Honeywell

Honeywell
301 Plainfield Road
Suite 330
Syracuse, NY 13212
315-552-9700
315-552-9780 Fax

May 10, 2010

Mr. Timothy Larson, Project Manager
Division of Environmental Remediation
Remedial Bureau D
New York State Department of Environmental Conservation
625 Broadway, 12th Floor
Albany, NY 12233-7016

RE: Onondaga Lake Bottom Subsite – Onondaga County, New York
Consent Decree 89-CV-815
Phase VI Pre-Design Investigation
Action Item Cap-19h
Phase VI Addendum 1 Carbon Isotherm Study Work Plan - Revised

Dear Mr. Larson:

This letter presents the Carbon Isotherm Study Work Plan. This letter provides the proposed scope of work and details for the collection of additional data to support the design of an isolation cap in Remediation Area D.

1.0 INTRODUCTION

As detailed in the Draft Onondaga Lake Capping and Dredge Area and Depth Initial Design Submittal (IDS), the isolation cap design in Remediation Area D, which encompasses the in-lake waste deposit (ILWD), and in other areas of the lake will include carbon as an added layer of protection (Parsons, 2009). The carbon amendment will be designed to adsorb dissolved organic contaminants for time-scales sufficient to allow biological activity to reach levels that would achieve long term-compliance of the cap performance criteria.

The design life of the carbon layer was predicted in modeling conducted as part of the IDS using isotherm data generated as part of the Phase IV PDI (Lowry et al., 2010 and Reible et al., 2010). Design life is affected by the *in situ* adsorptive capacity of the selected activated carbon for the porewater target constituents, the loading rates of these constituents in upwelling water, and the allowable exit concentration of these constituents from the carbon layer. The evaluation described in this work plan is designed to build on the work conducted during the Phase IV PDI and to substantiate our current understanding of carbon performance.

2.0 STUDY OBJECTIVES

The primary objective of the study is to experimentally determine *in situ* Freundlich carbon adsorption isotherm parameters for the target constituents expected to impact the design life of the cap. The site-specific isotherm testing is designed to improve the cap design by identifying any potential limitations to long-term sorption capacity that might be posed by porewater matrix effects, which may include competitive sorption of constituents or natural organic matter (NOM).

The study described here builds on previous adsorption isotherm testing reported by Lowry et al. (2010) for porewater generated from sediments in SMU 1 and SMU 6/7. In the first part of that study, preliminary isotherms were generated for benzene, toluene, ethylbenzene, total xylenes, chlorobenzene, dichlorobenzenes (1,2-, 1,3-, and 1,4-), and naphthalene onto four different activated carbons. Calgon Filtrasorb F400 was found to be the preferred activated carbon with which to conduct full isotherm tests. The full testing was performed using porewater that underwent sparging to remove VOCs and was then spiked to a range of starting concentrations. Testing resulted in a set of reported Freundlich isotherm parameters for each of the target compounds.

The isotherm study will build on the study reported by Lowry et al. (2010) as follows:

- A single spiked test water will be used, rather than a series of spiked concentrations. Equilibrium concentrations will then be measured after exposure to a range of activated carbon doses based on established methods (e.g., Calgon Carbon Corporation, Laboratory Evaluation of Granular Activated Carbon for Liquid Phase Applications).
- Test samples will not be sparged before testing in order to retain potential competitive adsorption effects caused by both target and non-target volatile and semivolatile compounds.
- The study will account for potential matrix effects arising from *in situ* conditions including pH and oxidation-reduction potential (ORP) as well as natural organic matter and competitive adsorption.

The isotherm study will be primarily conducted at room temperature (about 70°F), which will yield slightly conservative results. A limited study will also be conducted at *in situ* temperatures.

3.0 HEALTH AND SAFETY

The Project Safety Plan (PSP) for Onondaga Lake work will be followed for the isotherm study. The Parsons Treatability Laboratory Chemical Hygiene Plan (CHP) and Standard Operating Procedures (SOPs) will also be followed. Isotherm study-specific activity hazard analyses (AHAs)/Job Safety Analyses (JSAs) will be developed and documented as required by the PSP.

4.0 FIELD WORK

Bulk water samples for the isotherm study will be collected from an existing groundwater upwelling pump in Remediation Area D in accordance with SOP 16 (Parsons, 2005). Upwelling location TR05-B was selected as the most viable location because of its proximity to the shoreline, the integrity of the apparatus, and the DOC content of the porewater. Location TR05-B will be purged and then sampled over a two to three-day time period to obtain approximately 55 gallons of porewater. The water will be pumped into 5-gallon containers and brought to the Parsons Treatability Laboratory in Syracuse, New York (EPA Identification No. NYR000170670), where water from the containers will be composited for use in the isotherm testing.

5.0 TESTING LOCATIONS

All isotherm testing for the study described in this work plan will be conducted at the Parsons Treatability Laboratory in Syracuse, New York (EPA Identification No. NYR000170670). Contract analytical testing will be conducted by an independent NYSDOH Environmental Laboratory Accreditation Laboratory (ELAP) certified laboratory.

