# ONONDAGA LAKE PRE-DESIGN INVESTIGATION: PHASE III WORK PLAN - ADDENDUM 3 CAP DESIGN BENCH-SCALE COLUMN STUDIES Syracuse, New York

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# PHASE III PDI WORK PLAN – ADDENDUM 3

#### **1.0 INTRODUCTION**

The potential for biological degradation for contaminants within or below a sediment cap was evaluated as part of the Onondaga Lake Phase II PDI Addendum 6 (Parsons, 2006). Experiments were run using sediment slurries which showed a high likelihood for biological decay in SMU 6 and 7, while the initial studies in SMU 1 showed little microbial activity over the limited duration of the initial experiment. The studies from Addendum 6 of the Phase II PDI are ongoing at the University of Texas.

The column experiments proposed in this work plan will build on the initial slurry experiments, while reducing some of the variability associated with slurry experiments. Some of the slurry experiments showed short-term results that varied from substantial degradation to minimal degradation of contaminants under identical conditions. This is likely exacerbated by the dilute slurries in that the initial microbial population was more variable. Due to the dilutions (1 percent and 5 percent) used, it is likely some of the incubations did not receive viable bacterial populations. It is believed that under more realistic sediment, organism, and nutrient density conditions, that the degradation is likely to be more consistent with those slurries showing substantial degradation. Column experiments will also provide a better representation of conditions within the cap itself including redox potential, sorption to cap materials, buffering capacity of cap material (for SMU 1) and nutrient and microbial activity. These studies will be performed at the University of Texas in the same laboratory as the Phase II cap bench-scale studies.

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 PDI Sampling and Analysis Plan (SAP), Quality Assurance Project Plan (QAPP), Project Safety Plan (PSP), and Standard Operating Procedures (SOPs).

These studies will be focused on samples from areas of known high contaminant concentration, or previously observed non-aqueous phase liquid (NAPL). These areas have the highest potential to compromise the integrity of the proposed sediment cap and, therefore, require further consideration. Specific areas of uncertainty addressed by these studies include:

- 1) contaminant retardation factors and migration rates in typical cap material;
- 2) pH buffering of SMU 1 porewaters by a cap; and
- 3) biodegradation rates of chemical parameters of interest (CPOIs) in the cap material, especially in SMU 1.

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#### 2.0 PROJECT OBJECTIVES

The purpose of the Phase III PDI is to collect information required to conduct remedial design activities. The design of the isolation cap component of the remedy is based on an analytical 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 assumptions made in the cap model and to examine the potential for processes such as advection associated migration and biodegradation to impact the performance of the cap. 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 Project Safety Plan (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 III 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 a Vibracore or push core in accordance with the procedures outlined in the Phase I PDI SAP (Parsons, 2005). Cores will be located in areas that are representative of the sediment that will be capped. Eight locations will be sampled as described below in Table 1. The locations of the cores will correspond to a subset of the locations sampled in the Phase II PDI Addendum 6 for cap bench-scale slurry experiments.

Three 2 inch diameter cores will be collected at each location in SMUs 6 and 7. Three cores will be collected at three of the four locations in the ILWD (SMU 1). At the fourth location in

SMU 1, four cores will be collected. The cores will be collected from the 0 to 2 meter interval. A 14 inch segment (maximum length that can be shipped vertically in cooler) of each core will be selected for shipment to the laboratory for bench testing. Criteria for selecting the appropriate segment from each core will include:

- representative of materials within the core;
- biased toward the top of the core, but excluding the top 3 to 6 inch nepheloid layer, which may be aerobic and not representative; and
- excludes "crusty" layers that will be hard to handle in the laboratory.

