REAC

Response Engineering and Analytical Contract

J-FIELD PHYTOREMEDIATION PROJECT
FIELD EVENTS AND ACTIVITIES THROUGH JULY 31, 2000
ABERDEEN PROVING GROUND, EDGEWOOD, MARYLAND

AUGUST 31, 2000

U.S. EPA Work Assignment No.: 0-034
Lockheed Martin Work Order No.: R1A00034
U.S. EPA Contract No.: 68-C99-223

OFFICE OF EMERGENCY AND REMEDIAL RESPONSE

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1.0 INTRODUCTION

1.1 Site Background

J-Field is located at the tip of Gunpowder Neck, Edgewood Area of Aberdeen Proving Ground (APG) in Harford County, Maryland. The Toxic Pits of J-Field were once the disposal site for chemical warfare agents, munitions, and industrial chemicals. The Toxic Pits consist of two parallel disposal pits that are approximately 10 feet deep, 15 feet wide, and 200 feet long. Remnants of other pits extend into the marsh area to the east. The pits were used for open burning and detonation from 1940 through the 1970's.

During open burning, wood was first placed in one of the pits. Materials including high explosives, nerve agents, mustard agents, smoke materials, and solvent were then placed on top of the wood. The pit was then flooded with fuel oil and ignited. After the first burn, a second burning event of any remaining material was performed in the adjacent pit. Any remaining debris was then pushed into the surrounding marsh. Metals were recovered from the pushout area for recycling. The pits and surrounding land have been disturbed by the activities that took place at J-Field. The contaminants of concern in the groundwater adjacent to the toxic pits are: Trichloroethene (TCE), 1,1,2,2-tetrachloroethane (1122), 1,1,1,2-tetrachloroethane (1112),1,1,2-trichloroethane (TCA), trans-1,2-dichloroethene (t-DCE), cis-1,2-dichloroethene (c-DCE), trichloroethene (TCE), and tetrachloroethene (PCE). Focus has been primarily on TCE and 1122, the most prevalent contaminants.

1.2 Objectives of this Study

As part of the remedial action selected for the site, a pilot-scale phytoremediation study was implemented in the spring of 1996. Phytoremediation is an emerging technology which utilizes plants and their associated microorganisms to remove, degrade, or contain chemical contaminants from soil, sediments, and water. Various poplar species and hybrids are commonly used for phytoremediation because of their rapid growth and high transpiration rates (Chappell, 1998). A total of 183 hybrid poplar trees (*Populus deltoides x trichocarpa* cv. HP-510) were initially planted over an area of approximately one acre (Figure 1). The objectives of the phytoremediation study are to determine if the shallow aquifer underlying J-field can be intercepted and contained due to evapotranspiration by the poplar trees, and to determine if volatile organic compounds (VOCs) in the groundwater can be removed and/or destroyed through natural mechanisms by the poplar trees or their associated microorganisms.

Other objectives of the study are to determine the aquifer drawdown within the study area and the trees' zone of influence; to correlate findings from tree tissue and transpirational gas sampling with water quality data from the capillary fringe; and to determine the possible mechanisms responsible for VOC reduction. Methods of VOC reduction may include:

- Transpiration of groundwater through plant leaves without VOC degradation.
- Metabolism of VOCs in plant tissue leading to a release of degradation products through transpiration.
- Incorporation, with or without modification, of VOC contaminants into plant tissue.
- Degradation of VOCs in soil by microbial populations, which may be enabled or enhanced in the rhizosphere by the presence of root exudates.

These objectives are being met through field investigations which involve the collection and analysis of plant tissue, roots, transpiration gas, soil gas, and groundwater contaminant concentrations and water elevation data. The sap flow rate in trees along with transpiration gases are being measured regularly. These data will be correlated with weather parameter data (solar radiation, relative humidity, temperature, and wind speed) in order to estimate the effect the trees are having on the concentration of contaminants in the aquifer and the elevation of the water table.

It is necessary to experimentally determine if these objectives are being met at the phytoremediation plot. Possible outcomes of the phytoremediation pilot study are as follows:

A) Groundwater contamination remains the same or increases over time

1) Trees are not reducing VOCs.
2) Trees are reducing VOCs, but the contaminant source [soil or dense nonaqueous phase liquid (DNAPL)] is replenishing the groundwater.
3) Trees are reducing VOCs at an undetectable rate.

B) Groundwater contamination decreases over time

1) Trees are aiding in soil microbial biodegradation of VOCs in the rhizosphere.
2) Trees are removing and metabolizing VOCs.
3) Trees are removing and transpiring VOCs.
4) Trees are removing and accumulating VOCs.

This report summarizes the significant results obtained from the commencement of this project in spring of 1996 to July 31, 2000. Further details and actual data may be found in Roy F. Weston (1997a), Roy F. Weston (1997b), Roy F. Weston (1999).

2.0 FIELD ACTIVITIES

2.1 Groundwater Monitoring and Sampling

2.1.1 Monitoring Well Installation

Prior to the beginning of the J-field phytoremediation study, there were nine shallow aquifer monitoring, wells, P2, P3, P4, JF-53, JF-63, JF-73, JF-83, JF-173 and JF-183, in the vicinity of the study area. Five additional 2-inch groundwater monitoring wells, JFP-1 through JFP-5, were installed in 1996. The location of these additional wells was determined based on the objectives of the pilot-scale monitoring, site conditions, and accessability. Monitoring wells JFP-1 through JFP-5 are screened from approximately 3.5 to 13.5 feet below ground surface (bgs). The casing of Well P-2 was later destroyed and this well has not been sampled recently.

Monitoring well JFP-1 was placed as far upgradient of the phytoremediation study area as possible to obtain a representative sample of groundwater before being impacted by the trees. Wells JFP-2 and JFP-3 were placed within the study area to monitor the trees effect on water quality and water table levels. Well JFP-4 was placed in-line, down gradient of wells JFP-1, JFP-2, and JFP-3 so that the affect of a larger planting area on water quality and groundwater elevations can be determined. Well JFP-5 was placed in the wooded area to the south of the site approximately 100 feet from the study area border.

All of the wells in the shallow aquifer in the study area were sampled in May, July, and August 1998, July 1999, and July 2000. The wells were purged and sampled according to U.S. EPA and APG sampling Standard Operating Procedure (SOP) 2007 *Groundwater Well Sampling*. All of the water samples were analyzed for VOCs. Filtered and unfiltered groundwater samples collected in July 1999 were also analyzed for TAL metals.

2.1.2 Micro-wells

A Geoprobe® unit was used to install 24 micro-wells throughout the phytoremediation study area. The Geoprobe® micro-well clusters were installed using the ERTC/ REAC all surface vehicle equipped with a Geoprobe® attachment..

Once a micro-well was pushed to its completion depth, it was then developed using a peristaltic pump and dedicated tubing. The micro-well was developed until it produced a relatively steady flow and relatively turbidity free water. Physical parameters such as turbidity, pH, oxygen, and conductivity were recorded during the development After development, the micro-wells were purged an additional 5 gallons prior to sampling. During sampling, the peristaltic pump flow was reduced and a sample was collected. The micro-well groundwater samples were then analyzed for VOCs. Microwells were last sampled in 1999 with the exception of the microwell at tree No. 174 which is sampled more regularly, most recently in July, 2000.

2.1.3 Lysimeters

Two sets of two lysimeters were installed near monitoring wells JFP-2 and JFP-3. The lysimeters were placed in pairs and set at depths of approximately 4 and 8 feet bgs. The 4 foot deep lysimeter was placed closest to the well. These depths allow for sampling of the capillary zone during seasonal highs and lows in the groundwater table. However, these lysimeters have been recently problematic during sampling.

