

## Quality Assurance Project Plan

Phase I RI Low Resolution Coring/Sediment Sampling  
Lower Passaic River Restoration Project  
Newark, New Jersey

Section: Attachments  
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## Appendix D

### Bioavailability Protocols

This Appendix provides background, scope and methodology for the procedures to evaluate sample specific PCB organic carbon-water partitioning values (K<sub>oc</sub>) and assessment of the geochemical character of particulate organic matter in LPR sediments.

## 1) BACKGROUND

### National Review of Contaminant Bioavailability

In 2003 the National Research Council (NRC) (NRC, 2003). concluded that there was inadequate scientific understanding of bioavailability of contaminants in sediments, which has hampered the widespread consideration of bioavailability processes in remedial decision-making. The NRC recommended specific steps to improve the understanding of bioavailability of contaminants at individual sites for use in regulation and decision-making.

### U.S. EPA Contaminated Sediment Remediation Guidance

In 2005, the U.S. EPA provided guidance for remediation of contaminated sediments which identified contaminant bioavailability as a key parameter for remedial investigations, risk characterization, and feasibility studies (U.S. EPA 2005, Table 1). The guidance emphasized the importance of evaluating contaminant bioavailability in the RI/FS process and the need for assessing contaminant bioavailability in order to evaluate the feasibility of Monitored Natural Recovery (MNR) as a remedial action alternative. Although the EPA has defined contaminant bioavailability as an important parameter for developing site-specific sediment remedial action objectives (RAOs), little or no guidance has been provided on the analytical methods and approach for evaluating contaminant bioavailability.

**Table 1. Utility of bioavailability analysis im EPA Contaminated Sediment Remediation Guidance**

	<b>RI/FS Process</b>	<b>Activity</b>	<b>Application</b>
1.	Remedial Investigation Considerations	Establishing Cleanup Goals	Development of site-specific Remedial Action Objectives (RAOs)
2.	Feasibility Study Considerations	Evaluating Remedial Alternatives	Evaluation of residual risk from contaminants remaining following completion of remedial action
3.	Evaluation of Primary Remedial Alternatives	Assessing Monitored Natural Recovery	Natural processes that reduce toxicity through transformation or reduce bioavailability are preferred
4.	Monitoring During and After Remedial Action	Planning Long Term Monitoring	Support for fate and transport modeling and habitat restoration post remedial action

### Other background on bioavailability of PCBs and PCDD/Fs

Various approaches for characterizing the biological and chemical availability of PCBs and PCDD/Fs have shown that, in the presence of anthropogenic sources of “black” carbon, the

sediment/water partitioning ( $K_{oc}$ ) and bioaccumulation of PCBs is often lower than is typically assumed for natural organic matter (Cornelissen et al. 2005). For example, the sorption of PCBs (Jonker and Koelmans, 2002; Cornelissen et al. 2004; Bucheli and Gustafsson, 2003), and PCDD/Fs (Barrington et al. 2002), to carbonaceous geosorbents has been shown to exceed the sorption to natural organic matter by a factor of 10 to 100. This resistance to aqueous desorption has been shown to be more pronounced (one order of magnitude higher  $K_{oc}$ ) for planar PCBs and PCDD/Fs relative to their non-planar homologues (Cornelissen et al. 2005). This is an important finding because planar PCB congeners are generally more toxic than non-planar congeners.

In addition to variability in site-specific PCB and PCDD/Fs  $K_{oc}$  values in field collected sediments, many studies have shown that PCB desorption is biphasic or triphasic with fast and slow desorbing fractions, indicating sorption to different particle types is affecting the partitioning of PCBs from sediment to pore water (Carroll et al., 1994; Kan et al., 1997; Ghosh et al., 1999; Cornelissen et al., 1997). Kan et al. (1997) found that 2,2',5,5'-tetrachlorobiphenyl had a rapidly desorbing phase and a resistant phase with 30-50% of the mass being irreversibly sorbed to sediment. Carroll et al. (1994) found that desorption of PCBs from Hudson River sediment had a rapidly desorbing fraction and a slowly desorbing resistant fraction with the resistant component making up ~ 45% of the total PCB mass.

Studies have also shown that when black carbon is present in sediment PCBs will partition into the black carbon. Ghosh et al. (2003) analyzed particle types in PCB contaminated sediment and found that carbonaceous particles (black carbon) contributed 5-7% to the total mass of the sediment and 60-90% of the total mass of PCBs in the sediment. This is an important finding because it indicates that although PCBs do not enter aquatic systems sorbed to black carbon, they partition into the black carbon over time. Zimmerman et al. (2004) found that the addition of activated carbon to PCB contaminated sediment reduced the flux of PCBs from the sediment to the water column by 78% over the interval of 1-5 months. Over a six month contact period, the aqueous equilibrium concentration of PCBs was reduced by 92%, again indicating that black carbon in sediments naturally, or added as a remediation strategy, can greatly reduce the bioavailable fraction of PCBs.