Samples from each core will be used in column experiments as follows:

- one core from each location for column studies employing baseline flow rates and cap configuration (8 columns);
- one autoclaved (killed) control (autoclaved for one hour at a temperature of 130°C and 15 psi for each of three consecutive days) for each SMU employing baseline flow rates and cap configuration (3 columns);
- one replicate core from a SMU 1 location employing higher than baseline flow rates and baseline cap configuration as defined in Section 5.3 (1 column);
- one replicate core from a SMU 1 location employing lower than baseline flow rates and baseline cap configuration (1 column); and
- two replicate cores from SMU 1 and one each from SMU 6 and 7 that can be used to repeat other column experiments or to evaluate the need for and effectiveness of cap amendments (4 columns).

In addition to the sediment cores, lake water will be collected for the column tests. Approximately 10 gallons of water will be collected from the dock area in SMU 1 and shipped to the University of Texas.

SMU	Sample Location	Number of Cores	Notes from Slurry Testing
6	OL-STA-60098	3	No aerobic or anaerobic degradation observed for most compounds to date.
6	OL-STA-60100	3	Aerobic and anaerobic degradation observed for most compounds to date.
7	OL-STA-70048	3	Aerobic and anaerobic degradation observed for most compounds to date.
7	OL-STA-70050	3	No aerobic or anaerobic degradation observed for most compounds to date.
1	OL-STA-10115	4	No degradation observed to date.
1	OL-STA-10116	3	No degradation observed to date.
1	OL-STA-10117	3	No degradation observed to date.
1	OL-STA-10118	3	No degradation observed to date.

# TABLE 1SAMPLE LOCATION INFORMATION

Core segments will be capped and sealed immediately after collection and an effort will be made to minimize exposure to ambient air. A written description of each core will also be documented in the field. Photographs will be collected in the field of each core prior to shipment. The cores will be shipped vertically, and will be maintained at 4°C and sealed with no headspace until tests are conducted.

Cap material for the column tests will be selected in consultation with NYSDEC. Testing of the cap material will be conducted to define organic carbon content, porosity, and bulk density and/or grain size distribution, if not already available. Conventional sand capping materials will be part of the test, either from local sources or commercially available sands. Other cap materials, such as organoclays or other materials, will be tested in selected experiments.

#### 5.0 COLUMN STUDIES

#### 5.1 Objective

The column studies will be used to estimate contaminant mobility through the sediment cap in minimally disturbed cores, spatial variability of redox and pH throughout the column, sorption to cap materials, and contaminant fate processes in the cap material.

#### **5.2 Sample Preparation**

At the laboratory, cores will be transferred to an anaerobic glovebox (3% H2, 97% N2). The top 15 cm of sediment will be removed and transferred to 500 mL polycarbonate centrifuge bottles (Beckman). Bottles will be sealed and wrapped in parafilm, then centrifuged for 30 minutes at 10,000 rpm at 4C. The bottles will be returned to the glovebox and water will be removed by pipette. Both supernatant water and solids will be submitted to Test America for analysis for VOCs and mercury. The top 15 cm of sediment will be used to provide an estimate of initial concentrations. This is anticipated to provide the best estimate of initial concentration in a core without disturbing the integrity of the core sample. It is acknowledged that concentrations fluctuate with depth in the lake sediments; however, this estimate can be validated at the completion of the column experiment based on the final sediment concentrations which will be measured at the completion of the experiment, concentrations in the cap material, as well as the effluent water sample concentrations. An additional 15 cm of the glass column will be filled with cap material.

#### **5.3 Procedures**

#### Partitioning Experiments

Partitioning coefficient measurements on the cap material will be carried out in 50 mL centrifuge tubes using at least four replicates. Due to the expected low sorption capacity of sandy, cap materials, 50 g of these materials will be added to the centrifuge tubes and the tube filled with pre-made contaminated solution (approximately 25 mL) and sealed. The pre-made contaminant solution will contain levels of VOCs, nutrients, and ionic strength levels at concentrations similar to those observed in lake porewater. The solution will be developed based on the concentrations observed in the top 15 cm of the core as described in Section 5.2. The contaminant solution will be analyzed to insure stability of the initial concentration. The tubes will be tumbled for 48 hours. After tumbling, the tubes will be centrifuged for 30 minutes at 3000 rpm and 10 mL of supernatant collected for headspace analysis. The sorption coefficient on the cap material will be estimated by material balance. If more sorptive cap material is selected for specific experiments, the solid-water ratio will be modified to insure detectable concentrations in the supernatant water and to maximize the accuracy of the material balance.

