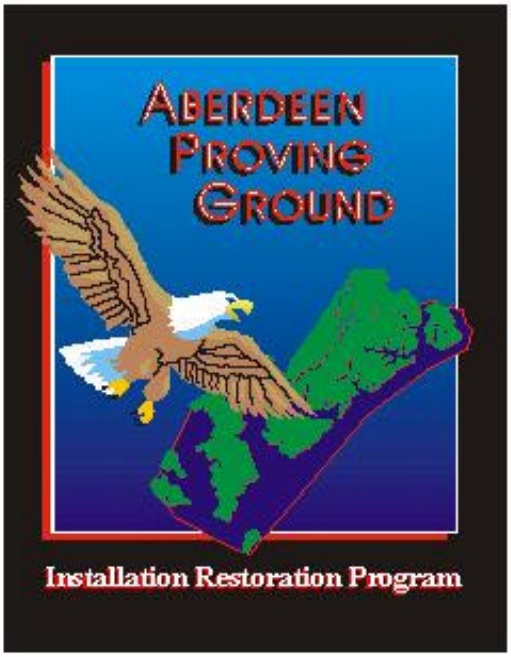

Work Plan-Performance Evaluation of Pytoremediation and Monitored Natural Attenuation Interaction in the J-Field Poplar Grove

June 2000
Aberdeen Proving Ground, Maryland
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1 STUDY OBJECTIVES

Past practices at J-Field have resulted in the contamination of groundwater with chlorinated aliphatics. Phytoremediation can play a prominent role in the reduction of chlorinated aliphatics in shallow subsurface systems. Trees may provide several functions: 1) direct uptake and metabolism of the aliphatics, 2) creation of a rhizosphere where aerobic and anaerobic microorganisms can biodegrade aliphatics and 3) altering the geochemical conditions in the aquifer downgradient from the trees. At J-Field, where a phytoremediation poplar grove is in proximity (within 200 feet) of areas where natural attenuation is thought to be occurring, evaluation of the contribution of the poplar grove to the overall natural attenuation of the chlorinated plumes is important (Figure 1). More information on the contribution of the trees to monitored natural attenuation is needed. In particular, what is needed is information from discrete depths spanning the vadose zone capillary fringe and the surface of the water table aquifer.

Currently a number of wells and piezometers are located within and outside of the grove. These give valuable information regarding the overall fate and transport of contaminants in this area of J-field. However, these sampling points are not able to provide the vertical or spatial resolution needed to differentiate between gross microbial reactions within the aquifer and more discrete plant-microbe interactions within the rhizosphere of the poplar trees. The results of this performance evaluation study can be used to examine the effects of the rhizosphere (which, due to unique planting techniques, is thought to exist from the surface to eight feet below ground surface) on VOC concentrations and distribution as well as geochemistry. A membrane dialysis sampler or “peeper” will be used to collect data at this resolution. This peeper has been specially designed to sample at the depths necessary for this type study. The effects of the rhizosphere on VOC concentrations and distribution may also be evaluated by analyzing plant material or environmental media for trichloroethene metabolites. In conjunction with the peeper sampling a number of wells and piezometers will be sampled to look at the gross changes in VOCs and root exudates in a flow line through the grove. The results of this study will help to determine the contribution of the poplar grove to the final fate of VOCs in the J-Field area.

1.1 Overview

The objective of the study is to evaluate the contribution of the poplar grove to the overall natural attenuation of VOCs occurring at J-Field. Specifically this will include two tasks.Task 1 will determine the concentration of chlorinated solvents, daughter products, and root exudates along a flow line within the Poplar Grove by sampling 15 piezometers, wells and lysimeters currently located within the Grove. The purpose of this task will be to locate promising locations for the installation of the peepers and to get some spatial information on VOC and root exudates concentrations. The sampling points are depicted in Figure 2. Task 2 will determine the vertical distribution of parent chlorinated solvents, daughter products, dissolved gases (H_2, CH_4, ethene, ethane),

organic acids and other carbohydrate root exudates in the rhizosphere at one location within the poplar grove and one location within the groundwater plume but away from the grove. In addition, if funding permits, plant material will be sampled and analyzed for parent and daughter compounds.

