment).

### PCB Analyses

PCB concentrations in tissues and digestive fluids were analyzed using standard EPA methods adapted to use smaller (about 100 mg) wet weights of tissue. Tissue and digestive fluid samples were sonicated using EPA method 3550B with the following modifications: solutes were extracted using a single volume of 10-mL hexane and sonicated at 50% pulse for 6 min using a microtip probe. Samples were cleaned and concentrated using methods based upon EPA 3630C with the exception that extracts were reduced to 40 μL. PCB congeners were analyzed using EPA 8270 and selective-ion monitoring on a Hewlett-Packard 5890 series II gas chromatograph–mass spectrophotometer (GC–MS) with detection limit <0.25 ng/kg wet weight. PCB concentrations in sediments were analyzed using standard method EPA 8270. PCB concentrations in the water phase were analyzed as described by Zimmerman et al. (17) with 14-day equilibration followed by colloid removal and hexane extraction.

Total sediment and tissue PCB concentrations refer to the sum of 31 selected congeners listed in Table 1. Congeners were chosen on the basis of occurrence in both tissue and sediment samples at concentrations above method detection limits, and on reproducible absence of peak coelution. Chosen congeners range from the tetra- through nonachloro-biphenyls. Mono- through tri-chloro-biphenyls constituted a very small fraction of total PCBs in the sediment (<1%).

| Table 1. List of 31 Selected PCB Congeners Used to Calculate Total PCBs in Tissues |
|---------------------------------|-----------------|-----------------|
| congener | IUPAC # | congener | IUPAC # |
| 2,2,3,4’ | 49 | 2,2,3,4,5’,6 | 175 |
| 2,2,3,4,4’ | 85 | 2,2,3,3,4,6 | 176 |
| 2,2,3,5,6 | 95 | 2,2,3,4,5’,6 | 177 |
| 2,2,3,4,5’ | 95 | 2,2,3,3,5,5 | 178 |
| 2,3,3,4,6 | 110 | 2,2,3,4,4,6 | 180 |
| 2,3,4,4’,5 | 118 | 2,2,3,4,4,5 | 183 |
| 2,2,3,3,4’,4’ | 128 | 2,2,3,4,5,5,6 | 185 |
| 2,2,3,3,4,5’ | 130 | 2,3,3,4,5,5,6 | 193 |
| 2,2,3,3,6,6 | 136 | 2,2,3,3,4,4,5,5’ | 194 |
| 2,2,3,3,4,4,5 | 138 | 2,2,3,3,4,4,5,6 | 195 |
| 2,2,3,3,4,5’,5’ | 146 | 2,2,3,3,4,4,5,6’ | 196 |
| 2,2,3,3,5,5,6 | 149 | 2,2,3,3,4,5,6 | 201 |
| 2,3,5,5,6 | 151 | 2,2,3,4,4,4,5,6 | 203 |
| 2,2,3,3,4,4’,5 | 170 | 2,2,3,3,4,4,5,5,6 | 206 |
| 2,2,3,3,4,5,5’ | 172 | 2,2,3,3,4,5,5,6,6 | 208 |
| 2,2,3,3,4,5,6’ | 174 |

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and sieved to remove coarse sediment from Sequim Bay, WA, were freeze-dried and stored at -20 °C for 10 min. After cooling, samples were vortexed with 4.8 mL of vanillin reagent (600 mg vanillin (Sigma) dissolved in 100 mL hot deionized water and 400 mL of 85% phosphoric acid (Sigma)). After 5 min, color intensity was analyzed by spectrophotometer at 490 nm against a reagent blank. Lipid content was derived by comparison with a soybean oil (Sigma) standard curve.

**Digestive Fluid Surfactancy and Enzyme Activity.** The effects of activated carbon on digestive fluid surfactancy and enzyme activity were measured using digestive fluids collected from the benthic deposit-feeding polychaete *Arenicola brasilienis*. The digestive fluid used was a composite of archived material collected using the methods of ref 25 and archived material collected using the methods of ref 25 and stored at -80 °C. Hunters Point sediment and a laboratory reference sediment from Sequim Bay, WA, were freeze-dried and sieved to remove coarse (>500 μm) particles. Dried sediments were then added to digestive fluids (100 mg dry weight sediment to 600 μL digestive fluid), shaken for 1 h, and centrifuged at 5000 rpm for 10 min. Supernatant was then removed for analyses of surfactancy and enzyme activity.

Digestive fluid surfactancy was assessed by measuring the static contact angle between a 10-μL droplet of digestive fluid and a hydrophobic surface (Parafilm) (26). Droplets were placed on Parafilm and the side view image of the droplet was entered into an image analyzer. The tangent was drawn at the droplet-Parafilm intersection, and the angle between this tangent and the base of the droplet was determined. Surfactant activity and micelle stability were investigated over a range of artificial seawater dilutions. Effects of activated carbon on digestive fluid protease, lipase, α-glucosidase, and β-glucosidase enzyme activities were measured using substrate monomers attached to fluorescently labeled water (excitation wavelength 355 nm, emission wavelength 440 nm) of the free MCA or MUF as it was hydrolyzed. For protease activities, alanine attached via a peptide bond to methylcoumarinyl amide (MCA, Sigma-Aldrich, St. Louis, MO) was used; for lipase activities, palmite esterified to methylumbelliferone (MUF, Sigma-Aldrich, St. Louis, MO) was used; and for α- and β-glucosidase activities, glucose attached by either α- or β-glucosidase bonds to MUF (Sigma-Aldrich, St. Louis, MO) was used. Methods were similar to those used in ref 26. For each enzyme analysis, 250 μL of digestive fluid supernatant was diluted to 25 mL with 0.1M pH 8 phosphate buffer, and 1 mL was placed in a fluorescence cuvette; 0.1 mL of tagged enzyme substrate (two replicates per enzyme) was added, vortexed, and the ensuing hydrolysis reaction was monitored by measuring the fluorescence (excitation wavelength λex = 355 nm, emission wavelength λem = 440 nm) of the free MCA or MUF as it was cleaved from the conjugate. Slopes of the plots of fluorophore release over time were converted to molar hydrolysis rates after correcting for fluorescence quenching by measuring the fluorescence of 1 μM solutions of unbound MCA or MUF (Sigma-Aldrich, St. Louis, MO) in the same diluted solutions.

**Statistics.** Lipid-normalized tissue concentrations and biological responses were compared using either one-way analysis of variance (ANOVA, for comparison of variables from both coarse and fine coke treatments with nonamended sediment) or Student’s t test (for all pairwise comparisons between both activated carbon-amended and nonamended sediment exposures and between 1- and 6-month contact times). Digestive fluid enzyme activities were compared using nonparametric ANOVA on ranks, because of heteroscedacity. Null hypotheses were rejected at the level $P \leq 0.05$. All statistical analyses were performed using SigmaStat 3.0 (SPSS Inc, Chicago, IL).

**Results and Discussion**

**Effect of Coke and Activated Carbon on PCB Bioavailability in Sediments.** The addition of identical proportions of coke and activated carbon resulted in very different effects on PCB bioaccumulation. Addition of 3.4% coke had no significant effect ($P > 0.05$) on PCB bioaccumulation in either *L. plumulosus* or *N. arenaceodentata* (Supplemental Figure S1). Additional data (not presented) showed that the low efficacy of coke was not improved by increasing dosage (from 3.4 to 8.5%) or increasing contact time (from 1 to 6 months) or decreasing particle size range (from 105 to 250 μm to 63–105 μm). Similarly, the previous physicochemical studies demonstrated little or no effect of these coke treatments on aqueous PCB concentrations (17).

Activated carbon reduced PCB bioaccumulation following 1-month contact time with sediment by 70% in *L. plumulosus* ($P = 0.003$) and 82% in *N. arenaceodentata* ($P < 0.001$) compared to nonamended sediment as shown in Figure 1a. These decreases in PCB bioaccumulation are of similar magnitude to the decreases observed in aqueous-phase PCBs (87%, Supplemental Figure S2a). These decreases are also similar to reductions in uptake by SPMD (up to 83%) and in the diffusive flux from sediment (up to 89%), using the same activated carbon-amended Hunters Point sediment (17). The effects of activated carbon on *A. brasilienis* digestive fluid solubilization of PCBs were less conclusive, with a statistically insignificant 36% decrease in total PCB solubilization in the treated sediment (Supplemental Figure S2b). Because ingested material can be the primary source for the bioaccumulation of highly hydrophobic contaminants by deposit feeders (27), we might expect that activated carbon would decrease both digestive-fluid PCB solubilization and bioaccumulation by similar magnitudes. Since this was not the case, the digestive-fluid solubilization method used in this study was not a good analogue of biological exposure. From Figures 1a and S2 we conclude that activated carbon reduces PCB bioaccumulation through reduced exposure via the aqueous, and possibly the ingested sediment, uptake routes.
The greater effectiveness of activated carbon compared to coke likely results from its high affinity for hydrophobic organic contaminants and interconnected micropores that yield a higher specific surface area per unit mass compared to coke particles. Jonkers and Koelmans (28) reported nearly 2 orders of magnitude higher $K_{ow}$ values for PCB adsorption on activated carbon versus coke. The specific surface area of coke used in our work was 3.2 m$^2$/g compared to 938 m$^2$/g for the activated carbon. Coke is somewhat porous, but the pores are largely unconnected voids, thus limiting PCB uptake due to small available specific surface area and extremely slow diffusion through solid coke material.

Increasing sediment–carbon contact time to 6 months resulted in additional, although not statistically significant, improvements in activated carbon effectiveness as shown in Figure 1b, with further reductions of total PCB content in $L$. plumulosus from 70% to 75% and in $N$. arenaceodentata from 82% to 87%. In Zimmerman et al. (17), we observed similar incremental improvements in decreasing equilibrium aqueous PCB concentrations from 87 to 92% after increasing sediment–carbon contact time from 1 to 6 months. We conclude under these laboratory-mixing conditions that the benefit of activated carbon is manifested relatively quickly and that the benefit in reducing either bioaccumulation or sorption-retarded diffusion is not lost after an additional 5 months of mixing.

PCB tissue concentrations were consistently lower in $N$. arenaceodentata than in $L$. plumulosus (Figure 1). The difference in tissue PCB concentrations between the two organisms may reflect dissimilarities in net rates of bioaccumulation, which might be explained by the 6-fold difference in the wet weight between the two species. Landrum et al. (29) demonstrated that a higher organism mass (and by inference higher volume and lower surface-area-to-volume ratio) resulted in lower aqueous uptake rates, presumably because of slower movement of hydrophobic contaminants to the lipid phase.

