Honeywell

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September 22, 2009

Mr. Timothy Larson NYSDEC Division of Environmental Remediation Remedial Bureau D 625 Broadway, 12<sup>th</sup> Floor Albany, NY 12233-7016

## RE: Onondaga Lake Bottom Subsite – Onondaga County, New York Consent Decree 89-CV-815 Phase V Pre-Design Investigation – Addendum 2 – Biological Decay Batch Study Work Plan

Dear Mr. Larson:

This letter presents a work plan Biological Decay Batch Studies to support cap design. This document is being submitted in accordance with the above-referenced Consent Decree.

#### **INTRODUCTION**

Biological decay batch studies were conducted by the University of Texas, under the direction of Dr. Danny Reible, during the Phase II Pre-Design Investigation (PDI) as a screening-level evaluation and to support development of column studies designed to evaluate biological decay rates employed in cap chemical isolation layer modeling. Biodegradation studies under various redox conditions were executed using lake sediment to evaluate the potential for biological decay of key contaminants likely to drive the cap design. Based on the results of these studies, biological decay column studies were implemented as part of the Phase III and Phase IV PDIs. The Phase IV column studies are ongoing.

The studies proposed in this Phase V Work Plan Addendum are designed to supplement column study data for prediction of biological decay rates and to further examine the mechanisms controlling biological decay through an evaluation of sediment geochemical conditions, effects of nutrient addition, and the impacts of inoculation and bioaugmentation. These studies are intended to produce results which can be used in conjunction with results from prior, ongoing, and potential future column studies to refine the biological decay rates used in cap chemical isolation modeling. The study results will also be used to evaluate the approach to promote biological decay within the cap in the area of the In-Lake Waste Deposit Sediments (ILWD) through pH neutralization, nutrient addition, and bioaugmentation.

Column studies will remain a primary source of biological decay rate information for use in modeling. Additional column studies may be appropriate depending on the results from the ongoing column studies and the batch studies discussed herein. However, experience of the biological decay technical team at other remediation sites incorporating biological decay indicates that batch studies can also provide predictions of biological decay consistent with full-scale conditions. Batch studies also offer the advantage of being simpler and quicker to implement then column studies, making it easier to generate a more robust data set. For example, execution of testing scenarios in triplicate to verify

repeatability is much easier using batch studies. The sediment to porewater ratio will be increased from that used in the Phase II PDI batch studies to increase the density of the microbial community and more closely simulate field conditions. The approach for using the column and batch study results to predict biological decay will be developed in conjunction with NYSDEC following completion of the testing.

## **BIOLOGICAL DEGRADATION SLURRY EXPERIMENTS**

Additional biological degradation slurry experiments will be conducted following the procedures specified in the November 2006 Onondaga Lake Pre-Design Investigation: Phase II Work Plan – Addendum 6 Cap Design Bench Scale Studies (Parsons, 2006). Clarification, deviations and additional detail on the tests proposed for Phase V are provided below.

## **Sample Collection**

Samples will be collected by Parsons in accordance with the procedures outlined in the Phase I PDI Sampling and Analysis Plan (SAP), Quality Assurance Project Plan (QAPP), Project Safety Plan (PSP), and Standard Operating Procedures (SOPs).

Sediment samples will be collected from a total of ten locations, with three locations in each of SMU-1, SMU-6, and SMU-7, and one final location in an area of SMU 5 that is not impacted by the target compounds. One of the sediment samples from each of SMU-1, SMU-6, and SMU-7 will be obtained from the vicinity of previous samples that showed the highest degree of contaminant loss under anaerobic conditions during prior slurry tests (i.e., OL-STA-10117, OL-STA-60100, and OL-STA-70049). These locations are referred to as the primary locations. Sample locations in SMUs 1, 6 and 7 are shown on Figure 1.