6.0 TEST PARAMETERS

The parameters that will be evaluated during the study include the target constituents (VOCs; SVOCs; and mercury), aggregate organics, cations, anions, and aggregate inorganics. VOCs and SVOCs will be added to the test water as needed in order to develop isotherm curves for these compounds. Isotherm curves for mercury will be developed based on unspiked test sample concentrations.

6.1 VOCs

The target VOCs for the isotherm study include the compounds listed below. It is the intent of the study to develop Freundlich isotherm parameters for these compounds.

1. Benzene
2. Chlorobenzene (CB)
3. 1,2-Dichlorobenzene (1,2-DCB)
4. 1,3-Dichlorobenzene (1,3-DCB)
5. 1,4-Dichlorobenzene (1,4-DCB)
6. 1,2,3-Trichlorobenzene (1,2,3-TCB)
7. 1,2,4-Trichlorobenzene (1,2,4-TCB)
8. 1,3,5-Trichlorobenzene (1,3,5-TCB)
9. Ethylbenzene (EB)
10. Toluene
11. o-Xylene
12. m-Xylene
13. p-Xylene

6.2 SVOCs

The target SVOCs for the isotherm study include phenol and polycyclic aromatic hydrocarbons (PAHs) including naphthalene. The PAHs comprise the list for which Probable Effects Concentrations (PECs) have been established. These PAHs will be analyzed using EPA Method 8270. It is the intent of the study to develop Freundlich parameters for phenol and naphthalene, both of which may be added to the test water. The test water will not be amended with other PAHs; isotherm data will be collected on these compounds to the extent that their unspiked starting and equilibrium concentrations provide useful data for developing Freundlich parameter values.

6.3 Mercury

Isotherm data for total mercury will be collected. Test samples will not be amended with mercury, in order to capture sorption effects for mercury in its *in situ* state. Therefore the isotherm study will rely on unspiked concentrations.

6.4 PCBs

PCBs will be analyzed in this study to help characterize the test water used in this study; however, isotherm data for PCBs will not be collected. Aqueous-phase concentrations of PCBs, calculated using partitioning principles applied to sediment PCB levels, were below 0.1 μg/L at the 99th percentile for samples collected in each Remediation Area D subarea. Due to their low *in situ* concentrations and generally recognized affinity to carbon, it is not expected PCB sorption would drive the design of the carbon portion of the cap nor pose significant competitive sorption effects. Their low concentrations would also be difficult to provide for meaningful isotherm data; Method SW8082 for PCB analysis has a PQL of 0.5 μg/L for each of seven Aroclors, which are mixtures of individual congeners, with a majority of individual compounds having an MDL above 0.1 μg/L.

6.5 Aggregate Organics

The following aggregate organic properties will be analyzed in this study to help characterize the test water. Isotherm data for these parameters will not be collected.

1. Chemical Oxygen Demand (COD)
2. Biochemical Oxygen Demand (BOD_5)
3. Total Organic Carbon (TOC)
4. Dissolved Organic Carbon (DOC)

6.6 Cations

The following cations will be measured during this study for the purposes of test water characterization only – isotherm data will not be collected for them.

1. Total Iron (Fe)
2. Sodium (Na)
3. Potassium (K)
4. Calcium (Ca)
5. Magnesium (Mg)
6. Manganese (Mn)

6.7 Anions

The following anions will be measured for test water characterization purposes only. Isotherm data will not be collected for them:

1. Chloride (Cl^-)
2. Fluoride (F^-)
3. Nitrate (NO_3^{-2})
4. Sulfate (SO_4^{-2})
5. Sulfide (S^{-2})
6. Total Phosphate (PO_4^{-3})

6.8 Aggregate Inorganics

The following aggregate inorganic properties will be measured for test water characterization purposes only. Isotherm data will not be collected for them.

1. pH (field measurement)
2. Temperature (field measurement)
3. Conductivity (field measurement)
4. ORP (field measurement)
5. Total Hardness
6. Total Alkalinity
7. Total Dissolved Solids (TDS)

6.9 Analytical Methods

The analytical methods that will be used for the above-listed parameters are presented in Table 1. Included in Table 1 are the standard sample volume requirements, method detection limits (MDLs), and PQLs. The following considerations have been made with regard to analytical methods:

- EPA Method 8270 – SIMS analysis allows for lower detection limits of PAHs (PQL 0.2 ug/L; MDL 0.03 ug/L) than the standard EPA 8270 method (PQL 10 ug/L; MDL 0.4 ug/L), which would allow the study to more capably address the low concentrations of some of the more complex PAH compounds. The SIMS analysis would be modified to include select SVOCs relative to this study (e.g., phenol) which would allow collection of only a single SVOC sample per isotherm test bottle.
- Porewater samples collected for the study will be analyzed for mercury using EPA Method 245.1, this method was selected based on anticipated mercury concentrations. Concentrations close to the detection limit will be evaluated to determine if samples should be reanalyzed using Method 1631 to provide for a lower detection limit. Use of Method 1631 for samples with higher mercury concentrations is likely to result in excessive sample dilutions that could compromise data quality. The threshold for selection will ensure that data of sufficient quantity and quality will be obtained across carbon doses from which an isotherm can be generated.