2.2 Soil Gas and Background Gas Monitoring

On July 31, 1997, flux samples were collected within the phytoremediation area. Stainless steel flux chambers were utilized to sample gases eminating from ground surface. This was done to determine if significant levels of VOCs were being released from the ground into the phytoremediation plot. These samples were analyzed for VOCs by Gas Chromatograph/ Mass Spectrometer (GC/MS) following U.S. EPA method TO14 at the REAC laboratories.

In addition, Open-Path Fourier Transform Infrared (OP-FTIR) analysis has been used to monitor ambient concentrations of VOCs within the phytoremediation area. Analysis has been performed near ground level and at approximately 10 feet above ground surface.

2.3 Sap Flow Rates

Determining the sap flow rates of the trees is one of the most important tasks during the monitoring event at the phytoremediation plot. It is important to know how much water the trees are removing from the shallow aquifer and results are used to model the effect of phytoremediation plot on the groundwater. In addition, this information can be used to model how quickly the trees are removing VOCs from this groundwater source. Sap flow rates will vary with season, weather, and tree age and the monitoring and modeling include these paramaters.

Dynamax Dynagage ™ collars and Thermal Dissipation Probes (TDPs) were used to measure sap flow one or more times annually. Tree Nos. 58, 60, 67, 69, 174,177,181, 184,187, and 189 have been historically measured during various sampling events. In addition, trees Nos. 55, 126, 150, and 176 were monitored on July 11-19, 2000, along with two sweetgum trees located next to the plot and having similar size, although greater age, than the poplars. The two sweetgums were designated G1, located in proximity to poplar tree No. 149, and G2, located close to poplar tree No. 55.

2.3.1 Dynagage Collars

A series of Dynamax Inc. Dynagage ™ collars were used to collect continuous sap flow rates on selected trees in the phytoremediation plot. A data logger was used to record the sap flow measurements for the duration of each session. Each individual sensor consists of a series of thermopiles, a heating strip, and insulating separators. The thermopiles are arranged to measure conducted heat transfer (heat flux) up and down the stem and radial heat flux (heat lost to ambient). The heat added by the heat strip is precisely regulated at a fixed wattage and monitored by a separate sensor.

In order to calculate the sap flow in the stem, the individual parameters are obtained and used in the following thermodynamic equation:

$$F = (Pin-Qv-Qr)/Cp \times dT$$

Where:
F = flow, grams water per second
Pin = power in watts applied to heater strip, watts
Qr = radial heat flux, joules
Qv= Qu + Qd
Qu = axial heat flux (upward component), joules
Qd = axial heat flux (downward component), joules
Cp = stem heat capacity constant, joules/gram degrees Celsius
dT = temperature increase of the sap, Celsius.

The mass of sap passing through the sensor is calculated using the heat capacity of sap and the observed temperature increase. Since sap is composed of more than 99 percent water, the heat capacity constant of water (4.186 joules/gram degrees Celsius) is used in the equation.

Each sensor installation was calibrated according to the manufacturer instructions for the thermal conductance of the stem/sensor assembly by measuring all of the thermopile outputs during a zero flow period. This is accomplished during the first pre-dawn period of the sampling session for each of the sensors. After calibration, the sensors record sap flow rates measured in gallons/hour at five minute intervals. During data processing, the calibration factor is used to adjust any uncalibrated data collected between sensor installation and sensor calibration.

2.3.2 Thermal Dissipation Probes

A series of Thermal Dissipation Probes (TDPs) were also utilized for measuring sap flow. The TDPs were used in conjunction with the Dynagage ™ collars, however, the TDPs have been utilized more frequently than the collars during recent field sampling events as the tree diameters have increased to a point where the collars no longer will fit correctly. The TDP consists of two needle-like sensors with a pair of thermojunctions in each sensor. One of the sensors in the pair also has a heating element. The thermojunctions are differentially wired to determine temperature differences between the heated needle and the non-heated (reference) needle. Pilot holes are drilled into the tree trunk using a jig and depth stop to ensure perfect alignment of the sensors. The diameter of the pilot hole is slightly smaller than the diameter of the sensor, providing a close fit and good thermal conductance. The sensors are placed into the holes and connected to a power supply and data logger.

The regulated power supply provides a constant heat input to the heated upper sensor through the heating element. The temperature difference between the heated needle and the lower reference needle is dependent on the thermal conductance of the surrounding plant tissue. At zero sap flow conditions, the temperature difference is at a maximum value, decreasing to a temperature difference of zero at infinite sap flow. This relationship is expressed as:

$$K = \frac{dTM - dT}{dT}$$

Where:
K = a dimensionless parameter
dT = temperature difference of the heated sensor and the reference (unheated) sensor
dTM = temperature difference at zero flow

The sap flow velocity, v, in centimeters per second (cm/s), can be found by using the calculated K in the following equation:

$$V = 0.119 \times K^{1.231}$$

The sap flow velocity is converted to a volumetric flow rate using:

$$F_s = A_s \times V \times \frac{3600\ \text{sec}}{1\ \text{hr}} \times \frac{1\ \text{gallon}}{3785\ \text{cm}^3}$$

Where:
F_s = sap flow rate, gallons per hour
A_s = trunk cross-sectional, in square centimeters.

2.3.3 Leaf Area Index

Leaf area index (LAI) is a measure of unit leaf area per unit ground area. It is useful to know LAI because it influences transpiration rate and helps model when transpiration rates and therefore removal of VOCs, should be maximum. LAI was initially measured at J-field by Dr. Michael VanBavel of Dynamax, Inc. Details may be found in Appendix A. A Delta-T SunScan Canopy Analyzer (Delta-T Devices, Cambridge, UK) was used by Dr. Erik Hammerlynk to determine LAI at representative sites within the J-Field poplar stand in July 2000. The SunScan system calculates LAI as a function of extinction of ambient light transmitted through the canopy. Light transmitted through the canopy is measured with a wand-array of 21 silicon photodiodes, with concurrent measurements of direct beam and diffuse light made with a beam fraction sensor consisting of an unshaded (direct beam) and shaded (diffuse beam) photodiode oriented to true north outside the canopy. The canopy wand was held level at the same height as the lowest branches encountered. Control software automatically calculates solar zenith angle from the latitude, longitude, and deviation from Greenwich Median Time of the site. The software assumes an ellipsoidal, spheroid canopy of randomly distributed leaves. The ellipsoidal leaf angle distribution parameter (ELADP) was set to 1 (roughly equal horizontal and vertical leaf angles) and 2, representative of a higher frequency of horizontal leaf areas, for each sampling session. Sampling centered on an area bounded by Tree Nos. 151, 117, and 115 in the southern portion of the poplar stand. Measurements were made between 09:00 and 11:00 EDT.

2.4 Plant Tissue Sampling

Plants tissue samples were taken at various intervals to see if VOCs present in the groundwater are also found in the plant tissue, indicating translocation of these compounds. Samples have been taken at least once annually from 1996 through 1999. Initial tissue sampling involved the homogenization of the tissue and loss of the volatile contaminants before the sample was placed in sampling vial was a concern. Therefore, a method adapted from a standard procedure for sampling VOCs in sludges was used after the 1998 season as it appeared to be more applicable. The sample tissues are placed directly into a weighed sampling vial, re-weighed, filled with a reagent grade solvent (methanol) and weighed a third time. Since the VOCs easily pass through the plant tissues, the VOC concentration in the solvent and tissue matrix soon reach an equilibrium. The solvent is then analyzed and a dilution factor is applied to the results to back calculate the original concentration in the plant tissue. These analyses are now performed at REAC laboratories, although some of the earlier samples were sent to Phytokinetics, Inc..

Leaves, stems, and trunk cores were collected and prepared for analysis using the above method. The leaves were packed into the sample vials whole. The stems were cut to the length of the sample vial using a decontaminated stainless steel knife blade and closely packed into the vial. The trunk cores were extracted from the tree using a decontaminated hollow tree corer. The coring tool extracts a core about 3/16 inch in diameter which is broken into lengths that will fit into a sample vial and are packed as closely as possible.