The database was reviewed to identify historical sampling locations in SMU 5 with limited impact by CPOIs. Sample location S100 was selected since CPOIs were not detected in deeper sample intervals. Phenol was detected in a surface sediment sample (0 to 2 cm) at this location at 45 ug/kg, which is less than sediment screening criterion. The top interval from the core at this location (0 to 30 cm) contained low-level detections of 1,2-dichlorobenzene (20 ug/kg) and naphthalene (35 ug/kg) which are both less than the PECs (239 ug/kg and 917 ug/kg, respectively). These CPOIs were not detected in the 30 to 60 cm and 60 to 90 cm samples at this location. Therefore, a sample from this location will be collected for use in the clean sediment inoculation testing (see Figure 2). The targeted sampling interval will be below the aerobic zone (i.e., sampling interval of 2 to 4 ft below the Lake bottom). The sample will be analyzed for VOCs and SVOCs to verify that it is clean prior to initiating the testing. These results will be provided to NYSDEC prior to using this sediment for the inoculation.

Five 3-inch diameter cores will be collected, at the primary location in each SMU; the remaining two locations will have three 3-inch diameter cores collected. The cores will be collected from the 0 to 2 meter interval. Criteria for selecting the appropriate segment from each core will be consistent with that specified in the Phase II Addendum 6 Work Plan. Samples will be shipped to SiREM (a division of Geosyntec), in Guelph Ontario for bench testing.

Geotechnical and chemical characterization sampling will be conducted on a representative core segment. These analyses will include:

- Grain Size by Method D422;
- Bulk Density by Method E1110-2-1906;

- Moisture Content by method ASTM 2216; and
- VOCs by Method 8260.

Porewater will be collected from each sediment sample and analyzed to identify the geochemical characteristics of the porewater. The results of these analyses will be used to formulate synthetic porewater for each SMU area. The same synthetic porewater will be used for testing sediment samples from each of the three locations within the same SMU.

## Sample Preparation, Methods and Reporting

Samples will be prepared as specified in the Phase II Addendum 6 Work Plan (Parsons, 2006). Porewater will be analyzed for terminal electron acceptors and contaminants of interest, including benzene, toluene, ethylbenzene, and xylene (BTEX), chlorobenzene (CB), individual dichlorobenzene (DCB) isomers, individual trichlorobenzene (TCB) isomers, and naphthalene, as specified in the Phase II Addendum 6 Work Plan (Parsons, 2006).

The sediment to porewater ratio will be increased from that used in the Phase II work plan to increase the density of the microbial community and potentially shorten the duration of the experiments. The sediment-to-porewater ratio in the microcosms will be approximately 50 grams(g) of sediment per 200 milliliter (mL) of deaerated synthetic porewater, which is 5-6 times higher (more solids) than was used in previous batch testing.

Consistent with the Phase II testing, microcosms will be constructed, under anaerobic conditions, by filling 250 mL (nominal volume) glass bottles with approximately 200 mL of synthetic porewater and 50 g of sediment leaving a nominal headspace for gas production (e.g., carbon dioxide, methane). All batch testing will be constructed in triplicate. Table 1 lists the basic microcosm experiments that will be conducted.

Sediment material added to the sterile control microcosms will be autoclaved three times before the addition of artificial porewater to the microcosms. Once artificial porewater has been added to the sterilized soil, the microcosms will be poisoned with mercuric chloride to a final concentration of 0.05% and sodium azide to a final concentration of 0.017%, in order to inhibit microbial activity. The addition of mercuric chloride and sodium azide to sterile controls is an added measure of precaution above that conducted during the Phase II testing to ensure that the sterile controls remain sterile throughout the experiment.

Each treatment and control microcosm will be spiked with a stock solution to bring the concentration of each of the target compounds to approximately 1 mg/L. The original Phase II Addendum 6 Work Plan specified an initial concentration of 10 mg/L, however, prior to execution of the Phase II experiments, it was determined that 1 mg/L would be a sufficient spiking concentration, and all Phase II experiments were run at 1 mg/L. Given the higher ratio of sediment to water to be used in these tests relative to previous tests, additional mass of some of the target compounds may be added to the bottles to achieve sufficient concentrations in the aqueous phase. The appropriate mass of each compound to spike will be estimated from site-specific data on the partitioning between sediment and pore water.

