

**ONONDAGA LAKE PRE-DESIGN INVESTIGATION:  
EQUILIBRIUM STUDY WORK PLAN**

**Onondaga County, New York**

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## **1.0 INTRODUCTION**

Porewater samples were collected during Phase I of the Onondaga Lake Pre-Design Investigation (PDI) using diffusion samplers commonly referred to as “peepers.” Based on literature recommendations and experience at other sites, these samplers were left in place for approximately three weeks to equilibrate with the surrounding porewater. At the end of the three week period, the samplers were removed from the sediment and porewater was extracted for chemical analysis. During Phase II of the PDI, samples will be collected and a lab study will be performed to validate the three week time period and ensure adequate time for porewater equilibration.

Equilibration time for diffusion based samplers is dependent upon a number of parameters including cell geometry, characteristics of species of interest, membrane type, and sediment conditions. The effects of cell geometry are well understood: the time required for equilibration increases with increasing cell depth (direction perpendicular to membrane surface). These effects can be evaluated by simple models (Harper et al., 1997; Webster et al., 1998). The chemical species and inherent properties such as the diffusion coefficient ( $D_c$ ), possible effects of species charge, and interactions with the sediment environment (typically evaluated under sediment conditions) are also important. Membrane type is typically evaluated by the permeation speed (km). Historically, applications have used cellulose acetate or polysulfone with a pore size of 0.45 or 0.2  $\mu\text{m}$ , and recently Teflon coated membranes have become available in similar sizes. Sediment conditions are important in determining the supply of chemical species to the area near the membrane and are the most difficult to estimate. Sediments with low bulk density and high porosities generally have faster equilibration times. Other important considerations include whether the species of interest have solid phase reservoirs (precipitates, or sorbed phases), which decrease equilibration times by buffering contaminant concentrations in the vicinity of the sampler. Sediment conditions are generally evaluated as buffered, diffusion controlled, or partially buffered where no porewater flow is present. The effects of sediment conditions are poorly estimated and are best evaluated experimentally with sediment from the site.

## **2.0 OBJECTIVES**

This work plan is designed to determine the permeation speed and estimate equilibration time for diffusion samplers (“peepers”) installed in Onondaga Lake sediments. This will be done through a series of experiments including equilibration time trials with site sediment, and a membrane evaluation. While actual site conditions cannot be replicated, the combination of known cell geometry, diffusion coefficients, membrane permeability, and sediment properties combined with experimental equilibration times using site sediments and contaminants, can produce robust estimations of *in situ* equilibration times.

## **3.0 OVERVIEW OF FIELD WORK ACTIVITIES**

Sediment samples will be collected from three locations for this effort during the Phase II PDI scheduled for the Fall of 2006. Sampling will be conducted in accordance with the

procedures outlined in the Onondaga Lake Pre-Design Investigation: Phase I Sampling and Analysis Plan (Parsons, 2005) with the modifications discussed herein.

Vibracore samples consisting of 20 L (approximately 5 gallons of sediment) will be collected from SMU 1, 2, and 7 (see table below) where isolation capping is a main component of the lake remedy and where porewater samples are likely to be collected in 2006. To obtain the volume necessary for this study, one 14 foot core will be collected from each proposed location at a depth below the approximate dredge prism for that area. Based on previous cores in the area, the locations in SMU 1 and SMU 2 will contain only Solvay waste. However, cores near the S4C location in SMU 7 contained some Solvay waste within the 0-14 ft zone. Therefore, multiple cores will be collected at this location to ensure that sufficient black silt is collected and homogenization with Solvay waste material will not be required.

Cores will be cut into sections <2-foot (to facilitate shipping) and labeled to indicate location and depth interval and placed in coolers for delivery to the Groundwater Analysis Laboratory (GAL) at Texas Tech University. Sample locations were selected based upon a general representation of sediment characteristics in the SMU as well as known elevated contaminant concentrations of VOCs, mercury and naphthalene in the vicinity. In SMU-1 the sample will be collected near OLA-STA-10009, in SMU 2 the sample will be located near OLA-STA-20006, and in SMU 7 the sample will be located in the vicinity of S4C. If the results from samples in SMU 1, 2, and 7 are highly variable and result in significantly different equilibration times, additional samples may be collected in SMU 4 and SMU 6 to obtain specific equilibration times for those SMUs. The table below specifies the sample locations and depth intervals at where samples will be collected.