2.5 Transpiration Gas Sampling

The objective of transpiration gas sampling was to determine if the trees are remediating the volatile organics in the groundwater, and if so, to determine the types and levels of volatile contaminants being emitted from the leaves of the trees. Sampling was performed utilizing a clear, 2 mil, 100 liter (30 x 36 inch) Tedlar® bag manufactured by SKC®, Inc., with dual stainless steel fittings. The valveless end of the bag was sliced open and placed over the ends of two or three branches of the tree. Branches were chosen for their sun exposure and healthy appearance. Plastic wire ties, ceramic clay (Standard Clay Mines Dover White), and home-made mechanical clamps (wood and viton tubing) were utilized to form a tight seal between the bag and the branches. Various methods have been experimentally used to prevent reduction in transpiration rate. These methods generally focused on maintaining ambient temperature with various “cold traps” made from wet or dry ice. In general, it has been difficult to compare these methods directly because of natural variability and lack of sample replicates.

2.5.1 Viking SpectraTrak

A Viking SpectraTrak 620 GC/MS was utilized in the field to provide quick turnaround analysis of the transpiration and flux chamber gas. A smaller 1-liter Tedlar bag was utilized to collect and transport a sample to the Viking SpectraTrak. A vacuum box system connected via a 0.25-inch teflon line was utilized to collect a sample from the larger bag on the tree. The Viking SpectraTrak was calibrated to analyze for three compounds of concern (TCE, TCA, and 1122) because of time constraints.

2.5.2 Summa Canister

Evacuated 6-liter stainless steel Summa® canisters were utilized to collect a near instantaneous gas sample from the Tedlar bag. Teflon® tubing (0.25 inch diameter) was utilized to connect the canister to the bag. Initial and final canister pressures were checked upon sampling. Samples were collected during major sampling events. These samples were analyzed by GC/MS following U.S. EPA method TO14 at the REAC laboratories.

2.5.3 Tenax/CMS Tubes

Tenax®/Spherocarb tube samples were collected in duplicate using a calibrated personal sampling pump. Teflon tubing (0.25 inch diameter) was utilized to connect the tubes to the bags. Samples were collected at a flow rate of 40 cubic centimeters (cc) per minute for a total volume of 4.8 liters. This method was experimentally performed during the1999 sampling events, but evacuation of the site during the procedure necessitates further trial. A similar method attempted in July 2000 but problems encountered during analyses prevented an accurate comparison at the time this report was written.

2.6 Transpiration Gas Condensate

Condensation gas has also been analyzed for VOCs because it is often present in the Tedlar bag while collecting transpiration gas. This condensation water was sampled after the transpiration gas was sampled and before the bag was removed from the tree. In order to collect the sample, a small cut was made in one corner of the bag and the condensate was transferred directly into 40 milliliter (mL) sample vials. The samples were placed on ice and brought to REAC laboratories for analysis by GC/MS.

2.7 Meterological Monitoring

A mobile meterological (MET) station was located at J-Field by REAC personnel to collect wind speed, relative humidity, precipitation, temperature, and net solar radiation during the sampling events. The station was placed away from the sampling activities at the edge of the plantation area in order to ensure that the readings were representative of the conditions for the entire phytoremediation plot. Data were collected as one minute averages from which a five minute average was calculated. These data were utilized to help develop a crop index for transpiration rates.

2.8 Tree Growth and Health Evaluation

Trees were examined visually to determine the status of their health since the initial planting. Pruning was performed on an as-needed basis. Insect damage, deer damage caused by rubbing, and leaf tip burn were recorded. Tree health was recorded for all trees. Trees were designated as healthy (large unblemished leaves) or significant and/or severe damage (loss of much of tree and or devegetation) and poor (small leaves, discolored leaves, excessive insect damage). Tree heights were measured with an optical height gauge and tree diameters were measured at breast height (4.5 feet above ground surface) with a tree diameter tape. As the trees matured, height measurements were eliminated. In 1999 LAI was calculated by Dr. Michael VanBavel of Dynamax, Inc. (Appendix A). Additional LAI were calculated in 2000 (see section 2.3.3).

Soil fertility analysis was performed at the beginning of the project and again in May of 2000 (Appendix B). Because the success of this project is ultimately linked to the health and continued growth of the trees, it is necessary to monitor agronomic factors, such as soil fertility, pH, and conductivity. In addition, leaf tissue was also examined in 1999 to determine the nutrient status of the trees.

2.9 Nematode Soil Community Analysis

Nematode analysis occurred annually in July to help determine how the poplar trees are effecting the soil food web and function. Three soil samples were collected from selected trees and homogenized. Based on espophageal morphology, these nematodes were classified as fungivores, bacterivores, herbiviores, omnivores/predators, or other (including immature or other individuals where characteristics were undeveloped or visually obscured).

Soil sample cores were taken from around selected poplar trees within the phytoremediation plot to assess the health of the soil community. Results were compared to sampling events of other years. Three soil samples were taken from 6 inches, 12 inches, and 18 inches of a selected tree using a two-inch diameter stainless steel auger with an acetate sleeve. The three samples were combined and homogenized within a one-gallon ziploc bag. From this bag three 20 grams of aliquot (wet-weight) were then collected by the laboratory and extracted for 48 hours. Nematodes encountered in each sample were placed into functional groups after examination at 120-160X magnification under a dissecting microscope. Samples were collected at poplar tree Nos. 17, 48, 58, 76 ,87, 107, 137, 139, 149, 174, 181, 185, 191, and 193. An additional control sample was taken from a nearby, mature woodland. Samples were sent to an outside laboratory, most recently Soil Food Web, Inc., for analysis. Analysis included total number of nematodes and division based on esophageal morphology into bacterivores, fungivores, herbivore, predator, hatchling, and unknown. Each sample, representing one tree location, was analyzed in triplicate.

2.10 Tree Root Development Evaluation

Three trees were excavated to evaluate their root development status in July 1999. Screening for the purpose of UXO avoidance was performed during the excavation. The excavation of a fourth tree was aborted when the UXO screening detected the presence of an unidentified anomaly near the tree.

A backhoe was used to dig a narrow trench beside the trunk to a total depth of 8 to 10 feet bgs. A fire hose was used to wash the soil away from the root mass of the first tree (No. 168) to avoid further damage to the smaller roots. The washing was continued until the tree was completely removed from the hole. After the root structure was measured and photographed, the tree was replanted in the original hole.

On tree Nos. 126 and 200, the backhoe was used to dig a trench on either side of the trunk but the soil was not washed away. The soil was chipped away to better expose the roots using a trowel attached to a long wooden pole.

It is predicted that the roots of at least one additional poplar tree (No. 55) will be examined in September 2000.

2.11 Additional Plantings

During the week of November 8, 1998, 65 additional trees were planted to extend the phytoremediation plot in two areas and to establish a reference area for future studies. Three species of trees, native poplar (*Populus deltoides)*, silver maple (*Acer saccharinum*) and tulip poplar (*Liriodendron tulipifera*) were planted in selected areas located south and southwest of the Hybrid Poplar plot.

Three planting methods were used to test the influence of different planting methods on the development of the new trees. Powered augers of two diameters were used to bore holes for the new trees. The first planting method used was similar to the original planting method having a bore diameter of 12 inches and drilled to a depth of 10 feet deep. The second method consisted of a 12 inch bore drilled to 10 feet deep which was backfilled followed by a 3-inch bore drilled to 6 feet. The third method consisted of only the 36-inch bore to a depth of 6 feet. The holes in all cases were backfilled with a soil and coarse sand mixture fortified with a 10*10*10 commercial fertilizer. The fertilizer was added to the mixture at a rate of 10 pounds per cubic yard of soil mixture. The trees were planted so that their root ball was at the same depth from the soil surface as it were before transplanting. The top three feet of all of the holes was backfilled primarily using the material excavated from the hole during boring.

