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Deployment of Phytotechnology in the 317/319 Area at Argonne National Laboratory-East

Innovative Technology Evaluation Report

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Notice

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Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This publication had been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Director
National Risk Management Research Laboratory

Abstract

In 1999, Argonne National Laboratory-East (ANL-E) designed and installed a series of engineered plantings consisting of a vegetative cover system and approximately 800 hybrid poplars and willows rooted at various predetermined depths. The plants were installed using various methods including the TreeMediation® TreeWell® Treatment System developed by Applied Natural Sciences. The goal of the installation was to protect downgradient surface and groundwater by hydraulic control of the contaminated plume. This goal was to be accomplished by intercepting the plume with the tree roots, removing moisture from the upgradient soil area, reducing water infiltration, preventing soil erosion, degrading and/or removing pollutants from the subsoil and groundwater.

The EPA Superfund Innovative Technology Evaluation Program (SITE) and ANL-E evaluated the demonstration for a three-year period (1999-2002). The effectiveness of the various plantings was monitored directly through groundwater and soil measurements and samples, and indirectly via plant tissue analysis, microbial surveys, geochemical analysis, soil moisture probes and sap flow monitoring. A weather station with data logging equipment was installed. ANL-E predicted physical effects of the plants on groundwater using a standard hydrological model. The treatment period will continue for up to 20 years.

This Innovative Technology Evaluation Report presents the results from sampling, monitoring, and modeling efforts to date. The project has demonstrated success in reducing contaminated groundwater flow and taking up contaminants at the source; it also provides insight into the techniques that are useful for measuring and predicting the effectiveness of future similar projects.

Contents

Contents (Con't)

Contents (Con't)

Tables

Figures

Acronyms, Abbreviations and Symbols

ac	acre
ANL-E	Argonne National Laboratory-East
ANS	Applied Natural Sciences
ARARs	Applicable or Relevant and Appropriate Regulations
ASTD	Accelerated Site Technology Deployment
bgs	below ground surface
BSE	Baseline Sampling Event
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
^{o}C	Degree Centigrade
CAA	Clean Air Act
CAHs	Chlorinated Aliphatic Hydrocarbons
CAP-88	Clean Air Act Assessment Package-1988
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CDD	Cooling Degree Days
CFR	Code of Federal Regulations
CLF	Chloroform
cm	centimeter
COE	Corps of Engineers
CSO	ANL-E Construction Safety Officer
CV	Coefficient of Variation
CWA	Clean Water Act
db	decibel
DCA	1,1-Dichloroethane
DCE	cis-1,2-Dichloroethene
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
^{o}F	Degree Fahrenheit
FD	French Drain or French Drain Plantation
FDCP	French Drain Control Plot
Fe	Iron
FID/ECD	Flame Ionization and Election Capture Detection
FSE	Final Sampling Event
ft	foot
FY	Fiscal Year
g	gram
gal	gallon (US)
GC/CD	Gas Chromatography/Conventional Detector
GDD	Growing Degree Day

Acronyms, Abbreviations and Symbols (cont'd)

ha	hectare
HASP	Health and Safety Plan
HAP	Hazardous Air Pollutant
HAZWOPER	Hazardous Waste Operations and Emergency Response
HC	Hydraulic Control Area
IEPA	Illinois Environmental Protection Agency (IEPA)
in	inch
ITER	Innovative Technology Evaluation Report
JSA	Job Safety Analysis
kg	kilogram
km	kilometer
L or l	liter
LCS/LCSD	Laboratory Control Sample/Laboratory Control Sample Duplicate
m	meter
mg	milligram
mi	standard mile
mm	millimeter
Mn	Manganese
MS/MSD	Matrix Spike/Matrix Spike Duplicates
MSE	Mid-term Sampling Event
NESHAP	National Emission Standards for Hazardous Air Pollutants
ng	nanogram
NPDES	National Pollution Discharge Elimination System
NPL	National Priority List
NPK	Nitrogen, Phosphorous, and Potassium
NRMRL	National Risk Management Research Laboratory
O&M	Operations & Maintenance
ORP	Oxidation Reduction Potential
OSHA	Occupational Safety and Health Administration
PCBs	Polychlorinated Biphenyls
PCE	Tetrachloroethene or Perchloroethene
pCi	picoCurie
PET	Potential Evapotranspiration
PLFA	Phospholipid Fatty Acids
pmol	picomole
PPE	Personal Protective Equipment
QA/QC	Quality Assurance/Quality Control
r^2	coefficient of determination
RCRA	Resource Conservation and Recovery Act
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
s	second
SAIC	Science Applications International Corporation
SB	Soil Bore
SITE	Superfund Innovative Technology Evaluation Program
SSI	Site Screening Inspection
SWMU	Solid Waste Management Unit
TCA	1,1,1-Trichloroethane
TCAA	Trichloroacetic Acid
TCE	Trichloroethene

Acronyms, Abbreviations and Symbols (cont'd)

TDP	Thermal Dissipation Probe
TOC	Total Organic Carbon
TSA	Technical Systems Audit
TSCA	Toxic Substance Control Act
USDA	United States Department of Agriculture
ug	microgram
VC	Vinyl Chloride
VOCs	Volatile Organic Compounds

Acknowledgments

This report was developed under the direction of Steven Rock, the EPA Technical Project Manager for this demonstration. Gratefully acknowledged are the participation and contributions by the ANL-E technical and management team, including Cristina Negri, John Quinn, Jim Wozniak, and Ray Hinchman (retired). Their tireless efforts were instrumental in making this project a success.

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Disclaimer

Project objectives evaluated in section 4, Treatment Effectiveness, were done so with data generated in accordance with the project-specific quality assurance project plan (QAPP), as is customary. However, data and information describing other (non-QAPP) technology performance indicators in section 4 were produced by ANL-E. Including their measurements and scientific analyses in this report helps significantly in forming a more complete picture of the behavior of this technology to date and identifying important operating trends that may manifest more fully in future years.

The methods and materials used by ANL-E are summarized in section 4 so that the validity of the measurements and scientific conclusions drawn therefrom may be assessed by the reader.

EXECUTIVE SUMMARY

Introduction

The Argonne National Laboratory-East (ANL-E) is a Department of Energy (DOE) research and development laboratory that performs a variety of research in the basic energy and related sciences (i.e., physical, chemical, material, computer, nuclear, biomedical, and environmental) and serves as an important engineering center for the study of nuclear and non-nuclear energy sources. ANL-E maintains an active and robust environmental protection program that supports its policy of protecting the public, employees, and the environment from harm that could be caused by ANL-E activities, and of reducing environmental impacts to the greatest degree practicable.

Among its environmental restoration duties, ANL-E is managing some 50 cleanup projects. Seven of the projects are located in what is referred to in this document as the 317/319 Area at ANL-E. It is located on the extreme southern end of the ANL-E site, immediately adjacent to the DuPage County Waterfall Glen Forest Preserve, an area used for public recreation and as a nature preserve. The principal environmental concern in the 317/319 Area is related to the presence of several volatile organic compounds (VOCs) in the soil and groundwater and low levels of tritium in the groundwater beneath and downgradient of the site. Several interim actions have already been implemented to reduce the VOC and tritium releases from this area; however, additional remedial actions are ongoing which should further restore the site.

This report discusses the accomplishments of a phytotechnology system deployed by ANL-E in the 317/319 Area to reduce the risks from the VOCs and tritium. Phytotechnology is a proven yet innovative remediation technology, which in this case is intended to improve the rate and effectiveness, while decreasing the overall cost, of the planned cleanup of the site. Phytotechnology relies on the natural process by which woody and herbaceous plants extract pore water and entrained chemical substances from subsurface soils and transpire them into the atmosphere. Degradation of VOCs also takes place in the zone of chemical and biological activity immediately surrounding the plant root system. Because of its lower deployment costs, phytotechnology is being applied in a more extensive and integrated fashion across the entire 317/319 Area than would be possible if the baseline approach (capping/extraction wells) were used.

Activities

During June and July 1999, ANL-E installed stands of hybrid poplars and hybrid willows and a supplemental ground cover of herbaceous plants with the following objectives:

- Hydraulically contain the VOC and tritium plumes south of the 317 Area French Drain and 319 Area Landfill
- Continue the remediation of residual VOCs within the 317 Area French Drain
- Minimize water infiltration into the 317 Area French Drain soils and stabilize the surface to prevent erosion, runoff, and downstream sedimentation.

Earlier in 1999, the U.S. Environmental Protection Agency (EPA) expressed an interest in participating with DOE in this study and subsequently included it as a demonstration project under the National Risk Management Research Laboratory (NRMRL) Superfund Innovative Technology Evaluation program (SITE). ANL-E anticipates an operating period for the phytotechnology deployment of up to 20 years; SITE's involvement covers the first three years of operations, from July 1999 through September 2001. During the program kick-off meeting held on April 7, 1999, specific scientific and engineering project objectives were discussed, and tasks designed to generate the data required to evaluate those objectives were divided between ANL-E and EPA.

Monitoring activities during the demonstration included the following:

- Groundwater Containment
- Groundwater Contaminant Removal
- Soil Contaminant Removal
- Contaminant Uptake and Degradation in Plant Tissue
- Geochemical and Microbial Indices of Reductive Dechlorination
- Modeling and Confirming Water Use and Hydraulic Control
- Health and Growth of the Planted System

The details on collection methods and evaluation results are presented in section 4.

Discussion

The phytotechnologies deployed at ANL-E are supplementary to and intended to eventually replace an existing pump-and-treat system. As the trees completed their third growing season in the field (2001), a significant amount of information had been collected to assess their performance at achieving the remedial objectives. From this data, the young plantations appear to have begun to influence the cleanup area. The deep-planted trees have tapped into the lower saturated zone and are consuming contaminated water. Degradation of volatile organics from the source area soil is occurring in the plants, and the rhizosphere is moving toward conditions that are capable of supporting reductive dechlorination. In ground water, pollutants are being removed (tritium) or degraded (VOCs) in some areas of the contaminated groundwater plumes. Overall, less contamination is reaching the extraction well system than before the plants were installed.

Probably the key remediation mechanism of this planted system is the interception and removal of water from the impacted aquifer (i.e. phytostabilization). Consequently, the magnitude of transpiration is one of the most important monitoring parameters: transpiration rates for the trees at the site provide information for evaluating current water removal as well as predicting future water usage. Quantified sapflow rates were used to estimate transpiration. Data show that maximum sapflow rates determined during the 2001 growing season are still below the plants' potential as estimated by the hydraulic flux at baseline. However, the year-to-year increase in rates suggests that across the plantation water use is closing the gap. These data complement others derived from the recording of continuous groundwater elevation at the site, which shows diurnal fluctuations of hydraulic heads in correspondence with elevated daily solar radiation (transpiration) during the vegetative season.

Multiple lines of evidence are often needed to demonstrate biodegradation processes at contaminated sites. The lines of evidence used to examine biodegradation for this project include (1) detection of TCE and its degradation products in tree tissue in the 317 FD; (2) groundwater chemical data that indicate decreasing concentrations of target VOCs and increasing concentrations of degradation byproducts (3) geochemical data that indicate depletion of electron donors and acceptors; and (4) laboratory microbiological data that indicate the bacteria present at a site can degrade contaminants.

Tissue analysis of willows growing at the contaminated source area indicate that TCE and PCE are taken up by the trees in measurable amounts, and that at least a portion of the transported contaminants is degraded in the leaf. The intermediate degradation product, TCAA, appears to be subsequently degraded further in the leaf litter to background levels.

TCE and TCA and their degradation byproducts are seen at nearly all groundwater wells throughout the study area, implying that microbial attenuation of some form has occurred. In a number of cases monitoring data are unclear about where or how degradation byproducts were formed, and at other locations VOC, geochemical, and biological indicators suggest that reductive dechlorination is ongoing.

Source area soils, which may have been aerated as a result of plant installation, have lost much of their initial aerobic nature. Obligate-anaerobic, iron and sulfate-reducing bacteria have established colonies across the 317 FD, and there appears to be a particularly strong anaerobic character building in segments of the source area where contaminant levels are greatest.

After enduring a transplant shock and below-optimal growth conditions during the first two years in the field, the trees grew at faster rates in 2001. Their increased size is reflected in increased transpiration rates, and presumably larger/longer root systems and enhanced rhizosphere to better influence contaminant reduction and hydraulic control. Modeling based on data collected during the first three years of the project predicts full containment of the 317 plume, and significant containment of the 319 plume. Figure ES-1 is a time-lapse compilation of a portion of the 317/319 Area collected at discrete periods during the course of the demonstration.

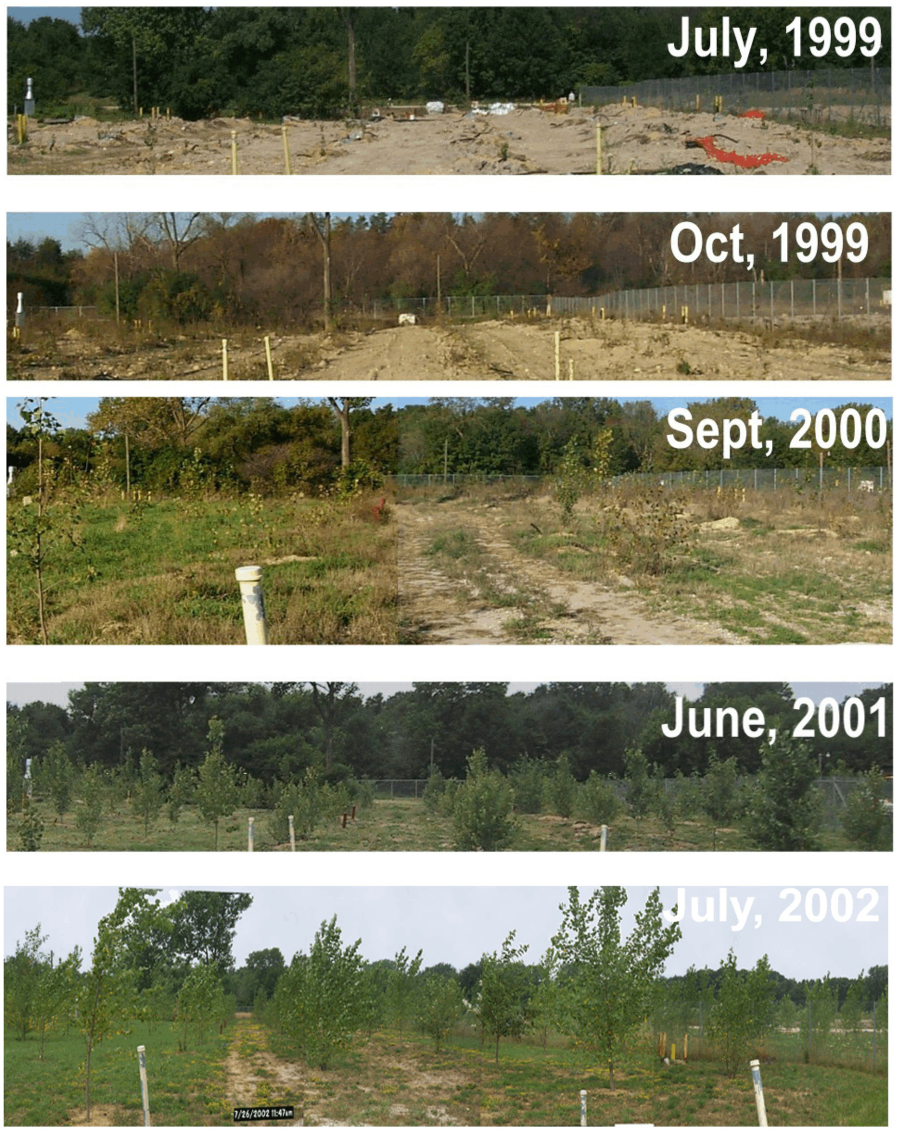

Figure ES-1. Hybrid Poplar Growth in 317/319 Area.

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SECTION 1
INTRODUCTION

This section provides a discussion of the origin and need for remediation of the study site, background on the analytes of concern, a description of phytotechnology, a summary of the Superfund Innovative Technology Evaluation (SITE) Program, and a statement regarding the purpose of this Innovative Technology Evaluation Report (ITER). For additional information about the SITE Program visit the U.S. Environmental Protection Agency (EPA) SITE Program web page at http://www.epa.gov/ORD/SITE/. For information on this SITE project and the technology involved, key contacts are listed at the end of this section.

1.1 The Study Site, Contaminants of Concern, and Potential Remedies

1.1.1 The Study Site

The 317/319 Area at ANL-E covers a surface area of approximately two hectares (five acres) and contains several release sites used in the past to dispose of solid and liquid waste from various laboratory activities. Consequently, solvents such as trichloroethene (TCE), perchloroethene (PCE), and others and tritium have been detected at soil and groundwater monitoring points throughout the 317/319 Area and in adjacent properties. Several interim actions have been completed at the site, and the functional requirements for the final remedial actions in the 317/319 Area are to (1) prevent the release of soil contamination to groundwater, (2) minimize the offsite migration of groundwater containing VOCs and tritium from source areas, and (3) minimize the release of contaminants to storm water runoff.

The DOE funded ANL-E to deploy a phytotechnology-based system across the site instead of a traditional pump-and-treat remedy on the assumption that phytotechnology is more cost effective and better suited to the complex stratigraphy underlying the area than the combination of mechanical extraction wells (currently removing groundwater as an interim measure) and an asphalt cap to achieve long-term objectives.

Turn to section 4.1 for a detailed description of the 317/319 Area and 4.2.4 for information on previous remedial actions taken.

1.1.2 Chlorinated Aliphatic Hydrocarbons

TCE, PCE, and other similar chemicals are from a chemical group known as chlorinated aliphatic hydrocarbons (CAHs). For decades these man-made compounds were used at ANL-E for purposes ranging from equipment degreasing to laboratory extraction solvents. Through intentional and unintentional releases at facilities nationwide, CAHs are now ubiquitous in the environment and include ten of the 25 most common pollutants found in groundwater (NRC, 1994). Because they have high specific gravity and low water solubility, CAHs migrate down through the subsurface soil as dense nonaqueous-phase liquids (DNAPLs) and form pools at the bottom of aquifers. These DNAPL pools act as continual sources of groundwater contamination and are often mobile and difficult to locate or gauge their size. In the vadose zone (soil above the water table), CAHs can commingle with soil pore water and volatilize into the soil gas. It is often the case that CAHs move upward and laterally in the subsurface and increase or re-distribute the area of the original release (Russell et al., 1992). These characteristics have been observed or suspected at the 317/319 Area.

