ONONDAGA LAKE PRE-DESIGN INVESTIGATION: PHASE IV: ADDENDUM 2 CAP AMENDMENT STUDY ISOTHERM DEVELOPMENT

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ADDENDUM 2

1.0 INTRODUCTION

Phase II and Phase III bench test data indicate that an amendment may be required as part of the Onondaga Lake Isolation Cap design to meet the performance criteria specified in the Record of Decision. Amendments under consideration include activated carbon, organoclay, and peat. Experiments will be conducted to measure sorption isotherms of volatile organic compounds of concern to activated carbon, organoclay, and peat. Representative porewater will be generated for isotherm testing from sediments in SMU 1 and from SMU 6 and 7. The activated carbon studies will be performed at Carnegie Mellon under the direction of Dr. Gregory Lowry and the organoclay and peat studies will be performed under the direction of Dr. Danny Reible at the University of Texas. TestAmerica Pittsburgh will be responsible for the initial generation of porewater and preliminary porewater analysis before experiments are performed. DHL in Austin, Texas will perform the analysis on samples generated following the experiments.

The sample locations, data-gathering methods, and details of the analyses and testing to be performed at each location are described in this document. The core samples will be collected in accordance with the procedures outlined in the Phase I Pre-Design Investigation (PDI) Sampling and Analysis Plan (SAP), Quality Assurance Project Plan (QAPP), Project Safety Plan (PSP), and Standard Operating Procedures (SOPs) (Parsons, 2005).

2.0 PROJECT OBJECTIVES

The purpose of the Phase IV PDI is to collect information required to conduct remedial design activities. The design of the isolation cap component of the remedy will be based on a model of contaminant fate and transport, as well as calculations to insure the physical integrity of the cap. The studies proposed in this work plan are designed to support long-term cap performance evaluations and specifically to predict the effectiveness of activated carbon, organoclay and peat as potential cap amendments. This information will be combined with the existing data set for use during design.

3.0 MOBILIZATION AND LOGISTICS

This section covers the mobilization and logistics to support the field tasks outlined in this addendum.

3.1 Health and Safety

Parsons ranks health and safety as the highest priority. Parsons PSP and our Subcontractor's Safety Plans (SSP) prepared for previous PDI activities will be used for this investigation and

will be strictly followed by all personnel. Any task outside of the current scope defined in the PSP will have a new Job Safety Analysis (JSA) completed before the task begins. Copies of the PSP and SSPs will be maintained at the support zone and on each vessel.

3.2 Site Facilities

Support zone and site facilities were established during the Phase I PDI near existing permanent structures at the west end of Wastebed B. These facilities will be utilized to support the Phase IV PDI activities including those covered in this addendum.

3.3 Decontamination and Waste Handling

Decontamination will be conducted at the decontamination area established during Phase I and on the various barges and vessels. The decontamination and waste disposal procedures will be conducted in accordance with the Phase I PDI SAP (Parsons, 2005).

4.0 SAMPLING LOGISTICS

Samples will be collected from a barge or a pontoon boat using vibracore lexan (or equivalent) tubes (3.5-inch) in accordance with the procedures outlined in the Phase I PDI SAP (Parsons, 2005). Samples will be located in areas that are representative of the sediment that will be capped. Upon retrieval, the samples will be placed in sealed 3 or 5-gallon buckets and refrigerated to approximately 4 C. Ultimately, the porewater generated from these samples will be composited into one total porewater sample from SMU 1 and one total porewater sample from SMU 6/7. As such, the sediment will not be composited or homogenized prior to porewater generation.

Locations will be sampled as described on Table 1a; sample locations are shown on Figure 1. Five locations will be sampled to a depth of 10 ft in SMU 1, and eight locations to a depth of 6 ft will be sampled in SMU 6/7. Locations and sample depths were based on representative cap areas and considering potential dredge depths along with know distribution profiles (i.e., ILWD area does not show strong vertical trends) areas. Samples were also located in areas and at depth intervals with high organic content as this is expected to have the greatest impact on sorption to amendments. The sample locations in SMU 1 are consistent with locations OL-STA-10114, 10116, 10117, 10118, and 10119 previously sampled for Phase II and Phase III bench testing. The levels of DOC measured in the top three meters of the ILWD in the vicinity of the selected sample locations are consistent with levels measured at depth and are generally representative of the levels throughout the ILWD. SMU 6 and 7 have similar levels of organic carbon and sediment/porewater from SMU 6 and SMU 7 will be combined as one area in the isotherm experiments. Sample locations in SMU 7 are evenly spread down the middle of SMU 7 focusing on areas with higher levels of DOC. Sample locations in SMU 6 are evenly spread across the SMU parallel to the shoreline and biased toward areas with high organic carbon measured in previous porewater samples.

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The tests outlined in the methods sections below may require as much as 9 liters of porewater be collected and composited per area (SMU 1 and SMU 6/7). Previous porewater generation efforts have produced 100 to 150 mL of porewater per liter of sediment. This translates to 90 liters (24 gallons) of sediment required per SMU. Estimated sample volumes are calculated in Table 1a. Note that the tables indicate volume above what is required to ensure sufficient sample volume.

Given the large volume of porewater required for these tests, samples will be collected in 3- or 5-gallon pails as mentioned above. As discussed in Section 5, following porewater generation the porewater will be sparged to remove existing volatile organic contaminants. The sparging in addition to collecting samples in buckets (as opposed to sealed cores) is not expected to impact the results of the isotherm experiments. However, to verify this assumption a subset of cores will be collected in each SMU, data from these cores will be used to spot check the isotherms and evaluate the effects of sediment and porewater processing, if any. It is anticipated that 1 L of porewater will be required for this evaluation. One 10-ft core will be collected in SMU 1, and two, 6 ft cores will be collected in SMU 6/7. The cores will be cut into 2-ft sections. These cores will be immediately capped making an effort to minimize headspace and exposure to oxygen. The porewater generated from these cores will be generated under nitrogen in a glovebox and used to determine any potential matrix effects from oxygen exposure and/or sparging Sample locations for these tests are provided in Table 1b.