Screening for the purpose of UXO avoidance was performed during the drilling operations. Many of the tree plantings required some relocation due to the detection of an unidentified anomaly near their intended location.

An additional area is being cleared on the southern part of the J-Field phytoremediation plot for future planting. It is possible that additional native tree species will be utilized in this expanded area. Due to previous problems with trees toppling and to the shallow nature of the groundwater, any trees planted in the future will most likely not be deeply planted or confined in such a way as to restrict root growth.

2.12 Modeling

Flow and contaminant transport modeling was performed to estimate the capacity for the poplar trees to remove contaminant mass and to predict the time to restore the shallow aquifer. Two methods of modeling have been utilized at J-Field. One is based on the analytical methods of Schnoor (Schnoor 1997), and the other utilizing numerical methods based on a three-dimensional groundwater flow (MODFLOW) and contaminant transport (RT3D) model (McDonald and Harbaugh, 1998; Clement, 1998).

3.0 RESULTS

3.1 Groundwater

VOCs are continuously monitored in the wells around the phytoremediation plot. Twelve to 14 wells have been samples one or more times per year since the commencement of the study. Figure 2 shows the major wells at J-Field and indicates and compares concentrations of TCE and 1122 found during July 1999 and July 2000, the latest sampling event. It appears that the VOC plume is splitting with half of the plume moving southeast and half moving roughly southwest of the phytoremediation plot. The actual concentration of VOCs has not yet been significantly reduced, probably due to the relatively high initial concentration and volume.

Continued monitoring of groundwater levels indicates a depression in groundwater at the phytoremediation plot. A groundwater depression of 12 centimeters or more has been recorded during the growing season (Figure 3). Complete groundwater level data may be found in the March 2000 report “J-Field Study Area Groundwater Elevation Monitoring Data Report” prepared by General Physics Corporation, Edgewood, Maryland.

Results of lysimeter sampling 8 feet bgs have detected both TCE and 1122 at the tree root zone.

TCE ranged from 5 to 29 micrograms per liter (ug/L) and 1122 was found at a concentration of 14- 36 ug/L. Sampling of the lysimeters has often been problematic. Data collection and analysis seem to indicate that the lysimeters are not optimally located. However, data obtained from the other wells located on the site has provided all of the necessary information.

3.2 Soil Gas and Background Gas Monitoring

TCE has been detected from gas flux chambers in 1997 at levels up to 38 parts per billion volume (ppbv), but 1122 was not detected. The fact that 1122 was not detected is noteworthy, as this contaminant is of greater importance and it is often found at the site groundwater concentrations greater than that of TCE. 1122 also has a greater vapor pressure than TCE. OP-FTIR analysis has never resulted in concentrations of VOCs above the minimum detection limit for all target compounds. Although some TCE and possibly other compounds may be off-gassing from the soil under natural conditions, the amounts are minimal at best and of little concern.

3.3 Sap Flow Rates

The continual monitoring of the tree transpiration at J-Field is necessary for long-term hydrologic modeling. Tree sizes (diameter at breast height) have been recorded annually. Meteorological data were also recorded by a portable MET station to estimate the overall evapotranspiration potential (ETP). The ETP in the plot is compared to the sap flow to generate a tree specific/site specific “crop index” and to support the long-term prediction model. Appendix A is the report generated by Dynamax, Inc., and gives detailed information on all sap flow calculations through the 1999 growing season with modeled predictions of future rates.

The diameter of each tree was measured with a digital tree caliper at breast height (4.5 feet above ground level). The number of the tree and its diameter in inches and centimeters were recorded (Figure 4). For the purpose of modeling water use of the phytoremediation plot, only the 156 original surviving trees are used. These are the oldest trees of the plot representing the first 200 trees planted, and therefore those most likely to have an effect on groundwater. As of this July 2000 sampling event, these trees averaged 11.14 centimeters in diameter. Stem diameter initially increased by 2.5 centimeters per year but declined to a 1.9 centimeter increase/year between July 1998 and July 1999. LAI was calculated to be an average of 2.59 and a maximum or 3.16 as of the 1999 growing season. In July 2000, LAI was calculated to be approximately 3.80, which corresponds to the Dynamax model predictions (Appendix A). A canopy closure is predicted to occur at a LAI of 4 and may occur during the 2000 growing season. Sap flow estimates for 1999 indicate that the poplar plantation is removing more than 4000 liters of water per day (based on a 200 day growing season) with individual trees removing more than 26 liters per day on average. It is predicted that the amount of water use will increase to 7500 liters per day for the entire poplar plantation (48 liters/tree/day). Note that these values are averages and that transpiration rates vary by individual tree, season, and weather patterns.

3.4 Tree Tissue Sampling

VOCs have been routinely found in some tissue samples. It is not possible to quantify these values but the presence of VOCs indicates that these compounds are being transported in the tree and may be found in tree tissues. Leaf bud data from March 1999 indicated TCE at levels of 0.14 to 0.17 milligrams per kilogram (mg/kg) wet weight and 1122 at 0.95 and 1.18 mg/kg wet weight. Leaf tissue analysis has also reproduced VOCs. See the J-Field 1997 Phytoremediation Study

Final Report, Roy F. Weston, Inc., for more detailed information.

3.5 Transpiration Gas Sampling

VOCs have been consistently detected in transpiration samples. TCE and 1122 have been found at concentrations ranging from 14 to 840 ppbv. Seasonal trends have been observed with levels increasing during the warmer months and then decreasing again in the fall, probably corresponding to higher midsummer transpiration rates. Although several different methods were utilized in an attempt to optimize the capture of VOCs from transpiration gas, no conclusions may be made as to which method is most optimal. This is because of the lack of replicates in methodology during the experiments and the extreme variability which is inherent to this type of data. Nearly all methods produced VOCs in the transpiration gas using a Tedlar bag, although VOCs have not been found in every tree tested within the phytoremediation plot. Unfortunately, it is not feasible to measure a great number of trees at one time so it is not possible to continuously determine which trees are demonstrating VOCs in their transpiration gas at any given time. Initial sampling efforts only found VOCs in a percentage of the trees sampled and later sampling efforts generally focus on these specific trees. Tree No. 174 is included in most transpiration gas sampling events because VOCs have been consistently found in the transpiration gas of this particular tree. VOC data will also vary from different branches on the same tree, time of collection, and weather conditions. The addition of various cold traps to theoretically maintain transpiration rate does not seem to have a great effect on improving VOC collection, but natural variability and lack of sample replicates prevent a thorough comparison. The flow through system needs to be further evaluated in the future to better compare it with the static systems. During analysis after the July 2000 sampling event, high levels of compounds collected in the Tenax tube during the flow test caused the analytical equipment to fail.

3.6 Condensate Sampling

Contaminants of concern are regularly found in condensate in conjunction with transpiration gas sampling. TCE has been found at levels of 2.5 ug/L and 1122 up to 156 ug/L in condensate. It is difficult to directly correlate levels of VOCs in condensate and transpiration gas, but elevated levels of VOCs in each indicate the presence of these VOCs transported to the upper parts of the trees and released into the ambient air.

3.7 Meteorological Monitoring

Meteorological data has been used in conjunction with sap flow rates. Where collected data were not available, weather data was obtained from the United States Department of Agriculture (USDA) Beltsville, Maryland weather stations. Additional weather reports from Beltsville, Maryland were analyzed to model the overall ETP demand of the phytoremediation trees. Dynamax, Inc., has indicated a correlation between weather patterns and sap flow rates in their report. For example, it is apparent that the trees transpire less water during an overcast day than on a sunny day.