1.1.3 The Fate of CAHs

The fate of CAHs in groundwater has been the subject of considerable investigation. Research has shown that many of these chemicals can naturally attenuate by either non-destructive or destructive means (Chapelle, 2000). Non-destructive mechanisms include dilution through recharge, sorption, and hydrodynamic dispersion (EPA, 1998) as well as diffusion into micropores and entrapment in immobile groundwater zones (NRC, 1997). Among the destructive attenuation mechanisms, biological degradation is the most important (EPA, 1998).

EPA (1998) reports that many laboratory and field studies have demonstrated CAHs are biodegradable naturally under three different processes: (1) CAHs as electron acceptors (reductive dehalogenation); (2) CAHs as electron donors (aerobic respiration); and (3) cometabolism, where degradation of CAHs is fortuitous and of no benefit to the microorganism. One or all of these processes may occur at a given site.

The most significant of these processes for highly chlorinated (i.e. highly oxidized) CAHs is reductive dehalogenation. Reductive dehalogenation is a reduction-oxidation (redox) reaction where a highly chlorinated CAH, e.g. PCE, is reduced by accepting electrons released during the metabolism (oxidation) of organic food sources by methanogenic bacteria. A chlorine atom is replaced on the molecule by electrons coupled to a hydrogen atom, which results in the transformation of PCE to TCE. The process can repeat itself with TCE to produce dichloroethene isomers, of which cis-1,2-dichloroethene (DCE) is the most commonly produced under these conditions (Bouwer, 1994). The rate of reductive dehalogenation decreases as the degree of chlorination decreases, so further degradation of DCE to vinyl chloride, while possible, is usually slow.

To a lesser extent, direct aerobic respiration and cometabolism have been observed as natural attenuation mechanisms. McCarty and Semprini (1994) describe investigations in which vinyl chloride (VC) and 1,2-dichloroethane (DCA) served as primary substrates. In contrast to reductive dehalogenation where the most chlorinated CAHs are preferred, aerobic respiration can utilize only the least chlorinated (i.e. least oxidized) of the CAH compounds. Murray and Richardson (1993) have reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation. During cometabolism, CAH compounds are coincidentally transformed by bacteria as they consume other organic compounds to meet their energy requirements. Vogel (1994) further elaborates that the rate of cometabolism increases as the degree of chlorination decreases.

1.1.4 Tritium

The other contaminant of concern for this project is tritium. Tritium is a radioactive form (radioactive isotope) of hydrogen. The normal hydrogen atom (also called protium) has one proton and one electron and accounts for 99.985% of natural hydrogen. Like hydrogen, tritium also has one proton and one electron, but differs because it also has two neutrons, which give it too much energy to be stable. Each atom of tritium releases its excess energy in the form of a low energy beta particle, whereupon the atom becomes a stable isotope of helium. This release of excess energy is called radioactive decay. Tritium has a radioactive half-life of about 12.3 years, which means that in that time half of the original tritium atoms will have decayed to helium (SRS, 2002).

Tritium is constantly produced both by natural processes (the interaction of cosmic rays with the atmosphere) and by human-made processes. Tritium is used in a wide variety of consumer products such as illuminated watches, thermostat dials, and exit signs. Both the natural and human sources contribute to a worldwide background level of tritium.

Because tritium is simply a hydrogen atom with two neutrons instead of none, its chemical behavior is essentially the same as regular hydrogen. In water, tritium isotopes very easily replace one or both of the normal hydrogen atoms. This behavior presents a unique cleanup challenge because, on a large scale, there is no technology that removes or separates tritium from groundwater (SRS, 2002).

1.1.5 Limitations of Conventional Treatment Technologies

The conventional strategies of excavating soil and pumping and treating contaminated groundwater are generally unsatisfactory at restoring DNAPL-contaminated sites (Pankow and Cherry, 1996). A 1994 National Research Council study of conventional groundwater cleanup systems at 77 contaminated sites determined that cleanup levels had been achieved at only eight of the sites and full realization of cleanup goals was highly unlikely with the in-place technologies at 34 of the 77 sites (NRC, 1997). Tables 1-1 and 1-2 list conventional technologies used to treat source areas and groundwater plumes and summarize their limitations.

Although the weaknesses of these technologies have become increasingly clear, their use is widespread. A U.S. Environmental Protection Agency (EPA) status report observed that as of 1996 conventional methods were in operation at 93% of Superfund sites (EPA, 1996a).

Table 1-1. Conventional Treatment Technologies for DNAPL Source Areas

Technology	Mechanism	Limitations
Steam	Volatilization, mobilization	Must be able to control steam flow and to heat units to appropriate temperature. Heterogeneity may increase treatment times and produce tailing. Must consider implications of DNAPL mobilization.
Surfactants	Dissolution, mobilization	Must be able to establish hydraulic control. Heterogeneity may increase treatment time and produce tailing. Must consider implications of DNAPL mobilization.
Solvents	Dissolution, mobilization	Must be able to establish hydraulic control. Heterogeneity may increase treatment time and produce tailing. Must consider implications of DNAPL mobilization.
Insitu oxidation	Chemical reaction	Must be able to deliver adequate reagent to source zone. Heterogeneity may increase treatment time and produce tailing. Reaction with other compounds may reduce effectiveness
Insitu vitrification	Thermal decomposition	Soil must produce appropriate melt. Vapor emissions must be controlled. Depth limited to 10 m (30 ft).
Soil vapor extraction	Volatilization	Must be able to induce adequate air flow through entire source zone. Heterogeneity and high water content may limit effectiveness.
Air sparging	Volatilization	Must be able to induce adequate air flow through entire source zone. Heterogeneity may limit effectiveness. Contaminants must be volatile at groundwater temperature, generally less than 15^{o} C (59^{o} F).
Electrical heating	Volatilization	Volatilized contaminants must be removed by another technology (typically vapor extraction or steam). Permeability must be sufficient for vapor flow.

Table 1-2. Conventional Treatment Technologies for Dissolved DNAPL Plumes

Technology	Mechanism	Limitations
In-well stripping	Volatilization	Treatment zone depends on groundwater flow pattern established.
Reactive barriers	Dechlorination	Treats only aqueous phase. Wall must intercept entire plume. Specific limitations attached to barrier type.
Electrokinetic systems	Electrically induced mobilization	Applications to DNAPL not well established. Must be coupled with technology for destruction or removal of contamination.
Physical barriers	Containment	Limitations vary with barrier type. If not keyed into impermeable unit at base, system will be open and contamination will not be contained.

Note: Tables 1-1 and 1-2 adapted from NRC, 1999.

1.1.6 The Case for Phytotechnology

1.1.6.1 Technical Characteristics

Phytotechnology can be defined as the purposeful use of green plants to affect pollutants in soil, sediment, surface water, and ground water. Phytotechnologies have been reported successful in laboratory, bench-scale, or full scale projects involving a variety of contaminants (ITRC, 2001):

- Organic contaminants, including petroleum hydrocarbons, gas condensates, crude oil, chlorinated compounds, pesticides, PCBs, and explosive compounds.
- Inorganic contaminants, including salts, heavy metals, metalloids, nutrients, and radioactive materials.

Six different plant-facilitated processes have been recognized as contributing to phytotechnology success. These processes are as follows:

- Phytoaccumulation, referring to a process where plant roots uptake and translocate contaminants (typically metals and radionuclides) from their roots to their above-ground biomass where the contaminants are concentrated and removed by harvesting the plants
- Rhizostabilization, which is a process whereby contaminants (typically metals) are sorbed onto plant roots and therefore not likely to migrate
- Rhizodegradation, which involves the complex interaction of roots, root exudates, and the surrounding soil and microbial community, and how these elements combine to break down contaminants, (typically organics) in situ
- Phytodegradation, which includes processes occurring inside the plant which can degrade contaminants, (usually organics)
- Phytovolatilization, referring to the process whereby contaminants are extracted from soil or ground water and then transpired into the atmosphere (typically organics)
- Phytostabilization, which describes how certain plants with high water demand (woody plants typically) can slow or reverse ground water flow paths thereby containing contaminated groundwater plumes.

Phytotechnology has been suggested as a strategy for treating CAH contamination. In the case of TCE (one of the contaminants of concern at the ANL-E site), hybrid poplars (*Populus* spp.) have been the subject of many lab and field-scale investigations (Chappell, 1997). These investigations propose several of the plant-facilitated processes described above as reasons why poplars are considered useful for treating TCE in soil and groundwater:

- Rhizodegradation (I) - Poplar root systems can break down TCE in soil by exuding certain *ex planta* enzymes (those released by the plant into the root zone). These include dehalogenases and laccases, enzymes which have important natural functions and have been shown to help degrade TCE and other CAHs (Negri et al., 1998).
- Rhizodegradation (II) - TCE degradation has been observed in soil with increased microbial activity. Roots exude complex secretions containing carbohydrates that feed and stimulate the microorganisms and natural chelating agents

that help mobilize both nutrients and contaminants (Negri et al., 1998). Significant mineralization of TCE has been documented in slurries of rhizosphere soil collected from a former solvent disposal site (Walton and Anderson, in Cunningham et al., 1996).

- Phytodegradation - Poplars can take up TCE and metabolize it into benign end products. In one study, xenic (sterile, homogenous) cell cultures were studied to examine the consequences of the metabolic activity of a poplar hybrid (*Populus trichocarpa x deltoides*, H 11-11) in the absence of soil, mycorrhizal flora, or microbial activity. The cells were incubated with TCE and later extracted and analyzed for metabolites. Chloral, trichloroacetate, dichloroacetate, and trichloroethanol were detected in the extracts. These compounds are known physiological oxidative metabolites of TCE; thus, researchers suspect that similar oxygenase activities exist in cells of this and other poplars (Newman et al., 1997).
- Phytostabilization - Poplars can provide hydraulic control of a contaminated plume until plant-stimulated activity, natural attenuation, or other processes degrade contaminants. Poplars and many other members of the willow family (*Salicaceae*) are phreatophytes, meaning their deep roots draw water from or near the water table. These trees are also known as fast growers and must transpire a substantial amount of moisture to meet their metabolic needs. These characteristics make poplars ideally suited to provide hydraulic control of groundwater.

In addition to the plant-facilitated mechanisms described above, it is estimated that a typical poplar plantation can produce as much as 120,000 km (75,000 mi) of fine roots per acre (EPA, 2000). Such a density allows roots more complete coverage of a waste site, particularly in a heterogeneous subsurface that limits the effectiveness of conventional technologies.

1.1.6.2 Other Potential Advantages

Beyond potential technical advantages, phytotechnology is an attractive strategy for several reasons. It is considered less expensive than conventional methods. Estimated costs are as low as 10% to 50% of other methods such as pump and treat (Rock and Sayre, 1998; Chappell, 1997). Phytotechnology is also viewed as an environment-friendly concept. Vegetation is a "natural" part of ecosystems, and tree plantations have a park-like aesthetic and provide shade, habitat, and windbreaks (Lay, 1999). Implementation may be less intrusive than the installation of mechanical equipment and utilities associated with conventional technologies.

1.1.6.3 Potential Regulatory Acceptability

Due to the potential utility of phytotechnology and its lower estimated costs, there is a great deal of interest on the part of site owners, managers, and their consultants and contractors in applying this technology to their sites. Balanced against this prospect are questions regarding the true rate and extent of cleanup using this technology, as well as other associated risk concerns. Specific regulatory standards on the efficacy and potential risks for phytoremediation have not been developed, and installations are currently approved on a site-by-site basis (Rock and Sayre, 1998).

One indication that a technique will be accepted for treatment of a given site is a track record of prior successful applications on similar sites. Because it is relatively new, phytotechnology does not have a long history of completed cleanups or site closures. Past results of studies done in greenhouses and on field test plots in different locales can be used generally to show proof of concept. Similar type studies performed on soil or water from the site can confirm the efficacy of site-specific treatment (Rock and Sayre, 1998).

1.2 Brief Technology Description

The primary technical challenge at the 317/319 Area is reaching polluted soil and groundwater as deep as 30 ft (9 m) below ground surface (bgs). Root-to-contaminant contact is the key to phytotechnology success; therefore, the depth to the affected media has to be shallow enough for the roots reach it. In the case of ground water, roots to must be able to develop to the capillary fringe, the zone above the aquifer where water is drawn upward by the capillary action of soil micropores. Given these limitations, phytosystems (prior to 1999) generally targeted affected media at depths of 20 ft (6 m) or less (EPA, 2001); however, Applied Natural Sciences, Inc (ANS), Hamilton, OH, the contractor hired by ANL-E to plan and install the system in the 317/319 Area, developed planting techniques that purportedly extend the treatment range to over 30 ft (9 m) bgs.

According to ANS, the TreeMediation® TreeWell® Treatment System (TTTS®) creates a permeable zone to promote and direct root growth by developing a column through the vertical extent of the affected media (see Figure 1-1). The existence of the column provides a preferential pathway for roots to develop either (1) throughout the area of contaminated soil, or, if the column is lined to prevent outward root penetration, (2) down into the capillary fringe of the contaminated aquifer.

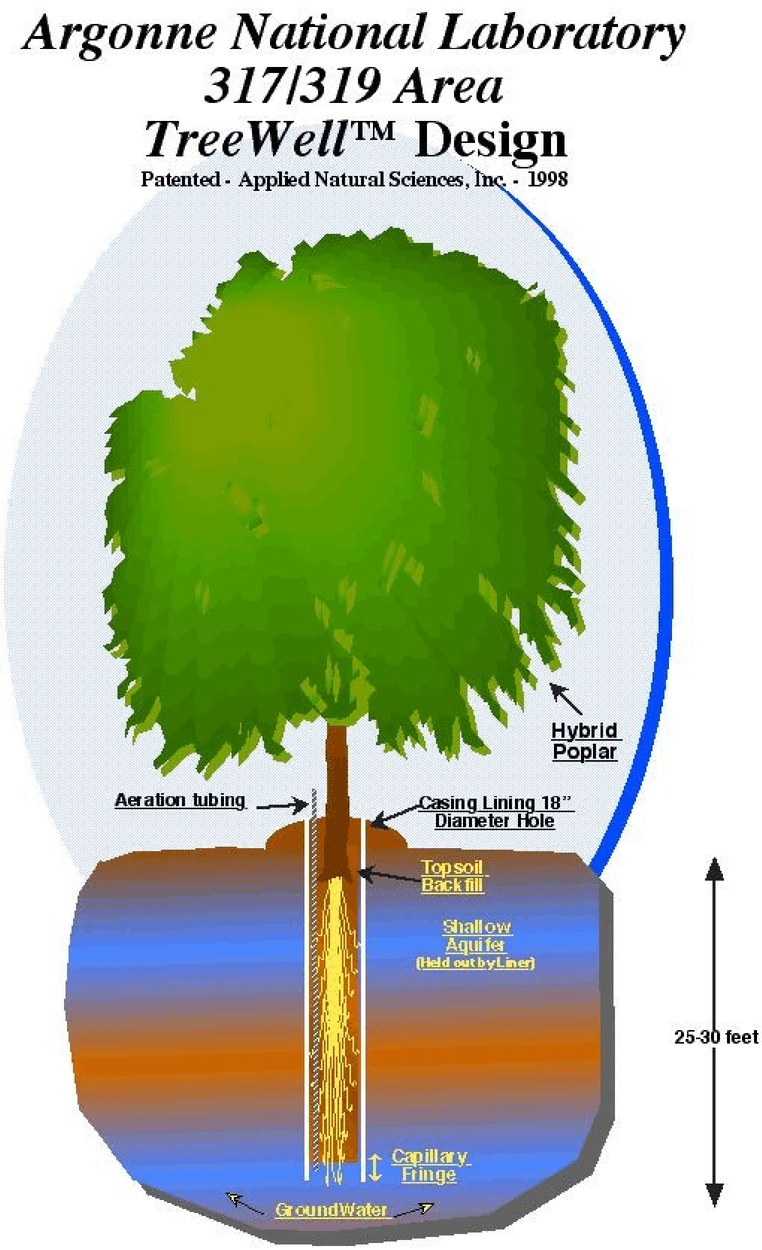

Figure 1-1. Diagram of the ANS TTTS®

The column also allows for ready upflow of the water to the root system. The installation depth of the root ball mass can be varied to better target subsurface soil horizons or decrease the distance and time the roots must travel to reach ground water.

During the summer of 1999, approximately 800 hybrid poplars and hybrid willows were planted using the ANS TTTS® in and downgradient of the 317/319 Area with the goal of intercepting the flow of ground water and preventing the offsite migration of pollutants. In the upgradient source area (i.e., 317 Area French Drain) hybrid willow trees were planted in a manner such that their roots could freely explore the contaminated soil and take up pore water and entrained chemicals. A vegetative cover of herbaceous plants was seeded among the trees to control soil erosion and minimize water infiltration.

Figure 1-2. 317/319 Area Phytosystem

Figure 1-2 is an aerial view of the 317/319 Area shortly after the phytosystem was installed. Turn to section 4.2.5 for a detailed description of the specific planting techniques used at the 317/319 Area.

1.3 Description of the SITE Program and Reports

The SITE Program is a formal program established by EPA's Office of Solid Waste and Emergency Response (OSWER) and Office of Research and Development (ORD) in response to the Superfund Amendments and Reauthorization Act of 1986 (SARA). The SITE Program promotes the development, demonstration, and use of new or innovative tech-nologies to clean up Superfund sites across the country.

The SITE Program's primary purpose is to maximize the use of alternatives in cleaning hazardous waste sites by encouraging the development and demonstration of new, innovative treatment and monitoring technologies. It consists of three major elements discussed below:

- the Demonstration Program,
- the Monitoring and Measuring Technologies Program, and
- the Technology Transfer Program.