Several additional treatment bottles will be prepared without spiking with DCB or benzene to better evaluate the degradation of CB which can be formed by the degradation of DCB. Treatments will also be

prepared without DCB or CB to better evaluate the degradation of benzene which can be formed by the degradation of CB (Table 1).

Microcosms will be sealed with Mininert<sup>™</sup> valves to allow repetitive sampling of each microcosm. The anaerobic microcosms will be maintained in an anaerobic chamber (containing a nitrogen/hydrogen atmosphere) for incubation and sampling to exclude exposure to oxygen throughout the study. The microcosms will be maintained in the dark to minimize photodegradation, and on their sides to minimize the potential for volatile losses via the Mininert<sup>™</sup> cap. These steps are consistent with the Phase II Work Plan.

The majority of the microcosms will be stored at room temperature (~22 °C), except for certain treatments that will be incubated at 12 °C, as shown in Table 1 (note that each of these treatments parallels a room temperature treatment). These bottles will be transferred to a sealed bag while in the anaerobic chamber and then stored in the dark in a refrigerator at 12 °C. The microcosms will be returned to the anaerobic chamber for sampling. Data from these bottles will provide information about the temperature dependence of the degradation rates and additional comparisons with previous work. One treatment per SMU (i.e., SMUs 1, 6, and 7) will be tested at both a reduced temperature (approximately 12 °C) and at room temperature (approximately 22 °C) to provide a temperature correction factor that can be applied to degradation rate information derived from other tests conducted at room temperature.

For SMU-1 sediment treatments, the pH in each microcosm will be adjusted to pH 7 using hydrochloric acid at the start of the test. Neutralization of individual microcosms will ensure the solids/ porewater mixture is initially adjusted to pH 7. One test will also be conducted with the pH as received to assess the degree of degradation obtained under these conditions. To support the observations from the Phase II testing, SMU 1 sediments will be inoculated with sediment from other locations in the lake where greater amounts of biological activity were observed and also with sediment from the core collected at the clean location as discussed above.

In addition to those tests described in Table 1 and as referenced in the Phase II work Plan, additional tests may be run under various conditions such as positive controls (including nutrient and/or electron acceptor additions), and negative controls (such as electron donor conditions).

## Analysis, Reporting and Quality Assurance/Control

Samples will be collected from each microcosm monthly. Analytical methods and quality assurance and control procedures will be consistent with those described in the Phase II Addendum 6 Work Plan. Microcosm tests will be performed by SiREM Laboratory (a division of Geosyntec) and analytical samples will be submitted to a laboratory consistent with the project QAPP (Parsons, 2005).

Sediment samples from each core location for SMUs 1, 6, and 7 will be analyzed initially according to the following methods:

- Volatiles (including naphthalene) using SW-846 Method 8260.
- Phenol using SW-846 Method 8270

The sediment sample from SMU 5 will be analyzed according to the following methods:

- TCL Volatiles using SW-846 Method 8260;
- TCL Semi-volatile SW-846 Method 8270

Sediment from select microcosms may be analyzed at the end of the study to confirm the total mass of each target compound remaining. Phenol analysis (SW-846 Method 8270) will be done on sediments at the completion of incubations. The triplicates for each test will be combined as one sample to ensure sufficient volume. Centrifuged pore water samples from a single core in each SMU will be analyzed according to the following methods:

- Volatiles (including naphthalene) using SW-846 Method 8260;
- Anions by Method 300.0;
- Ammonia by Standards Methods for the Examination of Water and Wastewater Method 4500;
- Dissolved oxygen by *Standards Methods for the Examination of Water and Wastewater* Method 4500-OG Membrane Electrode Method;
- pH by SW-846 150.1;
- Sulfide by EPA 376/SW-846 9030;
- Sulfite by EPA 377.1/SW-846;
- Phosphorus by EPA Method SW6010B;
- Dissolved metals (calcium, magnesium, potassium, sodium, iron, manganese) by SW6010B
- Alkalinity and unfiltered alkalinity by SM 2320B; and
- Total organic carbon by SM 5310B.