Sediment samples will be sealed immediately after collection and an effort will be made to minimize exposure to ambient air. A written description of each sample collected will also be documented in the field. Photographs will be collected in the field. The samples will be shipped while maintained at 4°C and sealed with minimal headspace.

5.0 POREWATER GENERATION

Sediment samples will be shipped to Test America Pittsburgh, PA for porewater generation. Porewater will be generated and analyzed in accordance with the procedure outlined in Attachment 1. Porewater from the lake may contain concentrations of the adsorbates. Since isotherm samples are being spiked to achieve a known initial mass of contaminant, native VOCs in the samples will be sparged with N2 for 15 minutes prior to use. A sample of the initial porewater before and after sparging will be analyzed for VOCs, TOC/DOC, cations/anions, pH, mercury, ORP, alkalinity and total dissolved solids (TDS) to ensure that any remaining VOCs are present at a significantly lower concentration than the spiked concentration, while other natural non-volatile organic compounds are retained in the porewater. This analysis will also be conducted on the sealed core tube sample. The following methods will be used in the analysis: pH - SW9040, TOC/DOC - SW5310B, cations/anions - E300.0, SW6010, VOCs SW8260B, Low Level Mercury – SW1631, ORP - SM 2580B, alkalinity - SM 2320B, and TDS - SM 2540C.

The sparging and initial analysis will be conducted by Test America prior to shipment to Carnegie Mellon and the University of Texas. Two-thirds (2/3) of any produced porewater will be shipped overnight to Carnegie Mellon University and one-third (1/3) will be shipped to the University of Texas.

Table 1a Bulk Sediment Collection

Sample Location	Depth (ft)	Volume Collected (3.5-in lexan) (gal)
SMU 1		
OL-STA-10114	10	5
OL-STA-10116	10	5
OL-STA-10117	10	5
OL-STA-10118	10	5
OL-STA-10119	10	5
Total Sediment Volume	25 gal/95 liters	
Anticipated PW Volume (100-150 ml/L sediment)	9.5-14.3 liters	
Note: Sediment volume from SMU 1 will be combined into 3- or 5-gallon pails and shipped to Test America (nine 3-gallon pails or six 5-gallon pails)		
SMU 6/7		
OL-STA-70116	6	3
OL-STA-70117	6	3
OL-STA-70118	6	3
OL-STA-70121	6	3
OL-STA-60099	6	3
OL-STA-60218	6	3
OL-STA-60219	6	3
OL-STA-60220	6	3
Total Sediment Volume	24 gal/91 liters	
Anticipated PW Volume (100-150 ml/L sediment)	9.1-13.7 liters	
Note: Sediment volume from SMU 6 and 7 will be combined into 3- or 5-gallon pails and shipped to Test America (eight 3-gallon pails or five 5-gallon pails)		

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Table 1b Core Collection for Evaluation of Processing Impacts

Sample Location	Depth (ft)	Volume Collected (3.5-in lexan) (gal)
SMU 1		
OL-STA-10117	10	5
Total Sediment Volume	5 gal/19 liters	
Anticipated PW Volume (100-150 ml/L sediment)	1.9-2.85 liters	
Note: Sediment volume from SMU 1 will be collected from one location in SMU 1 in a 3.5-in lexan (or similar) core tube, cut into 2-ft sections and capped.		
SMU 6/7		
OL-STA-70117	6	3
OL-STA-60099	6	3
Total Sediment Volume	6 gal/22 liters	
Anticipated PW Volume (100-150 ml/L sediment)	2-3 liters	
Note: Sediment volume will be collected from one location in SMU 6 and one in SMU 7 in a 3.5-in lexan (or similar) core tube, cut into 2-ft sections and capped.		

6.0 ISOTHERM DEVELOPMENT

6.1 Background and Experimental Design

The proposed sorption testing is designed to evaluate the influence of porewater matrix effects on the capacity of potential sorbents that may be part of an active cap for Onondaga Lake. Such testing was used previously in the Anacostia (Washington DC) active capping demonstration, at the McCormick and Baxter (Portland OR) organoclay capping project, and the EPRI manufactured gas plant MGP site (Hudson River, NY) active capping demonstration, as well as at a variety of other sites across the country. The site-specific sorptive characteristics testing is designed to improve the cap design by identifying any potential limitations to long-term sorption capacity that might be posed by matrix effects. Such effects may include competitive sorption of other contaminants or natural organic matter.

Isotherm experiments are designed to obtain an upper limit (referred to as equilibrium) on the mass of a given target chemical sorbed per mass of sorbent (activated carbon, organoclay, or peat). These tests are relatively quick to run (usually less than one month) and can indicate the mass of sorbent needed to achieve a certain contaminant removal. It may be necessary to

supplement these equilibrium studies with kinetic tests although for sediment capping applications, sorption kinetics are rarely necessary due to the relatively long residence times of contaminants in the cap layer. The need for kinetic tests based on predicted upwelling rates and contaminant concentrations in designated Onondaga Lake cap areas will be considered following completion of the isotherm experiments. The isotherm experiments will provide the Freundlich parameters (K_f and $1/n$) for activated carbon or linear partitioning coefficients (K_d) for organoclay and peat needed to simulate contaminant transport through a sediment cap amended with these materials (Murphy et al., 2006; Lampert and Reible, 2007). Further, these studies will identify the magnitude of the effect of dissolved organic matter and porewater matrix on the adsorption properties of the adsorbents.