Figure 1- Phytoremediation/Natural Attenuation Study Area

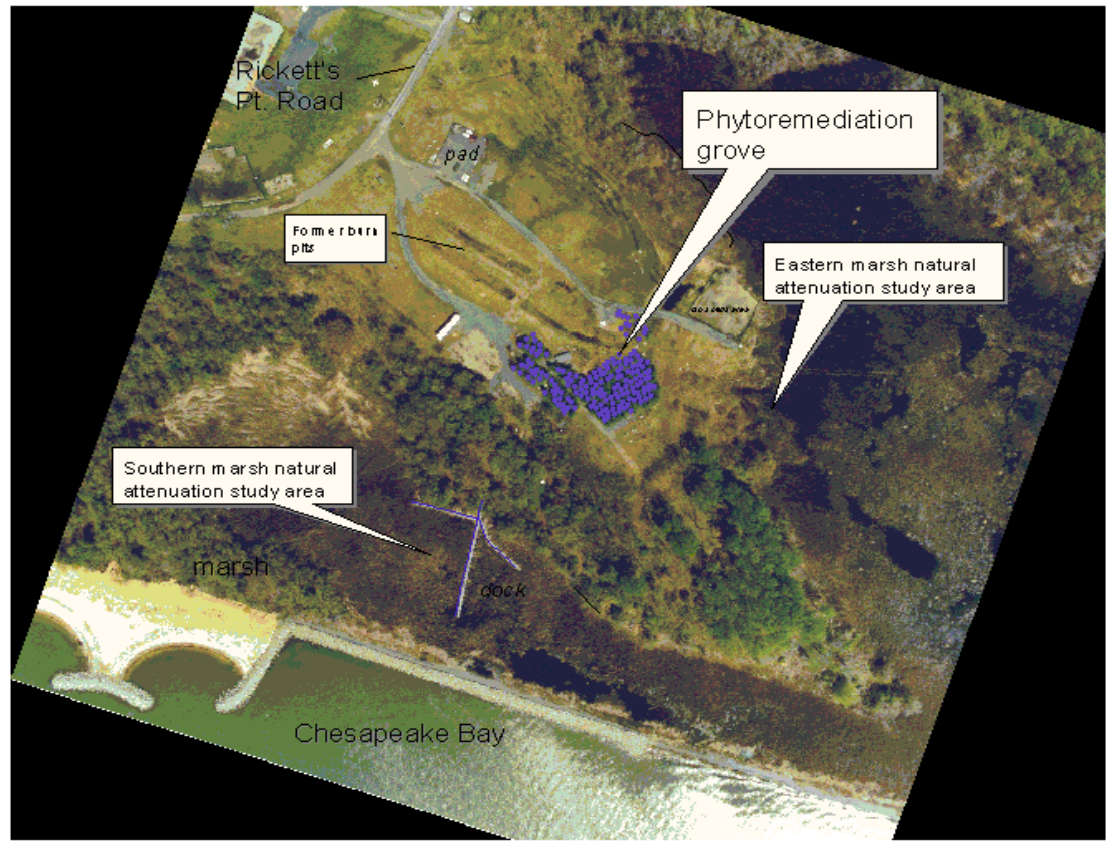
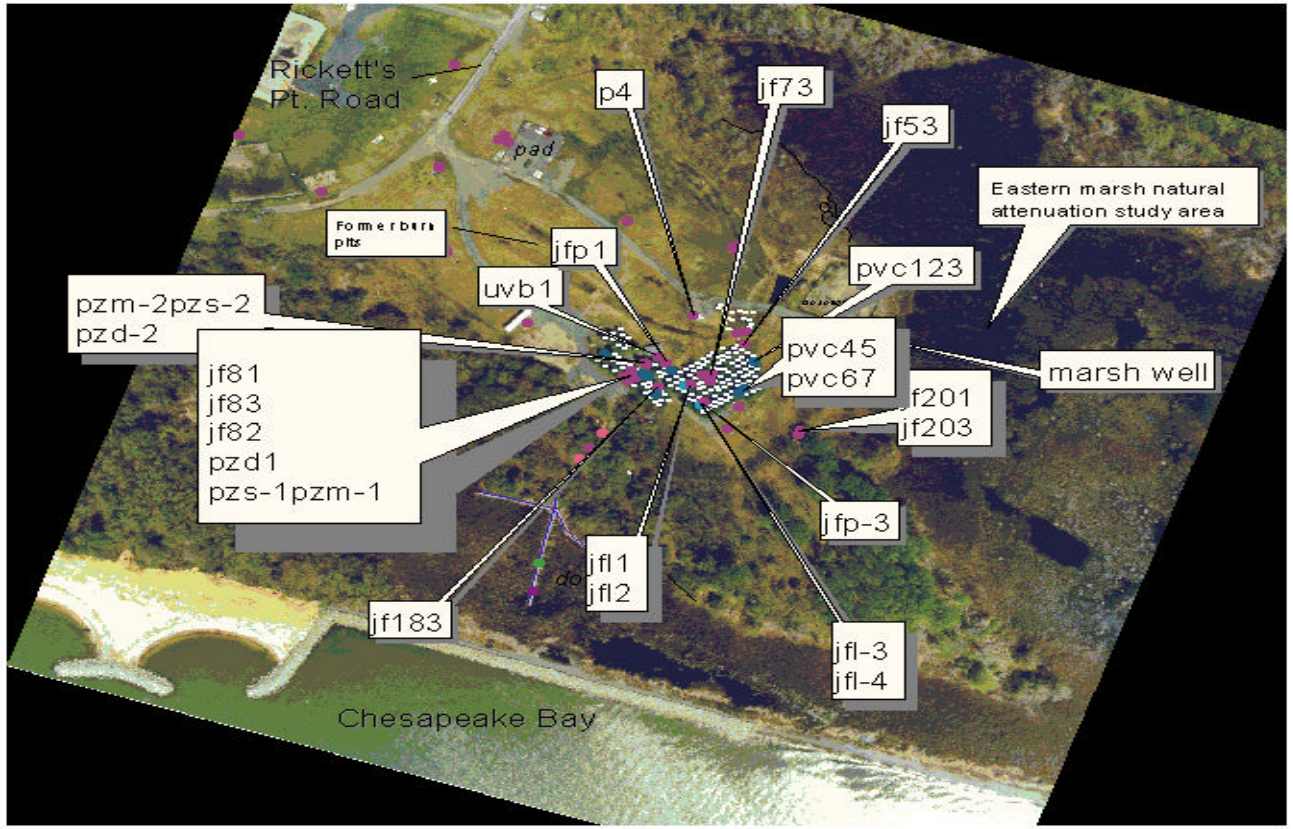