**Relationship between Congener $K_{ow}$ and Activated Carbon Effectiveness.** To address the effects of congener chlorination on activated carbon effectiveness, PCB congeners were summed by homologue group and percentage reductions in bioaccumulation were investigated for each group, using homologue $K_{ow}$ values from Erikson (21). Reductions in PCB bioaccumulation, PCB aqueous concentrations, and digestive-fluid extractions for activated carbon-treated sediment were inversely related to congener log $K_{ow}$ as shown in Figure 2. This is due to several factors including the greater mass-transfer resistance from sediment and the slower uptake in activated carbon for higher $K_{ow}$ congeners. Evidence for desorption resistance is demonstrated in Zimmerman et al. (17), in which higher $K_{ow}$ congeners show slower release rates and a lower fast desorbable fraction compared to congeners with lower $K_{ow}$ values. Under this scenario, a higher proportion of lower $K_{ow}$ congeners would be available for passage to the strongly sorbing activated carbon particles and hence become less bioavailable to organisms. Higher $K_{ow}$ congeners would be more prone to retention in the original sediment and hence maintain a bioavailability similar to that in the nonamended sediment. Further, the rate of internal transport of higher chlorinated PCB congeners in the activated carbon is slower because of chemisorption interaction with the carbon surface (30) and sorption-retarded diffusion.

Contacting activated carbon with the sediment for 6 months reduced the bioavailability of PCB congeners with log $K_{ow} < 7$ by more than 75%. The bioavailability of PCB congeners with a log $K_{ow} > 7$ may be reduced to a similar extent over longer time periods. Inferences about desorption resistance and bioavailability have been made in other studies. In a study on PAH bioaccumulation in a sediment-feeding oligochaete ($Hydradris templetoni$), Lu et al. (31) found that the prior extraction of a more easily desorbed fraction of phenan-threne from contaminated sediments using 2-propanol reduced subsequent bioaccumulation by 50%. They found for benzo(a)pyrene, which has a high log $K_{ow}$ value, that the prior extraction method did not change bioaccumulation significantly. Kraaij et al. (32) also found that laboratory-spiked sediment treated with Tenax adsorbent
resin for 48 h removed greater fractions of the lower $K_{ow}$ PAHs and PCBs compared to the higher $K_{ow}$ compounds. They also found that the treatment with Tenax resulted in a greater reduction in PCB and PAH bioaccumulation for the lower $K_{ow}$ compounds compared to the higher $K_{ow}$ compounds.

**Effect of Activated Carbon on Biota-Sediment Accumulation Factors.** The bioaccumulation potential of sediment-associated organic contaminants can be described using the biota-sediment accumulation factor (BSAF) (33):

$$\text{BSAF} = \frac{C_{\text{org}}}{C_{\text{sed}}} \frac{f_{\text{lipid}}}{f_{\text{oc}}}$$

where $C_{\text{org}}$ = individual congener or sum of 31 congeners in organism (µg kg$^{-1}$ wet weight tissue); $f_{\text{lipid}}$ = lipid content of organism (percent wet weight tissue); $C_{\text{sed}}$ = individual congener or sum of 31 congeners in sediment (µg kg$^{-1}$ dry weight sediment); and $f_{\text{oc}}$ = total organic carbon content of sediment (percent dry weight sediment).

Although a sediment-organism equilibrium state may not be reached in a short exposure test for many organisms, BSAF values for about a month exposure are widely published for various organisms and sediments and provide a mechanism for comparison of results across different studies. Ranges of BSAF (sum of 31 congeners) from exposure to unamended Hunters Point sediment were 0.87 to 0.88 ($L. \text{plumulosus}$) and 0.19 to 0.24 ($N. \text{arenaceodentata}$) (Supplemental Table S1). Ankley et al. (34) presented BSAF values for total PCBs of 0.87 derived from field-collected oligochaetes and 0.84 from oligochaetes exposed to the field sediment for 30 d in the laboratory, which are similar to our BSAF values for $L. \text{plumulosus}$. Calculation of BSAF for selected congeners using 28-d exposures to Hunters Point sediment revealed, for both species, an inverse relationship between BSAF and compound $K_{ow}$ (Supplemental Figure S3), in agreement with field data for high $K_{ow}$ PCB congeners (34). Kraaij et al. (35) observed tubifex worm BSAF values (for 21–34 days exposure) in the range of 1–4 for laboratory-contaminated sediments for four PCBs and seven PAHs. The BSAF for individual PCBs in this study are generally lower than those reported by Kraaij et al. (35). A possible reason could be the predominance of carbonaceous particles such as charcoal in Hunters Point sediment (10) that reduces the bioavailability due to stronger binding of the PCBs compared to natural organic carbons.

For coke-amended sediments, the BSAF increased compared to the untreated sediments from 0.88 to 1.89 for $L. \text{plumulosus}$ and from 0.24 to 0.57 for $N. \text{arenaceodentata}$. These trends reflect the increase in $f_{\text{oc}}$ by approximately 2.6 times for the coke treatments, without a significant reduction in 28-d PCB bioaccumulation. For activated carbon-amended sediments, the BSAF decreased compared to the unamended sediments, from 0.87 to 0.68 for $L. \text{plumulosus}$ and from 0.19 to 0.09 for $N. \text{arenaceodentata}$. Thus, the added activated carbon acts as a stronger sorbent than the native sediment organic carbon. Although tissue PCB concentrations in both organisms decreased by greater than 70% after treatment with activated carbon, the BSAF did not change to the same extent because the fraction of organic carbon in sediments also increased. These results indicate that BSAFs are affected by the nature of organic carbon responsible for contaminant binding, at least over the exposure periods used in this study. Introduction of activated carbon into the sediment changes the PCB partitioning behavior by out competing the partitioning among the sediment organic carbon and the aqueous and organism lipid phases.

**Effect of Activated Carbon on PCB Bioconcentration Factors.** The bioaccumulation of hydrophobic organic compounds from sediments has been described as a two-stage process, whereby organics partition from the sediment into either the aqueous phase or digestive fluid and are then available for partitioning from these solubilized phases into the lipid fraction of organisms (31). Kraaij et al. (35) showed that the bioaccumulation potential might be derived using pore water concentrations and associated bioconcentration factors (BCF) alone. Therefore, we investigated the degree to which the observed decreases in PCB bioaccumulation in the activated carbon-amended sediments might be explained by decreases in PCB concentrations in the aqueous phase. We calculated BCFs for both $N. \text{arenaceodentata}$ and $L. \text{plumulosus}$, using the sum of 14 PCB congeners (listed in Table 2) in organism tissues ($C_{\text{org}}$) and in aqueous phase ($C_{\text{aq}}$) presented in Zimmerman et al. (17) for untreated and treated sediment. BCFs were calculated using

$$\text{BCF} = \frac{C_{\text{org}}}{C_{\text{aq}}}$$

where $C_{\text{org}}$ = individual congener or sum of 14 selected PCB congeners in water at equilibrium (µg L$^{-1}$).

Figure 3 presents aqueous BCFs (L/kg) for the two organisms with the untreated and activated carbon-treated Hunters Point sediment (data for Figure 3 shown in supplemental Table S2). For the untreated sediment, BCFs (L/kg) for $N. \text{arenaceodentata}$ range from 4000–97000, whereas BCFs for $L. \text{plumulosus}$ range from 53000–476000. For sediment treated with activated carbon, BCF values for individual congeners changed, but the range of BCFs remained about the same (7000–107000 for $N. \text{arenaceodentata}$ and 61000–530000 for $L. \text{plumulosus}$). These results indicate that the relationship between aqueous concentrations and tissue PCB concentrations do not change after treatment with activated carbon. Thus, on the basis of evidence to date, PCB bioaccumulation reduction using activated carbon amendment can be related to aqueous PCB concentrations and congener BCF.

Kraaij et al. (35) found that the bioconcentration factors for PCBs in a deposit-feeding tubifex worm did not change after the treatment of sediments with Tenax for 48 h. They also found that the lipid-normalized bioconcentration factors were very similar to the log $K_{ow}$ of the PCB congeners. In our case we also found that the lipid-normalized bioconcentration factors are mostly within an order of magnitude of congener $K_{ow}$ (data not shown). An average bioconcentration factor of 31 200 L/kg for fish was used in developing EPA’s ambient water quality criteria for PCBs (36), and this value is also used for developing total maximum daily loads for PCBs in natural waters (37). Our measured BCF for $N. \text{arenaceodentata}$ for total PCBs in untreated Hunters Point sediment is 34 000 L/kg and is close to the value used by the EPA for fish. For $L. \text{plumulosus}$, we measured 5-fold higher bioaccumulation compared to $N. \text{arenaceodentata}$ and a corresponding higher bioconcentration factor. Different PCB exposure pathways and different surface area-to-volume ratios for the two organisms could be responsible for the observed differences in bioconcentration factors.

**TABLE 2. List of 14 Congeners Used to Calculate the Sum of PCBs in Digestive Fluid Extracts and the Aqueous Phase and Bioaccumulation Factors**

<table>
<thead>
<tr>
<th>congener</th>
<th>IUPAC #</th>
<th>congener</th>
<th>IUPAC #</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2',4,4',5</td>
<td>99</td>
<td>2,2',3,3',4,5,6'</td>
<td>174</td>
</tr>
<tr>
<td>2,2',4,5,5'</td>
<td>101</td>
<td>2,2',3,3',4,5,6</td>
<td>177</td>
</tr>
<tr>
<td>2,3',4,4'</td>
<td>115</td>
<td>2,2',3,3',4,5,5'</td>
<td>180</td>
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<tr>
<td>2,2',3,3',6,6'</td>
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<td>2,2',3,3',4,5,6</td>
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<tr>
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<td>146</td>
<td>2,2',3,3',4,5,5',6</td>
<td>194</td>
</tr>
<tr>
<td>2,2',3,5,5,6</td>
<td>151</td>
<td>2,2',3,3',4,5,5',6</td>
<td>201</td>
</tr>
<tr>
<td>2,2',3,3',4,5,5',6</td>
<td>172</td>
<td>2,2',3,3',4,4,5,5',6</td>
<td>206</td>
</tr>
</tbody>
</table>
Digestive Fluid
TABLE 3. Effect of Sediment and Activated Carbon on Enzyme Activities and Digestive Fluid Droplet Contact Angle in Polychaete

<table>
<thead>
<tr>
<th></th>
<th>digestive fluid</th>
<th>control sediment</th>
<th>control sediment + activated carbon</th>
<th>Hunters Point sediment</th>
<th>Hunters Point + activated carbon</th>
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</thead>
<tbody>
<tr>
<td>protease activity</td>
<td>270 ± 33</td>
<td>116 ± 20</td>
<td>138 ± 8</td>
<td>122 ± 45</td>
<td>113 ± 14</td>
</tr>
<tr>
<td>(µM/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lipase activity</td>
<td>20.2 ± 1.3</td>
<td>15.2 ± 3.0</td>
<td>15.2 ± 2.9</td>
<td>8.4 ± 0.6</td>
<td>16.6 ± 11.6</td>
</tr>
<tr>
<td>(µM/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-glucosidase activity</td>
<td>1.0 ± 0.0</td>
<td>0.5 ± 0.2</td>
<td>0.6 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.2 ± 0.2</td>
</tr>
<tr>
<td>(µM/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-glucosidase activity</td>
<td>6.0 ± 0.6</td>
<td>2.1 ± 0.2</td>
<td>2.8 ± 0.8</td>
<td>0.5 ± 0.0</td>
<td>2.1 ± 0.6</td>
</tr>
<tr>
<td>(µM/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>digestive fluid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>droplet contact angle (°)</td>
<td>27.1</td>
<td>28.3</td>
<td>34.5</td>
<td>36.4</td>
<td>36.9</td>
</tr>
</tbody>
</table>

**Effect of Activated Carbon on Enzyme Activity and Digestive Fluid Surfactancy.** Addition of 3.4% activated carbon to either Hunters Point or control sediment (Sequim Bay, WA) had no significant deleterious effect on protease, lipase, or α- or β-glucosidase activities, as shown in Table 3. This suggests that any sorption of digestive enzymes by activated carbon was not sufficient to decrease the functional efficiency of these key digestive enzymes. Droplet contact angle formed by pure digestive fluid from *A. brasiliensis* was not affected by the contact of the digestive fluid with control sediment. When 3.4% activated-carbon-amended control sediment was contacted with the digestive fluid, the contact angle increased from 28.3° to 34.5° indicating decreased surfactancy. However, digestive fluid contact angles were increased by the same extent in both the unamended and activated-carbon-amended Hunters Point sediment. This indicates that for Hunters Point sediment, there was no change in digestive fluid surfactancy from the addition of activated carbon. High digestive fluid surfactancy is common in deposit-feeding invertebrates (26). The role of surfactancy in digestion is not clear; it might be associated with solubilizing food particles, activating and deactivating digestive enzymes, enhancing solubility of lipids, preventing adsorptive loss of enzymes from the gut, and aiding gut lubrication (26). While it is possible that activated carbon particles can reduce *A. brasiliensis* digestive fluid surfactancy in some sediments with potential effects on nutrient assimilation, the addition of activated carbon did not contribute to any additional loss of digestive fluid surfactancy in the Hunters Point sediment.