7.0 ACTIVATED CARBON TYPE

During previous studies using porewater from SMU 1 by Carnegie Mellon University (Lowry et al., 2010), four different carbon types were evaluated including TOG, Centaur, DSR-A, and Filtrasorb F400 (Calgon Carbon Corporation). The study concluded that Filtrasorb F400 was the most effective carbon type for which a product specification can be obtained. Based on these results, the isotherm study described in this letter will use Calgon Filtrasorb F400.

F400 is a bituminous coal-based carbon that is commercially readily-available and comes with a product specification. The actual carbon samples used in the study will be pulverized and screened prior to use to promote attainment of adsorption equilibrium. Screening will be conducted to a specification of > 95% weight passing a 325 mesh. Parsons will obtain samples of the pulverized Filtrasorb F400 directly from Calgon.

Organoclay and peat have been shown to be less effective than activated carbon for the removal of VOCs and SVOCs from SMU 1 and SMU 6/7 porewaters. Reible et al. (2010) studied sorption of target organic constituents in porewater from SMU 1 and SMU 6/7 onto Organoclays PM-199 and XB-1 (CETCO) and peat. Results from this study were compared with those obtained by Lowry et al. (2010) for sorption of the same organics in porewaters from the same locations onto Filtrasorb F400. The comparison showed that the sorption capacities of the organoclays were approximately one order of magnitude lower than F400, and the sorption capacity of peat was lower still. Based on these results, other cap amendments are not being considered for this study.

8.0 EXPERIMENTAL DESIGN AND METHODOLOGY

8.1 Overview

The isotherm study will be conducted by adding different amounts of activated carbon to a series of test bottles each containing a known volume of test water and allowing sufficient time and mixing to allow target compounds to come to equilibrium with the activated carbon present in the bottles. The resulting liquid phase equilibrium concentrations of individual VOCs, SVOCs, and total mercury will be measured and the isotherm data will be interpreted. The Freundlich adsorption isotherm model will be applied individually to each target constituent to determine the model parameters for the constituent.

8.2 Test Water

One (1) test water will be tested. The test water will be sourced from a location within Remediation Area D that conservatively captures the matrix effects posed by *in situ* natural organic matter. It is currently anticipated the test water will be sourced from upwelling piezometer TR-05B since this well provides current access, and DOC levels from this well (822 mg/L) are toward the high end of the DOC range (approximately 100 – 1,200 mg/L) as measured across Remediation Area D during PDI activities.

Samples collected from the piezometer will be composited prior to testing. Depending on the concentrations of target constituents in the composited test water, select compounds may be added to increase the possibility of obtaining meaningful data across a range of applied carbon doses and reflect reasonably anticipated concentrations that may be found across Remediation Area D.

The test water will be collected and delivered to the Parsons Treatability Laboratory according to the protocol outlined in Section 4 of this work plan. A minimum of 45 gallons will be required to conduct the isotherm testing for the test water.

8.3 Preliminary Isotherm Test Design Considerations

Testing will be conducted using concentrations of target constituents according to the following considerations:

- Provide a conservative reproduction of *in situ* porewater concentrations based on measurements obtained during PDI efforts
- Maintain general relative ratios between constituents
- Ensure all constituents are present at high enough concentrations (e.g., 500 µg/L) to provide meaningful adsorption isotherm data across a range of activated carbon dose

8.3.1 Target Test Concentrations

Ninety-fifth percentile porewater concentrations of target constituents within each subarea of Remediation Area D as obtained during pre-design investigation (PDI) efforts are provided in Table 2. Aqueous-phase concentrations of VOCs and mercury were measured directly (ug/L); aqueous concentrations of PAHs, phenol, and total PCBs were calculated from sediment concentrations (ug/kg) by employing calculations using solid-water partition coefficients. Cumulative density function (CDF) statistical values were used.

Table 2 provides a summary of target concentrations of individual constituents to maintain general relative ratios of target constituents based on the highest subarea 95th percentile concentration obtained within Remediation Area D for each constituent, while simultaneously spiking to high enough concentrations to provide meaningful data across a range of carbon doses. These are:

- BTEX VOCs:
  - Benzene, toluene, and xylenes (o + m + p): 5,000 µg/L
  - Ethylbenzene: 500 µg/L

- Chlorinated VOCs:
    - Chlorobenzene: 10,000 µg/L
    - 1,2- and 1,4-Dichlorobenzene: 2,000 µg/L
    - 1,3-Dichlorobenzene: 500 µg/L
    - Trichlorobenzenes (1,2,3-, 1,2,4-, and 1,3,5-): 500 µg/L each
- SVOCs:
    - Phenol: 2,500 µg/L
    - Naphthalene: 10,000 µg/L
    - Other PAHs: Not spiked.
- Mercury: Not spiked.