#### Column Experiments

In each column, a 30 cm long column will be filled with approximately 15 cm of sediment extruded from a core tube. A cap of sand approximately 15 cm thick will then be placed on top of the sediment with a thin layer of glass fibers used to minimize intermixing between the cap material and underlying sediment. The filled column will be saturated with lake water. The column will be placed in a 12C environmental chamber for the duration of the experiment.

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Water will be injected into the sediment column at a baseline superficial (Darcy) velocity of 0.2 cm/day (73 cm/yr). This rate was selected such that breakthrough would likely occur in the columns within approximately two months. The water will be recirculated in a closed loop to minimize the introduction of any makeup water. It is anticipated that this will more closely resemble groundwater moving through the cap than would introducing fresh water in an open loop system. The sediment and cap materials have approximately equal pore volumes which will also minimize the introduction of outside makeup water into the cap prior to contaminant breakthrough.

One replicate core from each of SMU 1, 6, and 7 will be autoclaved and used as an abiotic control. Flow rates and column preparation for these experiments will be identical to the corresponding baseline core.

One replicate core from SMU 1 will be run at a higher flow rate (expected to be 0.5 cm/day) Darcy velocity) and one replicate core will be run at a slower flow rate (0.05 cm/day). The higher flowrate column experiments will be used to provide early feedback into the experimental approach and analysis procedures. The lower flow rate will evaluate sensitivity of the results to flowrate since all selected flows are substantially larger than expected in SMU 1 after placement of an onshore barrier wall (which is expected to limit Darcy velocities to approximately 0.006 cm/day or 2 cm/yr). The 0.5 cm/day flow rate provides an expected breakthrough time of approximately 15 days assuming a 40 percent porosity cap, 15 cm long while the 0.05 cm/day flow rate provides an expected breakthrough time of approximately 5 months. Flow rates may be adjusted based on observations made during the study (for example, if sorption related retardation in the cap material is greater than expected leading to much slower breakthrough times).

Contaminants can be released from the sediment by partitioning to the mobile water phase. Mobilized contaminants will be sampled by monitoring of effluent water via collection in vials containing hexane to insure VOC retention in the sample. Sampling will be initiated at 1/10 the modeled breakthrough time for each set-up, and as needed thereafter, to collect three to four samples along the breakthrough curve such that this portion of the curve is adequately characterized. An additional three to four samples will be collected along the steady state portion of the breakthrough curve such that the steady state portion of the curve is adequately defined. Sampling frequency will be adjusted depending on the preliminary analyses. The location of the sample extraction point will be as close as practical to the column exit. There will be a reservoir of makeup artificial porewater, one solution will be prepared per SMU based on the porewater concentrations and ionic strengths measured during sample preparation as described in Section 5.2. The APW reservoir will be attached to the inlet side of the column (i.e. not to the measured effluent, but to the bottom of the sediment column) during sampling. The pump will pull new fluid from this reservoir while simultaneously filling a sample reservoir. The volume of makeup water added will be equal to the volume of sample. The makeup water will not dilute the sample collected, and will not migrate into the cap layer without passing through and becoming equilibrated with sediment porewaters.

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Samples collected from the column will be analyzed for benzene, toluene, ethylbenzene, xylene (BTEX), dichlorobenzene (DCB), chlorobenzene (CB), and naphthalene, as well as pH, redox, DO, and inorganic constituents that will indicate flow behavior in the column (e.g. chloride from the high chloride porewater). After achievement of steady state with respect to VOC samples, an effluent water sample will be submitted for mercury analysis.