**Relevance to the Field.** The results from this work and a companion study (17) demonstrate that adding activated carbon to contaminated Hunters Point sediment can reduce PCB bioaccumulation in two benthic organisms, *L. plumulosus* and *N. arenaceodentata*, by nearly 1 order of magnitude. 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 risk to acceptable levels.
Ongoing laboratory work is testing the effects of activated carbon dose and particle size on reducing PCB bioaccumulation in organisms. Additional studies will be required to develop an understanding of both the underlying mechanisms and implications of the effect activated carbon had on the reduced growth of the exposed polychaete. Transitioning this in-situ treatment approach to the field requires testing the effectiveness of mixing activated carbon into contaminated sediment under field conditions where mixing may be less complete and where organism exposure conditions are more variable.

This technology may be applicable at low energy, net depositional, sediment environments where activated carbon loss through resuspension and transport would be minimal. These conditions exist at South Basin, adjacent to Hunters Point, where the cohesive nature of the sediment would further stabilize the added carbon particles. There may be several potential modes of application of activated carbon to sediments. Depending on particular site conditions, the carbon could be incorporated directly into sediments using a large-scale mixing device such as a rotovator or a hollow-stem mixing auger used for soil stabilization. Carbon could also be placed as a layer on the sediments with a clean sand cap and thus act as an active sorptive barrier to contaminant migration from sediments into the water column. Alternatively, carbon could be incorporated into sediments during dredging operations to stabilize the contaminants before disposal. The authors plan to investigate some of these challenges to field transition through a pilot field demonstration project and to evaluate site characteristics that may allow the successful application of this remediation technology.

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Supporting Information Available

Three figures and two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests

JOHN R. ZIMMERMAN,1 UPA L GHOSH,1 ROD N. MILLW ARD,1 T O D D S. BRIDGE S,1 AND R ICHARD G. LUTHY*1,2

Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020, Department of Civil and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250, and Environmental Laboratory, U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi 39180

The addition of activated carbon as particulate sorbent to the biologically active layer of contaminated sediment is proposed as an in-situ treatment method to reduce the chemical and biological availability of hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). We report results from physicochemical experiments that assess this concept. PCB- and PAH-contaminated sediment from Hunters Point Naval Shipyard, San Francisco Bay, CA, was contacted with coke and activated carbon for periods of 1 and 6 months. Sediment treated with 3.4 wt % activated carbon showed 92% and 84% reductions in aqueous equilibrium PCB and PAH concentrations, 77% and 83% reductions in PCB and PAH uptake by semipermeable membrane devices (SPMD), respectively, and reductions in PCB flux to overlying water in quiescent systems up to 89%. Adding coke to contaminated sediment did not significantly decrease aqueous equilibrium PCB concentrations nor PCB or PAH availability in SPMD measurements. Coke decreased PAH aqueous concentrations by 38–64% depending on coke dose and particle size. The greater effectiveness of activated carbon as compared to coke is attributed to its much greater specific surface area and a pore structure favorable for binding contaminants. The results from the physicochemical tests suggest that adding activated carbon to contaminated field sediment reduces HOC availability to the aqueous phase. The benefit is manifested relatively quickly under optimum contact conditions and improves in effectiveness with contact time from 1 to 6 months. Activated carbon application is a potentially attractive method for in-situ, nonremoval treatment of marine sediment contaminated with HOCs.

Introduction

Contamination of marine sediments with hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) is a concern at numerous harbors, estuaries, lakes, and rivers throughout the world. Approximately 10% of the sediment underlying surface waters in the United States poses potential risks to fish and to humans and wildlife that consume fish (1). Current approaches to contaminated sediment remediation rely heavily on dredging and disposal. Often this is very expensive and may temporarily increase contaminant exposure as well as destroy wildlife habitat. Furthermore, even when sediments are removed from a site, some contamination inevitably remains, becoming a potential long-term threat for exposure (2).

Contaminated sediment management at Hunters Point Naval Shipyard, San Francisco, CA, has been studied for several years (3, 4). A key area of concern is South Basin, a small inlet forming the southwestern border of the former shipyard. The inlet is also where storm sewer outfalls from an industrial area in San Francisco empty into the Bay. The San Francisco Bay Regional Water Quality Control Board reports that Hunters Point sediment contains up to 10.5 mg/kg total PCBs, one of the highest levels anywhere for the estuary (Fred Hetzel, San Francisco Bay Regional Water Quality Control Board, personal communication). Cleaning up contaminated sediment sites such as Hunters Point presents economic, environmental, and technical challenges; thus, innovative solutions are needed to meet sediment management cleanup goals while minimizing costs and environmental impacts. This paper describes results from physicochemical tests to evaluate a newly proposed method for in-situ treatment of HOCs in sediment that is based on addition of particulate carbon sorbent to sediment to achieve repartitioning and sequestering of PCBs and PAHs. This work builds on the discovery of the accumulation and strong binding of PAHs and PCBs in anthropogenic and naturally occurring particulate, black carbonaceous matter already present in sediments, which includes coal and charcoal in Hunters Point sediment (5, 6).

Strong sorption to solids can reduce contaminant bioavailability to organisms. Talley et al. (7) found that sediment bio-slurry treatment reduced PCB concentrations by 75% in the clay–silt fraction of sediment but did not reduce PAH concentrations in the lighter density, primarily coal-derived sediment fraction. In the same study, earthworms exposed to bio-slurry-treated sediment accumulated 75% less PAHs than earthworms exposed to untreated sediment, which indicated that PAHs on the clay–silt sediment fraction were readily available to both microorganisms and to earthworms. Kraaij et al. (8) showed that treating contaminated sediment by contacting with Tenax for 48 h reduced both the fraction of readily desorbing PCBs and PAHs and the biota–sediment accumulation factors (BSAFs) in tubificid worms. The authors concluded that the reduction in BSAF values was caused by the Tenax treatment decreasing the rapidly desorbing fraction of PCBs and PAHs.

Kosian et al. (9) and West et al. (10) used Ambersorb 1500 resin, a strong sorbent of hydrophobic organics, to sediment, which reduced PAH body burdens in Lumbriculus variegatus. Thus, results from several different studies with sediments and various organisms indicate that strong sorption to solids can reduce contaminant bioavailability.

The objective of this research was to investigate the effect of carbon addition in the form of coke and activated carbon on PCB and PAH availability in sediments. Changes in availability were measured through PCB aqueous flux and through PCB and PAH aqueous equilibrium and uptake in semipermeable membrane devices (SPMDs).
Experimental Methods

Sediment - Sorbent Contact. A composite sample of sediment was obtained from the intertidal region of South Basin, adjacent to the former landfill at Hunters Point (37°43.44′ N, 122°22.62′ W to 37°43.38′ N, 122°22.54′ W). Sediment was screened in the field to remove gravel and debris larger than 4 mm diameter and stored at 4 °C. PCB by congener and PAH (16 Priority Pollutant List PAH) concentrations on sediment solids were measured using sonication with 1:1 hexane:acetone extraction followed by cleanup using silica gel and analysis with GC-ECD and GC-FID, following U.S. EPA Methods 3550B, 3630C, 8082, and 8100, as described by Ghosh et al. (6). Sediment total organic carbon (TOC) was measured by combustion in an elemental carbon analyzer (Microanalytical Laboratory, University of Illinois at Urbana-Champaign) following treatment with acid to remove carbonates (11). Hunters Point sediment had a TOC content of 1.7%. Coke used in these experiments was 1–2 mm coke breeze obtained from Ispat Inland, Inc., East Chicago, IL, identified as “coke 1881” (Dr. Hardarshan Valla, Ispat Inland Research Department). The coke was ground in a ball mill and sieved to obtain particles in the 63–105 µm (fine) and 105–250 µm (coarse) size ranges. Type TOG activated carbon (75–300 µm), derived from bituminous coal and obtained from Calgon Corporation (Pittsburgh, PA), was boiled in water for 5 min prior to use to remove any air pockets in pores. Wet Hunters Point sediment, equivalent to approximately 3.8 kg dry weight, was placed in 1-gal glass roller bottles, followed by addition of sorbent and approximately 300 mL of 17 ppt seawater. Five different sorbent treatments were set up: fine and coarse coke at two and five times existing sediment TOC content of 1.7% (3.4% and 8.5%) and activated carbon at two times TOC content (3.4%). Controls were set up with no sorbent. Bottles were rolled at approximately 3 rpm for 28 or 180 d (1 or 6 months). At the end of the contact period, wet sediment slurry was placed in amber glass bottles and stored in a cold room at 4 °C. These sorbent doses were selected as a starting point to assess treatment effectiveness. Subsequent work has examined the effect of lesser activated carbon dose and smaller particle size on PCB availability.

Aqueous Equilibrium. Equilibrium distribution of PCBs and PAHs between sediment and aqueous phases was measured by placing approximately 100 g of coke-treated or activated carbon-treated or untreated wet sediment in 1.9-L glass bottles with 17 ppt seawater and 1 g/L sodium azide (practical grade, Mallinckrodt, Paris, KY) to inhibit microbial growth. The bottles were capped with Teflon-lined caps, shaken, and rotated at approximately 2 rpm for 14 d, after which the sediment-water mixture was allowed to settle and the supernatant cleared of any floating particles with a Pasteur pipet. Colloids were removed using the flocculation procedure described previously (12). PCBs and PAHs were extracted from the aqueous phase using liquid–liquid extraction with hexane. Extract cleanup with silica gel and PCB by congener and PAH (16 Priority Pollutant List PAH) analyses of extracts by GC-ECD and GC-FID from aqueous equilibrium, uptake by SPMs, quiescent flux, and desorption experiments were performed following U.S. EPA Methods 3630C, 8082, and 8100, as described previously (6).