Historical data from piezometer TR-05B (phenol) and porewater vibracore location OL-VC-10150 (VOCs; naphthalene) in the immediate vicinity were compared with the target test concentrations to preliminarily determine the levels of spiking that will be required. This comparison is provided in Table 3.

8.3.2 Test Water Spiking

Based on the comparison provided in Table 3, samples collected from TR-05B for isotherm testing will be spiked with standard solutions containing target VOCs and naphthalene to achieve the approximate target concentrations outlined in 8.3.1. The standard solutions will be prepared in methanol by a laboratory chemical supply company to facilitate dissolution into the test water.

The ability to achieve the exact target concentrations as presented in Section 8.3.1 will be limited by the following:

1. Unlike the previous Carnegie Mellon University study (Lowry et al., 2010), the test water(s) will not be sparged volatile-free prior to spiking. Although the non-sparging approach is being selected for this study in order to better retain potentially unknown volatile matrix effects, it will necessitate a loss of some control on targeting specific concentrations of target constituents.
2. Target constituent concentrations will not be known prior to initial characterization of samples collected for this study.
3. Procurement of spiking solutions with individually-specified concentrations of target constituents would be impractical, and would not necessarily result in attainment of exact target concentrations following spiking as described in items #1 and #2.

Standard spiking solutions of target constituents will be prepared by a vendor (e.g., AccuStandard or Sigma). Four (4) separate standard solutions will be prepared, as follows:

1. BTEX VOCs: Benzene, Toluene, Ethylbenzene, and xylenes
2. Mono-Chlorinated VOCs: Chlorobenzene
3. Di- and Tri-Chlorinated VOCs: Dichlorobenzenes and trichlorobenzenes
4. SVOCs: Naphthalene.

The use of these spiking solutions will allow for each group of parameters to be spiked independently to target the highest 95th percentile concentrations.

Table 3 summarizes the spiking solutions that will be formulated for this study and reflects a limit on the number of individually-specified concentrations within each solution. Table 3 also presents the resulting estimated concentrations for samples collected from TR-05B, based on the test water preparation described below. All four spiking solutions will be prepared in methanol, which is very hydrophilic and would not be expected to sorb appreciably to activated carbon, thereby eliminating a potential competitive adsorption effect that could not be attributed to *in situ* conditions.

With the exception of naphthalene, it is not advisable to augment test water with PAHs. The PAH spiking solution solvents are typically acetonitrile or a 50/50 blend of methanol and dichloromethane (DCM). Both acetonitrile and DCM would likely pose competitive sorption effects that could not be attributed to *in situ* conditions. Although 95th percentile concentrations from the west subarea were all above individual PAH compound MDLs, the attainment of these concentrations cannot be assured in the test samples collected for this study particularly when using DOC as a primary criterion for sample location selection, which may favor areas aside from or in addition to the west subarea.

As an alternative to augmenting PAH concentrations, naphthalene will serve as a surrogate compound for the PAH group for cap modeling. Naphthalene is smaller but otherwise chemically similar to the other compounds in the PAH group, is already a Honeywell associated contaminant in Remediation Area D, and is present at high levels in sediment as well as pore water. Additionally, the relatively low concentrations of the larger PAHs compared to other compounds would not be expected to provide a significant degree of competitive sorption.

8.4 Isotherm Test Bottles

To promote a robust data set for calculating the Freundlich adsorption isotherm parameters, twelve (12) target x/m carbon doses will be applied. Three (3) replicate bottles will be prepared for each target x/m dose. In addition, four (4) undosed controls will be prepared to evaluate losses in target compounds that are not attributable to carbon adsorption (e.g., volatilization, photolysis). The total bottle count would be forty (40).

A study will also be conducted at *in situ* temperatures using a temperature-controlled water bath. Due to water bath capacity, the *in situ* temperature study will be limited in scope with up to four (4) target x/m doses prepared in duplicate, plus two (2) undosed controls for a total of ten (10) bottles.

All isotherm tests will be prepared in amber glass bottles to mitigate potential photolytic degradation of target compounds. The bottles will be pre-washed with Liqui-Nox® cleaning solution, rinsed sequentially with tap water and distilled water, and dried at room temperature to remove any residual contaminants from production of the bottles. The bottles will be capped with Teflon-lined caps to mitigate sorption of target compounds to the cap. For these studies, 2-quart (1.9L) bottles will be used to provide sufficient sample volume for independent certified analytical laboratory analysis of all target compounds and associated performance-related parameters. Each bottle including cap will be pre-weighed empty prior to and following filling to allow exact volume determinations to be made after filling.