3.8 Tree Growth and Health Evaluation

Overall, the trees at the phytoremediation plot have thrived and grown as predicted. The trees have grown rapidly and will most likely reach canopy closure in 2000 or 2001. Stem area steadily increased from approximately 3000 square centimeters (cm^2) total in 1997 to 130,000 cm^2 in 1999. Tree mortality has declined with time after planting. The exception is the northern most section of the phytoremediation trees, designated as the"lead area." Trees in the lead area have done poorly. Levels of copper and zinc are high in the lead area (54 parts per million [ppm] and 156 ppm respectively). In addition, this area appears to be of lower elevation than the rest of the plantation and it maintains standing water for longer periods of time after storm events. Soil fertility samples taken in April 2000 (Appendix B) indicate that the trees would benefit from the addition of 2 pounds/1000 square feet of nitrogen, 2 pounds/1000 square feet of phosphorus pentoxide, and 2 pounds/1000 square feet of potash. The original poplar trees averaged 11.14 centimeters in diameter at breast height as of July 2000.

3.9 Nematode Sampling

The nematode population was found to increase in total abundance and specifically the fungivore community the first year after the trees were planted. It was believed that the presence of the trees may have enhanced the habitat for the nematode population. However, 1998 and 1999 showed a decrease in nematode population. It is speculated that this decrease may correspond to unusually hot and dry summers which occurred during these two years. Rainfall was more frequent and more evenly distributed during the summer of 2000. It will be critical to see if this difference in weather will cause a change in nematode population or population distribution.

3.10 Tree Root Development Evaluation

The roots of those poplar trees examined remained predominately within the narrow planting hole. The major roots spiraled within the planting hole and showed very little lateral root development into the surrounding native soil. This is probably due to the plastic barrier used in the planting hole to promote deep-rooting, the use of amended soil within the planting hole, or a combination of the two factors. The problem with this rooting regime was particularly evident when severe storms in 1999 caused several trees to lean or topple completely. Many trees now show evidence of thick, horizontal, extended roots at the soil surface but this does not occur from all of the trees. An effort needs to be made to perforate the plastic around the upper portion of the root zone to promote lateral root development. Any future planting probably should not be contained within an inorganic barrier to allow for a more natural rooting pattern.

3.11 Additional Plantings

After a high initial loss, the native trees planted appear to be doing relatively well, but are still considerably smaller in size than the hybrid poplars. These trees were subjected to two unusually hot and dry growing seasons after planting. The tulip poplars appear to have had a much harder time adapting than the other species. A future effort will be needed to compare the efficiency of these natives with the hybrid poplars for water uptake, transpiration, and removal of VOCs. Additional planting will probably occur in the future, particularly south of the existing plot. Additional species may also be evaluated in the future. In particular, native tree species may be selected based on availability, rooting habits, growth rates, and potential transpiration rates.

3.12 Modeling

The performance of the phytoremediation technology was simulated using both analytical and numerical models. Currently, four years of data exist to develop the models. These models were used to estimate the amount of contaminant mass that the poplar trees may remove from the surficial aquifer over the lifespan of the plantation and to predict the time required to restore its water quality. Although such models have their limitations, they do provide some guidance to the feasibility of cleaning up a particular site.

A method of estimating contaminant uptake rate has been popularized by Schnoor (Shnoor,1997). A 90% removal rate of the total VOC concentrations was arbitrarily chosen for calculating removal time below. Obviously a lot of parameters have to be taken for granted when using this equation (e.g. that all of the VOC of interest will become soluble) but the model still provides a rough means of estimating time frames. The use of this equation as applied to this particular site can be summarized below.

The uptake rate is given by the equation:

$$U = (TSCF)\,(T)\,(F)$$

where	U=	Uptake rate of the contaminant, milligrams per day
	TSCF=	Transpiration Stream Concentration Factor, dimensionless
	T=	Transpiration rate of the vegetation, liters/day
	C=	Aqueous phase concentration in soil or groundwater, milligrams per liter

After solving for "U", contaminant uptake and clean-up time are given by:

$$k = U/Mo$$

where	k=	First order rate constant for uptake, yr^{-1}
	U=	Contaminant uptake rate, kilograms per year (calculated from above)
	Mo=	Mass of contaminant initially, kilograms

An estimate for the mass of contaminant remaining at any time is $M = Mo\, e^{-kt}$
Solving for the time required to achieve clean-up of a known action level:

$$t = -(\ln M/Mo)/k$$

where	t=	Time required for clean-up to action level, year
	M=	Mass allowed at action level, kilograms
	Mo=	Initial mass of contaminant, kilograms

TCE: The total TCE at J-Field has been estimated at 215.86 kilograms (kg) in solution and an additional 593 kg associated with the soil. Concentration of TCE has been measured as 61mg/L. The J-Field hybrid poplar trees are estimated to be transpiring/removing 7500 liters of water/tree/year (at maximum).

There are approximately 200 trees on the site, which covers an area of about one acre. TSCF for TCE is 0.74.

Calculating for 90 percent removal of the soluble TCE: t= **7.3 years**. If it is assumed that all of the TCE (809.48 kg) on site will become soluble, then 90 percent removal is calculated: t= **27.52 years**.

1122: The total 1122 at J-field has been estimated at 589.54 kg soluble and 1978.11 kg total. Concentrations have been measured at 170mg/L. TSCF is 0.79.

For 90% reduction of the soluble 1122: t= **6.73 years**
If it is assumed that all of the 1122 (1978.11 kg total) on the site will become soluble in the aquifer, then 90 percent removal is calculated: t= **23.02 years.**

A more comprehensive numerical model was constructed to evaluate the performance of an integrated remedial system. The system is designed to hydraulically contain and ultimately reduce the VOC plume and consists of groundwater circulating wells or extraction wells located in the core of the plume to provide active source control. The source control is combined with monitored natural attenuation and phytoremediation instituted to further reduce dissolved-phase contaminants. The more detailed modeling effort was conducted to examine the effectiveness and optimal configuration of the integrated remedial technologies. The additional level of modeling was warranted based on field evidence that indicates the hybrid poplars are withdrawing VOCs from the shallow aquifer. Furthermore, field data indicates that natural attenuation and groundwater extaction/treatment are capable of reducing the VOC mass. Monitoring of natural attenuation parameters indicates that abiotic and biotic degradation is actively occurring and a 90-day pilot test of a circulating well provided 21 pounds of VOC removal (Weston, 2000).

A three-dimensional groundwater flow (MODFLOW) and contaminant transport (RT3D) model was constructed to estimate the capacity of the remedial system to satisfy the remedial objective. Model results indicate that the integrated remedial system is capable of removing up to 85 percent of the total 1122 mass after 30 years. Natural attenuation was determined to be the predominant mass removal mechanism unless four or more wells were employed. Sensitivity analyses indicate that variations in the rate constants impact these estimates and additional natural attenuation monitoring is needed to verify the results. Phytoremediation emerged as a favorable contributor to the remedial program by providing 7.5 percent of the total mass removal. Model results support field evidence that show the poplar trees generating partial hydraulic containment of the 1122 plume during the peak growing season (Schneider *et al.*, 2000)

4.0 Result Discussion

The poplar trees are growing very well at this site (Figures 5 and 6). The results obtained over several years thus far indicate that the project objectives are being met and that phytoremediation is a feasible remediation method for this particular site. The detection of VOCs and their degradation products in transpiration gas, condensate, and leaf tissue indicates that the trees are removing and degrading or releasing these contaminants of concern. Although the mechanism and rate of VOC removal are not known, the detection of these compounds offer strong evidence that the trees are actively withdrawing VOCs from the aquifer. Sap flow rates and shallow ground water levels provide evidence that containment and interception of groundwater flow is also occurring. In addition, it is possible that the trees may also be enhancing the soil community although further investigation is needed. Finally, models can be used to estimate contaminant removal at this site. Based on the two models presented, the site contaminants may be reduced by up to 85 percent in 30 years. This study provides evidence that phytoremediation can be successfully applied to sites that satisfy the application criteria and comprise similar hydrogeologic settings.