SPMDs. SPMDs are a biomimetic tool to assess the chemical and biological availability of PAHs and PCBs in sediment and water (13–17). SPMDs were used in this work to study the effect of sorbent addition on PCB and PAH release from contaminated sediments. Custom-made SPMDs (EST, St. Joseph, MO) were 100 mm long and filled with 0.1 g of triolein, a component of fish lipid (18). Approximately 12 g of wet, untreated, coke-treated or activated carbon-treated sediment was added to 40-mL clear glass vials with 17 ppt seawater and 1 g/L sodium azide, leaving approximately 1 mL of headspace. One SPMD was folded in half and placed in each vial; the vials were sealed with Teflon-lined caps and set on a rotator at approximately 20 rpm for 14 d.

After tumbling, the SPMDs were rinsed with deionized water; swirled for 30 s in 1 N hydrochloric acid (Fisher Scientific, Fair Lawn, NJ); rinsed with deionized water, acetone (pesticide grade, Fisher Scientific, Fair Lawn, NJ), and isopropyl alcohol (Mallinckrodt Baker, Paris, KY); and wiped and air-dried for approximately 30 s. The SPMDs were submerged in hexane and dialyzed at room temperature for 24 h. The dialysate was transferred to a second 250-mL bottle, and the dialysis with fresh hexane was repeated for 8 h. Dialysates were combined with hexane rinse, the total volume was recorded, and aliquots were taken for cleanup and analysis using methods described previously (6).

Quiescent Flux. Diffusive PCB flux from contaminated sediment was measured in quiescent systems with Amberlite XAD-4 (XAD) beads (20–60 mesh, Sigma Chemical Co., St. Louis, MO) suspended above the sediment in stainless steel mesh. XAD beads were cleaned using a methanol wash (pesticide grade, Fisher Scientific, Fair Lawn, NJ) and stirring periodically with a glass rod for 15 min; then draining and repeating three times each with methanol, 1:1 hexane:acetone, methanol, and deionized water; and then soaking in deionized water for 12 h. XAD beads were placed in precleaned stainless steel 40-mm diameter wire mesh baskets about half full, clamped with stainless steel wire, and shaken in deionized water to remove beads smaller than wire mesh openings.

Quiescent sediment systems employed approximately 20 g wet sediment in 250-mL beakers filled to 200 mL with 17 ppt seawater with 1 g/L sodium azide. A schematic of the experiment setup is shown in Figure 1. Four systems were set up: (i) untreated sediment; (ii) sand-capped sediment; (iii) activated carbon-capped sediment; and (iv) carbon-contacted sediment with 3.4 wt % activated carbon. The sediment-water mixtures were allowed to settle for several days and then 2 g of sand or 1 g of activated carbon were sprinkled slowly over the sediment, forming a uniform layer over the undisturbed sediment approximately 2 mm thick. The mass of carbon in the cap was approximately 7% of the whole sediment dry mass. Following addition of the sorbent caps, stainless steel mesh baskets containing the XAD beads were suspended above the sediment or cap and secured to keep the basket in the correct location. Any XAD beads that may have escaped from the basket were removed with a Pasteur pipet. Beakers were then covered with foil and placed in a dark cabinet at room temperature for 35 d. The baskets were removed, and a second set of XAD in baskets was suspended in the beakers for 134 d. XAD beads were extracted...
with 5 mL of 1:1 mixture of hexane:acetone, rotating end to end at approximately 2 rpm for 24 h, and repeating twice with hexane. The combined extracts were dried by adding a few grams of anhydrous sodium sulfate, concentrated to 1 mL, and cleaned and analyzed by the methods described previously (6).

PCB Desorption. PCB desorption kinetic studies with untreated Hunters Point sediment followed previously described procedures (5). Tenax beads (0.5 g) and sediment sample (5 g) were added to three 12-mL glass vials containing 10 mL of water and continuously mixed in a rotator. Sodium azide (1 g/L) was added to the mixture to prevent biological growth. At sampling times of 0, 1, 2, 3, 6, 14, 30, and 66 d, the Tenax beads were harvested by allowing the sediment to settle and the beads to float up, and then fresh beads were added. PCBs were extracted from the Tenax beads and analyzed by GC-ECD.

Results and Discussion

Reduction in PCB and PAH Aqueous Equilibrium Concentrations with Activated Carbon Addition. The total PCB concentration in composite, intertidal zone sediment samples was 9.9 ± 0.9 mg/kg (6). Figure 2 shows the distribution of PCBs by homolog group in Hunters Point sediment. The dominant PCBs in the sediment resemble Aroclor 1260 with hexa- and heptachlorobiphenyl homologs comprising 71% of the total PCBs. Figure 3 compares PCB concentrations by homolog group in the aqueous phase at equilibrium with untreated sediment and for sediment treated with 3.4% activated carbon for 1 or 6 months. At equilibrium the total aqueous concentration of PCBs is about 37 ng/L, mainly tetra-, penta-, and hexachlorobiphenyls. Compared to sediment, the aqueous samples show a shift toward lower molecular weight congeners due to their lower hydrophobicity and lesser tendency to sorb to sediment.

For activated carbon-treated sediment, the total aqueous PCB concentrations decreased by 87% and 92% for contact times of 1 and 6 months, respectively. This is a substantial reduction in aqueous PCBs and demonstrates under optimum conditions that activated carbon is a strong sorbent in sediment. With mixing, the effect of adding carbon to sediment on PCB aqueous equilibrium concentration is manifested relatively quickly and is not lost with time. Similar to the results with PCBs, adding activated carbon to sediment reduced aqueous equilibrium total PAH concentrations by 74% and 84% for 1- and 6-month contact periods, respectively.

The effect of activated carbon on lowering aqueous concentrations of PCBs is greatest for tetra- and pentachlorobiphenyl homologs, diminishing for hexa- and heptachlorobiphenyls. This is most likely due to the slower rate of release from sediment and slower rate of uptake by carbon for higher chlorinated PCBs. We measured PCB desorption rates from Hunters Point sediment, and the results in Figure 4 are shown as the fraction of PCBs desorbed by homolog group. These data indicate desorption rate decreases with increasing degree of chlorination. Nearly 70% of the tetrachlorobiphenyls are released over 2 months as compared to about 35% of the heptachlorobiphenyls. This trend is shown also in Figure 5 by comparing the percent reduction in aqueous phase PCBs by homolog versus homolog log $K_{ow}$ values (representative homolog log $K_{ow}$ values from Erickson; 19). Figures 4 and 5 are suggestive of a relation between the percent concentration reduction in the aqueous phase PCBs from addition of activated carbon and the extent of release of PCBs from the solid. The implications of these desorption results are discussed later in the context of other experimental results.

Effectiveness of Coke versus Activated Carbon in Reducing Aqueous Equilibrium Concentrations. Shown in Figure 6 is a comparison of total aqueous equilibrium concentrations of PCBs for 3.4% activated carbon-treated sediment with that for sediment treated with two size fractions of coke for applications at 3.4% and 8.5 wt % for 1- and 6-month contact periods. Coke has little or no effect on reducing aqueous equilibrium PCB concentrations over 6 months, compared to activated carbon achieving aqueous PCB concentration reductions of 87% and 92% for 1- and 6-month contact periods, respectively.
Figure 7 shows total PAH aqueous equilibrium concentrations for untreated and coke-treated and activated carbon-treated sediment for 1- and 6-month contact periods. Coke reduced aqueous phase PAHs up to 64% over 6 months. The increased effectiveness of coke for reducing aqueous PAH concentrations, as compared to PCBs, is likely due to the stronger sorption of the planar PAH molecules to coke, which bears some structural resemblance to soot. Several studies show elevated PAH organic carbon partition coefficients ($K_{oc}$) in the presence of soot (20–24). Soot has been described as “particles of multilayered macro-PAHs” (22), and coke is considered to consist of layers of PAH-type molecules (25). The elevated partition coefficient values ($K_{oc}$) observed for PAHs and coplanar PCBs in the presence of soot have been attributed to a combination of the ability of planar molecules to lie flat on the surface of soot particles allowing overlap of π bonds and to a greater extent of pore sorption due to the ability of planar molecules to penetrate soot pores or interlayer spacings (22, 24). Soot has greater porosity and specific surface area as compared to coke, approximately 8–59 m$^2$/g for soot (24) versus 3 m$^2$/g for our coke samples; the similarity in structural composition could explain why coke reduced PAH aqueous concentrations but did not affect aqueous concentrations of PCBs. A total of 94% of the PCBs measured in Hunters Point sediment are noncoplanar (i.e., containing more than one chlorine atom in ortho positions on the biphenyl rings). We did not see a significant difference in the behavior of coplanar and noncoplanar PCB congeners.

Reduction in PCB and PAH Uptake in SPMDs. Figure 8 shows a comparison of total PCB uptake in SPMDs for untreated sediment and sediment contacted with coke or activated carbon for 1 or 6 months. Activated carbon-treatment reduced SPMD uptake by up to 77% and 83% for PCBs and PAHs, respectively. Coke had little or no effect on SPMD uptake of PCBs or PAHs (data not shown), which is likely due to its smaller specific surface area and its pore structure being less favorable for binding HOCs as compared to activated carbon, as discussed above. The PCB homolog distribution for uptake in the SPMDs is similar to that for the sediment with a predominance of hexa- and heptachlorobiphenyl homologs. Ninety-nine percent of total PCBs in the SPMDs are tetra- to octachlorobiphenyl homologs. Similar to our results from aqueous equilibrium experiments, the effectiveness of activated carbon addition in reducing uptake by SPMDs decreased with increasing degree of PCB congener chlorination.

Reduction in PCB Flux from Sediment to Water. The quiescent flux experiments assessed how activated carbon treatment affects PCB flux to overlying water. The tests compared sediment mixed with activated carbon for 1 month with sediment having carbon applied as a cap. Untreated sediment and sediment with a sand layer on top were evaluated as well. The XAD beads maintain a constant driving force for PCB release from sediment by providing an infinite sink for PCBs because of the beads’ large sorption capacity and overwhelming affinity for HOCs.
$K$ is the organic carbon-normalized partition coefficient (L/kg), $C$ is the fraction of organic carbon in the sediment (mg/kg), $K_{oc}$ is the solid–water partition coefficient (L/kg), $f_{oc}$ is the fraction of organic carbon in the sediment (–), and $K_{oc}$ is the organic carbon-normalized partition coefficient (L/kg organic carbon). For HOCs, $K_{oc}$ is often correlated with compound octanol–water partition coefficient, $K_{ow}$. Six expressions for estimating $K_{oc}$ from $K_{ow}$ values are shown in Table 1 in the Supporting Information for data sets that include PCBs. These relationships are discussed below in the context of the aqueous equilibrium experiments performed as part of our study.