8.5 Filtrasorb F400 Dose and Application to Isotherm Bottles

Pulverized Filtrasorb F400 will be dried for at least 24 hours at 103-105°C and then weighed onto weighing paper using a Mettler Toledo AT261 DeltaRange® tabletop balance. The carbon will be added to the pre-weighed empty isotherm bottles.

For each test water a range of activated carbon doses will be applied to bottles containing identical test water. The method to apply a range of carbon doses to bottles containing the same test water is based on established test methods, including those prescribed by Calgon Carbon Corporation, but represents a departure from the previous work (Lowry et al., 2010) in which bottles were spiked to different starting COC concentrations while the carbon dose was kept constant.

A range of pulverized Filtrasorb F400 carbon doses was preliminarily selected to provide a range of equilibrium concentrations for each target constituent from which Freundlich model parameters can be calculated. Table 4 summarizes the anticipated doses to be applied to each test water. The final carbon doses will be refined as necessarily following initial characterization of test water samples.

Previously-obtained Freundlich parameters for Onondaga Lake studies (Lowry et al., 2010) show a wide range of values for both K_f and 1/n between compounds. Due to this variation in adsorptive properties, the actual x/m ratios resulting from given carbon doses based on equilibrium concentration measurements will be expected to vary from compound to compound.

8.6 Initial Characterization

To refine the experimental design, an initial characterization will be performed on the porewater samples upon receipt at the Parsons Treatability Laboratory. The samples will be analyzed on a rush turnaround basis to:

1. Establish unspiked concentrations of target constituents to refine the level of spiking of target VOCs and SVOCs and final carbon doses applied
2. Establish unspiked concentrations of PAHs and total mercury to estimate the potential to obtain meaningful isotherm data for these compounds and the usefulness of applying a surrogate compound for PAHs
3. Establish concentrations of test water characterization parameters (i.e., aggregate organics, cations, anions, and aggregate inorganics) as well as PCBs

These results and any significant refinements to the testing will be presented to NYSDEC before the spiking and testing begins. The test water will also be visually inspected for the presence of a free-phase non-aqueous phase liquid (NAPL) layer or sheen. If a NAPL layer or sheen is detected, the aqueous phase only will be transferred to the vessel used for final spiked preparation of the test water. If upon spiking a NAPL layer is observed, the aqueous phase of the prepared test water will be transferred to a separate vessel; this step will be repeated until no NAPL layer remains.

8.7 Test Water Preparation

A total of fifty (50) test bottles (40 for main study plus 10 for *in situ* temperature side study), each at around 2-liters volume, will be required for each test water. Therefore 100 liters (26.4 gallons) will be prepared for each test. Each test water will be spiked using the standard spiking solutions summarized in Table 3. Table 3 also illustrates estimated test water concentrations based on the historical data for piezometers TR-05B and porewater vibracore location OL-VC-10150 as discussed in Section 8.3.2 if 100 mL of each spiking solution were added to 100L of test water. Final spiking will depend on concentrations in each unsparged test water following the initial characterization of test water samples.

Test water will be prepared in a glass carboy and kept under a nitrogen blanket. The carboy will be pre-washed with Liqui-Nox® cleaning solution, rinsed sequentially with tap water and distilled water, and dried at room temperature to remove any residual contaminants from production of the carboy. The nitrogen atmosphere will be imposed to reduce the potential for oxidative effects during test setup. A tedlar bag will be used to accommodate filling and dispensing from the vessel while keeping the nitrogen blanket intact. Gentle mixing will be applied to disperse the standards while minimizing VOC volatilization.

The aqueous solubilities for individual compounds are generally much higher than the estimated final concentrations as well as the maximum measured *in situ* concentrations. The apparent solubilities of individual compounds will be affected by the presence of other compounds and by the higher TDS of the test water. Care will be taken to ensure that the target initial concentrations are modified if there is visual evidence that apparent solubilities have been exceeded.

8.8 pH and ORP

In situ pH and ORP conditions will be retained as much as possible.

- pH – the pH values measured during the time of sample collection from upwelling piezometer TR-05B in Remediation Area D will be recorded. The recorded value will be maintained in the test water by the addition of acid or caustic until the isotherm bottles are prepared. After equilibrium mixing, the final pH of each isotherm bottle will be measured and recorded.
- ORP – the ORP values measured during the time of sample collection from upwelling piezometer TR-05B in Remediation Area D will be recorded. The recorded value will be maintained in the test water by maintaining the samples under nitrogen blanket and through the addition of sodium sulfite (Na_2SO_3) or other chemical reducing agent. Resazurin dye may be added to the isotherm bottles to provide visual indication of ORP status during the equilibrium period.

8.9 Distribution to Test Bottles

The spiked test water will be distributed to the pre-weighed test bottles directly from the mixing vessel without any intermediate steps (e.g., measuring in a graduated cylinder) to minimize volatilization. The mixing vessel will be fitted with a glass hose barb affixed with flexible tubing and in-line valve. The tubing and valve seats will be Teflon to prevent sorption of target constituents.