The first step in designing isotherm experiments is to estimate the isotherm parameters using a screening study so that porewater volumes, concentrations of the target chemicals, and activated carbon doses can be estimated accurately. Initially, literature results will be used to design the screening study. Both Mangum et al. (2001) and Giffin et al. (1998) used Freundlich isotherm parameters for BTEX adsorption onto F-300 activated carbon reported by Calgon Carbon Corporation (Pittsburgh, PA). These parameters are listed in Table 2.

Table 2 Freundlich Isotherm Parameters for
BTEX Adsorption to F-300 Activated Carbon

Compound	K_f (mg/g)/(mg/L)^(1/n)	1/n (-)
Benzene	29.5	0.338
Toluene	69.1	0.272
Ethylbenzene	112	0.170
p-xylene	124	0.216

A range for C_e (the equilibrium compound concentration in the liquid, mg/L) and intermediate values need to be selected because porewater VOC concentrations are expected to vary within the site and change over time. Maximum and minimum concentrations measured in lake porewater, as provided on Table 3, as well as compound solubility will be considered in selecting C_e's for the isotherm experiments. Generally, 10 to 15 data points are needed per full isotherm for activated carbon and 5 to 8 for organoclay and peat (assuming linearity of the isotherm is confirmed) so that the resultant parameters have reasonably low degree of uncertainty.

**Table 3: Minimum and Maximum Porewater Concentrations
of the Target Chemicals as Measured During the Phase I-III PDI**

	Benzene ug/L		Toluene ug/L		EB ug/L		Xylene ug/L		CB ug/L		DCB ug/L	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
SMU 1	0.17	22,000	0.24	10,000	0.90	1,600	0.53	14,000	0.90	20,000	1.23	9,080
SMU 6	0.23	19	0.34	43	0.24	11	0.35	28	0.25	53	0.95	38
SMU 7	0.86	600	0.76	440	0.60	160	2.60	1,200	1.40	2,500	4.31	1,373

	Naphthalene ug/L		Hg ug/L		pH	
	Min	Max	Min	Max	Min	Max
SMU 1	1.10	61,000	0.00	1,380	6.9	12.7
SMU 6	0.26	390	0.05	1.60	6.7	7.8
SMU 7	0.46	5,600	0.01	32.10	6.4	10.8

An important first step is to determine the amount of porewater that is required to obtain measureable quantities of dissolved contaminant in the porewater at equilibrium. This is especially true for highly adsorptive materials like activated carbon. To estimate the porewater volumes required, it is necessary to perform a mass balance on the contaminant of interest in the isotherm bottle. Assuming each bottle has a known volume of porewater, mass of activated carbon, and initial VOC concentration, a mass balance on the contents of an isotherm bottle yields the following relationship:

$$VC_0 = M_i q_e + VC_e \qquad (1)$$

In equation (1), V is the liquid volume (mL), C_0 is the initial compound concentration (mg/L), M_i is the activated carbon mass (mg), q_e is the mass of compound sorbed per mass of activated carbon at equilibrium (mg/g), and C_e is the equilibrium compound concentration in the liquid (mg/L). To design the isotherm experiments (i.e. determine V and C_0 that yield practical values of M_i over the desired range of C_e) it is useful to rearrange the equation:

$$M_i = \frac{V(C_0 - C_e)}{KC_e^{1/n}} \qquad (2)$$

The Freundlich equation, $q_e = KC_e^{1/n}$ was substituted into equation 2 and is assumed to describe the adsorption of all compounds to activated carbon – this is a reasonable assumption given that many studies have found VOC sorption to activated carbons to be well described by the Freundlich model. Equation 2 allows you to determine V, M_i, and C_0 to give you an appropriate range of C_e, however, it requires a-priori a reasonable estimate of the Freundlich

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parameters that you will measure. The primary reason for the initial screening study proposed is to estimate K_f and $1/n$. Until demonstrated otherwise, $1/n$ will be set equal to 1 (linear isotherm) for organoclay and peat sorption, but this will be verified experimentally. Non-linearity, i.e. the value of $1/n$, has a large impact on the adsorptive property of the material. A very small value of $1/n$, e.g., 0.25 as if often the case with activated carbon, yields a very steep adsorption isotherm. This suggests exceptional performance at very low sorbate concentrations, but diminishing performance at higher sorbate concentration, i.e. lower overall sorption capacity. Thus, it is very important to determine the degree of non-linearity of adsorption over the range of sorbate concentrations expected.   Table 4 gives an exemplary outline for an isotherm experiment. Assuming V = 50 mL (as specified in the experimental procedure) and that a minimum measurable activated carbon mass is approximately 250 mg, C_0's were calculated for the BTEX compounds (using the Freundlich parameters provided in Table 2) and listed in Table 4. As noted above, the Freundlich parameters and $1/n$ value were taken from the literature for F-300. This is not the final design of the isotherm study, rather an example of what the setup will look like. Actual study design will be provided following completion of the screening study experiments. The exact volumes, activated carbon mass, and initial concentration will depend on the isotherm parameters determined in the initial screening study.

**Table 4. Initial Concentrations (C_0's) and Activated Carbon Masses (M_i's)
for the BTEX Isotherm Experiments**

Ce (mg/L)	V (mL)	Benzene		Toluene		Ethylbenzene		p-Xylene	
		C_0 (mg/L)	M_i (mg)	C_0 (mg/L)	M_i (mg)	C_0 (mg/L)	M_i (mg)	C_0 (mg/L)	M_i (mg)
0.01	50	35	281	100	253	270	264	250	273
0.03	50	50	277	140	263	320	259	300	258
0.07	50	65	270	170	253	370	260	350	251
0.1	50	75	276	200	271	400	264	400	265
0.3	50	100	254	250	251	470	257	500	261
0.7	50	140	266	320	255	550	261	600	261
1	50	150	253	350	253	600	267	700	282
3	50	230	265	500	267	700	258	800	253
7	50	300	257	600	253	800	254	1000	263
10	50	350	265	700	267	900	269	1100	267
30	50	500	252	900	250	1100	268	1400	265

A similar procedure will be followed to determine the C_0's and M_i's for o- and m-xylenes, chlorobenzene, 1,2-, 1,3-, and 1,4-dichlorobenzene, and naphthalene. Compounds will be in each isotherm bottle such that the resultant Freundlich parameters represent multi-solute conditions in the porewater at the site.