5.0 REFERENCES

Clement, T.P. *RT3D- A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers,* Version 1.0. 1998.

Chappell, J. *Phytoremediation of TCE in Groundwater Using Populus*. U.S. EPA Technology Innovation Office. 1998.

Dynamax. *EPA Phytoremediation Study-Aberdeen Proving Grounds J-Field.* Version 3.0, 2000

Finley, Mark. *J-Field Phytoremediation 1997 Phytoremediation Study Final Report. Aberdeen Proving Ground, Edgewood, Maryland.* Roy F. Weston, Inc. 1999.

McDonald, M.G. and A.W. Harbaugh. *A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model, Techniques of Water Resources Investigations, Book 6, Chapter A1*, U.S. Geological Survey, Reton, Va. 1998.

Quinn, R. L., Johnson, T.L., and L.E. Martino. *An Optimized Groundwater Extraction System for the Toxic burning Pits Area of J-Field, Aberdeen Proving Ground, Maryland.* Environmental Assessment Division, Argonne National Laboratory. Argonne, Il. 1996.

Schneider, W.H., Wrobel, J.G., Hirsh, S.R., Compton, H.R., and D. Haroski. *The Influence of an Integrated Remedial System on Groundwater Hydrology.* 2000

Schnoor, J.L. *Environmental Modeling Fate and Transport of Pollutants in Water, Air, and Soil.* John Wiley & Sons, Inc., Wiley-Interscience Publication,. 1996.

Schnoor, J.L. *Phytoremediation.* Ground-Water Remediation Analysis Center, Pittsburgh, Pa. 1997.

Weston, Roy F. *A Three-Dimensional Groundwater Flow and Contaminant Transport Model to Evaluate Remedial Alternatives at J-Field. Aberdeen Proving Ground, Maryland.* West Chester, Pa. 2000.

Appendix A
Dynamax, Inc.
January 2000 Management Report for Lockheed Martin EPA Phytoremediation Study-
Aberden Proving Ground, J-Field
Edgewood, Maryland
August 2000

Available on request

Appendix B
Rutgers Cooperative Extension Resource Center
Soil Testing Laboratory. Rutgers, The State University of New Jersey
May 2000 Soil Test Report for the J-Field Phytoremediation Study Area
Aberdeen Proving Ground- J-Field
Edgewood, Maryland
August 2000

Available on request

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Figures

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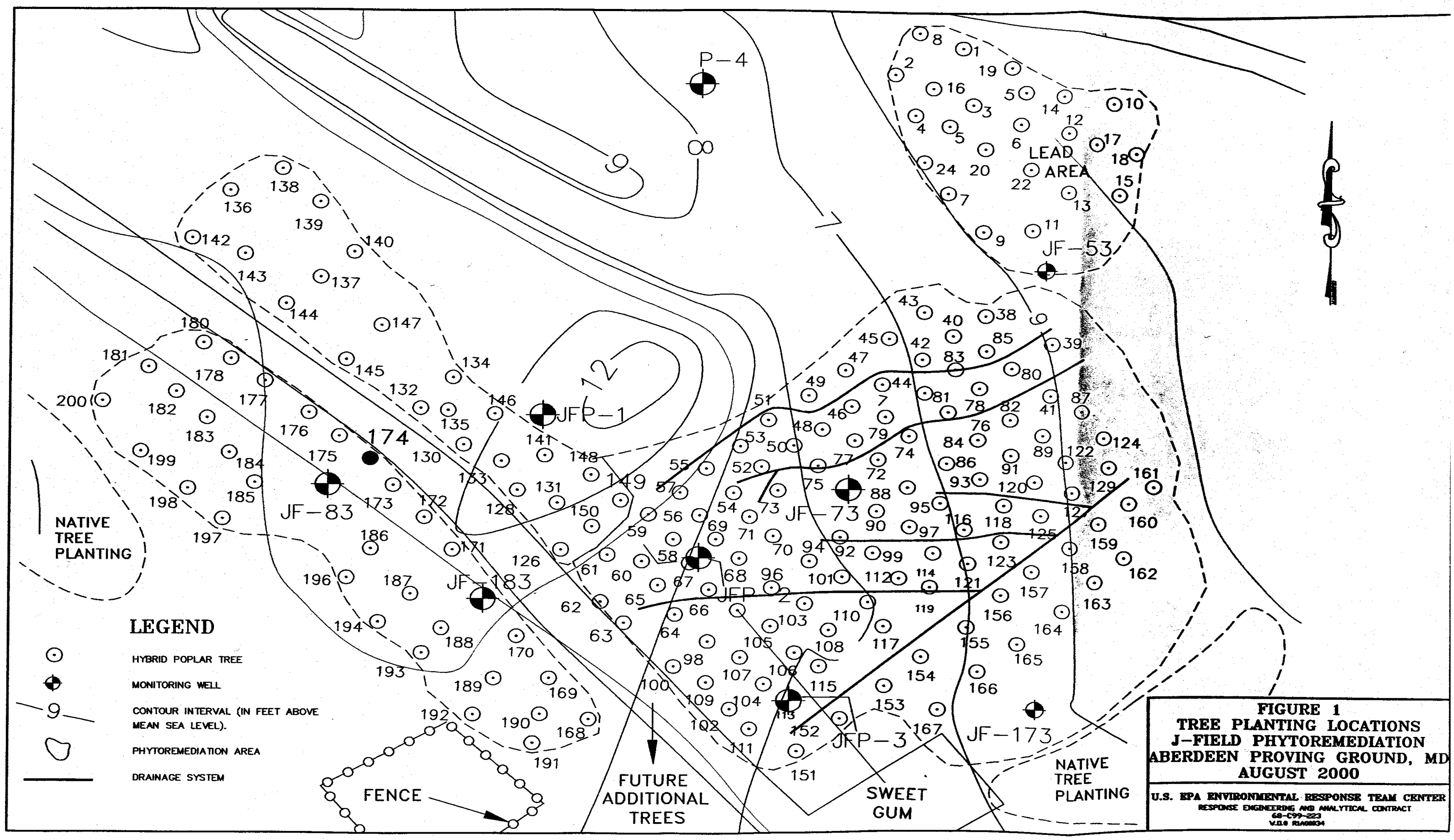
FIGURE 1
TREE PLANTING LOCATIONS
J-FIELD PHYTOREMEDIATION
ABERDEEN PROVING GROUND, MD
AUGUST 2000
U.S. EPA ENVIRONMENTAL RESPONSE TEAM CENTER
RESPONSE ENGINEERING AND ANALYTICAL CONTRACT
LEGEND
HYBRID POPLAR TREE
MONITORING WELL
CONTOUR INTERVAL (IN FEET ABOVE MEAN SEA LEVEL).
PHYTOREMEDIATION AREA
DRAINAGE SYSTEM
P-4
JFP-1
JFP-2
JFP-3
JF-53
JF-73
JF-83
JF-173
JF-183
LEAD AREA
NATIVE TREE PLANTING
NATIVE TREE PLANTING
FUTURE ADDITIONAL TREES
SWEET GUM
FENCE