Effluent samples will be analyzed for chlorides by ion specific probes. Effluent samples will be analyzed for CPOIs by direct injection using SW-846 Method 8260. Mercury will be analyzed by Test America using Method 1631. Any deviations from these methods due to sample volumes or other requirements associated with the sample experimental procedures will be documented in the final report.

The purpose of the effluent sampling is to define migration rate and breakthrough of the cap layer. Upon breakthrough and apparent achievement of steady state conditions, the experiment will be stopped. Some of the more hydrophobic compounds may not achieve steady state or may require a significantly longer period of experimentation. The flow and dimensions have been selected, however, such that all CPOIs (BTEX, naphthalene, and chlorobenzenes), with the exception of mercury, are expected to achieve steady conditions within six months. Following each column experiment, the cap and sediment layer will be profiled for pH and redox potential by insertion of appropriate probes at 1 cm intervals within the column sediment. The entire cap layer will be maintained anaerobic during the experiment to simulate the cap isolation layer. The redox measurement is designed to simply confirm this. The pH measurement will show any gradients that may develop in the cap.

The cap media and sediment will then be extruded and sectioned for analysis of contaminants of concern. Due to sample volume requirements, it is expected that sectioning will be in 5 cm intervals. The top interval (top 5 cm) in both the cap and sediment layers will be divided and the split samples will be sent for analysis at Test America. The remainder of the samples, and any samples collected with greater resolution (to inform process understanding), will be analyzed by solvent extraction SW-846 Method 8260. The lower layer of cap material will be sent to Test America for mercury analysis by SW846 Method 7471A. The sample will be collected from the interval of approximately 1 cm – 5 cm above the sediment layer or any sediment/cap intermixed layer to avoid direct incorporation of any mercury contaminated sediment. If mercury is detected in the cap material in the initial columns that are sacrificed or in the effluent water sample at steady state for VOCs, a more intensive effort to analyze for mercury in the effluent water samples and as part of the partitioning experiments will be considered in consultation with NYSDEC. This decision point will be added to the weekly action items list and tentatively scheduled for late October pending the progress of the experiments.

#### Cap Amendments

Two replicate cores from SMU 1 may be set up with an amendment added between the sediment and sand cap layer. These columns will be set up approximately two months after initiation of the initial cores. It is anticipated that organoclay and/or activated carbon will be used as amendments for organic sorption. The thickness of the amendment layer will be limited to approximately 1 cm. Due to the much higher sorption capacity of these layers, the time to achieve contaminant breakthrough is likely to be 100-1,000 times longer than through a sand layer. It is expected that substantially higher flow rates may be necessary before contaminants would be measurable in the effluent from these experiments. Other amendments (for example to control pH in the expressed porewater from SMU 1 sediments) may be employed after consultation with NYDEC. Other amendments may also be considered. These will be discussed with NYSDEC prior to initiation of the experiments.

#### SPME Exploratory Techniques

The primary measurement approach in these experiments is breakthrough time and concentration in the effluent from the columns. A secondary measurement is column sectioning at the conclusion of the experiment. It is also proposed to use a supplemental exploratory measurement during the experiment to determine porewater concentrations in situ through the use of solid phase microextraction fibers (SPME). Four to six 20 cm long SPME fibers will be inserted into the upper layer of sediment after extrusion of the core into the column barrel. The cap layer will be filled around the remainder of the fiber. At intervals during the experiment, an individual fiber will be removed, cut into 1-5 cm sections, and analyzed for contaminants of concern. These fibers are only 100-200 microns in diameter and are not expected to create preferential flow paths. Preliminary experimentation is underway to demonstrate that this is the case. SPME analysis will be via solvent extraction followed by conventional SW 846 Method 8260 analysis. Although the laboratory has extensive experience with this approach for PAH analysis, some method development is expected to be needed for volatiles. Analytical parameters that can be modified to maximize VOC detectability include reducing solvent extraction volume (as low as 50 µL), fiber length (e.g. up to 5cm), and fiber coating diameter (sorbent volumes per cm of fiber up to 10 times larger than standard fibers can be acquired commercially).