The objective of the Demonstration Program is to develop reliable performance and cost data on innovative technologies so that potential users can assess the technology's site-specific applicability. Technologies evaluated are either available commercially or close to being available for full-scale remediation of Superfund sites. SITE demonstrations usually are conducted on hazardous waste sites under conditions that closely simulate full-scale remediation conditions, thus assuring the usefulness and reliability of information collected. Data collected are used to assess: (1) the performance of the technology, (2) the potential need for pre- and post-treatment processing of wastes, (3) potential operating problems, and (4) the approximate costs. The demonstrations also provide opportunities to evaluate the long-term risks, capital and O&M costs associated with full-scale application of the subject technology, and limitations of the technology.

Existing technologies and new technologies and test procedures that improve field monitoring and site characterizations are identified in the Monitoring and Measurement Technologies Program. New technologies that provide faster, more cost-effective contamination and site assessment data are supported by this program. The Monitoring and Measurement Technologies Program also formulates the protocols and standard operating procedures for demonstrating methods and equipment.

The Technology Transfer Program disseminates technical information on innovative technologies in the Demonstration, and the Monitoring and Measurement Technologies Programs through various activities. These activities increase the awareness and promote the use of innovative technologies for assessment and remediation at Superfund sites. The goal of technology transfer activities is to develop interactive communication among individuals requiring up-to-date technical information.

1.4 The SITE Demonstration Program

Technologies are selected for the SITE Demonstration Program through annual requests for proposals. ORD staff review the proposals to determine which technologies show the most promise for use at Superfund sites. Technologies chosen must be at the pilot- or full-scale stage, must be innovative, and must have some advantage over existing technologies. Mobile and in-situ technologies are of particular interest.

Once EPA has accepted a proposal, cooperative agreements between EPA and the developer establish responsibilities for conducting the demonstrations and evaluating the technology. The developer is responsible for demonstrating the technology at the selected site and is expected to pay any costs for transport, operations, and removal of the equipment. EPA is responsible for project planning, sampling and analysis, quality assurance and quality control, preparing reports, disseminating information, and transporting and disposing of treated waste materials.

At the conclusion of a SITE demonstration, EPA prepares an Innovative Technology Evaluation Report (ITER), Technology Capsule, and Demonstration Bulletin. These reports evaluate all available information on the technology and analyze its overall applicability to other site characteristics, waste types, and waste matrices. Testing procedures, performance and cost data, and quality assurance and quality standards are also presented.

1.5 Purpose of the Innovative Technology Evaluation Report

This ITER provides information on the deployment of phytoremediation at the 317/319 Area of ANL-E and includes a comprehensive description of the demonstration and its results. The ITER is intended for use by EPA remedial project managers, EPA on-scene coordinators, contractors, and other decision makers in implementing specific remedial actions. The ITER is designed to aid decision makers in further evaluating specific technologies when considering applicable options for particular cleanup operations. This report represents a critical step in the development and commercialization of a treatment technology.

To encourage the general use of demonstrated technologies, EPA provides information regarding the applicability of each technology to specific sites and wastes. The ITER includes information on cost and performance, particularly as eval-uated during the demonstration. It also discusses advantages, disadvantages, and limitations of the technology.

Each SITE demonstration evaluates the performance of a technology in treating a specific waste or combination of wastes in a specific environmental setting. The characteristics of other sites likely differ from the characteristics of the site tested. Therefore, a successful field demonstration of a technology at one site does not necessarily ensure that it will be applicable at other sites. Data from the field demonstration may require extrapolation for estimating the operating ranges in which the technology will perform satisfactorily. Only limited conclusions can be drawn from a single field demonstration.

1.6 Key Contacts

Additional information on the ANL-E field demonstration and the SITE Program can be obtained from the following sources:

This SITE Demonstration
Steven Rock
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
5995 Center Hill Avenue
Cincinnati, OH 45224
Tel: (513) 569-7149

Fax: (513) 569-7879
Email: rock.steven@epa.gov

ANL-E Phytotechnology System

M. Cristina Negri
Argonne National Laboratory
9700 South Cass Avenue
Building 362
Argonne, IL 60439
Tel: 630-252-9662
Email: Negri@anl.gov

James Wozniak
Argonne National Laboratory
9700 South Cass Avenue
Building 331
Argonne, IL 60439
Tel: 630-252-6306
Email: Jwozniak@anl.gov

The SITE Program

Annette Gatchett
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, OH 45268
Tel: (513) 569-7697
Email: gatchett.annette@epa.gov

Information on the SITE Program also is available through the following on-line information clearinghouses:

- The Hazardous Waste Clean-up Information Web Site provides information about innovative treatment technologies to the hazardous waste community. It describes programs, organizations, publications and other tools for federal and state personnel, consulting engineers, technology developers and vendors, remediation contractors, researchers, community groups and individual citizens. CLU-In may be accessed at http://www.clu-in.org/.
- EPA REmediation And CHaracterization Innovative Technologies (REACH IT) is a system that lets environmental professionals use the power of the Internet to search, view, download and print information about innovative remediation and characterization technologies. EPA REACH IT will give you information about more than 650 service providers that offer almost 1,300 remediation technologies and more than 150 characterization technologies. EPA REACH IT combines information from three established EPA databases, the Vendor Information System for Innovative Treatment Technologies (VISITT), the Vendor Field Analytical and Characterization Technologies System (Vendor FACTS), and the Innovative Treatment Technologies (ITT), to give users access to comprehensive information about treatment and characterization technologies and their applications. used and the service providers that offer them. EPA REACH IT can be accessed at http://www.epareachit.org/.

Technical reports may be obtained by contacting the Center for Environmental Research Information (CERI), 26 West Martin Luther King Drive in Cincinnati, Ohio, 45268 at 1-800-490-9198 or (513) 569-7562.

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SECTION 2
TECHNOLOGY APPLICATIONS ANALYSIS

This section addresses the applicability of the phytotechnology system deployed by ANL-E at its 317/319 Area to other sites. This analysis is general in nature and intended primarily to highlight features of the ANL-E system and call out other issues to investigate further by readers considering a similar remedy. The information presented in this section is based upon the results of this SITE project and research conducted by others. A concise overview of the ANL-E phytosystem is on the ANL-E website at www.es.anl.gov/htmls/cbt10-phyto.html.

2.1 Key Features

Some of the key features of the ANL-E deployment include the following:

- Proprietary ANS TTTS® rooting techniques designed to reach ground water 30 ft (9 m) bgs. See section 1.2 for more details on the ANS TTTS®.
- Application designed to reduce or control the movement of contaminants until reductive dehalogenation, natural attenuation or other processes can reduce contaminant concentrations consistent with site goals.
- Full scale, with more than 800 trees. Hybrid poplars (600-plus) and hybrid willows (200-plus) planted in several engineered, strategically positioned plantations. (Turn to section 4.2.5 for an "as-built" map of the ANL-E phytosystem.)
- Trees of the *Salicaceae* family, poplar and willow, have high growth and transpiration rates. They are also phreatophytes (literally, "water-loving tree"). Phreatophytes are plants whose roots generally extend downward to the water table and feed on the capillary fringe. The combination of fast growth, large water demand, and the need to take in ground water makes poplars and willows ideal candidates for phytostabilization applications.
- Poplars and willows have a known, demonstrated ability to transform a variety of chlorinated VOCs, including TCE and PCE.
- Planting scheme (i.e., various depths, lined/unlined tree wells) promotes contact with soil pollutants in 317 Area French Drain and fast root growth to the water table in hydraulic control areas.
- 317 Area French Drain area seeded with a mix of legumes and grasses to minimize water infiltration and stabilize the soil.
- Eight-foot tall security encircling entire study area; radiologically-contaminated portion of site is access-restricted.

ANL-E plans to operate the system for a period of up to 20 years. Afterward, the trees will be harvested, chipped, and used at the ANL-E campus as landscaping material.

2.2 Operability of the Technology

2.2.1 Site Screening

2.2.1.1 Climate

There are a number of variables that affect the operability of phytotechnology systems. Chief among these are precipitation and evaporation. Phytostabilization of groundwater flow is more likely to succeed in areas where annual evaporation exceeds annual precipitation (Hauser et al., 1999). This can be expressed as a ratio:

Ratio = annual evaporation/annual precipitation.

Annual evaporation is best represented by calculating potential evapotranspiration (PET). However, PET is a fairly involved calculation requiring a large variety of data inputs. Perhaps more appropriate for an initial screening is to use Class-A pan evaporation. Data are available at state water surveys (e.g., www.sws.uiuc.edu) and the National Weather Service (e.g., www.crh.noaa.gov).

In areas were the ratio is greater than 1, the phytosystem should be able to lower the water table and control the migration of contaminants (Hauser et al., 1999). Where the ratio is below 1, engineering controls that may still allow successful phytostabilization. At ANL-E, where annual precipitation exceeds annual evaporation, the ground surface surrounding the poplar and willow trees was planted with vegetation to limit infiltration of precipitation to ground water.

2.2.1.2 Hydraulic Setting

In applications where hydraulic control is an important objective, phytostabilization success is more likely at sites where the water table is near the surface. Prior to 1999, tree-based systems were generally considered acceptable for groundwater depths to 20 ft (6 m). Below this depth severe reductions of water consumption were believed to occur (Hauser et al., 1999); however, the ANS TTTS® purportedly extends the treatment range to over 30 ft (9 m) bgs. (Refer back to section 1.2 for details on the ANS TTTS®.)

2.2.1.3 Soil Properties

During preliminary screening, data on surface soils, the vadose zone, and aquifer(s) of interest should be assembled and evaluated. Summary data are often available from the Natural Resources Conservation Service of the U. S. Department of Agriculture at either county or state offices. These data can help define the soil types likely to be found at the site if no significant construction or cutting and filling have occurred.

Cemented, high-density layers of soil may be strong enough to prevent root penetration. Such layers should be identified during preliminary screening because, if they exist, they must be modified. (Hauser et al., 1999). The ANS TTTS® claims to overcome the limitations of high density soil by creating permeable zones to promote and direct root growth through the vertical extent of the affected media. (Refer back to section 1.2 for details on the ANS TTTS®.)

2.2.1.4 Site Objectives and Plant Selection

An important principle of phytotechnology is to match the plant species and subspecies to the site and planned applications. Each site will be different: Some will be in wetlands, some in rubble, others in well drained sandy soils. Different plants thrive in these various conditions. Choosing the appropriate plants for the growing conditions is critical because if plants cannot grow, they cannot affect contaminants.

Different plants do well at remediating different types of contaminants. Some plants are better for treating heavy metals, others for volatile organics. Westphal and Isebrands (2001) lists some of the contaminants taken up by different species of poplars and willows: ammonium and nitrate nitrogen; barium, boron, cadmium, calcium, iron, magnesium, manganese, potassium, sodium, and zinc; BTEX, PAHs, TCE, and TNT; formaldehyde, herbicides, and pesticides; and cesium and strontium. It should be emphasized that not all poplar and willow species can metabolize these contaminants. Some varieties do, many do not.

A final consideration in selecting the appropriate plant type is whether it is native to the ecosystem where the phytotechnology is taking place. This criterion is particularly important for sites near natural areas that need to be protected (Westphal and Isebrands, 2001).

An important component of the ANS TTTS® is the selection of TreeMediation® vegetation (i.e., vegetation that is selected for its remedial capacity). ANS identified hybrid poplar and hybrid willow species known for their ability to treat TCE and other analytes of concern at the 317/319 Area. (Turn to section 4.2.5 for details on the selected poplar and willow species.) At the conclusion of the project, the poplar and willow trees will be harvested and the site will be re-planted with indigenous vegetation.

2.2.2 Engineering and Installation

2.2.2.1 <u>Plantation Design</u>

The design and performance assessment of phytotechnology systems requires a water balance. An important facet of the water balance is an understanding of the hydraulic framework surrounding the site. Data needs will include the following (EPA, 2001):

- Groundwater flow pathways, direction, and velocity
- Hydraulic gradient
- Average depth to ground water
- Aquifer thickness and recharge points
- Seasonal and diurnal groundwater level fluctuations,
- Connectivity of water bearing zones
- Interrelation of the contaminated aquifer with other aquifers or surface water features
- Principal mechanism of groundwater flow (intergranular or secondary porosity features)
- Volume of groundwater flows through treatment area
- Volume of ground water stored in aquifer underlying beneath treatment area
- Fraction of precipitation percolating to ground water
- Size and shape of the contaminant plume.

Past remedial investigations, corrective measures studies, or the information centers mentioned earlier should provide much of the required data. A numerical groundwater model may be needed to estimate flow rates and volumes. Such a model can be calibrated to actual site conditions and used throughout the project to evaluate hydrogeologic data as it is collected. Another component of the water balance is determining the rates at which the candidate plants consume ground water as they mature and over the life of the project. This directly affects design parameters such as the number, placement, and spacing of plants required to achieve site goals (e.g., hydraulic containment, alter subsurface geochemistry). ANL-E has developed a website that allows viewing of animated results of groundwater flow modeling in support of the 317/319 Area phytosystem. The website address is http://web.ead.anl.gov/phyto/.

A vegetative cover throughout a tree plantation helps to maximize total water use, control erosion, and keep shallow soil dry. Turn to section 4.2.5 for details on the vegetative cover deployed at the 317/319 Area.

For a number of plant varieties, a growing information base of water use characteristics is available from sources such as (but not limited to) U.S. and international universities, U.S. Forest Service and state agencies, and phytotechnology consultants.

The soil at treatment sites may have been significantly altered by past activities. Common adverse conditions include soil compaction and the addition of gravel or other oversized material. These conditions affect soil parameters such as bulk density, water holding capacity, porosity, and aeration. The soil at treatment sites should be investigated for its suitability as a growing medium. Hauser et al. (1999) lists important soil properties and associated test methods. One of the claimed advantages of the ANS TTTS® is that it can overcome the compacted soil in the 317 French Drain resulting from past soil mixing action. (Turn to section 4.2.4 for details about past treatment activities at the 317 French Drain.)

2.2.2.2 <u>Installation</u>

Ideally, plants should be installed early in the year to take advantage of the entire season. Early fall planting is acceptable since roots can begin to grow before the dormant season.

Trees are normally transplanted as either cuttings or growing trees. Smaller trees are less expensive, but the root mass of larger ones will likely begin treatment quicker. Trees should be watched closely to guard against drying during transport and inspected for damage upon delivery. For larger applications, a protected staging area will aid systematic monitoring for signs of plant stress (e.g. foliar discoloration) during an extended installation period that could take several weeks or more to complete. Figure 2-1 shows ANL-E scientists inspecting plants prior to planting.

Figure 2-1. Inspecting plants prior to Planting

It may be necessary to remove unsuitable native soil and foreign material in each tree installation point prior to placement. Soil borings (or “columns”) at each installation point is an new method pioneered by ANS. The drilling action removes heavy clay, hardpan, and other undesirable materials, which are then replaced by a combination of sand, peat, topsoil, and other materials to provide nutrients, wick water, and create a preferred growth path.

Inadequate aeration at depth may retard root growth. At ANL-E air inlet wells made of flexible perforated plastic pipe were installed to improve gas exchange within the rhizosphere.

For phreatophytic trees it desirable for the roots to reach and utilize ground water as quickly as possible. However, a brief period of surface irrigation may be necessary during and after installation to minimize transplant stress and meet the moisture needs of the plants, particularly if weather conditions are unseasonably warm and dry. Willows planted in the 317 French Drain were hand-watered periodically for several weeks after planting to alleviate stress from the hot, dry weather conditions.

2.2.3 Operation and Maintenance

2.2.3.1 <u>Monitoring</u>

(Turn to section 4.2.6 for monitoring activities undertaken specifically for the ANL-E phytosystem.)

Phreatophytic plants, with roots in or near the water table, can produce an obvious daily cycle of groundwater elevations beyond those exerted by variations in barometric pressure. The magnitude of these water level changes is more pronounced if the rate of groundwater recharge is less than the cumulative transpiration rate of the plantation. Continuous measurement of groundwater elevation within and outside planted areas will give a picture of the change in groundwater contours due to transpirative influence.

If a site goal is the reduction of contaminants in the ground water or soil as a result of root growth and influence or natural attenuation, then ground water and soil quality should be monitored. Sampling and analysis should be performed as required to determine the change in contaminants.

Climatological measurements should be obtained from either an onsite weather station (preferred) or one located nearby. Important parameters include precipitation, high/low daily temperature, humidity, wind speed, and solar radiation. These measurements permit the calculation of PET, which is useful in understanding changes in hydraulic conditions at the site and estimating transpiration rates for groundcover vegetation.

One method to assess the physiological development of plants is based upon the amount of heat absorbed during the growing season. This is described by a quantity known as the cooling degree day (Ball and Jones, 1998). There are several methods for calculating cooling degree days (CDD), including a widely-used variant known as the growing degree day (GDD) originally developed for corn crops (Eckert, 1990). The Climate Prediction Center of the National Weather Service gives brief descriptions of the different types of degree days as well as current and archived data for a number of regions across the nation (www.cpc.ncep.noaa.gov).

The quality of a growing season can be judged by comparing the current total site CDD against the average for the community. This is a simple and useful tool. A 1992 study of operational plantings on 50 to 100-acre agricultural-scale field plots in the north central United States indicated that among all the measured environmental characteristics, CDD had the strongest correlation (r^2=0.91) to poplar productivity (Downing and Tuskan, 1995). CDD may also provide a method to normalize or predict the performance of phytotechnology systems in different geographic regions to a proposed site during initial screening.

Evaluation of system performance is enhanced by measuring sapflow rate in individual trees after the plants have had a chance to recover from transplantation shock. Sap flow measurements are generally expensive and require a fair amount of expertise to collect and interpret. A number of different techniques and systems are available with varying degrees of accuracy (Smith and Allen, 1996). Indirect methods of determining sapflow rates are based upon correlations between sap flow and PET, basal diameter, or total leaf area. These methods are less accurate, but far less costly.

The overall health of the plants should be monitored on a regular basis. On-site inspections can determine whether disease, insects, wildlife, or lack of adequate plant nutrients is affecting rate of growth, water consumption, or plant health. Inspections should periodically include a sampling of basic measurements such as tree height, (basal) trunk diameter, and (after several growing seasons) canopy width.

2.2.3.2 Maintenance

The loss and replacement of plants during the treatment period should be expected. Losses are due to a number of reasons including transplant shock, nutrient deficiency, disease, wind or hail damage, and insect and animal predators, to name just a few. First year losses for willow and poplar trees have been reported between 5% and more than 50%. First year losses at ANL-E were less than 5%.