SMU	Sample Location	Depth Interval (ft)
1	OLA-STA-10009	6-20
2	OLA-STA-20006	6-20
7	S4C	0-14

## 4.0 MOBILIZATION AND LOGISTICS

### 4.1 Health and Safety

Parsons ranks health and safety as the highest priority. Parsons' Project Safety Plan (PSP) and our Subcontractors' Safety Plans prepared for previous lake work will be used for this investigation and will be strictly followed by all personnel. Any new task outside of the current scope defined in the PSP will have a new Activity Hazard Analysis (AHA) completed before the task begins. Copies of the safety plans will be maintained at the support zone and on each vessel. Each vessel will have the ability to communicate with land-based services by cell phone and marine VHF radio.

## 4.2 Site Facilities

The support zone and facilities established during the Phase I PDI will be used for the Phase II investigation.

## 5.0 MEMBRANE EVALUATION

The estimation of permeation speed ( $K_m$ ) will be conducted using a well mixed cell to prevent cell diffusion limitations or diffusive boundary layers, and a well mixed relatively constant bulk liquid phase which will be accomplished by using a much larger volume of bulk water containing the solute to prevent solute depletion. These experiments will be conducted using chloride as a conservative tracer to simplify the experimental approach and analysis and then adjusting the  $K_m$  by use of the following equation:

$$K_{m_x} = K_{m_{Cl}} * (D_{C_x}) / (D_{C_{Cl}})$$

Small bottle type samplers (2-5 ml) will be used, half covered with Teflon and the other half covered with Polysulfone membrane (0.45  $\mu$ m pore size). The samplers will be filled with distilled deionized water (DDI) and placed in a large container (100 times the volume of sampler) filled with a solution of NaCl (~100mg/l). Samples will be collected at increasing time intervals (0, 12, 24, 36, 48, 96, and 192 hours) using syringes and needles. Duplicate samplers (bottle peepers) will be evaluated for each time step and both membrane types. The concentration of chloride will be analyzed by Ion Chromatography (EPA method 301). Data will be plotted with respect to time and fitted to the following equation using non-linear regression.

$$C_t = C_o (1 - \exp(-K_m * t / F))$$

Where  $C_t$  is the concentration of chloride at time  $t$  in the sampler,  $C_o$  is the concentration at  $t=0$  in the bulk liquid,  $K_m$  is the membrane permeability constant, and  $F = V/A$  of the cell. Polysulfone membrane has been included as a basis for comparison as substantial information is available on its properties and applications.

## 6.0 SIMULATION OF SITE EQUILIBRATION TIMES

In order to test whether the results from the membrane permeability evaluation are reasonable, site sediment (~20 L) from three locations, as discussed in Section 3, will be sent to the laboratory. Sediment from each sample location will be homogenized and distributed into 500-1000 ml Teflon centrifuge bottles with zero headspace. Homogenization of cores from each site will be conducted in a  $N_2$  filled glove bag to prevent oxidation of the sediment. Since the porewater is already in equilibrium with the sediment from the lake, additional time for re-equilibration will not be necessary. Each centrifuge bottle will contain one bottle style diffusion sampler equipped with a Teflon membrane (0.45  $\mu$ m) and filled with DDI water. These bottle style samplers will have the same geometry ( $V/A$ ) as the individual cells of the extended peepers used during the Phase I PDI. In addition, the samplers will be oriented identically to the field samplers with the membrane face oriented perpendicular to the long axis of the bottle. Bottle volume will equal less than 5% of the total liquid volume of the sediment in the centrifuge bottle to prevent contaminant depletion during incubation. At varying time periods, duplicate

centrifuge bottles for each location will be sampled for reproducibility given the nature of sediment and potential for low concentrations. A total of 6 sampling times, including a time zero, will be conducted. Sampling intervals will be 3-5 days initially and increase to 7-10 days for the final time steps with a total sampling time of 30-45 days. Sample intervals will be determined based on initial results and adjusted accordingly based on each incremental time step result. The goal of the sampling program is to obtain the rate at which equilibration is achieved and also to experimentally reach >90% equilibrium. The final experimental matrix will then consist of a total of 6 time steps in duplicate for each sediment type to adequately develop equilibrium-approach type curves.