#### **5.4 Reporting**

The results from the column experiments will be a steady state contaminant flux and chemical concentration profile within the cap. The effluent contaminant concentrations and profiles of porewater and solid phase concentrations will be compared to predictions of the transient and steady state cap models (Lampert and Reible, 2007) for assessment of contaminant fate processes and rates. Specifically, chemical reactivity in the chemical isolation layer will be estimated by fitting the model to observations. Advection and diffusion/dispersion parameters are known to a high degree of confidence in the experiments but will be confirmed with nonsorbing inorganic effluent measurements (e.g. chloride). Breakthrough time of a particular

CPOI will provide an indication of sorption-related retardation and steady state concentration will provide an indication of average compound degradation rate. Comparison of biotic to abiotic control column effluent concentrations will indicate whether the observed degradation or loss was due to biotic or abiotic processes. Steady state concentrations will be the most sensitive indicator of compound degradation rate, but the transient concentration measurements (via *in situ* SPME and effluent measurements) and post-experiment concentration profile measurements can provide confirmation. The methods and results of this modeling analysis, including a comparison of fitted and observed concentration measurements, will be reported.

#### 6.0 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 NYSDEC prior to execution of the work or qualified in the final report if dictated by experimental process limitations during bench studies.

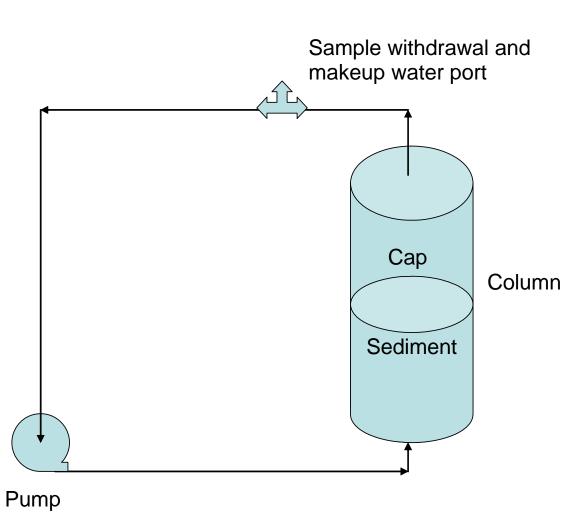
As a measure of quality, split samples representing key steps and milestones during these tests will also be submitted to a commercial laboratory approved by New York State Department of Environmental Conservation (NYSDEC). The top interval in both the cap and sediment layers will be divided at the conclusion of the column experiments and the split samples will be sent for analysis at Test America.

Analytical data will be collected and validated in accordance with the Onondaga Lake Quality Assurance Project Plan (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.

#### 7.0 REFERENCES

- Lampert, D. and D. Reible, 2007. An Analytical Modeling Approach to Design and Decision Making for Capping of Contaminated Sediments, submitted to *Journal of Soil and Sediment Contamination*.
- Parsons, 2005, *Onondaga Lake Pre-Design Investigation: Phase I Work Plan*. Prepared for Honeywell, Morristown, New Jersey. Syracuse, New York.
- Parsons, 2006, *Onondaga Lake Pre-Design Investigation: Phase II Work Plan.* Prepared for Honeywell, Morristown, New Jersey. Syracuse, New York.
- Parsons, 2006, Onondaga Lake Pre-Design Investigation: Phase II Work Plan Addendum 6. Prepared for Honeywell, Morristown, New Jersey. Syracuse, New York.