For organoclays, work at the University of Texas has estimated that hydrophobic organics are expected to sorb onto organoclays at approximately 1 to 10 times K_{oc} depending upon the

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compound and the organoclay. Sorption of chlorinated benzenes and BTEX aromatics have not been measured on commercially available organoclays used for sediment remediation but similar sorption is expected. Linear sorption has been observed on a variety of hydrophobic organic compounds reducing the number of contaminant concentrations needed to determine a water-sorbent partitioning relationship. Based on this experience, we will design the isotherm studies assuming linear partitioning (1/n=1) for organoclay. Similarly, peat is also expected to exhibit linear sorption and have a partitioning coefficient between 0.5 and 1 times Koc. Initial concentrations for organoclay and peat sorption will be defined in a similar fashion as activated carbon by estimation or by preliminary single concentration partition coefficient measurements. All compounds will also be employed for each organoclay and peat isotherm measurement as with activated carbon. The range of concentrations chosen will be selected to cover the range of interest of concentrations expected at each SMU.

6.2 Materials

Commercially available sorbent material will be used for the isotherm experiments. A preliminary screening study will be done with four commercially-available activated carbons with various pore size distributions and surface chemistries in which four isotherm points will be determined in organic-free water and the provided porewater from the lake. The results from the organic free water will be used to evaluate the impact of natural organic matter fouling on each activated carbon. Based on these results, one activated carbon will be selected for in depth analyses where multi-solute Freundlich parameters will be determined for all compounds in both organic-free water and porewater from the lake. Based on our experience evaluating fouling of activated carbon by natural organic matter, the following four activated carbons have been selected for preliminary screening: TOG (microporous, high surface oxygen), Centaur (microporous, low surface oxygen), AquaGuard (mesoporous, low surface oxygen), and a regenerated carbon. Mangun et al, 2001 demonstrated that activated carbon fibers with low surface oxygen led to enhanced BTEX sorption capacity. Based on McDonough et al., 2008 a mesoporous carbon has potential to perform better in the presence of natural organic matter.

A similar approach will be undertaken with organoclays. Organoclays to be screened include CETCO PM-199 and CETCO PM-200. Previous studies have shown that these organoclays, which have been applied commercially for sediment remediation, exhibit the greatest sorption for hydrophobic organic compounds. PM-199 and PM-200 are prepared by treating bentonite clay with bis(hydrogenated tallow alkyl)dimethyl ammonium chloride. The long chain tallow group (~ C18) encourages the sorption of the hydrophobic organics. Other organoclays which may be more effective for less hydrophobic compounds may also be tested if commercially available. Organoclays have been described as immune to the fouling and decrease of sorption capacity in the presence of organic matter that occurs in activated carbon (Wiles et al. 2005) but this will be demonstrated by preliminary testing with organic free and porewater.

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Testing of peat as a sorptive agent will also be undertaken at the University of Texas. These tests will parallel those conducted with organoclay for the screening portion of the study. The need to assess peat in a full scale isotherm will be determined based on the results of the screening studies. A source of peat local to Onondaga Lake will be used for these tests.

6.3 EXPERIMENTAL METHODS

6.3.1 Sample Preparation

The cap amendment material will be prepared according to method ASTM D5919-96 Sections 10 and 11. Any deviations from this method will be documented in the final report.

6.3.2 Screening Studies

6.3.2.1 Activated Carbon

The objective of the preliminary isotherm experiments is to obtain enough information to design an isotherm experiment to get Freundlich parameters for each of the seven target compounds on each of the four activated carbons (TOG, Centaur, and AquaGuard, and a regenerated one such as DSR-A). These experiments will also indicate the activated carbon that is most resistant to fouling by natural organic matter by comparing isotherms in organic free water with SMU 1 porewater. Finally, the time required to achieve equilibrium will be assessed by measuring the sorption parameters at three time steps (7, 14, and 28 days) for one type of AC. The compounds of interest are listed in Table 5, along with their respective Freundlich parameters on activated carbon from the literature (which are needed to predict the setup of the preliminary experiments), aqueous solubility, and maximum and minimum measured porewater concentrations in SMU 1 and/or SMU 6/7.

Table 5. Freundlich Parameters, Aqueous Solubility, and Maximum and Minimum Porewater Concentrations in SMU 1 and/or SMU 6/7 for the Compound of Interest.

Compound	K (mg/g)/(mg/L)^(1/n)	1/n	Aqueous Solubility (mg/L)	Measured Porewater Concentration (mg/L)	
				Minimum	Maximum
Benzene	29.5	0.338	1748	0.00017	22
Toluene	69.1	0.272	556	0.00024	10
Ethylbenzene	112	0.170	168	0.00024	1.6
Xylene	124	0.216	180	0.00035	14
Chlorobenzene	301	0.430	459	0.00025	20
Dichlorobenzene	250	0.300	130	0.00095	9
Naphthalene	277	0.430	32	0.00026	61

Note: K and 1/n for benzene, toluene, ethylbenzene, and p-xylene from Calgon Carbon Corp. (Pittsburgh, PA); K and 1/n for chlorobenzene, 1,2-dichlorobenzene, and naphthalene from Brasquet et al. (1999), Environmental Science and Technology, 33, 4226-4231. Values for m-xylene and, o-xylene are similar to the known values for p-xylene. The same is true for 1,3 and 1,4-dichlorobenzene.