Figure 2 - Potential Sampling Points



1.2 Sampling and Analyses Methods

Piezometers, Lysimeters and Monitoring Wells

Sampling of the piezometers, lysimeters and monitoring wells will be accomplished using standard techniques (Appendix J Standard Operating Procedures Work Plan for CERCLA RI/FS, December 1999) and CFR's SOPs. Piezometers and lysimeters will be purged and formation water collected for analysis. If wells are used to obtain samples, equilibration will be performed before sampling. Results of this sampling will produce 15 data points through the phytoremediation.

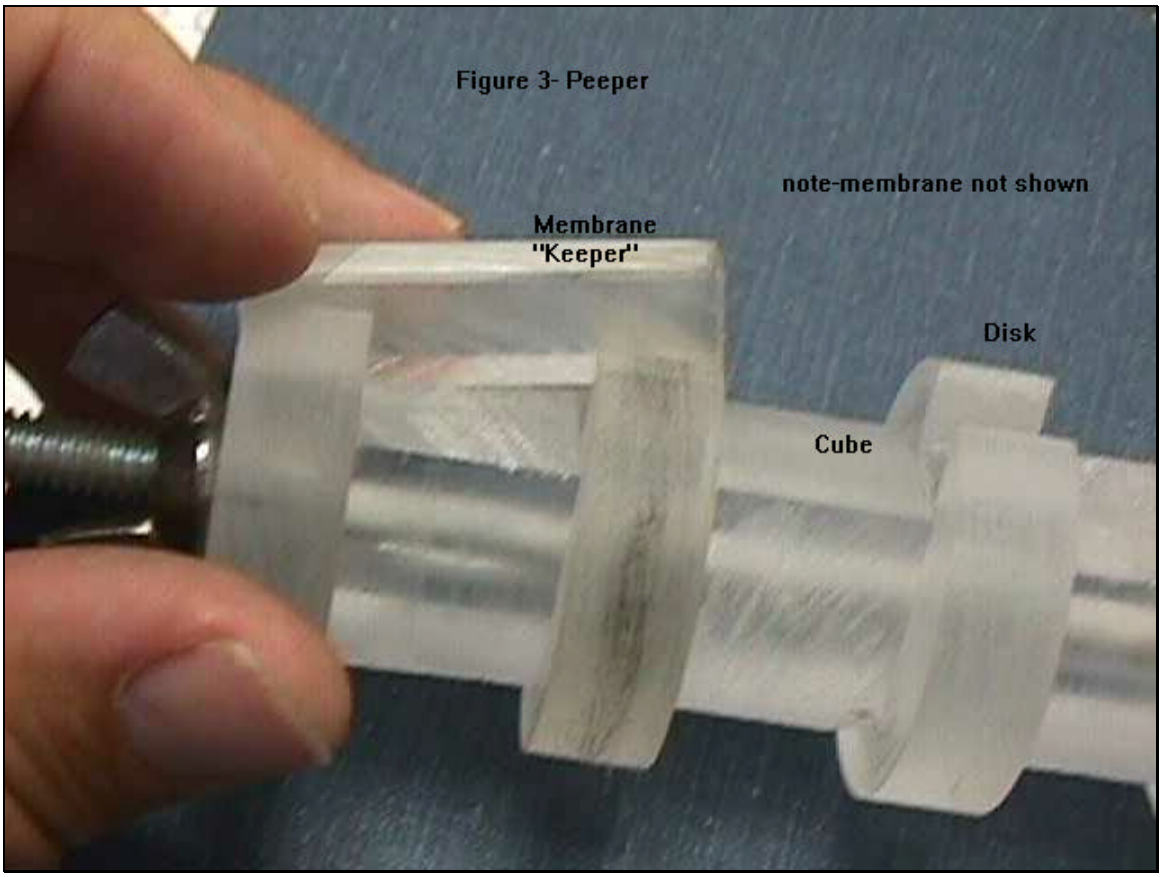
Phyto-Peeper

Sampling in the rhizosphere will be accomplished by using plexiglas peepers inserted in the rhizosphere by use of a Geo Probe. Locations for peeper insertion will be selected based upon the results of piezometer, lysimeter and montitoring well sampling as described below. Peepers are constructed of a series of plexiglas cubes and disks assembled into a four foot long sampling array. The wells between the cubes and the disks hold approximately 15 ml of de-ionized water. The wells will be covered with a 0.2 μm pore size membrane that allows dissolved constituents to pass between the porewater and the wells, but prevents particle transport. The membrane will held in place with a "keeper" that will be attached by nylon screws (Figure 3). Note the membrane is not shown in Figure 3. The design is a modification of the original peeper design by Hesslein (1976).

The peepers will be inserted into the rhizosphere and be allowed to equilibrate for 2-3 weeks. During this time the de-ionized water equilibrates with the pore water in the subsurface. The peeper will be removed after three weeks and the individual wells will be sampled. The result will be a vertical distribution of dissolved constituents at 4 cm increments over a 4ft depth resulting in approximately 24 data points.