Our understanding of the biological significance of carbonaceous geosorbents in contaminated sediments is rapidly developing. It appears that the bioaccumulation of PCBs in macrobenthic organisms and benthivorous fish are more strongly correlated to the bioavailable fraction of PCBs in the sediment than the bulk sediment concentrations. Moermond et al. (2004) found that the fast desorbing portion of PCBs in sediment better predicted the bioaccumulation of PCBs in benthivorous fish than bulk sediment concentrations. Kraaij et al. (2002) found that biota to sediment accumulation factors (BSAFs) were 2 to 27 times lower in sediments where the fast desorbing fraction of PCBs was removed, demonstrating the relationship between chemical measurements of availability and the bioavailability of PCBs. Kraaij et al. (2003) found that pore water concentrations were in equilibrium with the fast desorbing portion of PCBs in sediment and suggested that pore water measurements of PCBs could be used with appropriate  $K_{oc}$  values to calculate the bioavailable sediment concentrations of PCBs. These data have led to the proposed approach of adding activated carbon, coal or charcoal to sediments as a remedial strategy which results in an extensive reduction in bioaccumulation of PCBs by benthic aquatic organisms (Jonker et al. 2004).

## **2) RI/FS CONTAMINANT BIOAVAILABILITY WORK SCOPE**

This investigation is designed to address data gaps in the knowledge of PCB bioavailability in aquatic sediments in Passaic River sediments, specifically to survey the geochemical characteristics of the low density Passaic River particulate organic matter and to develop methods for characterizing the sediment pore water partitioning of PCBs. The goal is to develop

Table 2. Summary of Laboratory Testing

Sample Type	Matrix	Parameter	Purpose	Quantity	Laboratory <sup>1</sup>
<b>Organic Carbon Geochemical Characterization</b>	Sediment	Size/Density Classification & Microscopy	Characterization of organic carbon geochemistry	6	UMBC
		Petrography		6	Carbon Petro
		Total Organic Carbon (TOC), Soot Carbon		6	TestAmerica
<b>PCB Sediment/Water Partitioning Test</b>	Lab Experiment	Bulk Sediment PCBs (congeners)	Aqueous partitioning (K <sub>oc</sub> )	12 <sup>2</sup>	TestAmerica
		Dissolved PCBs (congeners)		12	
		POM-SPE (congeners)		12	
		Dissolved Organic Carbon (DOC)		12	

Note 1. UMBC - University of Maryland - Baltimore County, Baltimore MD

Carbon Petro - R&D Carbon Petrography, Inc., Monroeville, PA

TestAmerica - TestAmerica Laboratories, Inc., Knoxville, TN

Note 2. Six sediment samples analyzed in duplicate

**Table 3  
Laboratory Methods**

<b>Parameter</b>	<b>Method</b>	<b>Method Reference(s)</b>	<b>Laboratory<sup>1</sup></b>
Particle Size/Density Classification	Wet sieving into four size fractions: <63 µm, 63-250 µm, 250-1000 µm, and >1000 µm. Density separation of particles using centrifugation and a cesium chloride solution at specific gravity of 1.8.	Ghosh et al. 2000 Ghosh et al. 2003	UMBC
Particle Light Microscopy	Visible light using a Leica MZ16 stereo microscope	Kahlil et al. 2006	UMBC
Organic Particle Petrography	Optical microscopy of low density sediment particles using plane and polarized light ASTM D2797; D2798; D2799	Ghosh et al. 2003 Kahlil et al. 2006	R&D Carbon Petrography
PCB Congeners – Bulk Sediment	Soxhlet extraction, high resolution GC/MS analysis	EPA 1668A	TESTAMERICA
PCB Congeners – Water	Centrifugation, flocculation, high resolution GC/MS analysis	Ghosh et al. 2000 Khalil et al. 2006	TESTAMERICA
PCB Congeners – POM-SPE	Solvent extraction, high resolution GC/MS analysis	Cornelissen et al. (2007) EPA 1668A	TESTAMERICA
Dissolved Organic Carbon (DOC)	SM 5310C Persulfate-Ultraviolet Oxidation Method	APHA Standard Methods, 1992	TESTAMERICA
Total Organic Carbon (TOC)	Sample acidified to remove carbonates, triplicate analyses on sediments)	Lloyd Kahn	TESTAMERICA
Soot Organic Carbon (SOC)	Heat stable TOC following pretreatment at 375° C for 24 hrs	Gustafsson et al., 1997	TESTAMERICA