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Considering the maximum and minimum porewater concentrations measured in lake porewater, as well as solubility limits of the individual compounds and reliable detection limits, target equilibrium aqueous concentration ranges (C_e) of 0.001-0.01, 0.01-0.1, and 1-10-mg/L were selected for design for all seven compounds, corresponding to isotherm bottle volumes of 50-, 100-, and 250-mL, respectively. Freundlich parameters generated using these three ranges can be reliably extrapolated for concentrations approximately one order of magnitude above and below these ranges. The minimum practical mass of activated carbon per isotherm bottle (based on the ability to accurately weigh the mass) was determined to be 25 mg. Using a mass balance approach, initial concentrations (C_0) were calculated for each combination of chemical compound and the selected C_e. Based on these results, a spike solution of the seven compounds in methanol was selected at the concentrations listed in Table 6. The compounds selected are anticipated to be representative of the VOC contaminants in each SMU.

Table 6. Concentrations of Each Compound in Methanol for the Carbon Isotherm Spike Solution

Compound	Spike Concentration (mg/L)
Benzene	100
Toluene	1000
Ethylbenzene	3000
m-xylene	3000
p-xylene	3000
o-xylene	3000
Chlorobenzene	3000
1,2-dichlorobenzene	3000
1,3-dichlorobeneze	3000
1,4-dichlorobenzene	3000
Naphthalene	3000

Volumes of spike solution will be 0.25-, 0.50-, and 2.5-mL for 50-, 100-, and 250-mL bottles, respectively. These volumes match the selected values of C_e. Four activated carbons (generically referred to as #1, #2, #3 and #4) will be evaluated. Additionally, isotherms will be run with porewater and organic free water to evaluate the impact of natural organic matter fouling on each activated carbon. To ensure equilibrium is reached in the isotherm tests, bottles will be sacrificed at Days 7, 14, and 28 for one activated carbon (#1) only. Blanks (i.e. no activated carbon) for porewater and organic free water at all three C_e's will be run to quantify volatile losses (if any). A summary of the number of bottles needed, volumes of porewater and spike solution, and mass of activated carbon is presented in Table 7.

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Table 7 Summary of the Materials Needed for the Carbon Preliminary Isotherm Experiments

Activated Carbon	Target Ce's	Number Source Waters	Time Steps	Bottles	Volume (mL) Porewater	Spike	Mass (mg) Activated Carbon
#1	3	2	3	18	1200	9.75	450
#2	3	2	1	6	400	3.25	150
#3	3	2	1	6	400	3.25	150
#4	3	2	1	6	400	3.25	150
Blank	3	2	1	6	400	3.25	
Total				**42**	**2800**	**22.75**	**900**

As such, 42 bottles total to allow for each volume (50-, 100-, and 250-mL), multiple time steps on one carbon, the blank and the comparison against organic free water are needed for the preliminary isotherm experiments. Additionally, 2800 mL of porewater, 22.75 mL of spike solution, and 900 mg of activated carbon are needed.

6.3.2.2 Organoclay/Peat

The preliminary experiments for organoclay and peat sorption will be conducted similarly. Sorption analysis was based upon organoclay assuming an effective sorption coefficient of $5*K_{oc}$ as measured in previous research experiments with hydrophobic organic compounds. As with the activated carbon preliminary experiments, target equilibrium aqueous concentrations (Ce) of 0.001-0.01, 0.01-0.10, and 1-10 mg/L were selected for design for all seven compounds in isotherm bottle volumes of 50-mL for all three concentrations. In order to achieve the target equilibrium concentrations, different organoclay or peat masses will be introduced to these vials, as well as different spike solution concentration in the 3 target bottles. The starting spike solution of the seven compounds in methanol was selected at the concentrations listed in Table 8.

Table 8 Spike Solution for Organoclay/Peat Experiments

Compound	Concentration in methanol (mg/L)
Benzene	100
Toluene	500
Ethylbenzene	1000
p-xylene	1000
m-xylene	1000
o-xylene	1000
Chlorobenzene	1000
1,2-dichlorobenzene	1000
1,3-dichlorobenzene	1000
1,4-dichlorobenzene	1000
Naphthalene	1000

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The volume of spike solution and mass of organoclay or peat employed to achieve the estimated target concentrations are shown in Table 9

Table 9 Spike Solution Volumes and Sorbent (Organoclay/Peat) Mass Required To Achieve Estimated Equilibrium Concentration Ranges

Target Ce's (mg/L)	Volume (mL)		Organoclay/Peat
	Bottle	Spike	mg
0.001-0.01	50	0.25	10000
0.01-0.1	50	0.25	1000
1-10	50	2.5	100

The corresponding required total number of bottles, porewater volumes and sorbent mass required are shown in Table 10.

Table 10 Experimental Requirements for Organoclay/Peat

Organoclay Peat	Number				Volume (mL)		Mass (g)
	Target Ce's	Source Waters	Time Steps	Bottles	Porewater	Spike	Organoclay/Peat
#1	3	2	3	18	450	9	66.6
#2	3	2	1	6	150	3	22.2
Peat	3	2	1	6	150	3	22.2
blank	3	2	1	6	150	3	
Total				**36**	**900**	**18**	**111**

6.3.2.3 Summary of Screening Studies for Method Development

On the basis of these preliminary experiments with activated carbon, organoclay and peat, the best sorbent or sorbents will be selected and a full set of experiments for the determination of isotherms designed. These will include 10-15 individual concentrations over the approximate range of equilibrium concentrations targeted in the preliminary experiments for the activated carbon selected. Organoclay and peat isotherms will be determined from 5-6 individual concentrations over the same concentration range, given that preliminary experimentation suggests that linear isotherms apply. Tables detailing the design of the full isotherm experiments will be provided to NYSDEC upon completion of the screening studies.