A vibrant stand of young trees is an inviting sight to animal and insect predators. In most cases were a problem develops, a fence will be needed to protect the plants from being damaged by animals. (ANL-E constructed a gated 8-ft tall security encircling entire study area). GDD can be used as a tool for insect pest management. The University of California at Davis maintains a phenology database that relates insect life cycle to the number of degree days that have accrued. Many insects require a certain amount of heat in order to evolve from one stage of development to another. Such infor-mation can be useful in planning pest management options. The website, www.ipm.ucdavis.edu/PHENOLOGY/models.html, gives details about this database.

2.2.4 Site Closure

If the site does not require removal of the trees, they can be left in place. It is unlikely that the shoots (above ground tree material) will contain a significant amount of accumulated organic contaminants, particularly at the end of the remediation period when the concentration of contaminants in the water is low enough to meet cleanup goals. As a result, there should be no obstacles to the general disposal or reuse of tree parts or other biomass if they must be removed. However, if significant metals (determined on a case-by-case basis) were present in the groundwater plume, sampling of the roots may be required to determine disposal options (Hauser et al., 1999). At the conclusion of the ANL-E phytosystem deployment, ANL-E plans to harvest the trees and use wood on-campus.

2.3 Applicable Wastes

Generally, tree-based phytotechnology is best applied to sites with relatively shallow soil and groundwater contamination containing non-toxic levels of pollutants. Chappell (1997) reported separate case studies involving hybrid poplars treating groundwater containing more than 220 mg l^{-1} CAHs. The contaminants, whether organic or inorganic, should possess certain physical and chemical properties that make them amenable to phytotransformation, rhizosphere bioremediation, and/or phytoextraction. Burken and Schnoor (1998) reported that chemicals with moderate hydrophobicity (i.e., log K_{ow} = 1 to 3.5) make good candidates for extraction. Such chemicals include benzene, toluene, ethylbenzene and xylenes (BTEX), and short-chain (chlorinated and ono-chlorinated) aliphatic compounds.

2.4 Availability and Transportability of the Equipment

Unlike conventional technologies, phytotechnology systems do not involve mechanical equipment beyond that necessary for installation.

Figure 2-2. Tree Installation at ANL-E

Plants can usually be obtained from a nursery or tree farm and trucked to the site. Equipment required to install the system is entirely site specific, and to a large extent, dependent upon the soil conditions, target installation depth, and the size of the plots. For example, a pile driving crane with a 46-cm (18-in) auger was used to a depth up to 9 m (30 ft) bgs to install the poplars and willows at the ANL-E site. Site prep tasks such as clearing and grading can be out-sourced.

Other equipment that might be necessary during plant installation includes a backhoe, front-end loader and skid mounted loader for moving fertilizer, top soil and fill around the site, a mixing unit and a screen for blending the planting soil, a trencher for burying data cables, and discing and plowing equipment for loosening the ground surface and incorporating fertilizer and soil conditioners. This equipment can usually be rented locally. Figure 2-2 shows a portion of the tree installation process at ANL-E.

Typical monitoring equipment for sites where hydraulic control is a priority includes a network of monitoring wells. These wells can be equipped with electronic pressure transducers connected to data loggers for continuous water level monitoring. Weather stations are often installed at large plantations whenever other reliable data sources are not available.

2.5 Materials Handling Requirements

Materials handling is required mainly during three phases of the project: site preparation, plant installation, and site closure. Refuse from site preparation typically includes plant biomass and waste debris from clearing and surface soil and other material from grading. These items are usually uncontaminated and can be disposed of at a general landfill.

Treatment area soils may require incorporation of fertilizer and soil conditioners at the time of planting. Fertilizer could include any variety of commercially-available products depending on the desired nitrogen/phosphorus/potassium (NPK) ratios. Soil conditioners have traditionally included aged manure, sewage sludge, compost, straw and mulch. A mix mill/grinder and spreader can facilitate handling of these products. Screening equipment (i.e. subsurface combs, portable vibrating screens) may also be necessary to remove debris and cobbles from the soil. Turn to 4.2.5 for details about fertilization and soil conditioning at the 317/319 Area.

Installation byproducts, such as contaminated soil, may require specialized handling, storage and disposal. At ANL-E, the majority of drill cuttings were not considered contaminated and were spread across the ground surface at the site. Any drill cuttings that are considered contaminated are typically containerized (55-gallon drums, e.g.) and disposed of at a permitted facility. During installation, soil should be kept damp when being worked to limit dust production.

In a large-scale application, as many as 1,000 trees per acre may be planted initially to assure a significant amount of evapotranspiration in the first few years. In order to partially offset capital costs, the trees can be harvested on a periodic rotation and sold as fuel-wood or for pulp and paper production. The trees will grow back from the cut stump. ANL-E plans to operate their system for a period of up to 20 years. Afterward the trees will be harvested, chipped, and used at the ANL-E campus as landscaping material.

2.6 Site Support Requirements

Phytotechnology systems in general have minimal site support requirements and require few utilities to operate. Water is generally needed for irrigation and possibly decontamination purposes. A drip irrigation system may be installed and operated periodically over the first few growing seasons when the young trees are most susceptible to water stress. It may be operated at times afterwards to make up for rainfall deficits that occur during times of drought. Irrigation water would not necessarily have to be potable water. Depending upon local regulations, water from the contaminated aquifer might be used at no cost, with the additional benefit of enhancing groundwater treatment during the first few growing seasons when little remediation is expected.

The electricity needed to operate well pumps can be provided by small generators. Monitoring equipment (e.g., soil moisture probes, pressure transducers, data loggers, weather station components) can be powered by batteries or solar panels, as was the case at ANL-E.

Depending upon site location, security measures might be required to protect the public from accidental exposures and prevent accidental and intentional damage to the trees and monitoring equipment. A fence would also serve the purpose of discouraging local wildlife from using the trees as a food source.

2.7 Range of Suitable Site Characteristics

The suitability of the soil, groundwater, and climate for growing plants is assessed during initial site screening (refer back to section 2.2.1) and then refined for specific candidate plants and site objectives during the design phase (refer back to section 2.2.2).

A tree-based phytotechnology system is land intensive, requiring plenty of clear space, or at least a sufficient amount to hold the number of trees necessary to meet site goals. The site surface should be stable and capable of handling traffic from trucks, trailers, and construction-type heavy equipment.

2.8 Limitations of the Technology

Although current research continues to explore the boundaries of phytotechnology applications, there are some limiting factors that need to be considered.

Contaminant-to-root contact, a function of root mass and depth, is a limiting factor for direct uptake of contaminants. To overcome the depth barrier researchers (e.g., ANS) have developed and employed specialized (often proprietary) techniques that train the tree roots to penetrate to greater depths.

Contamination that is too tightly bound to the organic portions of a soil and root surfaces may also pose limitations. This is especially true with hydrophobic compounds ($\log K_{ow} > 3.5$) that cannot be easily translocated within the tree or are simply unavailable to microorganisms in the rhizosphere. Contaminants that are water soluble ($\log K_{ow} < 1.0$) simply pass through the roots unimpeded.

High concentrations of organics may inhibit tree growth (Dietz and Schnoor, 2001). Sites that possess toxic levels of organic contamination are best handled by other techniques. A tree-based phytotechnology system can then serve as a secondary step after hot spots have been treated.

A potential impediment from a regulatory standpoint is the transfer of contaminants or metabolites to the atmosphere. Transpiration of TCE to the atmosphere has been measured (Newman et al., 1997); however, there is little indication of releases of more toxic daughter products (i.e., vinyl chloride).

2.9 Technology Performance versus ARARS

ANL-E is a government-owned, contractor-operated research and development facility that is subject to environmental statutes and regulations administered by the EPA, the Illinois Environmental Protection Agency (IEPA), U.S. Army Corps of Engineers (COE), and the State Fire Marshal, as well as to numerous DOE Orders and Executive Orders. A detailed listing of regulations applicable facility-wide is contained in DOE Order 5400.1, which establishes DOE's policy concerning environmental compliance. Some of these regulations can be described as applicable or relevant and appropriate (ARAR) to the 317/319 Area phytotechnology site. Others may not, but are common to other cleanup sites and are worth examining in the present context. The list includes the following:

- Resource Conservation and Recovery Act
- Comprehensive Environmental Response, Compensation, and Liability Act
- Clean Water Act
- Clean Air Act
- Toxic Substances Control Act
- Worker Safety and Training
- Other Statutes

Much of the information presented was derived from the ANL-E document, *Site Environmental Report for Calendar Year 2001* (Golchert and Kolzow, 2002). ARARs are summarized in Table 2-1 located at the rear of this section.

The regulatory setting of each contaminated site is unique. Readers evaluating ARARs for a particular remediation project are strongly urged to seek experienced guidance.

2.9.1 Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) and its implementing regulations are intended to ensure that facilities that treat, store, or dispose of hazardous waste do so in a way that protects human health and the environment. The Hazardous and Solid Waste Amendments of 1984 created a set of restrictions on land disposal of hazardous waste. The HSWA also require that releases of hazardous waste or hazardous constituents from any Solid Waste Management Unit (SWMU) at a RCRA-permitted (RCRA Part B Permit) facility be remediated, regardless of when the waste was placed in the unit or whether the unit originally was intended as a waste disposal unit.

The IEPA has been authorized to administer most aspects of the RCRA program in Illinois. The IEPA issued a RCRA Part B Permit to ANL-E and DOE in September 1997 and it became effective in November 1997. The Part B Permit identifies 49 SWMUs and 5 areas of concerns, which includes portions of the 317/319 Area. The remediation program for the 317/319 Area as well as the other units is under the authority of the Part B Permit and is being conducted in accordance with IEPA-approved corrective action work plans.

2.9.2 Comprehensive Environmental Response, Compensation, and Liability Act

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), commonly known as Superfund, addresses the cleanup of hazardous waste disposal sites and the response to hazardous substance spills. Under CERCLA, the EPA collects data regarding sites subject to CERCLA action through generation of a Preliminary Assessment, followed up by a Site Screening Investigation (SSI). Sites then are ranked on the basis of the data collected according to their potential for affecting human health or causing environmental damage. The sites with the highest rankings are placed on the National Priority List (NPL) and are subject to mandatory cleanup actions. No ANL-E sites are included in the NPL.

Remedial actions to clean up any release of hazardous materials from inactive waste sites follows one of two main routes. The first is through the CERCLA program and is generally used for abandoned sites. The second route is the RCRA corrective action process, which is used frequently for waste sites on active facilities. SWMUs are the units subject to RCRA corrective action. Of the sites described in the ANL-E SSI reports, most are included as SWMUs in the RCRA Part B Permit. The ANL-E phytotechnology action is part of an effort to cleanup two SWMUs located in the 317/319 Area.

2.9.3 Clean Water Act

The Clean Water Act (CWA) was established in 1977 as a major amendment to the Federal Water Pollution Control Act of 1972 and was modified substantially by the Water Quality Act of 1987. Section 101 of the CWA provides for the restoration and maintenance of water quality in all waters throughout the country, with the ultimate goal of “fishable and swimmable” water quality. The act established the National Pollutant Discharge Elimination System (NPDES), which is the regulatory permitting mechanism designed to achieve this goal. The authority to implement the NPDES program has been delegated to those states, including Illinois, that have developed a program substantially the same and at least as stringent as the federal NPDES program.

The 1987 amendments to the CWA significantly changed the thrust of regulatory activities. Greater emphasis is placed on monitoring and control of toxic constituents in wastewater, the permitting of outfalls composed entirely of storm water, and the imposition of regulations governing sewage sludge disposal. These changes in the NPDES program resulted in much stricter discharge limits and greatly expanded the number of chemical constituents monitored in the effluent.

In November 1990, the EPA promulgated regulations governing the permitting and discharge of storm water from industrial sites. The ANL-E site contains a large number of small-scale operations that are considered industrial activities under these regulations and, thus, are subject to these requirements. There are two permitted storm water outfalls in the 317/319 Area. Parameters routinely inspected include flow measurements; analyses for certain specified pollutants including VOCs considered target analytes for this project; and dates, durations, and precipitation volumes for monitored storm events.

2.9.4 Clean Air Act

The Clean Air Act (CAA) is a federal statute that sets emission limits for air pollutants and determines emission limits and operating criteria for certain hazardous air pollutants. The program for compliance with the requirements is implemented by individual states through a State Implementation Plan that describes how that state will ensure compliance with the air quality standards for stationary sources.

A number of major changes to the CAA were made with the passage of the Clean Air Act Amendments of 1990. Under Title V of the Clean Air Act Amendments of 1990, ANL-E was required to submit a Clean Air Act Permit Program application to the IEPA for a sitewide, federally enforceable operating permit to cover emissions of all regulated air pollutants at the facility. All facilities designated as major emission sources for regulated air pollutants are subject to this requirement. ANL-E meets the definition of a major source. Facilities subject to Title V must characterize emissions of all regulated air pollutants, including oxides of nitrogen, sulfur dioxide, carbon monoxide, particulate matter, volatile organic compounds (VOCs), hazardous air pollutants (HAPs, a list of 188 chemicals, including radionuclides), and ozone-depleting substances. The ANL-E site contains a large number of air emission point sources; however, projected emissions from the 317/319 Area phytotechnology are considered minimal, so the site is not counted as an emission point source.

The National Emission Standards for Hazardous Air Pollutants (NESHAP) constitute a body of federal regulations that set forth emission limits and other requirements, such as monitoring, record keeping, and operational and reporting requirements, for activities generating emissions of certain HAPs. The only standards affecting ANL-E operations are those for asbestos and radionuclides. By the end of 2001, the IEPA had issued a total of 21 air pollution control permits to ANL-E for NESHAP sources. The 317/319 Area is not considered a NESHAP source and therefore does not require an air pollution control permit.

2.9.5 Toxic Substances Control Act

The Toxic Substances Control Act (TSCA) was enacted to require chemical manufacturers and processors to develop adequate data on the health and environmental effects of their chemical substances. The EPA has promulgated regulations to implement the provisions of TSCA. These regulations provide specific authorizations and prohibitions on the manufacturing, processing, and distribution in commerce of designated chemicals. The principal impact of these regulations at the ANL-E site concerns the handling of asbestos and polychlorinated biphenyls (PCBs).

PCB items in use or in storage for reuse are tracked by the ANL-E PCB Item Inventory Program. All PCB items identified by the PCB Item Inventory Program have been labeled appropriately with a unique number for inventory and tracking purposes. None of the PCB items are located currently within the 317/319 Area.

2.9.6 Worker Safety and Training

All SAIC employees and subcontractors who performed work in the 317/319 Area had to complete the initial 40-hr Hazardous Waste Operations and Emergency Response (HAZWOPER) training course per 29 CFR 1910.120(e)(3)(i) and the annual 8-hr HAZWOPER refresher training per 29 CFR 1910.120(e)(8) within the past 12 months. In addition, SAIC field managers directly responsible for overseeing field work had to complete the 8-hr Hazardous Waste Site Worker Supervisor training course per 29 CFR 1910.120(e)(4).

For the final sampling event SAIC added a Competent Person for Excavation and Trenching to the soil sampling field crew. Some months before, the ANL-E Construction Safety Officer (CSO) in charge of the 317/319 Area determined that using a Geoprobe® is considered "excavation." As such, he directed that the "excavation" operation be supervised by a "competent person" as defined by 29 CFR 1926.650.

SAIC included a sample shipping manager trained per 49 CFR 172.704, Hazardous Materials Packing and Handling. The methanol extracts developed as a component of the soil sampling program were considered a hazardous material.

All SAIC personnel and subcontractors were required to complete a computer-aided Radiological Worker Training I course (4 hours) per 10 CFR 839.902 and attend a contractor safety orientation (1-1/2 hours) prior to entering the field work area. The course and orientation were provided on-site by ANL-E.

In addition to the comprehensive health and safety plan (HASP) prepared for USEPA, SAIC prepared and submitted to ANL-E a series of Job Safety Analysis (JSA) documents. The JSA is the ANL-E equivalent of a HASP, except that it focuses solely on the tasks to be performed during a specific work event (field or laboratory). The JSA was updated and re-submitted prior to each work event.

SAIC obtained ANL-E dig permits for all field activities that involved penetrating the ground surface within the 317/319 Area.

All powered equipment and tools were inspected by the CSO prior to entry and use in the 317/319 Area. Any and all defects were replaced or corrected and re-inspected.

2.9.7 Other Statutes

Rock and Sayre (1998) have identified other statutes and rules potentially applicable to phytotechnology projects. Plants used for phytotechnology are potentially regulable under several U.S. statutes. The United States Department of Agriculture (USDA) administers several statutes that could be used to regulate such plants; e.g., The Federal Plant Pest Act (7 U.S.C. 150 et seq.), the Plant Quarantine Act (7 U.S.C. 151 et seq.), and the Federal Noxious Weed Act (7 U.S.C. 2801 et seq.). Pertinent regulations are found at 7 CFR parts 319, 321, 330, 340, and 360, respectively. Under USDA authorities one type of plant (transgenic or naturally-occurring) which would potentially be subject to review would be a plant considered to be a plant pest. For additional guidance on USDA regulations pertaining to plants, consult the USDA web site http://www.aphis.usda.gov/bbep/bp/.

The U.S. EPA does not currently regulate plants intended for commercial bioremediation, although EPA believes the TSCA gives EPA authority to do so, if such action is necessary to prevent unreasonable risk to human health or the environment. TSCA gives EPA authority to regulate " chemical substances". TSCA defines chemical substances broadly to mean all organic and inorganic chemicals and mixtures of chemicals, including products, byproducts and residues. Living organisms, such as plants, are mixtures of chemical substances and thus are subject to TSCA. Although TSCA could potentially be applied to plants used in bioremediation, EPA has not yet made a determination of whether such action is necessary to protect the environment and human health. EPA to date has only issued regulations for microorganisms under section 5 of TSCA (EPA, 1997). Further information on TSCA and biotechnology products can be found at http://www.epa.gov/opptintr/biotech/.