The bottles will be filled to ensure they are headspace-free without releasing any activated carbon. The filled bottles will be capped immediately. The filled bottles will be weighed to provide the exact volume of test water in each bottle, accounting for the carbon mass residing in the bottle.

Samples of each spiked test water will be collected and analyzed prior to distribution to test bottles, and also at the end of the distribution period. The bookend samples will be collected in order to account for loss during the distribution process.

8.10 Equilibration and Mixing Period

The capped isotherm bottles will be capped tightly and vigorously shaken for one (1) minute after filling with spiked test water. The bottles will be placed on a rotating mixing device to keep the contents of each bottle mixed during the equilibration period. The bottles will be placed on their sides, which will ensure the cap remains wetted and mitigate potential loss of VOCs. Bottles will be maintained at room temperature (about 70°F), which will yield conservative results compared to *in situ* temperatures. The mixing device will consist of multiple rotating PVC pipes loaded with the test bottles and rotated by a low rpm, low torque electric motor. Inert packing material (e.g., Styrofoam) will be placed between each bottle on the same device to prevent movement and thereby minimize the chance of breakage. The device will rotate the bottles continuously in the range of 5 to 20 rpm.

Bottles will be mixed for seven days, consistent with Lowry et al., (2010) which determined that seven days was sufficient to achieve equilibration for adsorption of VOCs and naphthalene with Filtrasorb F400 during isotherm testing. Upon completion of mixing, each test bottle will be placed upright for at least one hour to allow the carbon to gravity settle. The supernatant following settling will then be filtered at 0.45 μm pore size using a glass syringe with male luer-lok tip fitted with female luer-lok syringe filter with Teflon filter material, and dispensed to the appropriate analytical sample containers. The analytical samples will then be delivered for independent certified laboratory analysis.

9.0 DATA ANALYTICAL APPROACH

9.1 Freundlich Isotherm Model

The Freundlich Isotherm model is currently being used to model sediment cap activated carbon adsorption. The Freundlich model relates the equilibrium concentration of the adsorbate to the mass of adsorbate that is sorbed to the carbon as follows:

$$\frac{x}{m} = K_f C_e^{1/n} \qquad \textbf{Equation 1}$$

where:
x/m = mass of adsorbate per mass of adsorbent (synonymous with q_e)
C_e = equilibrium concentration of adsorbate in solution after adsorption
K_f = empirical constant
n = empirical constant

The parameters K_f and n are determined through logarithmic linearization of Equation 1 and linear, least-squares graphical analysis, as follows:

$$Log\left(\frac{x}{m}\right) = LogK_f + \frac{1}{n}LogC_e \qquad \textbf{Equation 2}$$

Equation 2 is in the form of a linear equation y = mx +b, with y = $log(x/m)$, x = $LogC_e$, m (slope) = $1/n$, and b (y-*intercept*) = $logK_f$.

9.2 Experimental Determination of Freundlich Model Parameters

The Freundlich isotherm parameters K_f and $1/n$ are experimentally determined by obtaining the equilibrium concentration (C_e) of adsorbate resulting from a range of adsorbent doses. For each applied absorbent dose, the x/m ratio is calculated as follows:

$$\frac{x}{m} = \frac{V(C_0 - C_e)}{M} \qquad \textbf{Equation 3}$$

where: C_0 = Initial concentration of adsorbate in solution before adsorption
V = Isotherm test sample volume
M = Mass of carbon applied to sorption experiment container

Running a range of adsorbent doses provides a set of x/m ratios, each associated with a measured value of C_e. By plotting *log(x/m)* versus *log(C_e)* and fitting a line to this data using a least-squares linearization, the slope of the fitted line would be 1/n and the y-intercept Log(K_f). K_f is then calculated by raising ten to the power of the y-intercept value (i.e., $K_f = 10^{\wedge\text{y-intercept}}$).

Actual x/m ratios will be calculated based on dry carbon doses and the reported equilibrium concentrations (C_e) of each target COC, including VOCs, SVOCs, and mercury. A plot of log(x/m) versus log(C_e) for each target COC will be prepared for each test using Microsoft Excel. Each COC plot will contain all data points for the test. A least-squares linear regression will be performed through each test's data log-log data plot. The Freundlich parameters 1/n (slope) and K_f (log transform of y-intercept) will then be reported based on the linear regression results for each COC.

10.0 REPORTING

Overall findings at the end of the study will be compiled in a draft isotherm study report, which will be submitted to the NYSDEC for review and comment. The report will include a materials and methods section that will discuss isotherm testing procedures, quality assurance/quality control (QA/QC), and analytical results. The report will be finalized after receipt and incorporation of comments.

Please feel free to contact Tom Abrams at 315-552-9670 or me if you have any questions.