For the duration of the study, microcosm samples will be collected for the following:

- Volatiles (including naphthalene) using SW-846 Method 8260;
- pH by SW-846 150.1 or by probe; and
- ORP by probe measurement.

An interim status report and/or presentation will be prepared approximately four months after microcosms have been initiated. Following the interim report and based on the initial degradation rates observed, a better estimate will be provided on the predicted experimental duration and final report schedule.

The results of these experiments will include the degradation rate of the parent compound as a function of time under site relevant conditions. Half lives or first order rate constants will be provided for comparison to rate constants employed in previous cap modeling.

Please feel free to contact Tom Abrams at 315.552.9670 or me if you have any questions.

Sincerely,

John P. Mulinliff

John P. McAuliffe, P.E. Program Director, Syracuse

Bob Nunes, USEPA (5 bound) cc: Mike Spera, TAMS/ET (1 bound) Bob Montione, TAMS/ET (1 bound) Mark Sergott, NYSDOH (1 bound,) Geoff Laccetti, NYSDOH (Cover Ltr Only) Gregg Townsend, NYSDEC (1 bound) Kenneth Lynch, NYSDEC (1 bound) Normal Spiegel, Env. Protection Bureau (Cover Ltr Only) Andrew Gershon, Env. Protection Bureau (Cover Ltr Only) Margaret Sheen, Esq., NYSDEC (Cover Ltr Only Argie Cirillo, Esq., USEPA (Cover Ltr Only) Joseph Heath, Esq., (1 bound) Thayne Joyal, HEFT/Onondaga Nation (1 PDF) Thomas Milch, Esq., Arnold & Porter (Cover Ltr Only) William Hague, Honeywell (1 PDF) Brian Israel, Esq., Arnold & Porter (1 PDF) Bob Edwards, NYSDEC (1 bound) Dave Scheuing, NYSDEC (1 bound) Steve Miller, Parsons (1 PDF) Edward Glaza, Parsons (1 bound) Tom Abrams, Parsons (1 bound)

## **Cited References**

- Parsons. 2005. Onondaga Lake Pre-Design Investigation: Phase 1 Work Plan. Prepared for Honeywell, Morristown, New Jersey. Syracuse, NY.
- Parsons. 2006. Onondaga Lake Phase II Pre-Design Investigation Work Plan; Addendum 6. Prepared for Honeywell, Morristown, New Jersey. Syracuse, NY.

# TABLE 1A

# TREATMENT CONDITIONS FOR BIOTREATABILITY BATCH TESTING FOR SMU-1

	Treatment #											
Application	1	2	3	4	5	6	7	8	9	10	11	12
Anaerobic (no additions)	X		X	X			X		X		X	X
Sterilized and Poisoned		X										
Stored at 12°C												X
Inoculation										-		
Addition of Sediment from SMU-7			X		X							
Addition of Sediment from Clean Area				X		X						
Sediment Location												
Sediment Location 1-A (near 10117)	X	X	X	X	X	X					X	X
Sediment Location 1-B							X	X				
Sediment Location 1-C									X	X		

## *Notes:*

All treatments will be spiked with 1 mg/L of each target compound

All treatments will be tested at room temperature  $(22^{\circ}C)$  unless otherwise noted.