6.3.2.4 Evaluation of Matrix Effects and Sparging (Analysis of Anaerobic and Non-Sparged Porewater)

The majority of sediment samples will be collected in three or five gallon buckets and transported directly in the centrifuge jars. A subset of samples will be collected in sealed core tubes and transported into centrifuge jars in a nitrogen environment. The porewater generated

from these cores will be compared to results generated from other isotherm experiments to determine any potential matrix effects from oxygen exposure and/or sparging.

The sparged and non-sparged porewater from these cores will be analyzed for the basic water quality parameters (pH, ORP, DOC/TOC, cations/anions, alkalinity, TDS, VOCs and Hg) to compare with similar results for the grab samples. This will indicate the representativeness of the grab samples to mimic the sediment porewater, and will indicate the effect of sparging and exposure to oxygen on the porewater chemistry. Several (2 to 3) isotherm points for AC will be developed using porewater from the sediment cores and compared to those from the grab samples. This will directly measure the effect of porewater sparging and exposure to air on the adsorption parameters. We expect these effects to be minor, if any at all. Further, we expect that these effects will be most evident in activated carbon and therefore only tested with these adsorbents. If sparging and exposure to oxygen have significant effects on the adsorption parameters for activated carbon, this process will also be conducted for peat and organoclay.

6.3.3 Procedures For Isotherm Development

Adsorptive capacity experiments on the activated carbon material will be carried out by adding 50 mg of adsorbent to 50-250 mL of porewater in a bottle. For the organoclay, 100 mg to 10,000 mg of adsorbent will be added to 50 mL of porewater. The need for full isotherm development using peat will be assessed based on the performance of peat measured during the screening studies. Each vial will be capped and placed on an orbital shaker at low speed (~120 rpm) for a minimum of 2 days to achieve equilibrium. A table detailing design of the full isotherm experiments will be provided upon completion of the screening studies.

Commercially available and certified solution standards will be used for spiking to achieve the initial sorbate concentration. These standards are provided with a certificate of analysis and eliminate the potential error associated with preparing standards individually. Ultra Scientific sells a matrix spike standard solution with the target compounds together in methanol in a 1 ml vial (e.g., Ultra Scientific CLP-102). Vials containing the required mixture of contaminants in methanol will be purchased for each isotherm, or they will be prepared in our laboratory using volumetric addition of each compound to methanol and subsequent dilution to achieve the required initial concentrations.

Once the centrifuge tubes have equilibrated, the tubes containing the sorbent in porewater will be removed from the rotator, and uncapped. Using a micropipette, the VOC solution will be added to each tube. The tubes will be quickly re-capped, and returned to the orbital shaker (~125 rpm) for incubation for 14 days in the dark at 12°C. After equilibration, the bottle contents will be centrifuged at approximately 2,000 RPM for 20 minutes to settle the activated carbon. The supernatant will be collected using a glass syringe and transferred to a 40 ml glass VOA vial with Teflon-lined septum for analysis. No headspace will be left in the VOA vial. If less than 40 ml of supernatant is available from some of the tubes with high concentrations of sorbent, it may be necessary to volumetrically add some volume (10 or 20 ml) of distilled water

to the VOA vials prior to adding the supernatant. The dilution factor will be recorded, and analytical results will be corrected for this dilution.

VOA vials will be stored in the dark at 4°C until analysis. Samples will be analyzed using purge and trap GC/MS by a commercial lab (SW5030B/8260B). Adsorption isotherms will then be calculated as recommended in ASTM standard practice D 5919-96.

Each isotherm for activated carbon will have 10 to 15 points such that an adequate isotherm can be achieved, while organoclay and peat samples will be limited to 5-8 point isotherms unless nonlinearity is observed. It is estimated that a total of 40 to 60 samples for each SMU for activated carbon studies and 15 to 24 samples for each SMU for organoclays and peat will be analyzed. This assumes that at least one full isotherm will be developed on one carbon per SMU which results in 10-15 samples per isotherm for porewater and organic free water. Isotherms will be developed in SMU 1 and SMU 6/7.

6.3.3.1 Isotherm Development for Mercury

A select set of experiments will be conducted to assess mercury partitioning to sand, activated carbon, organoclay, and potentially peat. Average mercury concentrations in SMU 1 porewater average 18 ug/L with a maximum porewater concentration of 1,380 ug/L. Concentrations in SMU 6 and 7 average 0.25 and 0.74 ug/L respectively, with maximum concentrations of 1.6 and 32 ug/L. Partitioning coefficients reported for mercury in the literature range over multiple orders of magnitude.

The activated carbon and organoclay used for the mercury isotherm development will be selected based on the screening study results for VOCs. Additional experiments run with a specially formulated organoclay may be conducted, if the organoclay is available from the manufacturer. Experiments will be run with peat pending the performance and results of the VOC screening studies.

For organoclay, these experiments will be conducted separately from those described in Section 6.3.3 because the current experimental design volume for organoclay and VOCs is only 50 mL, which is an insufficient sample volume to analyze for both VOCs and mercury. Mercury will be added to either 55 mL or 100 mL vials by mass of Hg++ as mercury chloride to achieve four concentrations. Concentrations will be selected to evaluate the multiple order of magnitude range of partitioning for mercury. Partitioning is expected to be linear; however, additional data points may be collected if initial experimental data indicates otherwise. Samples will be collect in 40 mL vials and analyzed at TestAmerica's North Canton facility in accordance with Low Level Mercury method SW1631. For activated carbon, mercury and VOCs will be analyzed together because the sample volume for AC isotherm development (200 mL) is sufficient to analyze for both. Mercury will be added as Hg++ in these experiments for at least four concentrations. . Samples will be collect in 40 mL vials and analyzed at TestAmerica's North Canton facility in accordance with Low Level Mercury method SW1631.