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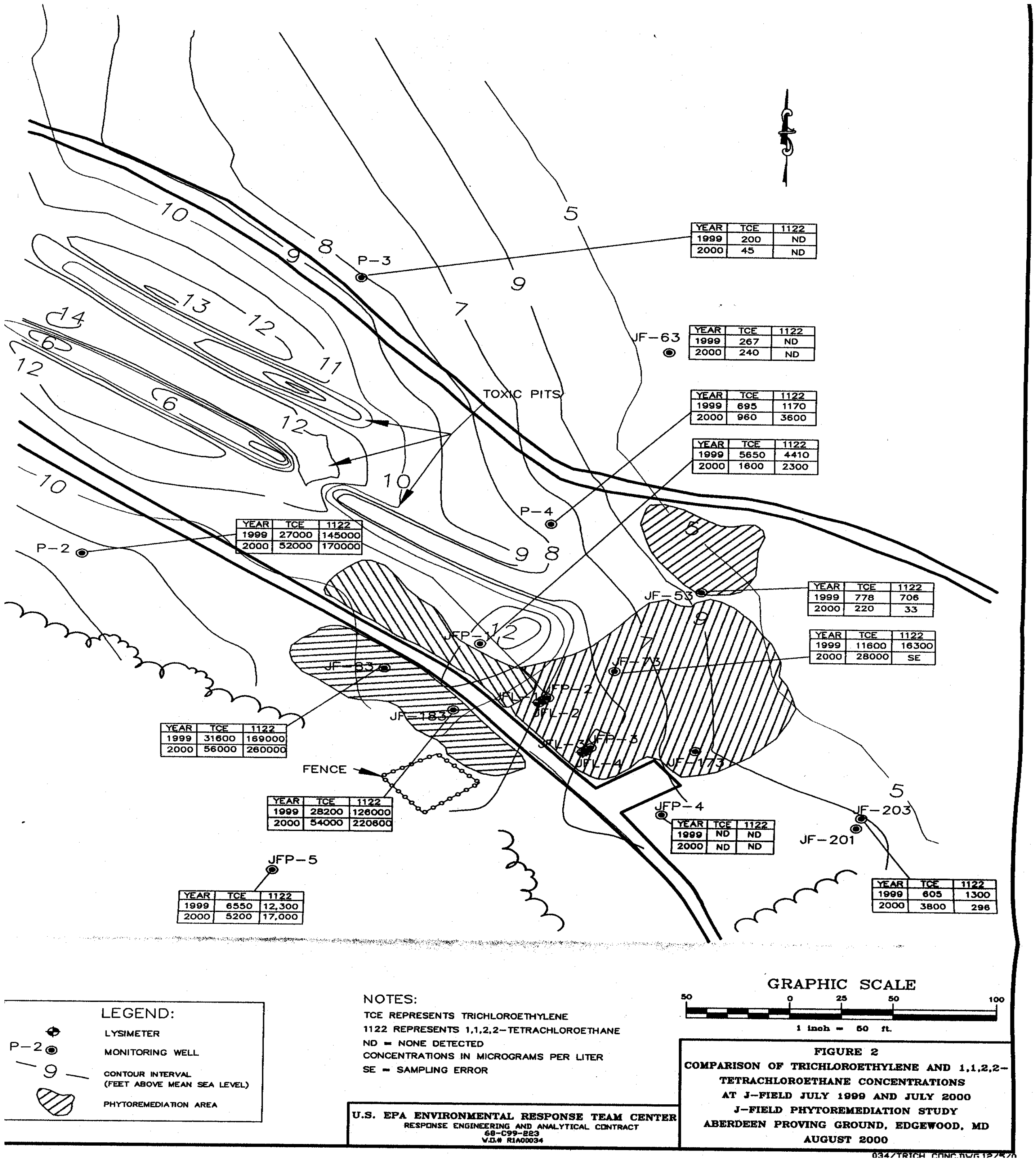

FIGURE 2
COMPARISON OF TRICHLOROETHYLENE AND 1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS AT J-FIELD JULY 1999 AND JULY 2000
J-FIELD PHYTOREMEDIATION STUDY
ABERDEEN PROVING GROUND, EDGEWOOD, MD
AUGUST 2000

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Figure 3
Groundwater Data at the J-Field Phytoremediation Plot
J-Field Phytoremediation Site
Aberdeen Proving Ground
Edgewood, Maryland
August 2000