Treatment 11 will be tested with pH as received; all other treatments will be tested with pH adjusted to 7

All treatments will be done in triplicate

# TABLE 1B

# TREATMENT CONDITIONS FOR BIOTREATABILITY BATCH TESTING FOR SMU-6

		Treatment #							
Application	1	2	3	4	5				
Anaerobic	X		X	Х	X				
Sterilized and Poisoned		X							
Stored at 12°C					X				
Sediment Location									
Sediment Location 6-A (near 60100)	X	X			X				
Sediment Location 6-B			X						
Sediment Location 6-C				X					

## Notes:

All treatment will be spiked with 1 mg/L of each target compound

All treatments will be tested at room temperature (22°C) unless otherwise noted

All treatments will be done in triplicate

# TABLE 1C

# TREATMENT CONDITIONS FOR BIOTREATABILITY BATCH TESTING FOR SMU-7

	Treatment #										
Application	1	2	3	4	5	6	7	8	9	11	
Anaerobic (no additions)	X		X	X	X	X	X	X	X	X	
Sterilized and Poisoned		X									
Stored at 12°C			X								
Modified Spike											
No DCB or benzene added				X							
No DCB or CB added					X						
Sediment Location											
Sediment Location 7-A (near 70049)	Х	X	X	X	X			X	X	X	
Sediment Location 7-B						X					
Sediment Location 7-C							X				

## *Notes:*

All treatment will be spiked with 1 mg/L of each target compound unless otherwise noted

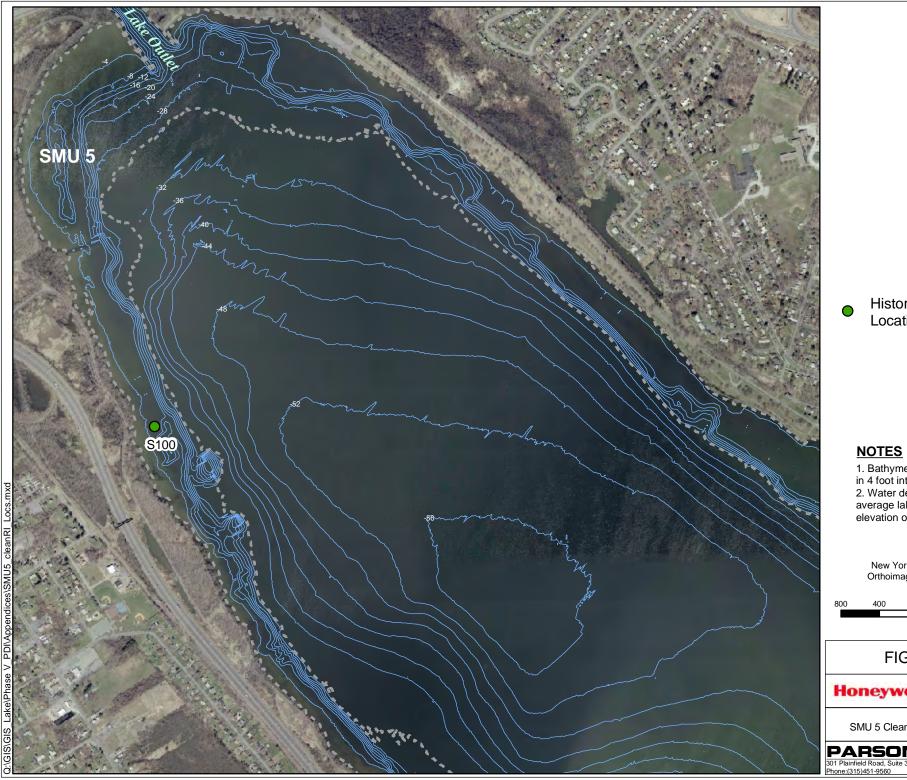
DCB - dichlorobenzene

CB - monochlorobenzene

All treatments will be tested at room temperature (22°C) unless otherwise noted

All treatments will be done in triplicate





Historical Sample Location

1. Bathymetry contours are in 4 foot intervals. 2. Water depth based on average lake elevation of 362.82 feet. New York State Digital Orthoimagery from 2003 800 400 0 800 Feet Feet FIGURE 2 Honeywell Onondaga Lake Syracuse, New York SMU 5 Clean Sample Location PARSONS 301 Plainfield Road, Suite 350; Syracuse, NY 13212 Phone;(315)451-9560