Table 2-1. Federal and State Requirements for a Tree-Based Phytotechnology System

Process Activity	ARAR	Description	Comment
Cleanup Process	CERCLA: 40 CFR 300 RCRA: 40 CFR 261 (or State Equivalent)	CERCLA generally applicable to abandoned sites, RCRA to active businesses or organizations.	ANL-E 317/319 Area cleanup under RCRA Part B Permit
Waste from drilling and excavation activities related to system installation	RCRA: 40 CFR 261 (or State Equivalent)	Determine waste components; may be hazardous if listed or characteristic waste is present.	Small amount of hazardous drill cuttings generated during installation at 317 French Drain
Wastewater or storm water discharges from site	CWA: 40 CFR 122 (or State Equivalent)	Discharges of wastewater and storm water from industrial facilities, including waste treatment sites.	317/319 Area has two storm water outfalls to nearby creek. Effluent permitted and monitored on routine basis.
Air emissions from large tree stand	CAA: 40 CFR 70 (State operating permit); 40 CFR 61 and 63 NESHAP	Stationary sources above threshold quantity of regulated pollutant require CAA permit. Under NESHAP, remediation at source owner site may constitute construction or modification.	ANL-E considered a major source; however, regulations not applicable to 317/319 Area activities.
All field activities	OSHA: 29 CFR 1910.120 DOE: 10 CFR 835	All field work conducted at CERCLA or RCRA sites requires OSHA worker training and monitoring; radiological sites may require additional training prescribed by DOE.	Applicable to field work at 317/319 Area.

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SECTION 3
ECONOMIC ANALYSIS

3.1 Introduction

The purpose of this economic analysis is to present the actual and planned (future) costs of the phytotechnology system deployed at the ANL-E 317/319 area. This evaluation is of a *full-scale* operation that is being implemented as part of an ongoing RCRA Corrective Action.

The primary source of the cost information is Mr. Jim Wozniak, the ANL-E project manager (630-252-6306). In describing project expenditures, Mr. Wozniak identified five major cost categories organized by fiscal year (FY). The categories are as follows:

(1) Inspection/Assessment and Develop Monitoring Plan (FY99)
(2) Engineering and Deployment (FY99)
(3) Non-O&M costs (FY00-FY02)
(4) O&M costs (FY99-FY02)
(5) Recurring O&M costs (FY03-FY19)

Amounts reported for the period FY99 through FY02 represent actual expenses. Costs attributed to the period FY03 through the end of the treatment (FY19) are estimates.

This section concludes with a cost comparison between the ANL-E phytosystem and the DOE baseline technology that features an asphalt cap and extraction wells.

3.2 Conclusions

The following conclusions have been drawn based upon the information provided by ANL-E:

- The cost for designing, installing, and maintaining the system for the first four years (1999-2002) is $2,382,632. This is the sum of Non-Recurring ($1,480,000), Non-O&M ($589,432), and O&M ($313,200) costs.
- The total amount of the system over the 20 year treatment period is $4,592,632 ($38/ft^2). This includes estimated O&M expenditures of $2,210,000 for the period FY03 to FY19.
- Approximately 32% ($1,480,000) of the total cost was incurred designing and installing the system. Over the duration of the project O&M is the dominant expense, estimated at 55% ($2,532,000) of total cost.

Table 3-1 presents the categorical breakdown of actual and future costs.

Table 3-1. Cost Estimates for the ANL-E Tree-Based Phytotechnology System.

ANL-E CATEGORIES	ITEMIZED COSTS		--------TOTALS--------		% of TOTAL COST
FY99 NON-RECURRING COSTS					
1. Inspection/Assessment & Develop Monitoring Plan [1]			$222,000		
2. Engineering & Deployment			$1,258,000		
2a - Engineering [2]		$262,400			
2b - Deployment		$995,600			
-- Drilling [3]	$170,800				
-- Planting [4]	$184,800				
-- Oversight [5]	$357,600				
-- Other Efforts & Subs [6]	$282,400				
			Total ANL-E FY99 Non-Recurring Costs →	**$1,480,000**	**32.2%**
NON-O&M COSTS (FY00-FY02)					
3. Non-O&M Costs					
3a - Applied Natural Sciences			$72,232		
3b - ANL-E Energy Systems			$517,200		
			Subtotal of Non-O&M Costs for FY00-FY02→	**$589,432**	**12.8%**
O&M COSTS					
4. FY99-FY02 O&M Costs			$313,200		
5. Recurring O&M Costs ($130,000 x 17 years)			$2,210,000		
			Subtotal of all O&M Costs for FY99-FY19→	**$2,523,200**	**55%**
			Projected Total ANL-E Phytotechnology Costs for FY99-FY19→	**$4,592,632**	**100%**

[1] Tasks associated with Inspection/Assessment & Develop Monitoring Plan include inspecting tree livestock at site (e.g., assessing root mass, taking and recording stem caliper measurements). Monitoring plan included the monitoring tasks for the first growing season (1999). Expenditures, which are estimated at about 95% labor, cover approximately three full-time ANL-E personnel during 1999.

[2] Of the $262,400, approximately 90% are labor. Tasks include collecting soil samples with a Geoprobe®, analyzing those soil samples for agronomic analyses by ANS. Tasks also included producing engineering specifications/drawings and installation details for IEPA review. Costs include all support from ANL-E project management for 1999.

[3] Drilling includes the drilling of tree holes in the French Drain area as well as in the hydraulic control area.

[4] Planting includes the physical placement of trees into the holes along with previously purchased soil amendments.

[5] Oversight includes the cost of furnishing the trees and the ANS scientific effort overseeing the entire planting operation.

[6] Other Efforts and Subs include a variety of miscellaneous costs. Major costs include the installation of about 60 monitoring wells, the purchase of topsoil, sand, and manure; and the deforestation (including stump removal) of the eastern portion of the 319 area.

3.3 Issues and Assumptions

3.3.1 Site Characteristics

Costs presented reflect the complexity of the type and method of treatment required at the 317/319 Area. For example, instead of using inexpensive whips or cuttings, the deep soil and groundwater contamination called for the installation of specially developed trees with large root masses capable of reducing the dormancy period before actual treatment begins. Instead of using picks and hand shovels, the ANS TTTS® installation processes demanded a heavy-duty auger and earth-moving equipment to emplace the trees at depth and clear and spread substantial amounts of drill cuttings. It is expected that cost differences will result at sites with less challenging treatment needs.

Although not evaluated in this cost analysis, it is anticipated that larger sites employing a similar treatment approach will experience greater economies of scale from certain fixed cost elements. In particular, those items identified in Table 3-1 as category 1, 2a, and 3 represent approximately 23% of the total figure and are less sensitive to total treatment area than other cost elements. Application of these outlays against a larger site would decrease their unit cost.

Table 3-2 provides the dimensions of the 317/319 planted surface.

Table 3-2. Total Tree Planted Surface Area

ANL-E AREA OF HYDRAULIC CONTROL/TREATMENT	ESTIMATED PLANTED SURFACE AREA
- 317 Area French Drain	270' x 75' = 20,250 ft^2
- Area South (Downgradient) of 317 Area French Drain	370' x 120' = 44,400 ft^2
- Area South (Downgradient) of 319 Area Landfill	400' x 130' = 52,000 ft^2
Total Area	**116,650 ft^2**

3.3.2 Design and Performance Factors

The number of growing seasons required for sufficient tree growth is a considerable variable. Climate has a direct impact on the growth of trees and, therefore, affects the total number years needed to achieve cleanup goals.

The need for specialized monitoring equipment utilized by EPA during this SITE demonstration is highly dependent on minimum data needs and budget. For this project, specialized monitoring equipment included sap flow sensors, electronic soil moisture probes, groundwater well pressure transducers, minirhizotrons, multi-parameter water quality meters used during groundwater sample collection, an onsite weather station, and solar-recharged dataloggers. The minimum data needs of other projects may not warrant the expense of some or all of these items; therefore, their costs have been excluded from this analysis.

3.3.3 Financial Assumptions

All costs are in U.S. dollars. For FY99 to FY02 amounts are actual expenses based upon the year in which they were incurred. Projected O&M costs (FY03-FY19) are in 2003 dollars and provided without accounting for interest rates, inflation, or the time value of money.

3.4 Basis for Economic Analysis

The five categories used in this cost analysis were provided by ANL-E, and each is discussed in this section.

3.4.1 Inspection/Assessment & Develop Monitoring Plan

The category referred to by ANL-E as Inspection/Assessment & Develop Monitoring Plan can be considered as a collection of site preparation-type costs. Inspection/Assessment consists mostly of the field activities conducted prior to actual tree planting. Tasks are reported to involve inspecting tree livestock at the site (e.g., assessing root mass, and taking and recording stem caliper measurements).

Monitoring Plan is reported to include monitoring tasks for the first growing season. The majority (an estimated 95%) of the $222,000 expenditure covered approximately three full-time ANL-E personnel during 1999. These personnel were higher level professionals (e.g., engineers and scientists).

3.4.2 Engineering and Deployment

3.4.2.1 Engineering

Engineering includes review and assessment of data for the purpose of determining the nature and extent of the required deployment. Some of the data were developed through Geoprobe® soil sampling and analysis for agronomic parameters. Agronomic analyses determine the condition and general ability of the soils to promote healthy tree growth. This category also includes production of engineering specifications, drawings, and installation details for review by IEPA. This category includes all ANL-E management support for 1999. Engineering cost was reported as $262,400, of which an estimated 90% is labor.

3.5.2.1 Deployment

Deployment consists of a number of pre- and post-planting activities that are described by four subcategories: Drilling, Planting, Oversight, Other Efforts and Subcontractors.

Drilling. This category includes the specialized tree installation services that produced the borings needed to place the trees at the proper depth. While all trees were deep planted, only those in the hydraulic control areas utilized the patented TreeWell® method. Total Drilling cost was reported as $170,800, which is a mix of labor, equipment rentals, and field supplies.

Planting. This category includes the physical placement of trees. Over 800 hybrid poplar and willow trees were planted during the summer of 1999 in and downgradient of the 317/319 Area at predetermined and varying depths. The trees were planted along with amendments (topsoil, sand, and manure). Planting also involved installing a vegetative cover among the trees to control soil erosion and minimize water infiltration. Planting costs were reported as $184,800, of which 100% is described as labor.

Oversight. This category covers the subcontracted ANS effort overseeing the entire planting operation. Oversight cost was reported as $357,600. This category also includes expenses for the 809-tree inventory ($107,266), which is a cumulative total comprised of the purchase of sapling poplars ($189 each) and willows ($61 each), two-years' nursery development, delivery of the tree livestock to the 317/319 Area by truck, and pre-planting care.

The use of an irrigation system was intentionally avoided in order to encourage root growth toward the target aquifer. The willows in the 317 Area French Drain were hand watered for several weeks after planting to lessen transplant shock and relieve the stress caused by a period of severe heat and dry conditions. The labor for manual watering is included in this category.

Other Efforts and Subs. This category represents a catch-all for tasks not covered under the previous categories. Significant activities include the installation of groundwater monitoring wells (about 60); purchase of amendments such as topsoil, sand, and manure; and deforestation and stump removal (via subcontractor) within the eastern portion of 319 Area. The total cost of Other Efforts and Subs was reported as $282,400, which is a mix of labor, equipment purchases (wells) and rentals, and field supplies.

3.4.3 Non-O&M Cost (FY00-FY02)

This category consists of efforts by ANL-E scientific investigators and ANS. ANL-E tasks focus on data collection and review, performance evaluations, and periodic internal progress reports. ANS tasks include assessments of tree stand health and replacement of dead trees. Non-O&M costs for ANL-E were reported as $517,200, which was 100% labor. Non-O&M costs for ANS were reported as $72,232 and represent a mix of labor, equipment purchases (trees) and rentals, and field supplies.

3.4.4 O&M Cost (FY99-FY02)

This category consists of establishing O&M routines during the early stages of the project and one-time maintenance events (e.g., perimeter fence repair). O&M routines were established for grass mowing; tree stand walk-throughs and, periodically, more intensive surveys to collect and evaluate physiological measurements (e.g., basal diameter, tree height, canopy width); and quarterly groundwater verification sampling and reporting for IEPA.

Approximately 20 of the 60 wells at the 317/319 area are monitored on a quarterly basis. ANL-E utilizes dedicated bailers to collect ground water samples from each well. Annual analytical laboratory costs are reported as approximately $26,000, which consists of 156 VOC samples at $120 per sample ($18,720) and 156 tritium samples at $46 per sample ($7,176).

The total outlay for O&M Costs (FY99-FY02) is reported as $313,200, which is primarily a mix of labor and subcontracted services.

3.4.5 Recurring O&M Cost (FY03-FY19)

This category represents a continuation of the O&M routines established during FY99-FY02. The total cost of Recurring O&M Costs is reported as $2,210,000, which is based on estimated expenditures of $130,000 per annum.

3.5 Comparison between ANL-E Phytosystem and DOE Baseline Technology

As described in section 1.1.1, the functional requirements for the final remedial actions in the 317/319 Area are to (1) prevent the release of soil contamination to ground water, (2) minimize the offsite migration of ground water containing VOCs and tritium from source areas, and (3) minimize the release of contaminants to stormwater runoff. Two approaches were considered: the DOE baseline, featuring traditional mechanical systems, and a phytotechnology alternative. These two approaches are discussed below.

3.5.1 Baseline Approach

Under the baseline approach, the specific actions taken would include (1) containing residual VOC contamination in the area under an asphalt cap and (2) preventing the release of contaminated ground water by installing a hydraulic containment system. The system would be installed within and downgradient of the 317 Area French Drain and include groundwater extraction wells to intercept the lateral migration of the plume. For the 319 Area Landfill, the objectives would be achieved by continuing to contain the waste material in the landfill under the existing impermeable cap, and operating the existing leachate and groundwater collection system at the 319 Area Landfill.

3.5.2 Phytotechnology Approach

Under the phytotechnology approach, a hybrid-tree-based system and a vegetative cap at the 317/319 Area was deployed to (1) hydraulically contain the VOC and tritium plumes south of the 317 Area French Drain and 319 Area Landfill, (2) continue the remediation of residual VOCs within the 317 Area French Drain, and (3) minimize water infiltration into the 317 Area French Drain soils and stabilize the surface to prevent erosion, runoff, and downstream sedimentation. (Turn to section 4.2.5 for further details about the deployed phytotechnology system.)

3.5.3 Technical Comparison

According to ANL-E (1999), the phytotechnology approach has several distinct technical advantages over the baseline approach. These advantages are discussed below.

3.5.3.1 More Effective Reduction in Plume Size

An engineered plantation across the southern portion of the 317/319 Area establishes an extensive root network in the desired areas. ANL-E believes this approach should be much more effective than employing the anticipated 36 groundwater extraction wells under the baseline approach. Previous (ANL-E) experience has shown that the zone of influence of groundwater extraction wells in the glacial till soil is very limited. (Turn to section 4.2.2 for details on the site's hydrogeologic setting.) In contrast, the roots of the hybrid poplar and willow trees penetrate throughout the soil column seeking out water in the saturated porous zones and shifting location in response to seasonal changes in groundwater location and flow.

3.5.3.2 Source Removal

As described in sections 1.1.6.1 and 2.2.1.4, hybrid poplar and willows have the ability to destroy the type of VOCs found at the 317/319 Area through rhizo- and phytodegradative processes. The baseline approach does not encourage the destruction of contaminants. As a result, the contaminated soil would remain as a potential source of contamination for decades, requiring careful maintenance of the cap and groundwater collection system.

3.5.3.3 Waste Prevention

ANL-E projects that the phytotechnology system significantly reduces the generation of secondary waste requiring additional treatment. The largest secondary waste stream under both options is ground water. The minimum design estimate of groundwater removal is approximately 1,000 gallons per day (3,900 liters per day), and increases depending upon seasonal fluctuations. Under the baseline approach the ground water would be pumped from the various wells and discharged to the ANL-E wastewater treatment facility. However, with the phytotechnology system in full effect, the ground water should be transpired by the trees and released directly to the atmosphere as water vapor.

3.5.4 Cost Comparison

According to ANL-E (1999), the phytotechnology approach has the potential to result in large cost savings over the baseline approach. Under the phytotechnology approach, system design and installation (FY99), other sunk costs (FY00-FY02), and non-recurring O&M (FY00-FY02), cost categories that represent items 1-4 in table 3-1, amount to $2,382,632. The equivalent cost for the baseline approach is approximately $400K more at $2,789,872. ANL-E estimated recurring O&M costs of $233,636 per annum, which is slightly more than $100K greater than the recurring yearly O&M costs of $130,000 (item 5 in table 3-1) for phytotechnology. Total costs for design, installation, operation, and maintenance of the baseline approach for twenty years is $6,994,520, which is approximately than $2.4 million greater than the phytotechnology approach ($4,592,632).

SECTION 4
TREATMENT EFFECTIVENESS

4.1 Project Overview

The 317/319 Area is located on the southern end of the ANL-E property. It contains a number of sites that were used before 1980 to dispose of a variety of solid and liquid wastes. These sites have been delineated and classified by IEPA as SWMUs and require corrective action pursuant to ANL-E's RCRA Part B Permit.

Past remedial investigations have identified two distinct plumes of contaminated ground water moving in a southeasterly direction below the 317/319 Area (Moos, 1997). One plume begins at the 317 French Drain (the suspected source area) and contains a mixture of chlorinated and aromatic VOCs. The other plume extends downgradient of the 319 Area Landfill and contains primarily tritium and some VOCs. Groundwater and leachate collection systems have been installed to intercept these plumes and prevent migration to a public forest preserve immediately south of the ANL-E boundary.

A series of interim remedial actions were conducted in the 317/319 Area to initiate the cleanup process and reduce pollutant migration to the underlying ground water (Wozniak, 1998). The DOE Accelerated Site Technology Deployment program and EM-40 funded ANL-E to deploy a phytotechnology system to complete the restoration of the site. As described in section 1.1.6, phytotechnology is the purposeful use of living plants for *in situ* treatment of contaminated soil and ground water. The process acts as a system of abatement mechanisms that include some or all of the following: sequestration, removal, stabilization, degradation, and mineralization. In the instant case, ANL-E has chosen phytotechnology over the baseline pump-and-treat technology because it appears to be less costly and is thought to offer technical advantages such as active cleanup, less residual waste generation, and better operation in the complex stratigraphy of the site.