**Note 1:** Laboratories

UMBC - University of Maryland - Baltimore County, Baltimore MD  
R&D Carbon Petrography, Inc., Monroeville, PA  
TESTAMERICA – TestAmerica Laboratories, Inc., Knoxville, TN

physical/chemical data on the low density particulate organic matter in the Passaic River and establish methods for characterizing PCB partitioning characteristics and bioavailability. If potentially significant impact on assessment of risk and remedial alternatives for the LPR emerges from this investigation, the program may be expanded to characterize aqueous partitioning of other nonionic organic chemicals such as chlorinated pesticides and PCDD/Fs later in 2008 and 2009.

The primary goal of the work scope is to develop the initial data necessary for establishing and evaluating the potential significance of a project specific method for quantifying the sediment/pore water partitioning coefficients for PCBs. The work will be conducted using chemical/physical methods which have been reported in the peer-reviewed scientific literature using EPA standard methods for quantitation of PCB congeners. The development of a method for PCBs will provide the framework for developing equivalent methods for other chlorinated pesticides and PCDD/Fs.

A secondary goal of the work scope is to conduct a preliminary survey of the site-specific PCB aqueous partitioning coefficients (partitioning between sediment and pore water) in 6 sediment samples which have been collected from different geochemical regimes of the Passaic River. These three areas are anticipated to be soft organic sediments in the river reach down-gradient from the salt water front, the sediments in the transition zone between fresh and salt water, and hard sediments in the freshwater reach below the Dundee Dam. A physical description of the nature of the organic carbon and the aqueous partitioning coefficient ( $K_{oc}$ ) for PCBs will be measured for each of the 6 sediment samples.

### **Sample Selection**

Screening level analysis of PCB concentrations, as measured in each of the bulk surface sediment samples, will be used to select a subset of samples with moderate to high concentrations (100 to 10,000  $\mu\text{g}/\text{kg}$ ) of PCBs for additional testing. Six samples will be selected for method evaluation, based on PCB concentrations and physical description of the sediment.

The selected sediment samples will not be frozen during storage since this may affect the partitioning characteristics of the sediment organic carbon. Sample holding times will be extended from project QA/QC standards to allow for experimental work and method development. All analysis of PCB congeners will be performed on duplicate extracts of each sediment sample. Other QA/QC procedures will follow Method 1668A requirements with adjustments as necessary for the matrices and goals of the project method.

### **Tests for Predicting Bioavailability**

A series of chemical/physical tests will be used to characterize the geochemistry of organic carbon present in Passaic River sediments and quantify sample specific aqueous partitioning coefficients ( $K_{oc}$  values) for estimating PCB bioaccumulation as described below.

#### **1. Geochemical Characterization of Sediment Organic Carbon**

The geochemical characterization of the sediment organic carbon will be carried out at the University of Maryland, Baltimore County through a Service Contract, and will be led by Dr. Upal Ghosh. The geochemical characterization will include petrographic analysis of low density particles conducted at R&D Carbon Petrography.

Low density organic matter present in Passaic River sediments will be characterized to identify the types of natural and anthropogenic particles that may control the aqueous partitioning and bioavailability of PCBs and other hydrophobic organic contaminants. Analysis will include:

- 1) the separation of sediment particles into size and density classes, and

2) the identification of organic particle types by light microscopy with confirmation through petrography analysis.

This work will be conducted by Dr. Upal Ghosh, University of Maryland Baltimore County (UMBC) and R&D Carbon Petrography, Inc. In addition, the total organic carbon (TOC) and heat-stable (soot) carbon will be analyzed in each sample by TestAmerica. These data will provide a physical description of the low density sediment particles that modify the aqueous partitioning and bioavailability of hydrophobic contaminants present in the sediments.

Petrography analysis of particle types will include two components:

1) identification of organic particle types by light microscopy and confirmation through petrography analysis, and

2) semi-quantitative analysis of volume fractions of primary organic particle type.

Optical microscopy analysis will be performed at UMBC in visible light using a Leica MZ16 stereo microscope. The petrography analysis using plane and polarized light will be conducted by R&D Carbon Petrography on lighter density size fractions of sediments using 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 D2799-Microscopic Determination of Volume Percent of Physical Components of Coal. These methods are used to determine the kinds or morphology of carbonaceous particles and the relative abundances of carbonaceous solids such as soot, coal, coke, and tars as described in Ghosh et al (2003). TestAmerica will determine TOC using the Lloyd Kahn method and soot carbon using the modification of this method proposed by Gustafsson et al. (1997) and Accardi-Dey and Gschwend, (2002).