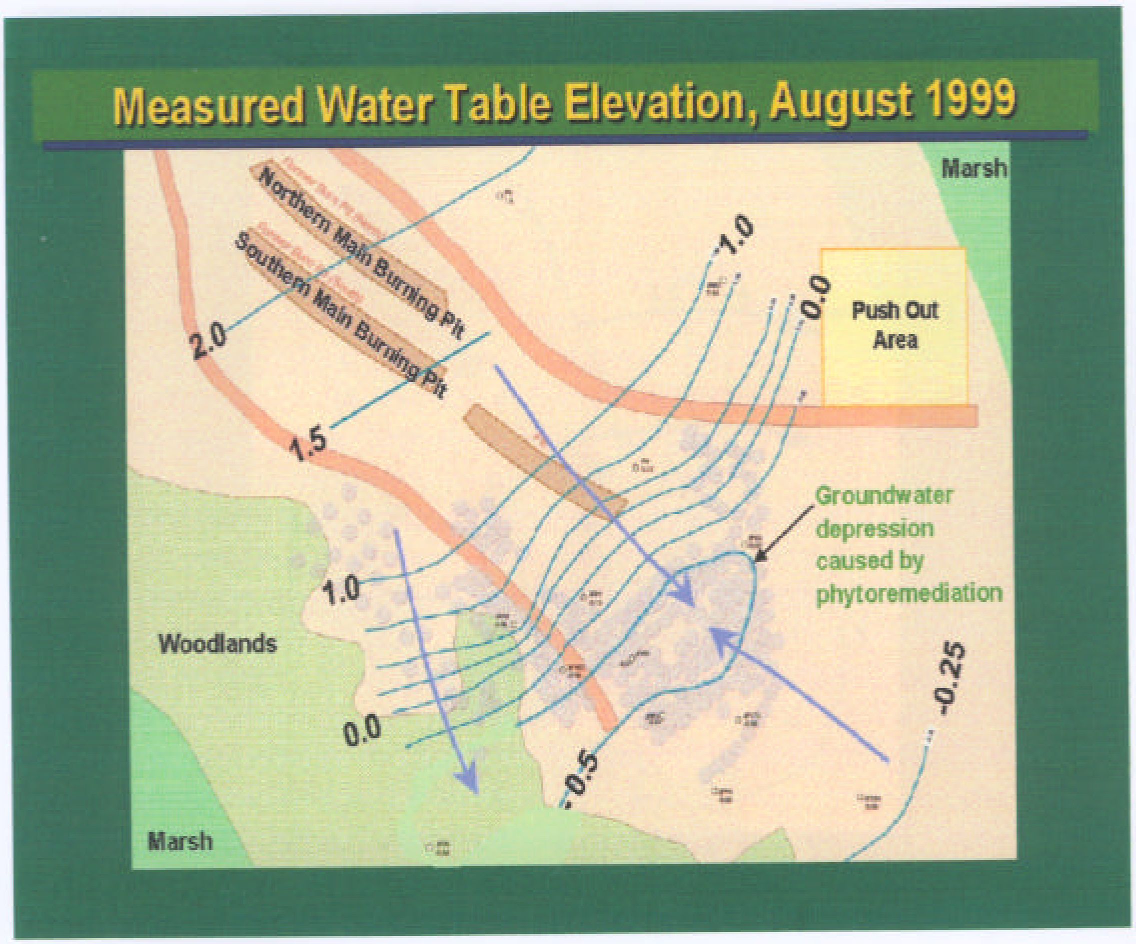

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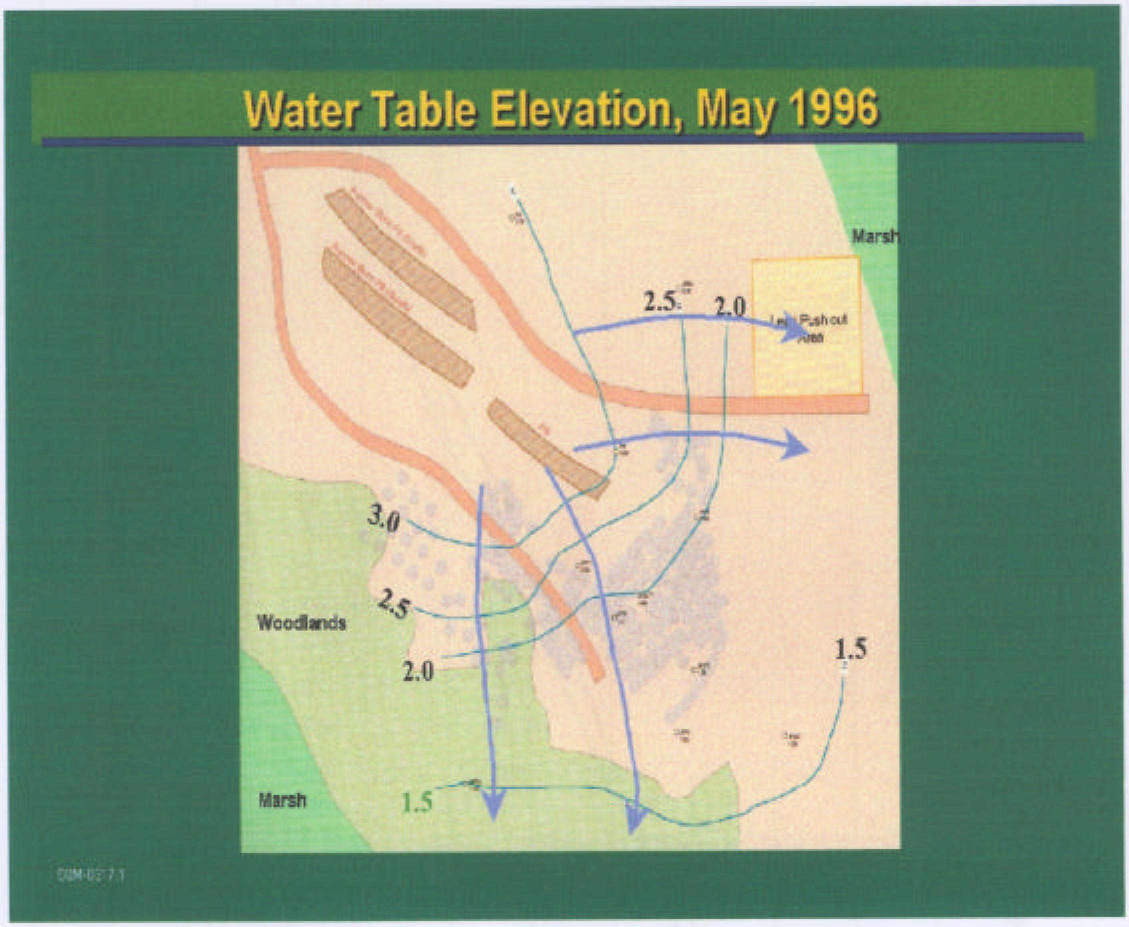
Figure 3 (Continued)
Groundwater Data at the J-Field Phytoremediation Plot
Water Table Elevation, May 1996, Before Tree Maturation
Aberdeen Proving Ground
Edgewood, Maryland
August 2000



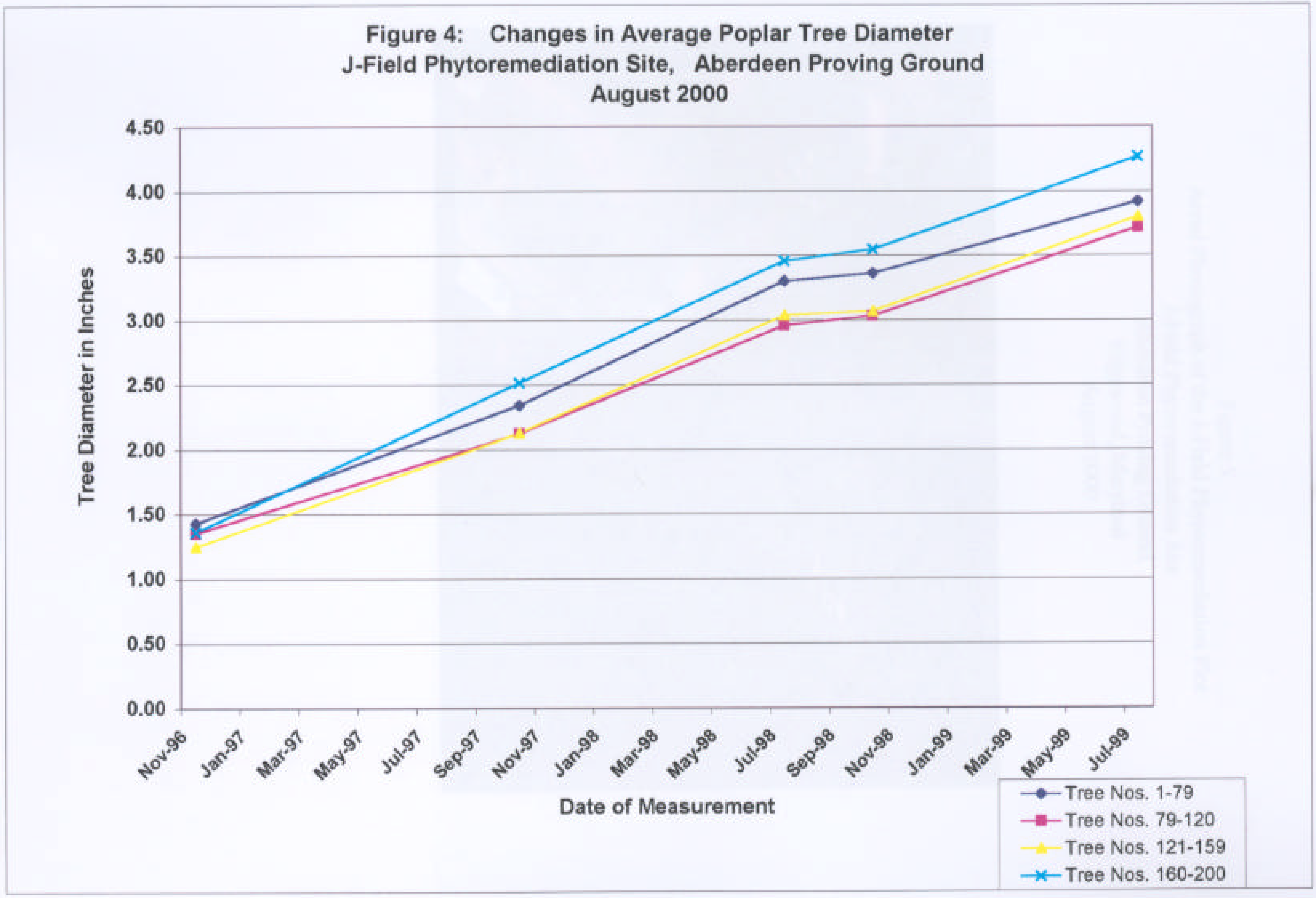


Figure 4: Changes in Average Poplar Tree Diameter
J-Field Phytoremediation Site, Aberdeen Proving Ground
August 2000
Tree Diameter in Inches
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
Nov-96
Jan-97
Mar-97
May-97
Jul-97
Sep-97
Nov-97
Jan-98
Mar-98
May-98
Jul-98
Sep-98
Nov-98
Jan-99
Mar-99
May-99
Jul-99
Date of Measurement
Tree Nos. 1-79
Tree Nos. 79-120
Tree Nos. 121-159
Tree Nos. 160-200

Figure 5
Aerial Photograph of the J-Field Phytoremediation Plot
J-Field Phytoremediation Site
Aberdeen Proving Ground
Edgewood, Maryland
August 2000

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Figure 6
J-Field Phytoremediation Plot During a Monitoring Event
J-Field Phytoremediation Site
Aberdeen Proving Ground
Edgewood, Maryland
August 2000