During June and July 1999, ANL-E installed stands of hybrid poplars and hybrid willows and a supplemental ground cover of herbaceous plants with the following objectives:

- Hydraulically contain the VOC and tritium plumes south of the 317 Area French Drain and 319 Area Landfill
- Continue the remediation of residual VOCs within the 317 Area French Drain
- Minimize water infiltration into the 317 Area French Drain soils and stabilize the surface to prevent erosion, runoff, and downstream sedimentation.

Earlier in 1999, EPA expressed an interest in participating with DOE in this study and subsequently included it as a demonstration project under the National Risk Management Research Laboratory (NRMRL) SITE program. Through a written commitment between the two organizations, ANL-E and EPA agreed to share the responsibility for monitoring the system and evaluating its performance.

ANL-E anticipates an operating period of up to 20 years; EPA's involvement covers the first three years of operations, from July 1999 through September 2001. A number of monitoring and measurement activities were planned, and these are described in section 4.3.

4.2 Detailed Project Description

4.2.1 317/319 Area

ANL-E comprises more than wooded 600 ha (1,500 ac) approximately 40 km (25 mi) southwest of Chicago, Illinois. The 317/319 Area occupies 2 ha (5 ac) at the southern end of the property. Figure 4-1 shows the location of ANL-E relative to the Chicago area (left) and the position of the 317/319 Area within the ANL-E campus (right). (Larger, easier-to-view versions of these maps are available at www.anl.gov.)

The 317 Area French Drain, IEPA SWMU No. 11, is described as an active hazardous and radioactive waste processing and storage area. According to ANL-E, liquid chemical wastes were disposed of at this site during the 1950s in shallow, gravel-filled trenches (Moos, 1997). The types and volumes of products disposed of were not documented; however, they likely consisted of cleaning solvents, oils and lubricants, and laboratory chemicals. Over time, these chemicals migrated into the surrounding environment. Data show that VOCs were detected in soil and groundwater samples from the French Drain (various depths to 10.3 m, 34 ft) and the downgradient fence line at levels above applicable standards (Moos, 1997). These data are summarized in Table 4-1.

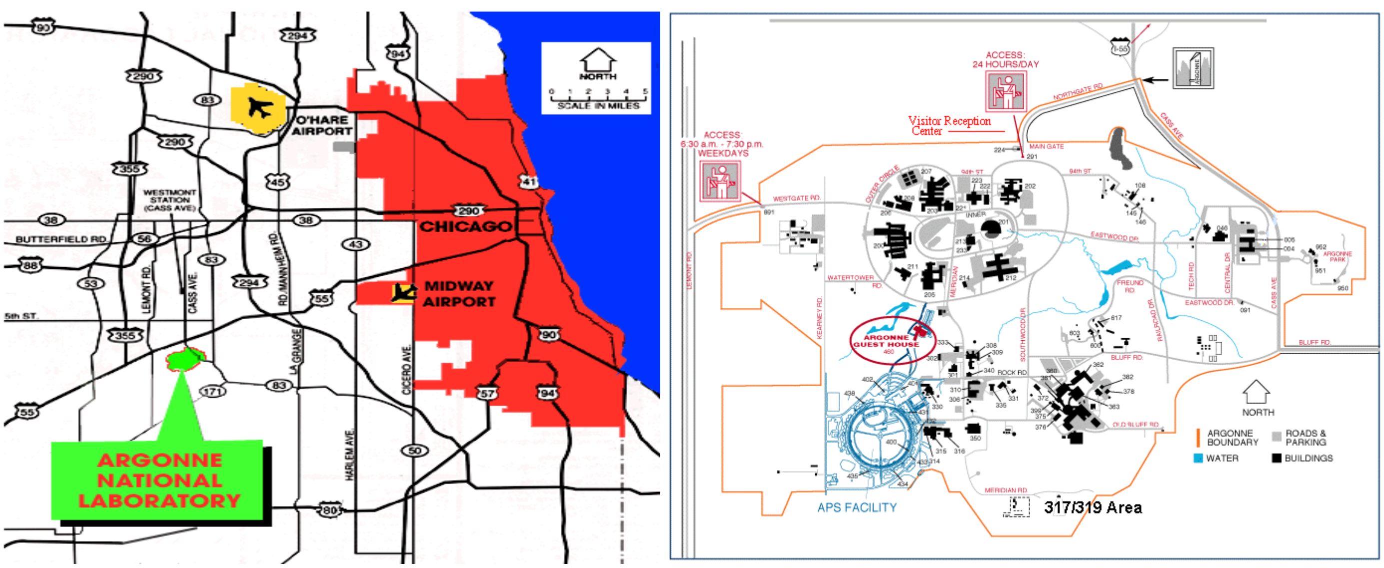

Figure 4-1. Locations of ANL-E (left) and the 317/319 Area (right)

Table 4-1. Maximum 317 Area VOC Concentrations above Applicable Remediation Objectives [1]

Analyte	317 French Drain Soil (ug/kg)	317 French Drain Ground water (ug/l)	ANL-E Fence-line Ground water (ug/l)
Benzene	3,200 (80)[2]	--	--
Carbon tetrachloride	54,000 (1,024)[2]	--	8 (5)[4]
Chloroform	21,000 (1,670)[2]	380 (211)[3]	4 (0.02)[4]
Methylene chloride	--	--	14 (5)[4]
Tetrachloroethene	190,000 (152)[2]	50,000 (316)[3]	--
Trichloroethene	47,000 (80)[2]	8,600 (127)[3]	6 (5)[4]
1,2-Dichloroethane	--	--	6 (5)[4]
4-Methyl-2-pentanone	78,000 (28,200)[3]	--	--

[1] Remediation objectives in parentheses

[2] Tier 2 value recommended by IEPA, March 1, 1999.

[3] Tier 2 value presented in Moos, 1997.

[4] Tier 1 value presented in Moos, 1997.

– Data not collected

The 319 Area Landfill, IEPA SWMU No.2, was previously operated as a solid waste landfill by the trench-and-fill method. Wastes disposed of within the landfill included general rubbish, construction and demolition debris, old equipment, metal scrap, wood, concrete, and other miscellaneous items. According to ANL-E, tritium and three VOCs were detected in groundwater samples from the southern tip of the landfill and the downgradient fence line at levels above applicable standards (Moos, 1998). These data are summarized in Table 4-2.

Table 4-2. Maximum 319 Area Tritium/VOC Concentrations above or Equal to Applicable Remediation Objectives [1]

Analyte	319 Landfill Ground water (ug/l or pCi/l)	ANL-E Fence line Ground water (ug/l or pCi/l)
cis-1,2-Dichloroethene	240 (70)[2]	--
Trichloroethene	24 (5)[3]	5 (5)[3]
Vinyl chloride	5 (2)[2]	--
Tritium	233,000 (20,000)[3]	--

[1] Remediation objectives in parentheses

[2] Tier 1 value presented in Moos, 1997.

[3] 35 IAC 620.410, Groundwater Quality Standards for Class 1

– Data not collected

4.2.2 Hydrogeology

According to ANL-E, the subsurface within the study area is a complex arrangement of approximately 18 m (60 ft) of glacial deposits over dolomite bedrock (Quinn, 1999). The glacial sequence is comprised of two main bodies that are dominated by fine-grained, low-permeability till. Permeable zones of varying character and thickness are present in each. These materials range from silty sands to sandy, clayey gravels to gravelly sands. In some locations, pure silt was encountered. If deep enough, this silt was typically saturated, and it is assumed to play a role in the flow of ground water in the study area. The permeable zones have a wide range of shape, including thin, lenticular, alluvial deposits; thick plugs of possible slump or channel-fill material; interfingerings; and a thick, basal, proglacial sand and gravel. In general, the permeable units are poorly sorted and many of them may represent slope-induced mass movement, resulting in transport and mixing of sediments. Their thickness range from 0.3 m (1 ft) to more than 4.6 m (15 ft), and data suggest short lateral extent.

The use of the term “aquifer” in this glacial setting is applied to any of the relatively permeable materials, including pure silt, and is not related to a permeable unit’s thickness, lateral extent, or ability to yield water at any certain rate.

The focus of this demonstration is the uppermost contaminated aquifer. The depth to the top of this unit ranges from 6.7 to 8.5 m (22 ft - 28 ft) in the 317 Area French Drain vicinity and 6.7 m to 10.4 m (22 ft - 34 ft) near the southern fence line. It is not a continuous feature in the study area. The aquifer is best described as numerous permeable subunits of varying character and geometry that share some similarity in depth and likely have some degree of hydraulic connection (Quinn, 1999). Based on well data, aquifers above this unit are assumed to be clean south of the 317/319 Area, though aquifers below it are impacted somewhat by VOCs and/or tritium.

Ground water in the aquifers flows generally to the southeast. ANL-E states that this is supported by head measurements reported in site investigation documents, and it is in keeping with the notion of regional flow following the topography and moving toward the Des Plaines valley.

The aquifer of interest is assumed to receive input from upgradient sandy units to the northwest and from downward infiltration. The recharge from infiltration may be localized, originating from shallower perched aquifers or directly from precipitation and conveyed by fractures within the overlying till.

The hydraulic conductivity determined from slug tests at monitoring wells throughout the 317/319 Area ranges from 4E-6 cm s^{-1} to 6E-2 cm s^{-1} (0.01 ft day^{-1} - 170 ft day^{-1}), with an average of 3.8E-3 cm s^{-1} (10.8 ft day^{-1}). The slug tests indicate variable permeability across the site without any trend (Quinn, 1999).

4.2.3 Climatology

ANL-E and the greater Chicago area are in a region of frequently changeable weather. The climate is predominantly continental, characterized by wide seasonal temperature swings. This continentality is partially moderated by Lake Michigan, and to a lesser extent by the other Great Lakes as air masses gain or lose heat to the underlying water bodies. Very low winter temperatures most often occur in air that flows from the north, west of Lake Superior. High summer temperatures are the result of south or southwest flow not influenced by the lakes (GRC, 1977). Average maximum daily temperatures are highest during July (29 ^oC, 84 ^oF) and lowest during January (-2 ^oC, 29 ^oF).

There is a 50 percent likelihood that the temperature will fall to 0 ^oC (32 ^oF) or lower by October 26, and that the last temperature of 0 ^oC (32 ^oF) or lower in spring will have occurred by April 20. However, temperatures this low have been recorded as early as September 25 in autumn, and as late in spring as May 14 (GRC, 1977). The Illinois State Climatologist’s Office estimates that the median growing season for the area surrounding ANL-E is between 155 and 165 days. Seasonal CDD (May through October) averages approximately 750 degree days (base 65).

Precipitation falls mostly from air that has passed over the Gulf of Mexico. Summer thundershowers are often locally heavy and variable; parts of the Chicago area may receive substantial rainfall and other parts none. Longer periods of continuous precipitation are mostly in autumn, winter, and spring. Annual precipitation averages approximately 91 cm (36 in), of which about 48 cm (19 in) falls during the growing season (May through September).

The amount of sunshine is moderate in summer and quite low in winter. A considerable amount of cloudiness, especially in winter, is locally produced by lake effect. Days in summer with no sunshine are rare. The total sunshine in December, partly because of shorter days, is only a little over one-third the July total (GRC, 1977). Annual pan evaporation (May through October) for the area is estimated at approximately 73 cm (29 in).

4.2.4 Remedy Selection

4.2.4.1 <u>Interim Measures</u>

In 1997, ANL-E installed seven extraction wells at the southern fence line and just south of the 319 Area Landfill to intercept contaminated ground water. The wells capture a portion of these plumes along with uncontaminated ground water; the water collected, estimated at 26,500 L d^{-1} (7,000 gal d^{-1}), is forwarded to Argonne's treatment plant before being released.

In 1998, ANL-E performed a voluntary interim corrective action on soils within the 317 Area French Drain. The goal was to remove the majority of VOCs from selected highly-contaminated areas with the intent that the larger, surrounding, lightly-contaminated area could be treated by another approach at a later date. The primary method of treatment was soil mixing combined with hot air/steam and vapor extraction. This technology was chosen because the soils are stiff glacial till and thought to require considerable (mechanical) energy to work the matrix and increase permeability. The secondary method was zero-valent iron injection in conjunction with further soil mixing. Removal rates in excess of 95% were reported (Lynch et al., 1998).

4.2.4.2 <u>Phytotechnology</u>

ANL-E decided against using DOE's "baseline" technology, which would have involved installing an asphalt cap and adding additional extraction wells. ANL-E believed the site's complicated subsurface would make it too difficult to predict where to place wells to produce a significant zone of influence. Instead, site managers chose phytotechnology. At the time, phytotechnology had been (at least on a limited basis) demonstrated feasible on VOCs in soil and ground water, and the following had already been shown or hypothesized about tritium: (1) tritium can be directly incorporated into water and biological tissues; (2) plants transpire tritiated water vapor; (3) tritium can accumulate in plant tissues, but the contaminant mean residence time is only about 4 to 37 days; and (4) contaminated ground water can be controlled using engineered plant-based systems. (Refer to section 3.5 for a comparison between the baseline technology and phytotechnology.)

To gain regulatory approval for the phytotechnology project, ANL-E had to prove that the plants would not release hazardous quantities of airborne VOCs or tritium. Emissions were calculated using EPA's CAP-88 (Clean Air Assessment Package-1988) exposure equations assuming worst-case scenarios. The highest concentrations detected in ground water after interim treatment were assumed to be in contact with and transpired by the plants. Emission levels were then calculated for an entire mature plantation with the expectation that transpiration rates would range from 8 to 190 L d^{-1} $tree^{-1}$ (2 to 50 gal d^{-1} $tree^{-1}$), depending on the season. The results indicate that VOC and tritium emission rates would be several orders of magnitude lower than what is allowed under NESHAP.

4.2.5 Plantation Installation

In June and July 1999, an engineered phytotechnology system was initiated and completed. It has the following components: (1) a herbaceous cover that is designed to minimize water infiltration and soil erosion; (2) shallow-planted TreeMediation® hybrid willows, which are intended to address the VOC source area; and (3) deep-planted TreeWell® hybrid poplars, which are expected to achieve hydraulic groundwater control. The latter were planted in lined columns where the roots are cut off from all shallow sources of water and are forced to grow downward in search of ground water. ANL-E stated that plume velocity and winter dormancy were considered when the number of trees to include in the phytotechnology design was determined.

A total of 809 trees were planted across the 317/319 Area. The trees were nursery raised for two years by ANS using proprietary techniques to maximize root mass prior to delivery and installation. Some 200 willows were planted on 3-m centers (10-ft) directly over the foot print of the former 317 Area French Drain (317 FD). The mix of willow species planted include laurel (*salix pentandra)*, golden weeping (*salix alba* 'Niobe') and the prairie cascade hybrid (*salix* x 'Prairie Cascade'). A total of 481 poplar saplings were planted on 5-m (16-ft) centers south of the demolished 317 Area South Vaults and south of the 319 Area Landfill. These plantings are known as the hydraulic control areas (HCs). The mix of poplars planted included a hybrid species (*populas charkowiiensis x incrassata*, NE 308). An additional 128 poplars were planted to fill in gaps and extend the treatment area. In the southwest corner of the 317 HC, the extra poplars increase the density of the tree stand by halving the distance between plants, i.e. 2.5-m (8-ft) spacing. At least two rows of hybrid poplars were planted along the southern edge of the willow plantation just north of the still-active North Vaults. The poplar trees were planted on both sides of the chain-link fence bounding the southernmost perimeter of the 317 Area Radioactive Control Zone. South of this fence, rows of poplar trees extend about 49 m (160 ft) to the southern property line.

Poplars in the 317/319 HC were planted in 9.1 m (30-ft) columns with the root mass installed to a depth of approximately 3.0 m to 4.6 m (10 ft - 15 ft) bgs. The 0.6-m (2 ft) diameter columns have a 6-m (20-ft) plastic liner that reportedly "trains" the roots to develop in a downward direction past clean surficial aquifers (5 m, 16 ft bgs) toward the contaminated aquifer. ANS states that the root system can grow as much as several centimeters per day during the growing season. The hybrid willows in the 317 FD were planted in 3-m (10-ft) unlined wells, with the root mass installed just below ground surface. Without a liner, the root system is free (presumably) to develop horizontally as well as vertically throughout the soil volume so that the rhizosphere can reach and affect the soil contaminants. All columns were backfilled with layers of blended top soil (10% manure) and sand to provide nutrients and wick ground water to the developing roots.

The 317 FD was seeded with a mix of legumes (*Lotus corniculatus*) and grasses (*Lolium perenne* and *Phalaris arundinacea*) to minimize water infiltration and stabilize the soil. Control cells were set up at the ANL-E greenhouse area to represent background conditions.

Figure 4-2 is an "as-built" drawing of the planted system as of September 11, 1999. Note: While the legend and other details of this drawing are not legible, the location and extent of the plantations are clearly visible. The "x" symbols represent willow trees planted within the 317 FD. The "+" symbols represent poplar trees, which have been planted in a wide, generally continuous band below the 317 FD and 319 Landfill. For reference purposes, it should be helpful to the reader to compare figure 4-2 with figure 1-2 (photograph of the site taken at about the same time frame in which the drawing was developed) and figure 4-3, which is a schematic representation of the 317/319 Area.