## **2. Sediment Organic Carbon–Water Partitioning (K<sub>oc</sub>)**

Aqueous partitioning tests will be conducted at the TestAmerica laboratory with technical review and support by Dr. Upal Ghosh (UMBC).

The aqueous partitioning of a selected set of PCB congeners will be determined for the 6 sediments in laboratory batch equilibrium tests. The aqueous partitioning of the selected congeners will be determined using laboratory methods published for estimating K<sub>OC</sub> values (U.S. EPA, 2000c; Ghosh et al., 2000; Khalil et al., 2006). The analysis of dissolved PCBs in water samples is complicated by the presence of micro-particulate and colloidal organic matter and its ability to interfere with the measurement of freely dissolved PCBs. To address this analytical problem, the measurement of PCBs in water samples will be conducted after alum flocculation to settle colloidal particulates as described by Ghosh et al. (2000). The batch equilibrium experiments will be conducted in 1L amber glass bottles with Teflon-lined caps. The bottles will be filled with 200 ml of wet sediment and 800 ml of site water (or DI water). Sodium azide (1000 mg/L) will be added to minimize biological activity in the bottles. After 1 month of equilibration on a roller or shaker, the contents will be allowed to settle over 24 hours before flocculation of the unsettled particulates using alum flocculation. High resolution GC/MS analysis of PCBs (EPA Method 1668A) will be conducted on the sediment and water extracts. Dissolved organic carbon in the water extracts will also be measured to adjust the estimate of the freely dissolved PCB concentration. The laboratory tests will be performed in duplicate for each sediment sample collected in order to obtain an estimate of the variance in the sample-specific K<sub>oc</sub> values.

Polyoxymethylene-solid phase extraction (POM-SPE) method has been used to measure low aqueous concentrations of PAHs and PCBs in sorption isotherm studies with strong sorbents (Jonkers et al. 2001; McDonough et al, 2008). Recent work by Cornelissen et al. (2008) developed calibrations for 55 micron thick POM that achieves equilibrium more readily than some of the other SPE devices, and used the approach to measure in-situ porewater and overlying

water concentrations of PAHs in Oslo Harbor sediments. Work at UMBC has extended the calibration of the POM samplers for a larger range of PCB congeners. We propose to test the application of POM samplers in measuring low levels of porewater PCB concentrations that may be difficult to achieve using the water extraction method. To measure equilibrium aqueous concentrations using POM-SPE, 100 mg of POM will be introduced into each sediment slurry batch equilibrium bottle. The POM-SPE will be separated from the slurry after 1 month of equilibration, gently rinsed with DI water to removed attached particles, and extracted with hexane to measure PCBs. The aqueous PCB concentration will be calculated based on the PCB concentration in the equilibrated POM and previously measured POM-water distribution coefficients. The POM measurements will be conducted in duplicate using the same bottles from which aqueous samples are collected. A comparison of the aqueous concentration measured following alum fluctuation will be made to the aqueous measurements using POM-SPE.

### **3) PROJECT REPORTING AND ACADEMIC RESEARCH SUBCONTRACTORS**

Each laboratory will prepare a data package, providing the results of the analysis, along with backup information. Data deliverables will be specified in a task-specific QAPP. Any data quality issues will be discussed in a case narrative included with the data report. The completed copies of the COC records (both external and internal) accompanying each sample from time of initial bottle preparation to completion of the analyses will be attached to the analytical reports.

The data packages provided by the laboratories will be validated by a project chemist. The chemist will summarize the results of the data validation in a summary report, which will be attached to the final project report. The project chemist will contact the laboratories, as necessary, to obtain additional information regarding any data deficiencies prior to issuance of the validation report.

**Dr. Upal Ghosh** of the University of Maryland – Baltimore County will provide the technical lead on the characterization of Passaic River organic carbon geochemistry and PCB aqueous partitioning and bioavailability in contaminated sediments. Dr. Ghosh pioneered sub-particle scale characterization methods of organic contaminants associated with sediments and the development of in situ remediation of PCB-contaminated sediments using activated carbon. His collaboration with the other team members in the development of SPME as tools for assessing PAH bioavailability has provided the fundamental mechanistic understanding of PAH sorption processes that is necessary for regulatory acceptance. Dr. Ghosh is the Co-PI for several Department of Defense technology research and development projects including *Characterization of Contaminant Transport Potential Through In-Place Sediment Cap; Field Testing of Activated Carbon Mixing and In Situ Stabilization of PCBs in Sediments; In Situ Stabilization of Persistent Organic Contaminants in Sediments*.

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