$K_{oc}$ and $K_{ow}$ were calculated for PCBs and PAHs in untreated Hunters Point sediment using sediment and aqueous equilibrium concentrations. Tables 2 and 3 in the Supporting Information show average values of log $K_{ow}$ from the literature and measured values of log $K_{oc}$ for PCBs and PAHs, respectively. Values of log $K_{ow}$ for PCB homologs in Table 2 (in the Supporting Information) are representative values reported by Erickson (19) from Shiu and Mackay (27). Our measured PCB log $K_{oc}$ values and the log $K_{ow}$ correlations presented in Table 3 (in the Supporting Information) are plotted against congener or homolog log $K_{occ}$ values in Figure 10. For the most part, the PCB log $K_{oc}$ values measured in this study are larger and lie outside the range of the various correlations. In contrast, log $K_{oc}$ values reported in recent studies with carbon materials such as soot and charcoal (24) and with soot-containing sediment (28) are closer to our measured values. The larger log $K_{oc}$ values observed for Hunters Point sediment likely result from the presence of anthropogenic black carbon particulate organic matter. Ghosh et al. (6) showed that 68% of the PCBs and 89% of the PAHs are associated with particulate organic matter in sediment at the site, which comprises 6% of the total sediment mass. The agreement of our log $K_{oc}$ values with those from other studies where PCB sorption is dominated by soot or charcoal, supports the concept that, given sufficient time, PCBs bind preferentially to charcoal or coal-derived particles, which are present in Hunters Point sediment.

Comparison of results in Figure 11 shows that our measured PAH log $K_{oc}$ values are about 2 orders of magnitude larger than log $K_{oc}$ values predicted by others for PCBs and other hydrophobic compounds. PAHs were measured at three sites within Boston Harbor, as reported by McGroddy and Farrington (20).
both studies contained soot, which plays an important role in PAH sorption. Jonker and Koelmans (24) measured solid–water distribution coefficients for soot sorbents–water systems (i.e., no sediment), and we calculated log K_{sw} values from these distribution coefficients and normalized their reported values by sorbent percent carbon. As shown in Figure 11, the similarity between log K_{sw} values measured in these three studies (28, 24, 20), where sorption is dominated by soot or charcoal, and our measured log K_{sw} values supports the concept of the dominance of strong sorption to black carbon particles (e.g., char, charcoal, coke) in Hunters Point sediment.

Comparison of Treated Sediment Equilibrium Partitioning with Literature Values. Aqueous equilibrium contaminant concentrations in water in contact with untreated and activated carbon treated Hunters Point sediment were used as an indicator of whether adding carbon sorbents decreases PCB and PAH release to the aqueous phase. The greater effectiveness of activated carbon is attributed to a combination of its greater effective surface area (940 vs 3 m²/g for coke) and its pore size distribution and structure that are favorable for binding contaminants (24). Jonker and Koelmans (24) measured sorbent–water distribution coefficients for soot and soot-like material and reported activated carbon–water partition coefficients (K_{AC}) ranging from 10^{13.5} to 10^{16.77} for several tri- to hexachlorobiphenyls in clean water. These values were about 3 orders of magnitude greater than measured values for soots and about 1 order of magnitude greater than for a charcoal. They found that K values for added PCBs correlated well with average pore diameter for soot and soot-like material and proposed that pore sorption dominated PCB binding mechanisms. We calculated K_{AC} values using homolog sediment PCB concentrations in the composite sediment sample (e.g., C_{w,penta-PCB} = 878 µg/kg), the fraction of activated carbon in the sediment, f_{AC} = 0.034, and aqueous homolog PCB concentrations (e.g., C_{w,penta-PCB} = 4.1 x 10^{-4} µg/L for 6-month contact), obtaining log K_{AC} values of 7.6–8.1 for tetra- through nonachlorobiphenyls. Though significantly larger than PCB distribution coefficients for amorphous sediment organic carbon, these values are smaller than those reported by Jonker and Koelmans (24) for activated carbon–water systems.

One reason for finding smaller distribution coefficients in this study, compared to those from activated carbon–water systems, is that only about 40% of the total PCBs may be available for mass transfer to carbon due to kinetic limitations. Another factor is the abundance of natural organic matter (NOM) in the sediment, which may reduce the fraction of activated carbon available for binding PCBs by both competing for sorption sites and by blocking entrance to micropores, where the majority of sorption capacity is located. Ebie et al. (29) showed that NOM reduced activated carbon sorption capacity of four organic pesticides up to 90% and attributed the reduction to competitive sorption and micropore blockage by NOM. A third possibility is competition among the PCBs and PAHs present in the sediment. Nonlinearity is often evident with sorption to activated carbon, and the total PCB concentration in our aqueous systems is approximately 2 orders of magnitude greater than in Jonker’s systems. This could explain the lower K_{AC} value from our work, relative to Jonker’s results (24).

A comparison of aqueous equilibrium PCB concentrations for samples from 1- and 6-month sediment–activated carbon contact periods indicates that mass transfer limitations are playing an important role for the higher chlorinated PCBs. Tetrachlorobiphenyls do not show a significant change in aqueous phase concentration for sediment–activated carbon contact times of 1 and 6 months. This is likely because release of tetrachlorobiphenyls from sediment is relatively fast as shown in Figure 4, resulting in little additional mass transfer after 1 month. Nonachlorobiphenyls show little change in aqueous concentrations for sediment–activated carbon contact times of 1 or 6 months because only a relatively small amount is released from the sediment and the system may be far from equilibrium. An observable difference in aqueous equilibrium PCB concentrations for sediment–activated carbon contact times of 1 or 6 months was evident for hexachlorobiphenyls. Following an initial fast release from sediment, activated carbon uptake becomes limited as hexachlorobiphenyls diffuse slowly from sediment into activated carbon pores.

Implications. The results from this work demonstrate that adding activated carbon to contaminated sediments can reduce PCB and PAH aqueous equilibrium concentrations, PCB and PAH uptake by SPMDs, and diffusive PCB flux to overlying water. A companion study (30) shows that contacting Hunters Point sediment with activated carbon reduces bioaccumulation of PCBs by benthic organisms. Results from the present study and our bioaccumulation work indicate that application of activated carbon to PCP-contaminated sediment can be an effective in-situ stabilization method to reduce contaminant availability to surrounding water and biota. Further work is required to address issues related to the application of activated carbon in the field for in-situ control of PAH and PCB availability in sediments. This includes work to understand the effects of activated carbon dose and particle size and contaminant mass-transfer kinetics with limited mixing. Also, activated carbon deployment and particle dynamics under various hydrodynamic conditions need to be assessed. Each contaminated sediment site will require specific consideration to find an appropriate management strategy and treatment method.

Depending on site conditions, activated carbon could be mixed or injected into sediment, used in conjunction with sand or gravel to hold carbon in place, or used as an “active cap”. For the case of Hunters Point sediment, we envision that treatment with activated carbon would involve mixing of the carbon into the upper 0.3–0.5 m of sediment, which comprises the biologically active zone. Hunters Point sediment at South Basin is cohesive, and the site is slightly depositional and protected from extreme hydrodynamic forces. Activated carbon could be mixed into sediment at low tide when the mudflat treatment area is exposed. In this situation, activated carbon treatment may be an attractive, cost-effective alternative to sediment dredging and disposal and possibly at other sites comprising large-volume, low-concentration material or as an adjunct to dredging to manage residuals after more highly contaminated sediments have been removed.

Acknowledgments
Funding for this research was from the Department of Defense through the Strategic Environmental Research and Development Program (Contract DACA72-01-C-0002). Supplemental support was provided by Schlumberger, Ltd.

Supporting Information Available
Three tables and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
(22) Gustafsson, O.; Gschwend, P. M. In Molecular Markers in Environmental Geochemistry; Eganhouse, R. P., Ed.; ACS Symposium Series 671; American Chemical Society: Washington, DC, 1997; pp 365–381.

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ES034992V
APPENDIX B

University of Maryland Baltimore County
Analytical Methods - Standard Operating Procedures
ANALYTICAL METHODS

STANDARD OPERATING PROCEDURES

PREPARED BY
DR. UPAUL GHOSH

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
UNIVERSITY OF MARYLAND BALTIMORE COUNTY

Updated August 6, 2006
Sediment PCBs will be extracted following EPA publication SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) method 3550B using three volumes of 40 mL each of acetone-hexane mixture (1:1) and sonicating the slurry for 6 minutes (pulsing for 15 seconds on and 15 seconds off). There are no modifications to this EPA method and the method will be followed exactly. The URL of the online publication of the method is provided below.

http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3550b.pdf
PCB cleanup is based on EPA publication SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) methods 3630C (Silica gel cleanup), 3665A (sulfuric acid cleanup) and 3660B (Sulfur removal with copper). In the silica gel cleanup process, the dried and concentrated extracts are passed through a 3% deactivated silica gel column for the removal of organic interferences and to separate the PCBs and PAHs. Silica gel (chromatographic grade, 100-200 mesh, Fisher Scientific, Fair Lawn, NJ) is activated by heating at 130°C for 16 hours, then deactivated by gradually adding 3% by weight deionized water and rotating on a roller at approximately 2 rpm overnight. The sulfur cleanup procedure will be followed only when there is evidence of contamination from elemental sulfur as shown in example chromatogram below. The three standard methods will be followed without any modifications.

The URLs of the online publications of the methods are provided below.


![Figure A1. Example chromatogram showing heavy contamination from elemental sulfur.](image-url)
PCB congener analysis using GC-ECD

PCB congener specific analysis will be performed using EPA publication SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) EPA SW846 Method 8082. The URL of the online publication of method 8082 is provided below.

The only modification to EPA method 8082 involves the use of a congener-level PCB calibration based on Mullin (1994) and the use of a single capillary column analysis. Any changes or deviations beyond those listed here will be documented in the final report. A multi-level calibration table has been prepared using dilutions of a PCB standard 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. Concentrated stock solution of this standard mixture and concentrations of individual PCB congeners in the standard mixture have been obtained from the EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, Michigan (Mullin M., 1994). Serial dilutions of this standard have been used to prepare calibration standards. The two internal standards used are 2,4,6-trichlorobiphenyl and 2,2’,3,4,4’,5,6,6’-octachloro biphenyl, which are not present in commercial Aroclor mixtures. Using this protocol, 91 PCB congeners or congener groups could be identified and quantified as shown in Table A1. Co-eluting peaks are calibrated as sum of congeners. Congener identification is performed based on congener relative retention times and based on the comparison of a standard chromatogram with a sample chromatogram obtained from Mullin (1994).

Sample preparation protocol:
After PCB extraction and cleanup, place 1 ml of the cleaned sample in a 2 ml autosampler vial with Teflon-lined septa. The sample may need to be concentrated or diluted prior to placement in the autosampler vial for injection. Decision to concentrate or dilute the sample will be based on expected concentration range of the sample and the concentration range of the calibration curve. Concentration will be carried out using nitrogen evaporation apparatus (N-evap model 11155-DA) and ultra pure nitrogen gas.

Remove the internal standards from the freezer, and equilibrate to ambient temperature for approximately 1 hr before addition. Add 10 microliters of the internal standard solution (containing 400 µg/L of the two internal standards) using a 25 microliter glass syringe to the autosampler vials containing PCB samples in hexane. This will result in a final concentration of about 4 µg/L of each internal standard. The sample vials will be labeled using a permanent marker and placed on the autosampler tray.