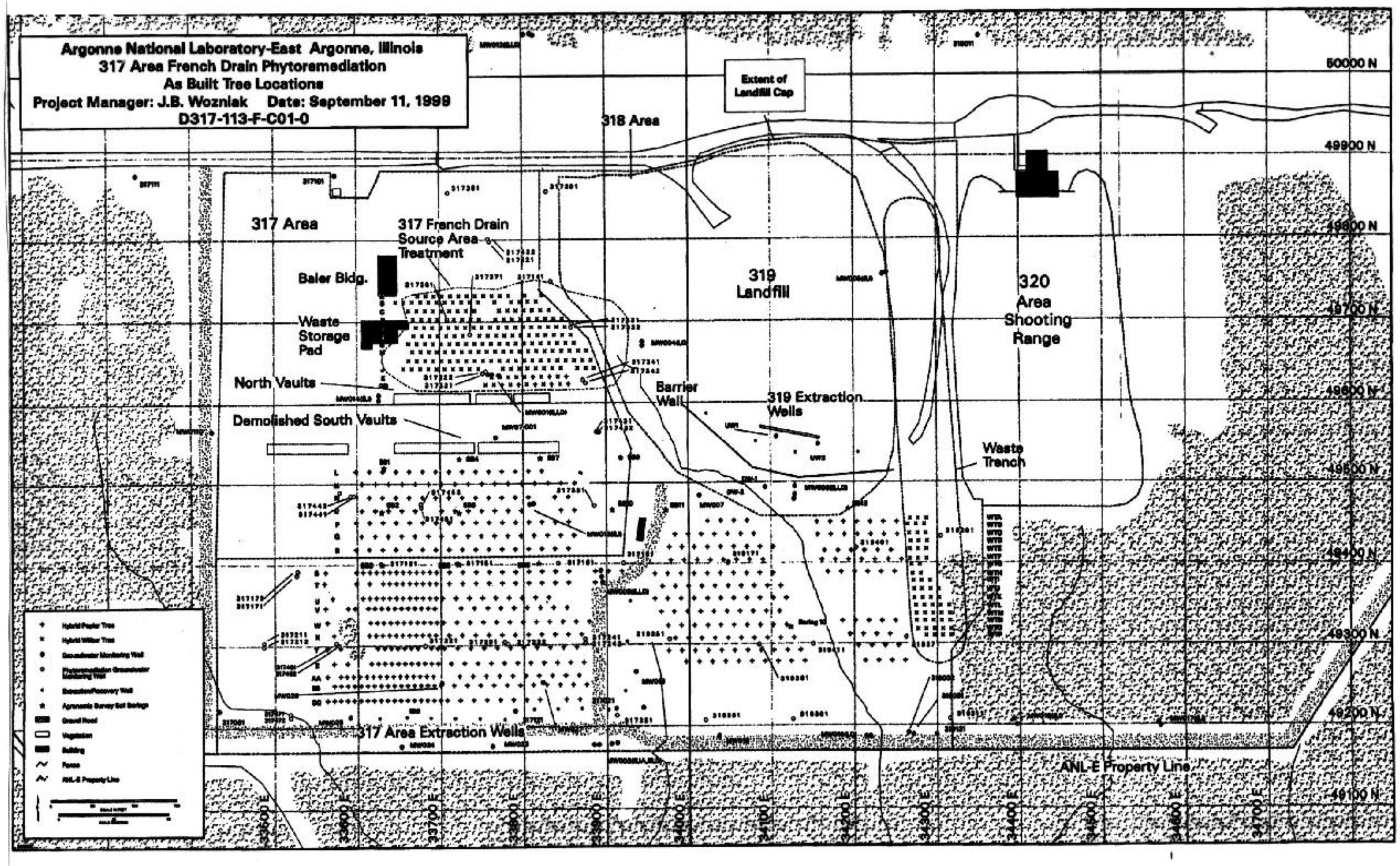

Figure 4-2. As-built Drawing of 317/319 Area Plantations

4.2.6 Monitoring

The monitoring system was designed to measure incremental changes in site conditions over time. The monitoring strategy for this study was more extensive than would be required for a typical phytotechnology project due to its research nature. Data collected for the monitoring program were used to determine how well the system performed during the demonstration period and to predict future system performance. The following monitoring stations were employed in this study:

- Approximately 60 wells upgradient, within, downgradient of the 317/319 Area were used to calibrate a groundwater model (MODFLOW) to assess hydraulic control.
- A total of 13 groundwater monitoring wells were sampled for selected VOCs, tritium, and other parameters.
- Pressure transducers were installed in 7 monitoring wells, including 2 upgradient of and 5 within the planted area.
- A weather station was installed to collect site-specific climate data
- Thermal dissipation probes were used during the 2000 and 2001 growing seasons to measure sap flow in selected trees.

Figure 4-3 (not to scale) depicts the location of monitoring points used by the SITE program with respect to the tree plantations, which are represented by the shaded rectangles.

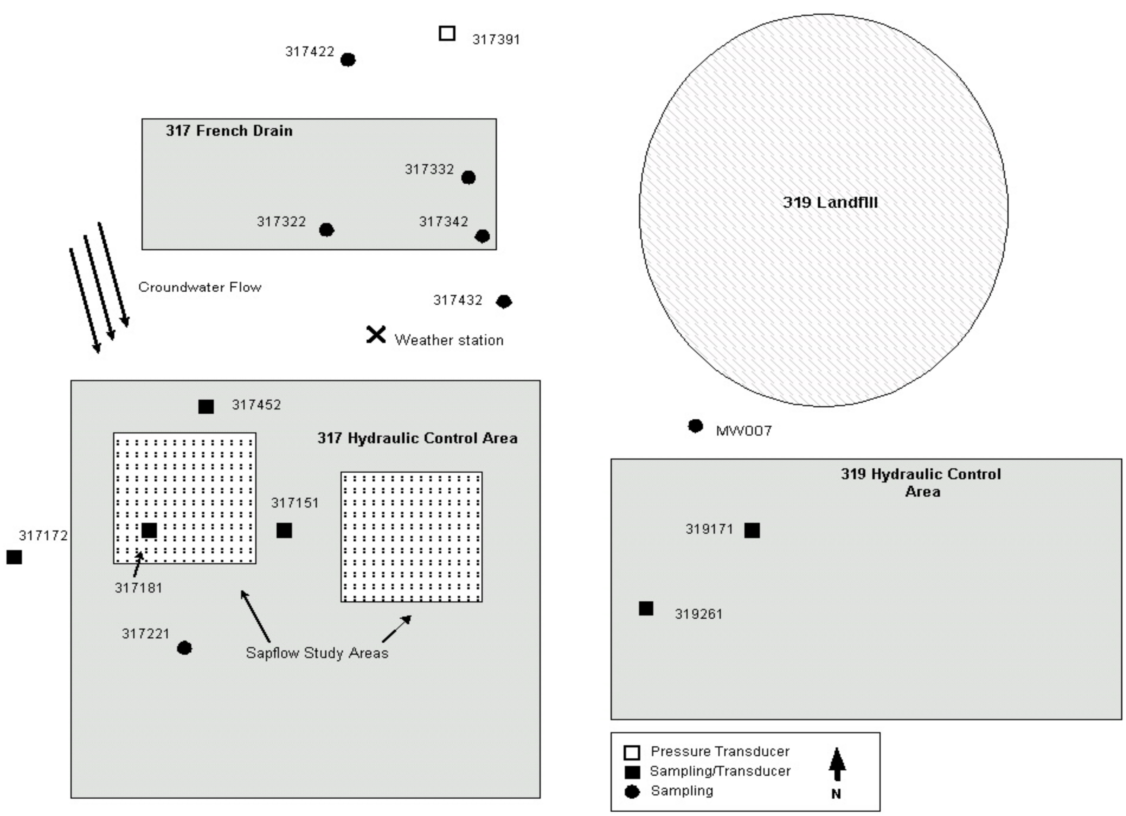

Figure 4-3. SITE Demonstration Monitoring Locations

4.3 Project Objectives

The deployment of phytotechnology at the 317/319 Area at ANL-E was studied to determine the ability of a purposefully-planted tree system to reduce the hazards of past releases of solvent-type VOCs and tritium into the environment. For the term of this SITE demonstration (1999-2001) monitoring and assessment duties were shared between the ANL-E and EPA. During the program kick-off meeting held on April 7, 1999 at ANL-E, specific scientific and engineering project objectives were discussed, and tasks designed to generate the data required to evaluate those objectives were divided among the organizations. The objectives, collection methods, and evaluation results are presented in this section.

4.3.1 Primary Objectives

4.3.1.1 <u>Groundwater Containment</u>

The first primary objective of this technology demonstration was to measure the sap flow of a small portion of the trees within the hydraulic control area and extrapolate the results stand-wide. The goal was to determine whether the extrapolated, stand-wide sap flow during the height of the second full growing season (2001) matches the estimated groundwater flow at baseline (1999).

An important mechanism for this system is the containment of polluted ground water through the interception and removal of water from the aquifer of interest. It was hypothesized that containment is achieved if the hybrid poplars take up water (represented by sapflow measurements) at a rate at least equal to the groundwater flux beneath the tree stands. Implicit in this hypothesis were several assumptions:

- The combination of deep planting and fast root growth would allow the plants to reach and establish the aquifer of interest as an unrestricted source of water (luxury consumption) at some point prior to the measurement period.
- The lined caissons would prevent hydraulic contact with shallow, uncontaminated water-bearing units scattered throughout the 317/319 Area.
- Based upon previous research and experience, ANS estimated that hybrid poplars in-ground for four years could transpire as much as 150 L d^{-1} (40 gal d^{-1}). The ANL-E trees were in-ground for two years when sap flow was measured in 2001.
- Trees planted in the area known as the 319 Waste Trench were not included because they do not intercept the aquifer of interest.

Monitoring Protocol. SITE installed thermal dissipation probes (TDP-30, Dynamax, Inc., Houston, TX) on 20 hybrid poplar trees inside the 317 HC within 30 m (100 ft) of one of two data collection systems located 53 m (175 ft) apart. TDPs measure sap flow via the temperature difference between a (non-heated) reference probe and a heated probe that is cooled proportionally by the movement of the sap liquid. Figure 4-3 shows the relative position of the instrumented trees within the 317 HC. The trees were instrumented beginning June 28, 2001 and monitored through October 18, 2001 (112 days). At the time of probe installation, all instrumented trees were greater than 30 mm in diameter (minimum requirement). The cross-sectional (basal) area of each instrumented tree was determined by measuring the trunk diameter at the point of probe insertion approximately 15 cm (6 in) above ground surface. Trunk diameter was measured along the north-south aspect and the east-west aspect and averaged to determine basal area. These measurements were made at the beginning of the data collection period and again the following spring (June 2002). The mean of these two values was used to calculate specific sap flow (i.e., sap flow normalized to basal area) for each instrumented tree. Basal area measurements for all hybrid poplars in the 317 HC and 319 HC were collected during June 2002 and used to extrapolate the mean sapflow rate from the 20 instrumented trees to the entire 317/319 HC tree stand (509 trees).

SITE employed two remote data collection systems (AM 416 Multiplexer, Campbell Scientific, Inc., Logan, UT). Each system was powered by a 12-volt battery recharged by a 60-watt solar panel. A voltage regulator (AVRD, Dynamax, Inc.) maintained the output from the multiplexers to the TDPs at approximately 2.8 volts. Data from the 20 TDPs were collected at 10-second intervals. Sixty-minute averages and minimum and maximum values were recorded daily by a datalogger (CR10X Datalogger, Campbell Scientific, Inc. Logan, UT). Stored data were downloaded periodically by a site worker, generally on two-week intervals. SITE converted sapflow measurements to gross water use using methods outlined by Dynamax, Inc. The following notation is used to describe how stand-wide transpiration was determined.

Define mean specific sap flow as $\bar{x}$ (g hr^{-1} cm^{-2}), the mean of individual specific sapflow measurements, x_i (g hr^{-1} cm^{-2}), where

$$\bar{x} = \frac{1}{n_s}\sum_{i=1}^{n_s} x_i \qquad \textbf{(Eqn. 4-1)}$$

for i = 1,2,3…, n_s instrumented trees. Define the basal area of the entire 317/319 HC tree stand as B (cm^2), the sum of basal area measurements for individual trees, b_i (cm^2), where

$$B = \sum_{i=1}^{n_p} b_i \qquad \textbf{(Eqn. 4-2)}$$

for i=1,2,3..., n_p trees in the 317/319 HC tree stand. Define total sap flow as Y (g hr^{-1}), where

$$Y = \bar{x}\,B \qquad \textbf{(Eqn. 4-3)}$$

SITE compared total sap flow (after conversion to L day^{-1}) using a statistical test of hypothesis to the estimate of baseline groundwater flux developed by Quinn (1999).

4.3.1.2 Groundwater Contaminant Removal

The second primary objective was to determine how effective the planted system could be in reducing the concentration of VOCs in the contaminated aquifer.

In addition to hydraulic control, poplars have a demonstrated ability to remove a variety of compounds from ground water. For this study it was hypothesized that the trees would remove contaminated water from the aquifer by means of their root systems, followed by the physiological alteration and incorporation of some compounds within the tree stems or the transpiration and volatilization of others into the atmosphere. The trees would also promote microbially-mediated reductive dechlorination of dissolved CAHs within the aquifer. Implicit in this hypothesis were several assumptions:

- The trees would establish contact with the saturated zone with ample time to influence subsurface geochemistry and promote reducing conditions.
- Treatment of tritium is primarily from groundwater uptake and volatilization, with a fraction retained for a brief period of time within the plant stem.

- The effect of non-destructive attenuation mechanisms (dilution, dispersion, sorption, etc.) is not known, but is thought to be negligible.

Monitoring Protocol. Data supplied by ANL-E from ongoing monitoring programs were used by SITE to identify a group of contaminants to be used in calculating VOC reduction. The top five VOCs were identified in terms of concentration and frequency of occurrence (i.e. lack of reported non-detects). These contaminants were (in descending order of concentration): 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), cis-1,2-dichloroethene (DCE), chloroform (CLF), and trichloroethene (TCE).

SITE collected groundwater VOC samples with a bladder pump using low-flow purging techniques (EPA, 1996b) to prepare the well. Samples were analyzed by (baseline) EMAX Laboratories, Torrance, CA and (final) Analytical Laboratory Services, Inc., Middletown, PA. All samples were analyzed by gas chromatography with flame ionization and election capture detection (GC/FID/ECD) according to EPA SW-846 Method 8021B (EPA, 1986).

SITE collected one sample per day for six days from each of seven primary monitoring wells during the baseline sampling event (BSE, August 1999) and again during the final sampling event (FSE, June 2002). Consequently, a total of 42 baseline and 42 final samples were available to evaluate the project objective. A number of sample results were also available from non-primary monitoring wells. These non-primary data in conjunction with the primary well data assist in shaping a better understanding of conditions throughout the study area. In addition, a limited data set was available for all monitoring wells from the mid-term sampling event (MSE). The MSE was conducted during November 2000; the timing and data from the event can add some perspective in gauging the progress of the system.

There are five target analytes per sample (CLF, DCA, DCE, TCA, and TCE), which equates to 210 analyte results per data set. In the BSE data set 33 of 210 results were non-detect, and 19 of 210 results were non-detect in the FSE data set. Non-detect results were set equal to the reporting limit, generally 1 ug l^{-1}. The concentrations of the five target analytes were summed to yield a “total VOC” concentration for each sample.

SITE collected groundwater tritium samples with a disposable Teflon® bailer and shipped to and analyzed by (baseline) Barringer Laboratories, Golden, CO and (final) Paragon Analytics, Ft. Collins, CO. All samples were analyzed by liquid scintillation according to EPA Method 906.0 (EPA, 1980).

SITE collected one sample per day for six days from each of two primary monitoring wells during the BSE and again during the FSE. Consequently, 12 baseline and 12 final samples were available to evaluate the project objective. All sample concentrations were above the reporting limit of 1,000 pCi l^{-1}.

4.3.1.3 Soil Contaminant Removal

The third primary objective was to determine how effective the planted system could be in reducing the concentration of TCE in the 317 FD soils.

In addition to poplars, willows also have a reported ability to remove a variety of compounds from soil-pore water. In the instant case, it was hypothesized that the trees would remove soil-pore water from the 317 FD soils by means of their root systems, followed by the physiological alteration of TCE within the trees or the transpiration and volatilization of TCE into the atmosphere. It was believed that the trees would also promote microbially-mediated reductive dechlorination of TCE. Implicit in this hypothesis were several assumptions:

- The tree roots can develop vertically and horizontally to reach and affect TCE throughout the 317 FD.
- After the interim soil-mixing activities undertaken in 1998, the tight clay-like soil matrix does not hamper root growth or channel roots away from polluted areas via preferred growth pathways.
- The residual levels of TCE and other contaminants are not toxic to the plants.

Monitoring Protocol. SITE collected soil samples via Geoprobe® from 28 boreholes arrayed in regular spacings across the 317 FD. Composite samples were drawn from three different subsurface intervals: 4 ft to 8 ft (1.2 m to 2.4 m), 8 ft to 12 ft (2.4 m to 3.6 m), and 12 ft to 16 ft (3.6 m to 4.9 m). SITE extracted the samples promptly onsite using methanol and then shipped to and analyzed by (baseline) EMAX Laboratories, Torrance, CA and (final) Analytical Laboratory Services, Inc., Middletown, PA. All extracts were analyzed by GC/FID/ECD according to USEPA SW-846 Method 8021B. Results were reported on a dry weight basis.

SITE collected a total of 84 baseline and 84 final samples from the 317 FD producing a combined data set of 84 paired samples. A large number of non-detections were reported, including 43 of 84 and 46 of 84 in BSE and FSE data, respectively. All non-detect results were set equal to the reporting limit, which ranged from 4 to 69 ug kg^{-1}.

4.3.2 Non-primary Objectives

Non-primary objectives were included in the study to elucidate the biological, hydrological, and biochemical processes that contribute to the effectiveness of the ANL-E deployment on contaminated ground water and soil. Since planted systems can take several years to become fully effective, much of the data associated with the non-primary objectives were collected to build predictive models to determine future performance. Measurements are primarily related to tree physiology (tree growth and contaminant translocation) and aquifer characteristics (hydraulic, geochemical, microbiological). Scientists at ANL-E and Science Applications International Corporation (SAIC) conducted the work related to the non-primary objectives in coordination with the EPA SITE program.

Non-primary objectives and the scope of the associated data collected are described herein.

4.3.2.1 <u>Contaminant Uptake and Degradation in Plant Tissue</u>

While it is known (Gatliff et al., 1998; Newman et al., 1997) that trees such as poplars and willows are capable of taking up a number of organic compounds (including CAHs), there are varying opinions on the fate of those compounds in the rhizosphere and plant systems. These compounds can be degraded in the root zone (Nzengung et al., 2001), taken into the plant and vented through the bark (Burken and Ma, 2002), and degraded in leaf tissue (Newman et al., 1999). Portions of these contaminants have also shown to be vented out by the same trees into the air via the transpirative flow or, during winter, by gas diffusion through the plant's air conducting tissue (Nietch et al., 1999; Vroblesky et al., 1999; Davis et al., 1998).