Sincerely,

John P. McAuliffe

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

cc: Bob Nunes, USEPA (5 hard copies, 1 PDF)
Mike Spera, AECOMM (2 hard copies, 2 PDF & Orig)
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Table 1. Analytical Methods and Sample Summarization

Constituent	Analytical Method	Sample Volume	Holding Time	MDL	PQL	Units	Analytical Measurements	
							Characterization and Isotherm Bottles$^{(2)}$	**Characterization Only$^{(3)}$**
Benzene	EPA 8260	3 x 40 mL (VOA)	14 days (HCl preserved) 7 days (unpreserved)	0.1	0.5	µg/L	X	
Chlorobenzene				0.1	0.5	µg/L	X	
1,2-Dichlorobenzene				0.1	0.5	µg/L	X	
1,3-Dichlorobenzene				0.1	0.5	µg/L	X	
1,4-Dichlorobenzene				0.1	0.5	µg/L	X	
1,2,3-Trichlorobenzene				0.1	0.5	µg/L	X	
1,2,4-Trichlorobenzene				0.1	0.5	µg/L	X	
1,3,5-Trichlorobenzene				Note (1)		µg/L	X	
Ethylbenzene				0.1	0.5	µg/L	X	
Toluene				0.1	0.5	µg/L	X	
o-xylene				0.1	0.5	µg/L	X	
m-xylene				0.2	1	µg/L	X	
p-xylene				0.2	1	µg/L	X	
Chemical Oxygen Demand (COD)	EPA 410.4	100 mL	28 days	5	10	mg/L	X	
Biochemical Oxygen Demand (BOD$_5$)	Std Mtds 5210B	200 mL	48-hrs	5	5	mg/L		X
Total Organic Carbon (TOC)	Std Mtds 5310B	40 mL	28 days	0.35	1	mg/L		X
Dissolved Organic Carbon (DOC)	Std Mtds 5310B	40 mL	28 days	0.35	1	mg/L	X	
Metals / Cations	EPA 200.7	125 mL	6 months	Note (4)	Note (4)	--		X
Total Hardness			28 days	6.6	6.6	mg/L		X
Anions	EPA 300.0	100 mL	48-hrs$^{(5)}$	Note (4)	Note (4)	--		X
Total Alkalinity	Std Mtds 2320B	250 mL	14 day	10	10	mg/L		X
Total Dissolved Solids	Std Mtds 2540C	100 mL	7 days	10	10	mg/L		X

(1) 1,3,5-trichlorobenzene is not included in the standard calibration mixture and, as such, would be reported with a J-listing as a "tentatively identified compound."

(2) Includes 50 isotherm bottles, triplicate initial characterization samples, and duplicate spiked test batch water samples at both beginning and end of distribution to isotherm bottles.

(3) Triplicate initial characterization samples.

(4) Varies by individual parameter.

(5) 48-hr for nitrate; 28 days for others anions.

Table 1 (Continued). Analytical Methods and Sample Summarization

Constituent	Analytical Method	Sample Volume	Holding Time	MDL	PQL	Units	Analytical Measurements	
							Characterization and Isotherm Bottles[6]	Characterization Only[7]
Acenaphthene	EPA 8270 - SIMS Analysis[8]	1000 mL	7 days	0.03	0.2	µg/L	X	
Acenaphthylene				0.03	0.2	µg/L	X	
Anthracene				0.03	0.2	µg/L	X	
Benzo(a)anthracene				0.03	0.2	µg/L	X	
Benzo(a)pyrene				0.03	0.2	µg/L	X	
Benzo(b)fluoranthene				0.03	0.2	µg/L	X	
Benzo(g,h,i)perylene				0.03	0.2	µg/L	X	
Benzo(k)fluoranthene				0.03	0.2	µg/L	X	
Chrysene				0.03	0.2	µg/L	X	
Dibenzo(a,h)anthracene				0.03	0.2	µg/L	X	
Fluoranthene				0.03	0.2	µg/L	X	
Fluorene				0.03	0.2	µg/L	X	
Indeno(1,2,3-cd)pyrene				0.03	0.2	µg/L	X	
Naphthalene				0.03	0.2	µg/L	X	
Phenanthrene				0.03	0.2	µg/L	X	
Pyrene				0.03	0.2	µg/L	X	
Phenol				0.03	0.2	µg/L	X	
Total Mercury	EPA 245.1/1631	125 mL	28 days	0.05	0.2	µg/L	X	
Total PCBs	SW8082	500 mL	7 days	Note (9)	0.5	µg/L		X

[6] Includes 50 isotherm bottles, triplicate initial characterization samples, and duplicate spiked test batch water samples at both beginning and end of distribution to isotherm bottles.

[7] Triplicate initial characterization samples.

[8] The EPA 8270 - SIMS analysis is a GC/MS technique different than that used in the standard EPA 8270 method that allows for much lower detection limits for the PAHs (compare to those for phenol analyzed by the standard EPA 8270 method). The method would be modified to include phenol.

[9] Total PCBs include Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260. Individual MDLs range from 0.0147 (Aroclor 1016) to 0.1395 (Aroclor 1254).