Instrument:
An Agilent gas chromatograph (model 6890N) with a fused silica capillary column (HP-5, 60 m x 0.25 mm inner diameter), and a micro electron capture detector will be used for analysis.
An Agilent 7683 autoinjector module will be used or sample injection. To start the GC analyses follow these steps:

1. Make sure the GC has been turned on for at least an hour
2. Make sure the autosampler tower is placed over the front inlet for PCB analysis.
3. Ensure sufficient carrier gas (ultrapure grade helium) and make-up gas (ECD grade argon/methane mixture P5) are in the cylinders to complete the runs.
4. Change inlet septum if more than 1 month has passed since last replacement or more than 50 samples have been injected.
5. Change the solvents in the autosampler wash vials, and empty out and clean the autosampler waste vial.
6. Load the method “PCB3” and check to make sure that the method parameters match those listed under “INSTRUMENT CONTROL PARAMETERS” in the SOP.
7. Start a new sequence table and give it a name with the date of analysis (e.g. PCB-Dec25-04).
8. Enter the sample names. Samples will be analyzed in sets that will include blank hexane, standards, and QC samples as follows:

| Vial 1: | Hexane |
| Vial 2: | Lab reagent blank sample |
| Vial 3: | PCB standard sample |
| Vial 4-11: | Experimental Samples |
| Vial 12: | PCB matrix spike sample |
| Vial 13: | Lab reagent blank sample |
| Vial 14: | PCB standard sample |
| Vial 15-22: | Experimental Samples |
| Vial 23: | PCB matrix spike sample |
| Vial 24: | Lab reagent blank sample |

9. Place the sample vials in the correct spots in the autosampler tray.
10. Verify that the correct method name has been entered in the sample log table for each vial.
11. Save the sample sequence.
12. Start the sequence.
13. Check to make sure that the first sample injection operates smoothly.
14. After the sequence is complete, check to make sure that all sample vials have been run. Check for needle puncture marks in the autosampler vial septa.
15. Proceed to PCB data analysis.

References:
Preparation of Calibration Standards:

Standard:

(1) Stock solutions used (From Ultra Scientific):
   Aroclor 1232: 100.3±0.5 ug/ml
   Aroclor 1248: 100.3±0.5 ug/ml
   Aroclor 1262: 100.3±0.5 ug/ml

(2) Diluting process
   Aroclor 1232: 100.3±0.5 ug/ml, 1 ml stock solution + 9 ml hexane--- 10000 µg/l
   Aroclor 1248: 100.3±0.5 ug/ml, 1 ml stock solution + 9 ml hexane--- 10000 µg/l
   Aroclor 1262: 100.3±0.5 ug/ml, 1 ml stock solution + 9 ml hexane--- 10000 µg/l

In the standard:
   Aroclor 1232: Aroclor 1248: Arocolor1262 = 25:18:18
   Take
   Aroclor 1232: 10 ml
   Aroclor 1248: 7.2 ml
   Aroclor 1262: 7.2 ml

Then add hexane to reach 40 ml and the final solution conc. of 6100 µg/l.

The 6100 µg/l stock is diluted as follows:
   3 ml stock to 10 ml hexane : 1830 µg/l
   1 ml stock to 10 ml hexane: 610 µg/l
   3 ml of 610 µg/l to 10 ml hexane: 183 µg/l
   1 ml of 610 µg/l to 10 ml hexane: 61 µg/l
   0.5 ml of 610 µg/l to 10 ml hexane: 30.5 µg/l

Internal standards:
   2,4,6-trichlorobiphenyl, Stock solution: 100.4 ±0.5 ug/ml
   2,2‘,3,4,4’,5,6,6’-octachloro biphenyl, Stock solution: 100.4 ±0.5 ug/ml.

Diluted:
   10 times, 10 µg/ml =10*10³ µg/l
   Take 5ml of these two diluted solutions, respectively to the 200 ml bottle and add 115 ml hexane, the final concentration is: 400 µg/l.

Surrogate standards:
   PCB#166, #65 and #14 are used as surrogates.
   The final concentrations for the calibration are: 2, 5 10 and 20 ug/l.
Safety:

Some of the analytes used in this method have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

Researchers working in the laboratory should follow UMBC laboratory Safety guidelines with attention to the following:

1. A lab coat is necessary when working in the lab.
2. Eye protection with splash resistant safety glasses or safety goggles is required.
3. Nitrile gloves should be used while handling PCB samples or standards.
4. Special solvent resistant gloves should be used while handling large amount of solvents.
5. All solvent work should be done in working and certified fume hoods.
6. Full-length trousers and covered shoes are required in the laboratory.
7. Avoid working alone in the laboratory. If work must be performed after hours or in the weekend inform the supervisor or other staff so that your presence is known and will be accounted for in case of an emergency.
8. Store chemicals and solvents under the hoods in flame-proof cabinets. Acids must be separated from bases.
9. A rubber bucket is required to transport any chemical.
10. Gas cylinders should be well secured at all times.
11. Discard disposable gloves and wash hands well after work.
12. No food or drinks are allowed in the laboratory.
13. In case of a minor spillage, use spillage kit to clean the area. A major spill requires the UMBC Environmental Health and Safety and Fire Department to be contacted and the working area evacuated.
14. MSDS sheets should be stored in the laboratory and easily accessible to the researchers.
15. All chemicals and standards must be labeled with chemical name, date, and initials of person to contact.
16. All chemicals and standards will be entered in the laboratory chemicals inventory.
17. Empty chemical bottles should be flushed out with water, or, in case of liquid, allowed to evaporate under a hood before discarding.
18. Label waste solvent containers as `chlorinated waste' and `non-chlorinated waste'. Glass bottles used for waste are placed under hoods for convenience. When full, call UMBC Environmental Health and Safety for hazardous waste disposal.
INSTRUMENT CONTROL PARAMETERS

6890 GC METHOD “PCB3.M”

OVEN

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Run time: 98.00 min

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**FRONT DETECTOR (µECD)**

- **Temperature:** 300 °C (On)
- **Mode:** Constant makeup flow
- **Makeup flow:** 60.0 mL/min (On)
- **Makeup Gas Type:** Argon methane 5%
- **Electrometer:** On

**SIGNAL 1**
- **Data rate:** 10 Hz
- **Type:** front detector
- **Save Data:** On
- **Zero:** 0.0 (Off)
- **Range:** 0
- **Fast Peaks:** Off
- **Attenuation:** 0

**SIGNAL 2**
- **Data rate:** 20 Hz
- **Type:** front detector
- **Save Data:** Off
- **Zero:** 0.0 (Off)
- **Range:** 0
- **Fast Peaks:** Off
- **Attenuation:** 0

**7673 Injector**

**Front Injector:**
- **Sample Washes:** 1
- **Sample Pumps:** 2
- **Injection Volume:** 2.0 microliters
- **Syringe Size:** 10.0 microliters
- **PostInj Solvent A Washes:** 2
- **PostInj Solvent B Washes:** 2
- **Viscosity Delay:** 0 seconds
- **Plunger Speed:** Fast
- **PreInjection Dwell:** 0.00 minutes
- **PostInjection Dwell:** 0.00 minutes

**Back Injector:**
No parameters specified
Table A1. List of PCB Congeners Quantified

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<td>(81+87)</td>
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Figure A2. PCB congener internal calibration plots showing good linear fit of the 4-level calibration data for congeners 28 (left) and 183 (right).
UMBC-SOP-4.


Analysis of sediment TOC will be conducted with all four sediment samples. The TOC analysis will be performed using a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). Carbon in the sample is combusted to form CO₂ which is detected by a non-dispersive infrared gas analyzer (NDIR). The sediment TOC analysis follows an operating procedure recommended by the manufacturer.

Sample homogenization and acidification:
The sediment sample will first be homogenized in a clean ceramic mortar to a powder. Three 0.5 g sub-samples of the homogenized sample 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.

Soil TOC measurement:
The prepared sample in a ceramic combustion boat is then inserted in the 900 °C combustion furnace. The high temperature and pure oxygen environment in conjunction with a platinum catalyst provides complete oxidation of carbon compounds into CO₂ gas and water. The produced CO₂ gas is detected by a non-dispersive infrared (NDIR) detector. The total organic carbon concentration is determined by generating a calibration curve with known standards and comparing area counts of the unknown sample to that of the best fit line in the calibration curve.

Soil TOC calibration:
The instrument shall be calibrated using a carbon-source standard (e.g., reagent grade glucose or naphthalene). A series of calibration curves, that accommodates the expected working ranges of the samples, shall be generated as per instrument manufacturer’s recommended procedures. The generally accepted measurement range for most carbon analyzers is from 0.1 mg to 30 mg of carbon in a solid sample; maximum sample size is limited to 1.0 g. For TOC analysis in sediment samples, this instrument’s minimum detection limit for carbon, based on a 0.5-g, dried sample, is 0.04%.

Appropriate QA/QC samples shall be analyzed along with each batch of ten sediment samples, to include:
1) Background blank
2) Blind duplicate sample
3) Carbon QC-check sample

The acceptance criteria are as follows: ± 20 % relative percent difference (RPD) for duplicate analysis; and percent recovery of carbon from C-check sample, 90-110%. The
background blank sample should not give a value higher than the stated minimum
detection limit of 0.04% carbon. If a batch run does not meet the above quality
standards, the analysis of all samples within the failed batch shall be repeated until the
run is in full compliance with the QC requirements.
UMBC-SOP-5.

Sediment Moisture Content Standard Operating Procedure.

The moisture content of the four sediment samples will be determined using a modified version of American Society for Testing and Materials (ASTM) Method D2216. The method is modified as follows: approximately 5-10 g of sediment will be placed in a pre-weighed, aluminum weighing pan. The initial weight will be recorded, and the pan will be placed in a drying oven at 110±5°C. The oven temperature will be verified at the start and end of the drying period using a digital thermometer. The sample will be dried to constant weight overnight, cooled in a desiccator for at least 30 minutes, and weighed again to obtain the dry weight. The sediment moisture content will be calculated as \(1 - \frac{(\text{dry weight}/\text{initial weight})}{100}\%\). The percent dry weight will be calculated as \(\frac{(\text{dry weight}/\text{initial wet weight})}{100}\%\).

Duplicate analysis will be performed for moisture content of each sediment sample for which PCB analysis is performed. Analytical balances will be calibrated annually.
APPENDIX C

University of Maryland Baltimore County
In-Situ PCB Biouptake Studies with *L. variegatus* –
Method Description and Standard Operating Procedures
In-Situ PCB Biouptake Studies with *L. variegatus*

Method Description and Standard Operating Procedure

Prepared by

Upal Ghosh

Department of Civil and Environmental Engineering
University of Maryland Baltimore County
Baltimore, MD 21225

Updated Aug 7, 2006
METHOD DESCRIPTION:

PCB uptake in the freshwater oligochaete *L. variegatus* will be measured in-situ to assess the change in PCB bioavailability to benthic organisms after amending sediments with activated carbon. This organism was selected for in-situ tests based on the USEPA method for testing bioaccumulation in freshwater sediments (USEPA, 2000), as well as previous studies by Burton et al. (2005) and Sibley et al. (1999), which have demonstrated the use of this organism for in-situ bioaccumulation measurements in freshwater sediments. Bioaccumulation tests will be conducted before treatment, and during the 12-month and 24-month post-treatment surveys. Results from the before treatment in-situ studies will serve as the baseline conditions for comparison of the effects of activated carbon addition to the sediments. During these surveys, *L. variegatus* will be deployed in screened cages or bioassay chambers at six sampling locations and one reference location for an exposure period of 14 days, following the draft ASTM method described in the Draft Standard Guide for Assessing Freshwater Ecosystem Impairment Using Caged Fish or Invertebrates (Burton et al., 2002). In support of this in-situ approach, trial field deployments will be performed in Summer 2006 (prior to the baseline studies) to evaluate the logistics associated with deploying and retrieving the caged worms in the lower Grasse River and the survival of the worms in field conditions.