FIGURES



# FIGURE 1

# Schematic of Column Set-Up

# ATTACHMENT 1

# pH SOURCE IDENTIFICATION AND BUFFERING EVALUATION

#### **MEMORANDUM**

October 12, 2007

To:	Tim Larson, NYSDEC
From:	Parsons
Subject:	pH Source Identification and Buffering Evaluation

The potential for biological degradation was evaluated as part of the Onondaga Lake Phase II Pre-Design Investigation (PDI). Experiments were run using sediment slurries which showed a high likelihood for biological decay in SMU 6 and 7 while the initial studies in SMU 1 showed little microbial activity over the limited duration of the initial experiment. Addendum 3 to the Phase III PDI Work Plan described column studies that will be initiated to further evaluate the ability of a cap to contain contaminant migration in Onondaga Lake and provide an environment where biological decay can occur. The integration of biological decay measurements into cap design requires detailed discussion with NYSDEC and will be initiated prior to conceptual design submittal.

The factors limiting decay in SMU 1 samples are currently under investigation at the University of Texas; however, it is likely that pH is playing a significant role. Porewater pH studies, as described in this memorandum, will be initiated to understand the source of the high pH and the potential long-term pH neutralizing capacity requirements of a cap. At the completion of the batch and column experiments underway at the University of Texas and pending the results of the studies describe herein, the need for a cap amendment to neutralize pH will determined and design implications will be assessed. If it is determined that an amendment would be required, the modeling described below will be used to predict potentially suitable amendment materials. Amendments will then be evaluated through a series of batch testing and column studies to evaluate their effectiveness in neutralizing pH and allowing for biological decay.

The work will be completed at the mineralogy/geochemistry laboratory facilities in the Geology Department at Portland State University in Portland, Oregon under the direction of S.S. Papadopulos & Associates (SSP&A) senior geochemist. SSP&A has extensive experience in conducting solid phase/mineralogical characterization of soil, sediment and waste materials applied to remedial investigation, feasibility studies, and remedial design, and has done similar work for numerous projects including: Berkeley Pit, Butte, MT; Bay Road site, East Palo Alto, CA; Factory Lane site, Middlesex, NJ; Anaconda Smelter site, MT; Seattle-Tacoma International Airport, WA; Barbee Mill site, Renton, WA; and Calvert Industries site, Snohomish, WA. SSP&A has a long history of collaboration with mineralogy/geochemistry laboratories located at several universities including Portland State University.

P:\Honeywell -SYR\443582 - Capping\09 Reports\P3 WP\_Addendum 3\_Column Studies and pH\_Final.doc October 22, 2007 The work discussed in the memorandum is an addendum to Phase III PDI Work Plan -Addendum 3 and therefore the associated core samples will be collected 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). Any modifications to these procedures are discussed in the text below.

#### **OBJECTIVE**

Biological degradation is an important process in evaluating contaminant fate and transport. Initial bench testing results indicate that pH may have an impact on the biological decay rate. The porewater pH-control studies discussed herein are designed to:

- understand the source of the elevated porewater pH and potential long-term pHneutralizing capacity requirements of the cap; and
- facilitate identification of potential amendment(s) that can be added to the cap material to buffer pH to meet the potential long-term pH-neutralizing capacity requirement.

### SAMPLING LOGISTICS

The sample locations, data-gathering methods, and details of the analyses and testing to be performed at each location are described in Addendum 3 to the Onondaga Lake Phase III PDI Work Plan. Samples for the pH buffering studies will be collected at the six locations in SMU 1 sampled during the execution of the Phase II PDI (Addendum 6) Cap Bench Testing work scope; four of these locations are also being sampled per the scope in Addendum 3 to the Phase III PDI Work Plan (Parsons, 2007). Sample locations are provided below in Table 1. A two-inch diameter 10-foot long core dedicated to the pH buffering work will be collected at each location. Three 14-inch sections from each core will be selected as described in Addendum 3, i.e. a 14-inch segment (maximum length that can be shipped vertically in cooler) of each core will be selected for shipment to the laboratory for testing. Criteria for selecting the appropriate segment from each core will include:

- Representative of materials within the core;
- Biased toward the top of the core, but excluding the top 3 to 6 inch nepheloid layer, which may be aerobic and not representative; and
- Excludes "crusty" layers that will be hard to handle in the laboratory.