Table 2. PDI 95th Percentile(1) Porewater Concentrations and Target Test Concentrations

Constituent	Units	95th Percentile Porewater Concentration			Target Test Concentration
		West	Center	East	
Benzene	µg/L	2539	**5450**	2856	5000
Chlorobenzene	µg/L	1261	1554	**11935**	10000
1,2-Dichlorobenzene	µg/L	316	449	**1431**	2000
1,3-Dichlorobenzene	µg/L	44	**72**	67	500
1,4-Dichlorobenzene	µg/L	383	408	**2052**	2000
1,2,3-Trichlorobenzene	µg/L	80	**153**	60	500
1,2,4-Trichlorobenzene	µg/L	78	**99**	77	500
1,3,5-Trichlorobenzene	µg/L	44	**72**	58	500
Ethylbenzene	µg/L	132	**278**	212	500
Toluene	µg/L	2464	**3520**	1316	5000
o-xylene	µg/L	2893	**5994**	2536	5000
m-xylene	µg/L				
p-xylene	µg/L				
Acenaphthene	µg/L	**24**	5.2	1.6	Not Spiked
Acenaphthylene	µg/L	**49**	11	6.7	
Anthracene	µg/L	**21**	7.2	4.0	
Benzo(a)anthracene	µg/L	**1.3**	0.28	0.16	
Benzo(a)pyrene	µg/L	**0.31**	0.053	0.042	
Benzo(b)fluoranthene	µg/L	**0.40**	0.063	0.049	
Benzo(g,h,i)perylene	µg/L	**0.041**	0.0062	0.0063	
Benzo(k)fluoranthene	µg/L	**0.16**	0.03	0.02	
Chrysene	µg/L	**0.49**	0.11	0.07	
Dibenzo(a,h)anthracene	µg/L	**0.015**	0.0029	0.0018	
Fluoranthene	µg/L	**7.6**	2.0	1.0	
Fluorene	µg/L	**51**	12	3.9	
Indeno(1,2,3-cd)pyrene	µg/L	**0.18**	0.026	0.024	
Naphthalene (PAH/VOC)	µg/L	**8783**	8407	5391	10000
Phenanthrene	µg/L	**86**	22	9.2	Not Spiked
Pyrene	µg/L	**4.0**	0.91	0.57	
Phenol	µg/L	**2521**	1336	1290	2500
Total PCBs	µg/L	0.00060	0.0082	**0.024**	Not Spiked
Total Mercury	µg/L	67	22	**173**	Not Spiked

(1) Based on Cumulative Density Function (CDF) data values as derived in Draft Capping IDS (Parsons, 2009).

Table 3. Preliminary Estimate of Test Sample Spiking

Constituent	Estimated Unspiked Concentration (μg/L)[1]	Target Test Concentration (μg/L)	Estimated Degree of Spiking Required (μg/L)	Spiking Solution Concentration (μg/mL)	Estimated Spiked Concentraction (μg/L)[2]
1. BTEX VOCs					
Benzene	556	5000	4400	4000	4600
Toluene	209	5000	4800	4000	4200
Ethylbenzene	126	500	370	400	520
Xylenes (o + m + p)	1536	5000	3500	4000	5500
2. MONO-CHLORINATED VOCs					
Chlorobenzene	1021	10000	9000	9000	10000
3. DI- AND TRI-CHLORINATED VOCs					
1,2-Dichlorobenzene	739	2000	1300	1500	2200
1,3-Dichlorobenzene	10	500	500	500	510
1,4-Dichlorobenzene	461	2000	1500	1500	2000
1,2,3-Trichlorobenzene	< 14	500	500	500	500
1,2,4-Trichlorobenzene	< 14	500	500	500	500
1,3,5-Trichlorobenzene	< 10	500	500	500	500
4. SVOCs					
Naphthalene	3645	10000	6400	6400	10000
UNSPIKED COMPOUNDS					
Phenol	3,750	2000	None	--	3,750
Mercury	694	--[3]	None	--	694

[1] Based on PDI Phase IV data from TR-05B (phenol), OL-VC-10150 (VOCs; naphthalene).

[2] 100 mL of Each Spiking Solution added to 100L Test Water Volumes.

[3] No target test concentration was established; isotherms to be based on concentration in porewater sample collected for isotherm testing.

Table 4. Pulverized Filtrasorb F400 Carbon Dosing(1)

x/m ID:	x/m_1	x/m_2	x/m_3	x/m_4	x/m_5	x/m_6	x/m_7	x/m_8	x/m_9	x/m_{10}	x/m_{11}	x/m_{12}
F400 Dose (mg/L):	2.5	5	10	17.5	35	50	100	250	500	1000	10000	100000
Mass/Bottle (mg)(2):	4.8	9.5	19	33.3	66.5	95	190	475	950	1900	19000	190000

(1) To be refined as required following initial characterization of test water samples.

(1) Bottle Volume of 1.9L