1.3 Analyses

Analysis will be performed to obtain data for each of the Phyto-Peeper well volumes. The analytes are the chlorinated VOCs, dissolved gases (methane, CO_2, ethane and ethylene), organic acids (acetate, benzoate, butyrate, propionate, formate, salicylate and lactate), and any other root exudates. The significance of each analysis is as follows. Analysis of chlorinated solvent parent and daughter products can be used to determine fate of each constituent as it passes through the rhizosphere. The light gases (ethene, ethane and methane) are potential daughter products (ethene and ethane) and an important redox indicator (methane). Organic acids serve as the intermediate step between the degradation of the plant matter and the H_2 used by the halorespiring organisms as an electron donor and are commonly observed as root exudates. The presence of certain types of slow H_2



releasing organic acids (e.g., propionate) is a strong indication that the biodegradation process is robust. Chlorides are the conservative tracer of dechlorination processes and can be a valuable indicator of dechlorination reactions as opposed to oxidation by methanotrophic bacteria. However, chloride data must be evaluated with caution because of the potential for chloride-containing estuarine waters to periodically enter the freshwater marshes at J Field during significant storm and tidal events.

1.4 Data Evaluation

The results of the sampling provide data on the effect of the poplar grove on VOCs and provide insight on the processes occurring in the rhizosphere helping to establish the contribution of phytoremediation to the project. As discussed above, data can be used for a wide variety of purposes including natural attenuation evaluation and modeling.

2 PROCEDURES

2.1 Field Methods

2.1.1 Sampling

Two peepers will be inserted and removed in Summer 2000. One peeper will be inserted within the poplar grove and one peeper will be inserted just adjacent to the poplar grove. The peepers will be installed at a depth sufficient to sample the rhizosphere while penetrating the capillary fringe and the shallow aquifer. The peepers will be inserted using Geo Probe direct push technology (DPT), and will then be removed 2-3 weeks later using Geo Probe DPT . Once the peepers are removed after the 2-3 week equilibration period, the water within the wells will be immediately sampled using a glass syringe and transferred to zero headspace vials.

2.2 Laboratory Methods

2.2.1 Analytical Methods

Chlorinated VOCs will be measured using EPA Method 8260B, with typical detection limits of 40 ug/L, and lower detection limits of 5 ug/L when needed. Dissolved light gases (methane, ethane, ethylene) will be measured using a gas chromatograph (GC) with a flame ionization detector (FID). For both light gases, CFR's SOP will be used with the following modification. Since volumes recovered from the peeper are so small, a five mL water volume will be utilized instead of a 40 mL VOA vial.

The concentrations of organic acids in the piezometers and peepers will be measured using HPLC using CFR's SOP. Organic acids are common root exudates. Three additional measurements of potential root exudates will also be made: 1) total dissolved organic carbon will be measured using CFR's SOP as an indicator of bulk carbon constituents; 2) carbohydrate root exudates will be measured using HPLC using a column specific for simple sugars; and 3) finally three specific degradation products for TCE in poplars: trichloracetic and dichloroacetic acid and trichloroethanol will be measured after derivitization on the GC-MS. Chloride will be measured using ion chromatography. The VOCs, electron donors and gases to be measured are listed in Table 1. Copies of analytical methods for gases and donors are attached as Appendix A.

Table 1. Analytes for Peeper Study

Volatile Organic Compounds	Organic acids	Root exudates/ degradation products	Gases
1,1,2,2-tetrachloroethane 1,1,2-trichloroethane 1,1-dichloroethane chloroethane tetrachloroethylene trichloroethylene cis-1,2-dichloroethylene trans-1,2-dichloroethylene vinyl chloride	Lactate butyrate benzoate acetate proprionate formate salicylate + any additional detects	DOC Total carbohydrates Trichloroacetic acid Dichloroacetic acid Trichloroethanol	CO2 methane ethane ethylene

3 REPORTING

Data will be reported in a standard data format including final calculations of concentrations (in mg/L or ug/L of water). An interpretive report will be written describing and interpreting the significance of the results.

4 REFERENCES

Hesslein, R.H. 1976. *An in situ Sampler For Close Interval Pore Water Studies*. Limnol. Oceanogr. 21:912-914.

US Army, Aberdeen Proving Ground, December 1999. *Appendix J Standard Operating Procedures Work Plan for CERCLA Remedial Investigation/Feasibility Study (Generic Work Plan.*