Core segments will be capped and sealed immediately after collection and an effort will be made to minimize exposure to ambient air. A written description of each core will also be documented in the field. Photographs will be collected in the field of each core prior to shipment. Prior to shipment, the cores will be individually placed in double Ziploc bags which will be purged with air free nitrogen gas before sealing. The cores will be shipped vertically and will be maintained at 4°C and sealed with no headspace until tests are conducted.

SMU	Sample Location	Number of Cores	Notes from Slurry Testing
1	OL-STA-10114	1	No degradation observed to date, pH 12.
1	OL-STA-10115	1	No degradation observed to date, pH 12.
1	OL-STA-10116	1	No degradation observed to date, pH 12.
1	OL-STA-10117	1	No degradation observed to date, pH 11.
1	OL-STA-10118	1	No degradation observed to date, pH 12.
1	OL-STA-10119	1	No degradation observed to date, pH 12.

 TABLE 1

 Sample Location Information for pH Buffering Studies

#### **Sample Preparation**

Cores will be split open using a spatula in an oxygen-free atmosphere (anaerobic glove box). Oxidation-reduction potential (ORP) and pH will be measured at intervals along each core, and three representative areas from each core will be sub-sampled for further analysis. Approximately 500-gram samples of each representative core section will be collected in labeled 16-oz glass containers and homogenized. Subsequently, three aliquots will be collected from each sample for bulk analysis (100 grams), mineralogy (50 grams), and sequential extraction testing (100 grams). The remaining samples will be sealed and stored in a refrigerator.

#### **PROCEDURES**

To understand the source of the high pH and the potential long-term pH-neutralizing capacity requirements, representative sediment samples from areas in SMU1 with porewater pH >11 will be analyzed for the following:

- 1. Bulk chemical analysis
  - a. iron, manganese, aluminum, calcium, magnesium, sodium, potassium, silicon, sulfur, and chorine by X-ray fluorescence (or microwave digestion and analysis by EPA 6010B);
  - b. moisture content (ASTM D 2216-90);
  - c. total organic carbon and total inorganic carbon (EPA 9060A);
  - d. total sulfur, sulfate, acid-volatile sulfide (AVS), and chromium reducible sulfide (CRS) (AVS and CRS not analyzed if total sulfur is below detection); and
  - e. soil (paste) pH.

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- 2. Powder X-ray diffraction (XRD) to identify crystalline mineralogy; and
- 3. Scanning electron microscopy (SEM) with EDX analysis to characterize X-ray amorphous phases and phase associations.

Following collection of the sediment characterization data, potential amendments will be evaluated for suitability in lowering porewater pH and maintaining an appropriate pH level for biodegradation using appropriate geochemical modeling tools. In these model simulations, porewater with elevated pH will be incrementally reacted (i.e. titrated) with an amendment. The initial pH and porewater chemistry used in the model simulations will be constrained by assuming equilibrium with one or more phases identified in the sediment characterization. The amount of the amendment dissolved, pH, and quantities of any precipitates predicted to form will be tracked as a function of the titration process. Through this procedure, potentially suitable amendment materials will be identified. These materials will then be ranked and screened relative to cost and availability.

#### **REPORTING**

The initial sediment characterization data will elucidate the mechanisms responsible for elevated porewater pH in SMU1 and provide an estimate of the source strength and duration.

#### **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 III PDI Work Plan (Parsons, 2007). Any deviations from these procedures will be discussed with 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 Quality Assurance Project Plan 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 scope. 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.