At each time interval, duplicate bottles will be sampled. First the bottle diffusion sampler will be removed from each Teflon centrifuge bottle and the lid quickly replaced. The bottles will then be centrifuged at 4°C for 10-20 minutes at rpm>10,000 to separate the porewater and sediment. The supernatant will then be removed using a glass syringe and injected through a 0.45 µm Teflon syringe filter in a no-headspace vial for analysis. While some very minor losses of volatile contaminants may occur, the limited surface area of the bottle compared to its volume and the short time required to remove the diffusion sampler will greatly reduce these losses. Filtration will also likely induce small losses due to the cold temperature of the supernatant and the use of slow rate filtration and techniques designed to minimize bubbles and turbulence. Samples will be analyzed within 48 hours or preserved and stored appropriately. Water from each diffusion sampler will be removed using a glass syringe and needle and placed in zero headspace vials as above. While these samples do not require filtration, they will be filtered to insure that the processing of the sediment porewater and sampler water are identical to minimize any differences due to sample handling.

## 6.1 Analytical

Filtrates will be analyzed for benzene, chlorobenzene, dichlorobenzene, naphthalene, xylene, ethylbenzene, toluene, mercury (in SMU 1), as well as chloride (see table below). These compounds were chosen as they currently drive the lake cap design and address hot spot removal criteria. For this work plan, mercury analysis is limited to SMU 1 based on the relatively low levels of mercury observed in previous porewater studies. Each two-foot section from the core in SMU 1 will be analyzed for mercury and the section with the highest concentration will be used to conduct the mercury equilibration experiment as described above. As there is some indication that high pH values may correlate with high porewater mercury concentrations, pH will be determined for all sections and time steps. If mercury concentrations are not sufficient in the core from SMU 1, the sediment from the SMU 7 core will be analyzed to determine if those concentrations are appropriate for this study. If the mercury equilibrium times differ substantially from the times for organics, additional analyses will be performed for mercury in other SMUs (not included in this work plan). Chloride has been included as it serves as a useful conservative tracer not subject to sample processing alterations.

Sample Location	Depth Interval (ft)	VOCs (see list above)	Chloride	Mercury	pH
OLA-STA-10009	6-20	12 samples	12 samples	12 samples	12 samples
OLA-STA-20006	6-20	12 samples	12 samples		12 samples
S4C	0-14	12 samples	12 samples		12 samples

The organics will be analyzed by purge-and-trap GC/MS generally following EPA Method 8260, and chloride will be analyzed by Ion Chromatography following EPA Method 300. These methods will be used as a starting point and modified as appropriate for optimum sensitivity and specificity to the target analytes. Total soluble mercury will be determined using EPA Method 7470A.

Analytical data will be collected in accordance with the Onondaga Lake Quality Assurance Project Plan (QAPP) (Parsons, 2005) as Level III data and will not undergo formal data validation. However, 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 FACILITIES

These studies will be conducted by the Groundwater Analysis Laboratory (GAL) at Texas Tech University which is located at Reese Technology Center (Building 790) as part of The Institute of Environmental and Human Health (TIEHH).

The GAL has conducted analyses for the U.S. Fish and Wildlife Service, the Texas Commission on Environmental Quality (formerly the Texas Natural Resource and Conservation Commission, TNRCC), as well as provided analytical support for ongoing projects at TIEHH funded by the Strategic Environmental Research and Development Program (SERDP) and the U.S. Army Corps of Engineers/Brazos River Authority. Significant expertise also exists within the GAL related to volatiles analysis using an HP 6890/5973 Purge and Trap GC-MS with autosampler.

## 8.0 DATA REPORTING

A draft report detailing the experimental results, model predictions, estimate of sediment impact and recommendations will be produced within ten weeks following sample collection. This report will include site specific equilibration rates and recommendations for appropriate diffusion sampler membranes. The final report will be completed approximately two weeks after receipt of comments.

## 9.0 REFERENCES

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