7.0 REPORTING

The results from the isotherm experiments will include Freundlich parameters describing sorption of each of the target chemicals to each sorbent. A recommendation regarding any future testing will be made.

8.0 QUALITY ASSURANCE/QUALITY CONTROL

The sample names, QA/QC procedures, sample collection, data entry, and data validation for this portion of the work will be conducted in accordance with the Phase I PDI Work Plan (Parsons, 2005). Any deviations from these procedures will be discussed with New York State Department of Environmental Conservations (NYSDEC) prior to execution of the work or qualified in the final report if dictated by experimental process limitations during bench studies.

Analytical data will be collected and validated in accordance with the Onondaga Lake QAPP (Parsons, 2005) as Level III data. The data will be evaluated by the laboratory in relation to the established laboratory and project control limits for accuracy and precision with factors impacting data quality being identified in the laboratory analytical report. The data will be evaluated by the project manager as to consistency with site conditions and developed conceptual models, to determine whether field and analytical data meet the requirements for decision making. The results of the measurements will be compared to the Data Quality Objectives (DQOs) described in Section B3 of the QAPP and in this Work Plan. The DQOs will be considered complete and satisfied if the data are identified as usable for the intended purposes and if no major data gaps are identified.

9.0 REFERENCES

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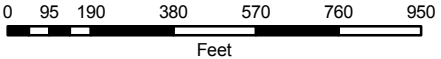
FIGURES

Proposed Isotherm Testing Sample Location

NOTES

1. Bathymetry contours are in 4 foot intervals.
2. Water depth based on average lake elevation of 362.82 feet.

SMU 6

SMU 8

SMU 1

SMU 7

ILWD Area B
ILWD Area A

OL-STA-60219

OL-STA-60218

OL-STA-60220

OL-STA-10114

OL-STA-70118

OL-STA-60099

OL-STA-10117

OL-STA-70117

OL-STA-10118

OL-STA-10116

OL-STA-10119

OL-STA-70121

OL-STA-70116

-30 -24 -16
-28 -20 -12 -8
-4

0 95 190   380   570   760   950
Feet

FIGURE 1

Honeywell   Onondaga Lake
Syracuse, New York

SMUs 1-6-7
Phase IV PDI Addendum 2
Proposed Sample Locations
for Isotherm Development

PARSONS

290 ELWOOD DAVIS RD, SUITE 312, LIVERPOOL, NY 13088 Phone:(315)451-9560

Q:\GIS\GIS_Lake\Phase_IV_PDI\SMUs1-6-7_prop_isotherm.mxd

ATTACHMENT 1

Honeywell

PROJECT SPECIFIC PROCEDURE NOTE

CORE PROCESSING AND POREWATER GENERATION FOR ISOTHERM TESTING IN SUPPORT OF PHASE IV WORK PLAN

Sample Storage

1. Bulk sediment samples will be collected via vibracore using lexan tubes (or equivalent), emptied into 3 or 5 gallon buckets, and placed in coolers. The coolers will be shipped and stored upright.

2. A subset of samples will be collected in 2-ft sealed core tubes. These samples will be handled separately as noted in certain steps below.

3. The samples will be stored in a secure cold room at 4°C ± 2°C under internal chain of custody control until sample preparation procedures are initiated, at which time the analyst will sign the samples out of sample management. The samples will not require equilibration to room temperature for the porewater generation procedure.

Sample Processing

4. The desired number of samples to generate porewater will be transferred to centrifuge vessels. Bulk sediment from the buckets will be placed directly into Teflon centrifuge vessels. The sealed core tubes will be opened in a nitrogen purged glove box and emptied into Teflon centrifuge vessels.

Sediment Processing and Porewater Generation from Buckets

5. The sediment from the buckets will be added to 500 mL Teflon bottles then loaded into the centrifuge. These vessels will be one-time use containers and will be discarded after this procedure. Overlying water in the buckets will be considered porewater that has settled during shipment and will be incorporated back into the sample.

6. Two Beckman J-6M Centrifuges set to 2000 rpm and 4 degrees C will be used for porewater generation. These settings have been determined to be adequate to generate maximum porewater from samples. The samples will be spun on the centrifuge 30 min. All samples will be centrifuged for the same period of time to ensure consistency.

7. After centrifugation, the Teflon bottles will be gently moved into a glove box for compositing of the porewater. The glove box will be purged with nitrogen for a period of 30 minutes prior to sample handling.

8. To the degree that it can be done without disturbance of the sediment, the supernatant porewater will be decanted into a clean 9.5 L glass flask. The flask will be sealed with a rubber stopper in between batches of porewater until the porewater generation is complete.

9. Porewater from sample locations in SMU 1 will be composited and porewater from sample locations in SMU 6 and 7 will be composited. Once porewater generation for each location is complete; a sample will be collected from the composited porewater and will be analyzed for the parameters specified below in Step 12.

10. The composited porewater will be sparged with nitrogen for a period of fifteen minutes to remove any oxygen and volatiles. The composited porewater will be sparged using rubber tubing that has been run into the glovebox from the nitrogen tank.

11. Each set of samples will be recorded in the porewater generation log book and a copy will be included in the final data package.

12. After sparging, the porewater will be analyzed for the following parameters. One sample from each location will be collected and placed in the appropriately preserved bottles. The volume for DOC, mercury anions, cations and pH will be filtered through a 0.45 um filter prior to being placed in the bottle. Filtering will be conducted outside the glove box.