The in-situ deployment will follow the ‘surficial sediment and pore water exposure’ method outlined in Burton et al. (2002). This in-situ testing method is designed to achieve organism exposure to surficial sediment and sediment porewater at the site. In-situ exposure chamber design will follow Burton et al. (2002) with some modifications as described in the operating procedure. The chambers are constructed of cellulose acetate butyrate tubes 12.7 cm in length and 7 cm outside diameter in which two 4x8 cm openings are constructed and covered with a nylon mesh attached using aquarium grade silicone sealant. Each caged deployment will consist of five replicate cages and an additional cage for water quality measurements and for deployment of any additional experimental monitoring tests. At each sampling location, the six chambers will be deployed together mounted on a rack for ease of retrieval. One set of six test chambers will also be deployed at each sampling time at the chosen reference location. To initiate the caged exposure, surficial sediment will be collected from the location, homogenized, and split for use in in-situ and ex-situ bioaccumulation tests. Sediment will be placed in each in-situ chamber, filled with site water, allowed to equilibrate and settle for 15 minutes before introduction of the worms. Due to the large depth of water column at the test site, the worms will not be flushed down an inlet tube as suggested in the ASTM draft method. The amounts of sediment and worms placed in each in-situ bioassay chamber will be similar to the amounts used for the ex-situ bioaccumulation studies for ease of comparison. The bioassay chambers will remain in the river for 14 days. After the exposure duration, the cages will be located and retrieved, and the worms separated from the sediment. The worms will be placed in depuration chambers and weighed before being frozen and shipped to the laboratory for PCB extraction and analysis. Congener level PCB analysis will be conducted on worms retrieved from each exposure chamber separately.

Volume of sediment per chamber: 150 ml
Mass of worms per chamber: 0.5 g
OPERATING PROCEDURE FOR FIELD DEPLOYMENT OF WORM CAGES AT GRASSE RIVER

Laboratory Tasks Before Deployment:

1. Prepare worm chambers following design provided in the ASTM draft method and arrange 6 chambers into a basket with bricks attached as weights.

2. Test worm chambers in aquarium containing Grasse River sediments and water and check on worm behavior and survival.

3. Purchase the necessary quantity of worms from Aquatic Research Organisms for field deployment.

4. Separate worms into required quantity for each chamber and maintain organisms in Grasse River water in 20 ml glass scintillation vials. Fill tubes with 80-90% water and add a small quantity of pureed unbleached paper towel. Place tubes in styrofoam tube holders and tightly pack in a cooler with ice. Do not allow worm tubes to touch the ice to prevent over-cooling. Make arrangements to transport cooler to Alcoa field lab. It is preferable to drive the worms and deployment chambers to Massena due to the potential of damage to the cages and stress on the worms during shipment in hot weather.

5. Prepare and run parallel control tests in the laboratory:

   a. First control to observe health of organisms from the same batch used for the field test. The control tests will be run in duplicate 20 ml glass vials with Grasse River water and pureed unbleached paper towel used as food. Twenty five worms will be used in each control test.

   b. Second control to observe any effect of transportation on the health of the organisms. These organisms will be carried to the field and returned back to the lab for the duplicate control tests. At the conclusion of the control tests, the number of surviving organisms will be counted and compared with the starting number to check for any significant mortality.

Figure 1. Three worm chambers in a basket
On-site tasks during in-situ cage deployment:

1. Inspect transported organisms in the cooler and make sure they have survived transport.

2. Carry cooler on the boat to the site and equilibrate organisms to river water temperature by placing the worm vials in a tray containing site water.

3. Locate cage deployment site with GPS coordinates and perform water quality measurements. Use a probe to measure pH, Temp, DO, turbidity, and conductivity at the surface, middle, and near the bottom of the river.

4. Collect about 1 gallon of sediment from the site using a petite ponar and inspect for the presence of indigenous organisms. If organism levels are found to be high enough to interfere with the in-situ measurement, screen sediments to remove organisms. Also examine for any obvious presence of predatory organisms. Past work at Grasse River indicates low density of native organisms in the sediments.

5. Place about 150 ml sediment into each chamber and pack remaining sediment (about 2L) for shipment to UMBC for parallel ex-situ laboratory tests.

6. Collect river water in a deep tray and place the chamber basket in the tray so that each chamber is completely submerged and full of water.

7. Keep chambers submerged in river water in a horizontal position in a large tray and partially close end caps leaving the hole uncovered at the top.

8. Allow sediment in chambers to settle for 15 minutes.

9. Introduce worms with a plastic pipette into each chamber through the two holes in the chamber (see Figure 2). Use a plastic pipette to transfer worms from the 20 ml glass vials to the worm chambers.

10. Close end caps completely covering the hole after allowing all air to escape and completely fill the chambers with water. The cages should have ropes tied to all four ends and balanced with the weights in a way to enable lowering of the setup in a horizontal, position under water.

11. Slowly lower the chamber basket on to the sediment bed without lifting the chambers out of the water. This can be achieved by submerging the tray into the river.

Figure 2. Inserting worms through an opening in the worm cage
water to transfer the chambers (see Figure 3).

12. Use an underwater camera to observe and document positioning of the chamber basket on the sediment bed. Check to make sure that the basket is placed in a horizontal position and the worm chambers are only partially sunk into the sediments. If the worm chambers get completely submerged in soft sediments there may be a concern with oxygen transfer into the tubes. The underwater video observation will be performed at the first deployment location during each of three deployment times (baseline study and once a year for two subsequent years).

13. Tie the tethering rope to a submerged buoy appropriately to enable retrieval after 14 days. Use decoy floating buoys as placement markers and submerged small buoys for in-situ test locator (see Figure 4).

14. Monitor water quality at test initiation and end. One in-situ chamber will be set aside for water quality measurements. To measure water quality, the chamber will be placed in a vertical position in a tray of water with the end slightly above the water surface. The end-cap will be opened and a YSI probe inserted to measure pH, Temp, DO, and conductivity. The YSI probe and a turbidimeter will also be used to measure ambient water quality in the water column close to the test location.

Figure 3. Six worm chambers in a basket being lowered into the river from a boat.
Figure 4. Worm chambers tied to a barely visible submerged buoy with a placement location buoy nearby that is tied to a brick.

Figure 5. Underwater video image capture showing the placement of the cages on the sediment and a curious yellow perch sniffing.
On-site tasks during in-situ cage retrieval:

1. Find in-situ cage location using GPS coordinates and decoy buoys.

2. Perform water quality measurements. Use a probe to measure pH, Temp, DO, turbidity, and conductivity at the surface, middle, and near the bottom of the river.

3. Use underwater camera to observe and document the state of in-situ chambers before retrieval for one of the locations. Look out for any obvious damage, disruption, or burial of the test setup. Save images.

4. Very slowly lift the cage basket to near the water surface keeping the cages just submerged in the river water and tie the rope on the boat to keep the cages hanging in the water.

5. Cut the two plastic ties on each cage and gently slide the cage into the 500 ml plastic beaker under water. Take care not to press against the screen mesh windows.

6. Turn the beaker with the cage to a vertical position under water and lift above water and place in the slotted tray (see Figure 6).

7. Monitor water quality parameters in one of the test chambers by opening the top end cap and inserting the YSI probe into the water.

8. Place the cages in a cooler with river water in beakers and transport to the field laboratory.

9. At the field laboratory retrieve worms from each cage and place in depuration beakers.

10. After 6 hours of depuration, remove worms, and place in pre-weighed glass scintillation vials for transport in ice to UMBC.

Figure 6. Slotted tray and beakers to place the worm chambers after retrieval
Procedure for harvesting of worms from sediment and depuration:

1. Pour sediment with worms into a U.S. Standard No. 40 sieve with 0.425 mm mesh opening.

2. Add potable water to a wide, shallow pan and gently sieve sediments to remove fine material. Use tweezers to remove coarse material as necessary.

3. Gently remove remaining sediment matrix and worms from the sieve and place in a separate pan with potable water. Inspect sieve to make sure transfer is complete.

4. Gently stir or swirl the contents of the pan to evenly distribute the contents of the sediment matrix across the pan to locate the worms.

5. Transfer the worms using a plastic pipette to a smaller pan with fresh water. Use the pipette to remove any solid materials from the pan.

6. Sieve a second time if necessary to maximize recovery of the worms and repeat steps 4 and 5.

7. Transfer about 20 ml stream/river water to a pre-weighed 25 ml vial and place the cleaned worms in it. Let the worms purge for 6 hrs. Make sure there is no sediment carried over to the purging vials. Note the time when depuration is initiated for each vial.

8. After 6 hours of depuration, remove the water and feces from the vials, and then wash the vial and worms two times with stream/river water. Make sure there is no sediment or feces remaining in the vial.

9. Pick up two worms from each vial and place in two clean vials for duplicate lipid measurements.

10. Take all of the water out from the vials after the depuration period and use a paper towel to blot out excess water if necessary. Cap the vials and freeze the sample for shipping.

11. Weigh the vials after making sure there are no visible droplets of water on the vial.
Typical Deployment, Retrieval, and Depuration Schedule:

Deployment:

Previous day: Travel to Massena and make sure the worms and cages have survived the transport.

6:00 am: Set out on a boat with equipment required to deploy worm cages. Depending on the site weather conditions, safety requirements, and actual time taken to deploy the cages at each location, the deployment may take more than one day.

Next day: Travel back to the laboratory with control worms in a cooler.

Retrieval and depuration:

Previous day: Travel to Massena and make sure the worms and cages have survived the transport.

6:00 am: Set out on a boat with equipment required to retrieve worm cages.

12:00 pm: Complete retrieval of cages and return to shore.

1:00 pm: Bring chambers to the Alcoa laboratory.

2:00 pm: Start screening worms and place worms into pre-weighed 20 ml depuration vials. Carry worm depuration vials to the hotel in a small cooler.

8:00 pm: End depuration at specific times for each vial by emptying water and feces with a pipette, closing vial, and placing in ice.

Next day: Retrieve remaining cages, if any, and complete screening and depurating worms at the Alcoa Lab.

Next day: Return to UMBC with depurated and frozen worms in a cooler.
Equipment Checklist for In-Situ Test:

1. Worm cages
2. Worm cage baskets
3. Bricks
4. Ties: small and big
5. Plastic tray
6. Plastic pipettes (10)
7. Worms weighed in required number of 20 ml glass vials
8. Ropes
9. Floats, Buoys
10. Knife
11. Cutting tool for ties.
12. Coolers for transporting worms.
13. Ice (buy locally)
14. Various size ziplock bags
15. Bubble wrap for shipping
16. Duct tape
17. Clear tape
18. Plastic beakers
19. Slotted Trays
20. Pre-weighed 20 ml Glass vials for collecting depurated worms.
APPENDIX D

University of Maryland Baltimore County
Laboratory Studies
Method Descriptions and Standard Operating Procedures
Laboratory Studies

Method Descriptions and Standard Operating Procedures

Prepared by

Upal Ghosh

Department of Civil and Environmental Engineering
University of Maryland Baltimore County
Baltimore, MD 21225

Updated Aug 7, 2006
LABORATORY STUDIES

Laboratory activities will include a suite of physicochemical and biological tests conducted before and after the application of activated carbon to sediments to monitor the effectiveness of the field treatment in reducing PCB flux from sediments and uptake by benthic organisms. Studies will include examination of aqueous equilibrium, PCB desorption rates, and measurement of PCB uptake in freshwater oligochaetes. These studies will follow methodologies previously employed by UMBC in other studies involving application of activated carbon to sediment. Details regarding each of the experimental studies are provided below.

1. Ex-Situ PCB Uptake in Biota

1.1. Method description.
PCB uptake in oligochaetes (*L. variegatus*) will be measured to assess the change in PCB bioavailability to benthic organisms after amending sediments with activated carbon. The test method will be based on the USEPA *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates* (USEPA, 2000).

The first modification to USEPA (2000) that is being proposed is the reduction in the size of test chambers primarily because we have determined that our organism tissue requirement for PCB analysis is much smaller for the range of sediment PCB concentrations expected during this study relative to the USEPA document. Also, the use of a smaller volume of sediment per replicate reduces the amount of PCB-containing sediment that needs to be transported to the laboratory without compromising the results. The sediment amount used per replicate will conform to the guidance of maintaining a ratio of 50:1 of sediment TOC and organism dry weight. About 0.5 grams of wet worms will be introduced to about 150 ml of wet sediment in 400 ml glass beakers (as opposed to 1g wet worms suggested in USEPA [2000]). Others (Kukkonen et al., 2005) have used a similar modification of exposure chamber size (250 ml beaker) for PCB bioaccumulation testing with *L. variegatus*. There are two reasons for a reduced sediment volume requirement for the bioaccumulation studies. First, the USEPA method is designed to allow bioaccumulation monitoring even at background sites where PCB levels are low. The PCB concentration range we are targeting at the Grasse River sediment is several ppm. Second, the USEPA method guidance on minimum tissue requirement (1 gram) is based on 1990 data on PCB analytical chemistry. Current PCB analytical methods using the latest GC-micro-ECD instruments and long capillary columns can provide much better detection limits than the 0.6 ppm for a 1 gram sample cited in the USEPA method based on work by Schmitt et al. (1990). The calculated total PCB detection limit for 0.5 grams of wet worms is less than 0.1 ppm wet tissue. The expected tissue PCB concentration based on previous work with Grasse River sediments is about 2 orders of magnitude higher than our detection limits.

The second modification to the bioaccumulation test method was suggested to Alcoa by the EPA. This modification involves reducing the exposure time for the organisms from 28 days to 14 days for all exposures. The operating procedure has been modified accordingly.
1.2. Setup of laboratory PCB biouptake studies.
Laboratory PCB bioaccumulation tests will be conducted for the sediments collected from six treatment locations and one reference location. Sediments used for the laboratory biouptake studies will be collected simultaneous to the sediment collection for the in-situ bioaccumulation tests. Fresh *L. variegatus* will be obtained from Aquatic Research Organisms, Hampton, New Hampshire. The worms will be maintained in the laboratory using standard culturing procedures outlined in the EPA (2000) document. Essentially the culturing method involves maintaining the worms in plastic containers with pureed unbleached paper towel and stream or site water with daily renewal of the overlying water. The water in the culture chamber should be aerated using an aquarium air pump and an air stone.

Worms will be exposed to the sediments in 400 mL glass beakers (150 ml sediment and 0.5g worms per beaker; with 4 replicates per sample) for 14 days and maintained at 23 ± 1 °C in a aquarium maintained with a 16 hour light:8 hour dark photoperiod. The aquarium will contain water to a depth of 3” (partially immersing the exposure beakers) to maintain a constant temperature for all the beakers. A thermometer placed in the aquarium water will be used to monitor temperature of the test.

At the termination of the experiment, worms will be removed from the sediments and allowed to depurate for 6 hours in a clean beaker containing site water. The depurated worms are then homogenized with excess sodium sulfate and extracted with a 50:50 mixture of hexane and acetone under sonication.

**Table 1. List of activities for conducting PCB bioaccumulation study in *L. variegatus*.

<table>
<thead>
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<th>Day</th>
<th>Activity</th>
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<tr>
<td>-1</td>
<td>Isolate worms for conducting bioaccumulation test. Add sediment into each test chamber, place chambers into exposure system, and start renewing overlying water. Ensure the lighting arrangement is working correctly according to the specified photoperiods.</td>
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<tr>
<td>0</td>
<td>Measure total water quality (pH, temperature, dissolved oxygen, hardness, alkalinity, conductivity, ammonia). Transfer appropriate amount of worms (based on weight) into each test chamber. Sample a subset of worms used to start the test for PCB analyses. Observe behavior of test organisms.</td>
</tr>
<tr>
<td>1 to 6</td>
<td>Measure temperature and dissolved oxygen. Observe behavior of test organisms.</td>
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<tr>
<td>7</td>
<td>Measure total water quality.</td>
</tr>
<tr>
<td>8 to 13</td>
<td>Same as Day 1 to 6</td>
</tr>
<tr>
<td>14</td>
<td>Measure total water quality. End the uptake by collecting the worms with a sieve. Separate any indigenous organisms from <em>L. variegatus</em>. Determine the weight of survivors. Eliminate the gut contents of surviving worms in water for 6 hours.</td>
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</table>
1.3. Procedure for harvesting of worms from sediment and depuration:

1. Pour sediment with worms into a 500 ml beaker.

2. Add stream/river water and mix very gently with glass/plastic bar to make into a slurry.

3. Sieve the sediment slurry through a stainless steel sieve with about 250 µm openings. Use small quantities of the slurry at a time to prevent overloading the sieve with large particles that are retained.

4. Use a squirt bottle to wash the sieved materials and remove clays/fines if necessary.

5. Put the screened material containing worms and large particles in a shallow pan with river water. Suspend the screened materials in the water and remove with a plastic transfer pipette. Avoid handling the worms with tweezers as far as possible.

6. Sieve the slurry multiple times if necessary to maximize recovery of the worms.

7. Transfer the worms using a plastic pipette to another shallow pan with fresh water. Use the pipette to remove any solid materials from the pan.

8. Transfer about 20 ml stream/river water to a pre-weighed 25 ml vial and place the cleaned worms in it. Let the worms purge for 6 hrs. Make sure there is no sediment carried over to the purging vials. Note the time when depuration is initiated for each vial.

9. After 6 hours of depuration, remove the water and feces from the vials, and then wash the vial and worms two times with stream/river water. Make sure there is no sediment or feces remaining in the vial.

10. Pick up two worms from each vial and place in two clean vials for duplicate lipid measurements.

11. Take all of the water out from the vials after the depuration period and use a paper towel to blot out excess water if necessary. Cap the vials and freeze the sample for shipping.

12. Weigh the vials after making sure there are no visible droplets of water on the vial.
Table 2. Parameters to be measured during the worm exposure experiment

<table>
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<tr>
<th># of Day</th>
<th>Temp (°C)</th>
<th>DO (mg/l)</th>
<th>pH</th>
<th>Ammonia (mg/l)</th>
<th>Hardness (mg/lCa(CO₃)₂)</th>
<th>Conductivity (mS)</th>
<th>Alkalinity (mg/lCa(CO₃)₂)</th>
<th>Water exch.</th>
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1.4. Lipid measurement. 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 °C 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 °C for 10 minutes. After cooling, the color is developed by pouring vanillin phosphoric acid regent 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 µl/l made from soybean oil (Fisher Scientific.).


1.5. Water quality measurements of overlying water in bioaccumulation test beakers.

**Temperature:** Water temperature is measured using a thermometer.

**DO:** The DO is measured with portable DO 100 meter (Oakton 35640-series).

**pH:** The pH is tested by oyster pH/mV, temperature meters.

**Conductivity:** Conductivity is measured by dual channel pH/ion meters (Accunet research).

**Alkalinity, hardness and ammonia** are measured colorometrically using the alkalinity test kit (Model AL-AP), Tetratext GH/KH, and ammonia nitrogen test kit, respectively.
1.6. List of key equipment and laboratory supplies

1. *L. variegatus* from Aquatic Research Organisms
2. 400 ml glass beakers
3. Large glass aquarium with temperature control and artificial lighting to place beakers
4. Thermometer to measure water temperature
5. Timer to control lighting duration
6. Alkalinity test kit
7. DO probe
8. Nitrate test kit
9. Ammonia test kit
10. Conductivity probe
11. Plastic transfer pipettes
12. Tissue homogenizer
13. Genesys 10 spectrophotometer (Thermo electron corp. Waltham, MA)
14. Water bath
2. PCB Aqueous Equilibrium measurement.

2.1. Method description:
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.

2.2 Setup of equilibrium experiment.
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.

2.3. List of key equipment and laboratory supplies.
1. Shaker table
2. 1L glass bottles with Teflon-lined caps
3. 1L glass separatory funnels with glass stoppers
4. Aluminum foil to cover bottles
3. PCB Desorption Rate measurement.

3.1. Method description.
Measurement of PCB desorption rate will be done to evaluate the change in PCB desorption kinetics in sediments after amending with activated carbon in the field. Tenax adsorbent resin will be used to perform the extraction of PCBs from sediment slurries.

3.2. Setup of desorption kinetics experiments.
The PCB desorption kinetic studies will follow previously used procedures (Ghosh et al., 2003). Tenax beads (1.0 g, 40-60 mesh, Suppelco, Pennsylvania) and sediment sample (5.0 g wet) will be added to a 40 mL glass vial containing 35 mL of water and continuously mixed in a rotator at 2-3 rpm. The vials will be positioned to achieve a end-over-end rotation. Sodium azide (1000 mg/L) will be added to the mixture to prevent biological growth. At each sampling time (2 hours, 6 hours, 1 day, 2 days, 5 days, 10 days, 30 days, and 60 days), the Tenax beads will be harvested by allowing the sediment to settle and the Tenax beads to float up. The Tenax beads containing the desorbed PCB will be scooped out of the test tube and fresh Tenax will be added at each sampling time. These studies will be conducted in duplicate. PCBs will be extracted from the Tenax beads by agitating the beads in 10 mL of hexane and acetone (50:50 mixture) for 12 hours and repeating two more times. The extracts will be combined and concentrated, cleaned using silica gel chromatography, and analyzed by gas chromatography-electron capture detection (GC-ECD).

3.3. List of key equipment and laboratory supplies

1. 12 ml glass vials with Teflon-lined caps
2. Roller apparatus
3. Plastic roller bottles to place glass vials.
4. Tenax adsorbent resin (40-60 mesh, Suppelco)