Parameter	Method Reference	Bottle Type	Preservative	Location
TOC	SM 5310B	1 x 40ml glass vial	Sulfuric Acid	Pittsburgh
DOC	SM 5310B	1 x 40ml glass vial	LAB FILTERED, then preserved with sulfuric acid	Pittsburgh
VOCs (CPOI List)	SW846 8260B	2 x 20ml glass vial	Hydrochloric Acid	Pittsburgh
Anions (Chloride, Nitrate, Orthophosphate, and Sulfate)	EPA 300.0	1 x 50ml plastic	LAB FILTERED, None	Pittsburgh
pH	SW846 9040	Can be taken from Anions bottle	LAB FILTERED, None	Pittsburgh
Cations (Ca, K, Na, Mn, Mg, Fe)	SW846 6010B	1 x 125ml plastic	LAB FILTERED, Nitric Acid	Pittsburgh
Low Level Mercury	EPA 1631E	1 x 125ml bottle	LAB FILTERED, Nitric Acid	North Canton
ORP	SM 2580B	1 X 500 mL bottle	None	Pittsburgh
TDS	SM 2540C	1 X 500 mL bottle	None	Pittsburgh
Alkalinity	SM 2320B	1 X 500 mL bottle	None	Pittsburgh

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13. The composited porewater from each SMU will be decanted into 1 L bottles in the glove box under nitrogen atmosphere. It is anticipated that at least 9 liters of porewater will be generated per area, SMU 1 and SMU 6/7 (18 liters total). Thus after centrifugation there should be one composited porewater sample from the SMU 1 bulk sediment (at least 9 liters) and one composited porewater sample from bulk sediment collected in SMU 6 and 7 (at least 9 liters).

14. From the remaining porewater 2/3 will be shipped via overnight delivery to Julian Fairy, Carnegie Mellon University and 1/3 will be shipped to Danny Reible, the University of Texas at Austin.

Core Processing and Porewater Generation from Core Samples

15. The samples shipped to TestAmerica in sealed core tubes will be handled separately from the bulk samples discussed above, as described in the main body of the work plan. The sealed core tubes, prep supplies, and 500ml Teflon bottles will be sealed in the glove box and the glove box will be purged for a period of 30 minutes prior to sample handling. The cores will be extruded and the sediment will be added to the Teflon bottles. These vessels will be one-time use containers and will be discarded after this procedure

16. Two Beckman J-6M Centrifuges set to 2000 rpm and 4 degrees C will be used for porewater generation. These settings have been determined to be adequate to generate maximum porewater from samples. The samples will be spun on the centrifuge 30 min. All samples will be centrifuged for the same period of time to ensure consistency.

17. After centrifugation, the Teflon bottles will be gently moved into a glove box for compositing of the porewater. The glove box will be purged with nitrogen for a period of 30 minutes prior to sample handling.

18. To the degree that it can be done without disturbance of the sediment, the supernatant porewater will be decanted into a clean beaker or volumetric flask. If the porewater generation requires multiple batches, the flask will be sealed between batches.

19. Porewater from sample locations in SMU 1 will be composited and porewater from sample locations in SMU 6 and 7 will be composited. Once porewater generation for each location is complete; a sample will be collected from the composited porewater and will be analyzed for the parameters specified below in Step 23.

20. The porewater generated from the cores will be kept separate. One half of this porewater volume will be sparged and the remaining half will remain unsparged. Samples will be labeled appropriately.

21. There will be one porewater blank generated with the SMU 1 cores, and one porewater blank generated with the SMU 6/7 cores. The porewater blank will be retained for analysis at TestAmerica only.

22. Each set of samples will be recorded in the porewater generation log book and a copy will be included in the final data package.

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23. The porewater (both sparged and unsparged) will be analyzed for the following parameters. One sample from each location will be collected and placed in the appropriately preserved bottles. The volume for DOC, mercury, anions, cations, and pH will be filtered through a 0.45 um filter prior to being placed in the bottle. Filtering will be conducted outside the glove box.

Parameter	Method Reference	Bottle Type	Preservative	Location
TOC	SM 5310B	1 x 40ml glass vial	Sulfuric Acid	Pittsburgh
DOC	SM 5310B	1 x 40ml glass vial	LAB FILTERED, then preserved with sulfuric acid	Pittsburgh
VOCs (CPOI List)	SW846 8260B	2 x 20ml glass vial	Hydrochloric Acid	Pittsburgh
Anions (Chloride, Nitrate, Orthophosphate, and Sulfate)	EPA 300.0	1 x 50ml plastic	LAB FILTERED, None	Pittsburgh
pH	SW846 9040	Can be taken from Anions bottle	LAB FILTERED, None	Pittsburgh
Cations (Ca, K, Na, Mn, Mg, Fe)	SW846 6010B	1 x 125ml plastic	LAB FILTERED, Nitric Acid	Pittsburgh
Low Level Mercury	EPA 1631E	1 x 125ml bottle	LAB FILTERED, Nitric Acid	North Canton
ORP	SM 2580B	1 X 500 mL bottle	None	Pittsburgh
TDS	SM 2540C	1 X 500 mL bottle	None	Pittsburgh
Alkalinity	SM 2320B	1 X 500 mL bottle	None	Pittsburgh

24. The composited porewater from each SMU will be decanted into 1 L bottles in the glove box under nitrogen atmosphere with zero head space. It is anticipated that 1 L of porewater will be generated from the core samples for each area (2 liters total). Thus, after centrifugation there should be one composited porewater sample from the SMU 1 cores opened under nitrogen and sparged and one composited porewater sample from the SMU 1 cores opened under nitrogen and not sparged. The same would be true for the samples from SMU 6/7.

25. All of the porewater generated from the core tubes will be shipped via overnight delivery to Julian Fairy, Carnegie Mellon University.

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