ANL-E sampled plant tissues (leaves and stems) to determine the presence of VOCs and their degradation intermediate trichloroacetic acid (TCAA). Finding VOCs in leaf and/or branch tissue above background levels would provide a clear indication that the trees are indeed taking up the contaminants from soil or ground water and translocating it to the aboveground tissues. Finding TCAA in these tissues would provide proof that at least a portion of the parent compound is being degraded by the plant. In principle, by multiplying contaminant concentrations in the sap by sapflow rate, a measure of contaminant removal by plant uptake can be obtained. However, this is still a very imprecise measurement because of unknown diffusion rates from the sap through cell walls into external air, and because it is still unknown how much of the total contaminant detected in tissue is in the freely moving sap and how much is adsorbed to the plant tissues.

ANL-E collected samples of leaves and branches by cutting with sharp scissors and placing into airtight crimped headspace vials. Samples for VOC and TCAA analysis were directly placed into headspace vials for gas chromatographic analysis within 24 hours. While analysis of VOCs was conducted via direct headspace techniques, samples for TCAA analysis were thermally decarboxylated at 90°C before being analyzed via headspace. Control samples from plants growing in non-contaminated soil were also sampled and analyzed using the same methods. Detection limits were 0.5 ng g^{-1} for CLF, TCAA, TCE, and 0.2 ng g^{-1} for PCE.

ANL-E collected samples from more than 30 different trees at the 317 FD area, plus willows at the greenhouse control plots, at various times during 1999, 2000, and 2001. In each sampling event, six samples were collected from each sampled tree, including two of branch tissue, and four of leaves growing on that branch.

4.3.2.2 <u>Geochemical and Microbial Indices of Reductive Dechlorination</u>

Davis et al (1996) in Chappell (1997) reports that microbial degradation of TCE can take place either aerobically or anaerobically. The aerobic process is an oxidative mechanism catalyzed by a mono-oxygenase enzyme. The anaerobic mechanism is reductive dechlorination, which is primarily carried out in the rhizosphere by methanogens. EPA (1998) suggests that reductive dechlorination is the most frequently encountered biodegradation mechanism in the subsurface. Furthermore, Bouwer (1994) in EPA (1998) reports that *cis*-1,2-DCE is a more common daughter product than either *trans*-1,2-DCE or 1,1-DCE. Baseline data from this project shows a preponderance of *cis*-1,2-DCE as compared to the other two congeners, which indicates that reductive dechlorination likely has occurred at the site. It was surmised that the action of the planted trees would re-activate the microbial population responsible for reductive dechlorination.

Trees can induce subsurface oxygen utilization by providing organic matter that stimulates aerobic microbial activity and depletes oxygen levels. SITE collected geochemical samples to assess the development of subsurface anaerobic conditions over time, along with any associated reductive dechlorination of CAHs. SITE collected samples and measurements from monitoring wells and soil throughout the study area. BSE, MSE, and FSE groundwater field measurements include specific conductance, dissolved oxygen (DO), oxidation reduction potential (ORP), temperature, pH, and ferrous iron (Fe II); laboratory analyses include sulfate, nitrate, manganese, total iron, and dissolved organic carbon (DOC). The ratio of TCE to DCE is also examined. Soil measurements (unsaturated zone) include total organic carbon (TOC), manganese, iron and pH.

SITE conducted a microbial survey to determine if the planted trees have driven the local microbial community structure to one that supports reductive dechlorination. SITE collected BSE and FSE samples of ground water and soil throughout the study area. Bacterial enumeration assays were performed for aerobic and anaerobic total heterotrophic plate counts by method 9215A/B (AWWA, 1971). Analyses of phospholipid fatty acids (PLFA) were performed to describe the classes of microbes present in the system and how they are reacting to environmental factors. PLFA analysis (White et al., 1997) is based on the extraction, separation, and recovery of lipid classes (Bligh and Dyer, 1959), followed by identification and quantitation using gas chromatography and mass spectrometry (GC/MS).

4.3.2.3 <u>Modeling and Confirming Water Use and Hydraulic Control</u>

As a means of evaluating the potential of the planted system for hydraulic containment, a finite-difference numerical flow model was constructed by at ANL-E Quinn et al. (2001). This model uses the U.S. Geological Survey code MODFLOW

(MacDonald and Harbaugh, 1988) and focuses on the confined, perched, glacial drift aquifer that extends below much of the 317/319 Area at a depth of approximately 7.6 m (25 ft) bgs. Modeling was directed initially toward calibrating to seasonally changing hydraulic heads based on over ten years of water level measurements at site wells. The effect of the ANS TTTS® of the plantation was then incorporated by assuming a best estimate for the water use of the trees under luxury consumption conditions. Both the growth phase and the mature phase of the plantations were modeled. ANL-E has developed a website that allows viewing of animated results of groundwater flow modeling in support of the 317/319 Area phytosystem. The website address is http://web.ead.anl.gov/phyto/.

In November 1999, as part of the phytotechnology system-monitoring program, SITE installed seven water level sensors (Druck model PDCR 1830, New Fairfield, CT) in monitoring wells in the 317 and 319 Areas. The water level data, along with weather station data, were collected hourly at several battery or solar-powered data loggers and were used by ANL-E to verify the validity of the predictions generated by the groundwater model.

4.3.2.4 Health and Growth of the Planted System

ANL-E monitored tree vitality by periodically measuring the height of the above ground stem (or tallest branch) and the diameter of the stem at 30 cm (1 ft) above ground level. ANL-E randomly selected approximately 10% of the trees for these measurements. ANL-E also carried out visual inspections were also carried out throughout the year to monitor aspect, presence of leaves, and branching, mortality, and presence of insects or other pests on the trees.

Three observation areas for the herbaceous cover were also randomly chosen and established. ANL-E conducted observations periodically and included the determination of percent plant cover versus bare soil, and percent coverage for each herbaceous species. From a reference tree center, using a sighting compass, a measuring tape was directed outwards at 160˚ from the tree. A 1-m^2 rigid quadrant (the survey area) was then placed on the ground, parallel to the tape on its west side at 1 m from the tree. The percent cover was defined as the amount of ground surface covered by living parts of plants, including but not limited to leaves.

4.4 Performance Data

The following sections present a discussion of the technology's performance with respect to the primary and non-primary project objectives. The purpose of the following sections is to present and discuss the results specific to each objective, provide an interpretive analysis from which the conclusions are drawn, and, if relevant, offer alternative explanations and viewpoints.

4.4.1 Primary Objectives

4.4.1.1 Groundwater Containment

TDP data were evaluated per manufacturer's guidelines. Some data were found unusable due to factors that led to extraneous or negatively reported numbers. Factors that may have caused data glitches include a poorly charged battery, cross signaling within the lines, and shorts within the system from electrical pulses or broken wires. Each data set was checked carefully for daily fluctuations and cross-checked against evapotranspiration data. Erroneous data were excluded from water use calculations. Four probes (N48, P96, R0, and T16) continuously reported negative or extreme values that did not correspond with evapotranspiration (e.g. night-time sap flow). Consequently, data from these trees were not used to assess groundwater containment.

Average transpiration (L day^{-1}) for each tree measured during the 2001 monitoring period is presented in Table 4-3. The results show that cumulative water use was highest during the month of July (62.5 L day^{-1}). Accordingly, transpiration rates from July 2001 were used to evaluate the project objective.

The June 2002 survey of the 317/319 HC poplars (509 trees) generated a cumulative, stand-wide basal area of 8,592 cm^2. This area combined with the July 2001 transpiration data yields a mean stand-wide transpiration of 1,440 L day^{-1}, with a 90% confidence interval between 1,270 L day^{-1} and 1,610 L day^{-1} (see p. 4-10 for calculation method). The underlying baseline groundwater flux was estimated previously by Quinn (1999) to be 4,870 liters day^{-1}. Thus, the mean July 2001 transpiration rate was approximately 30% of the baseline groundwater flux. (A statistical test of hypothesis (α = 0.10) confirmed statistically that the 317/319 HC plantation did not reach its target.)

Table 4-3. Transpiration Rates for Instrumented Trees during 2001 Growing Season

	Tree ID							
Month	**N32**	**P64**	**P112**	**Q24**	**S32**	**T72**	**T256**	**U200**
July	0.95	6.76	2.55	1.33	2.09	2.58	6.61	5.62
August	0.72	4.71	2.20	1.52	2.70	2.66	6.80	6.69
September	0.65	3.72	2.28	1.33	2.20	2.20	5.13	5.02
October	0.53	4.56	2.36	1.06	1.63	2.20	3.69	2.47
	N192	**O200**	**O248**	**Q200**	**S176**	**S224**	**T160**	**T208**
July	2.39	6.23	2.32	4.86	2.89	2.70	7.87	4.75
August	2.85	5.55	2.96	3.42	2.58	3.53	5.85	5.09
September	1.98	3.61	1.98	2.39	0.80	2.51	3.50	4.67
October	0.80	1.48	1.60	1.37	1.14	1.90	3.61	2.36
	Sum		**Mean per Tree**					
July	62.50	L day^{-1}	3.9	L day^{-1}				
August	59.83	L day^{-1}	3.7	L day^{-1}				
September	43.97	L day^{-1}	2.7	L day^{-1}				
October	32.76	L day^{-1}	2.0	L day^{-1}				

Transpiration rates for individual trees during July 2001 range from 0. 95 L day^{-1} to 7.9 L day^{-1} with an average value of 3.9 L day^{-1}. Not surprisingly, these rates were substantially below the ANS estimate of 150 L day^{-1} for poplars four years in-ground, which suggests that (1) the plants are not fully mature, and (2) the plants have not yet established luxury consumption conditions. However, Table 4-4 informs on encouraging year-to-year gains in transpiration rates despite the restricted water availability. Preliminary sapflow measurements were made on a sampling of 317 HC poplars from August 4 to September 18, 2000. This was a trial run for the purpose of testing the methods of installation and data gathering prior to the 2001 growing season when critical data would be generated. Table 4-4 compares the average transpiration rate from this trial period to a similar period during the 2001 study. Results show that the transpiration rate increased for individual trees between 0.2% (P64) to 81% (S32) with a cumulative increase of 18%. It is anticipated that the average year-to-year increases in transpiration will improve significantly once the plant roots are fully established in the saturated zone.

A plot of mean results from the 2001 study (July-October) describes a modest correlation between basal diameter and transpiration rate (Figure 4-4). Further confirmation of this relationship after luxury water consumption conditions have been established may provide in future years a rough estimate of stand-level transpiration without direct sapflow measurements.

Table 4-4. Sapflow Change between 2000 and 2001

Tree Number	Mean Sap Flow 2000	Mean Sap Flow 2001	Increase in Sap Rate
N32	0.54	0.70	30%
P64	4.73	4.74	0.2%
P112	1.89	2.22	17%
S32	1.17	2.12	81%
T72	1.98	2.43	23%
Total	10.31	12.21	18%

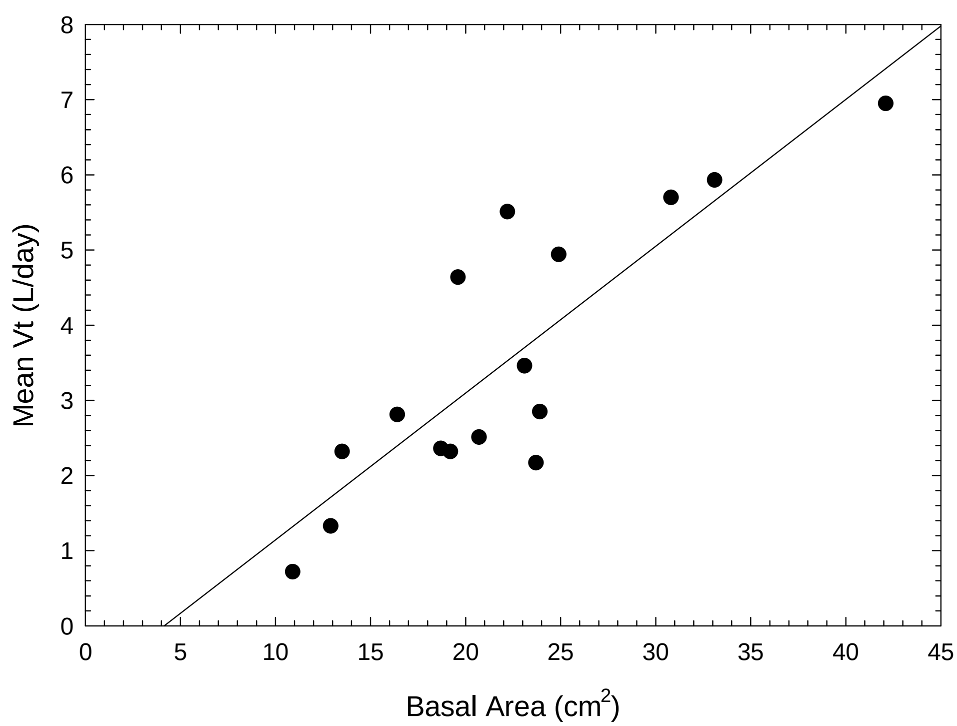

Figure 4-4. Relationship between July-October 2001 Sap Flow and Mean Basal Area

SITE calculated daily PET with REF-ET software (Allen, 2000) using data obtained from a weather station located at ANL-E. Values for PET were paired with daily water use and regressed. This was done for each instrumented tree for the 2001 growing season. Results show weak-to-moderate correlations between PET and transpiration rate with coefficient of determination (r^2) values ranging from 0.09 to 0.65 (data not shown). This is further evidence that unrestricted water use conditions have not been established.

4.4.1.2 <u>Groundwater Contaminant Removal</u>

Data are summarized in Tables 4-5 (VOCs) and 4-6 (tritium), and figure 4-5 compares BSE and FSE VOCs concentrations at each of the groundwater sampling locations across the study area.

VOCs: Baseline Conditions. Well construction information and the observed minimal difference in measured water levels (less than 1.5 ft / 0.5 m) at project outset suggest that the five wells within, upgradient, and downgradient of the 317 FD are situated in the same water bearing unit (data not shown). As such, the differences in groundwater total VOC concentration across the 317 FD at baseline are thought to be attributable mainly to the VOC content of the soil surrounding each well. For example, the baseline level of TCE in ground water at 317322, 317332, 317342, and 317422 was 4.3, 0.38, 0.09, and <0.001 mg l^{-1} (non-detect), respectively. TCE in soil sampling locations adjacent to each well was 47, 1.5, 0.24, and <0.061 mg kg^{-1} (non-detect).

Well construction information and measured water levels of the five monitoring wells within and upgradient of the 317 HC suggest greater variability in aquifer physical characteristics. Well completion depths range from 27.6 ft / 8.4 m (317181) to 42.5 ft / 13 m (317172), and water levels were between 16.9 ft / 5.2 m (317151) and 30.8 ft / 9.4 m (317172). Baseline VOC concentrations also varied widely. Wells 317452 near the beginning of the HC plantation and 317221 near the end of the stand had low total VOCs levels of 0.0053 mg l^{-1} and 0.35 mg l^{-1}, respectively. In contrast, 317151 and 317181, both located in the center of the 317 HC, had much higher total VOC concentrations, 62 mg l^{-1} and 8.2 mg l^{-1}, respectively. In general, baseline total VOC levels in the vicinity of the 317 HC do not appear to be spatially correlated.

Information for the three monitoring locations within and upgradient of the 319 HC suggest that the wells may be located in two different water bearing units. Well 319261 appears to be screened in a shallower aquifer because its completion depth (17 ft / 5.2 m), which presumably represents the bottom of the formation, is above the water level of 319171 (26.8 ft / 8.2 m) and MW007 (22.9 ft / 7.0 m). Baseline concentration of total VOCs was low for all three wells, as expected, ranging from 0.28 mg l^{-1} (319171) to 0.010 mg l^{-1} (319261).

VOCs: Changes in Concentrations. A comparison of BSE and FSE data for the four monitoring locations within and downgradient of the 317 FD shows that the concentration of total VOCs increased in two wells (317322 and 317332) and decreased in two locations (317342 and 317432). The upgradient well that serves as a control (317422) remained constant at a non-detect level (<0.005), as anticipated. Table 4-7 shows mean water level data collected during the periods when groundwater wells were sampled by SITE. In general, changes in water column size are small and do not appear to have an impact on the interpretation of groundwater analyte data.

The increase in total VOCs in 317322 was attributable to a single compound, DCE. The other four target analytes exhibited moderate to strong declines ranging from 36% (DCA) to over 99% (TCA). There is geochemical and biological evidence that the decreases in these analytes were brought about microbially under sulfate-reducing conditions (turn to section 4.4.2.2). Such an environment is generally conducive to dechlorination of each of the target analytes. The increase in DCE is thought to stem from coincidental leaching from the surrounding soil matrix, which is known to contain substantial amounts of the analyte (data not shown). Aerobic conditions (>1.0 mg l^{-1}) were observed at 317332 during the study period (section 4.4.2.2). Aerobic conditions preclude the possibility of reductive dechlorination. Increases in concentration, possibly due to transport processes, were noted for each target analyte. The slight decrease in total VOCs observed at 317342 from 2.6 mg l^{-1} to 2.4 mg l^{-1} is probably an artifact of analytical variability. The decline in total VOC levels at 317432 (0.31 mg l^{-1} to 0.12 mg l^{-1}) involves comparatively minor pollutant levels; however, the decrease between the BSE and FSE sampling events (61%) is significant (α = 0.10) when evaluated by single factor analysis of variance (ANOVA), where n=6 for each data set (means only shown in Table 4-5). The underlying attenuation mechanisms are

Table 4-5. Mean Target VOC Concentration in Ground water (mg l^{-1})

				Above 317 FD			**West of 317 HC**					
				317422			317172					
Analyte				BSE	MSE	FSE	BSE	MSE	FSE			
TCA				<0.001	<0.001	<0.001	0.004	<0.001	<0.001			
DCA				<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
CLF				<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
DCE				<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
TCE				<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
Total				<0.005	<0.005	<0.005	0.008	<0.005	<0.005			
Within and below 317 FD												
	317322			317332			317342			317432		
Analyte	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE
TCA	8.3	0.68	0.030	3.7	4.8	13	1.9	1.9	1.5	0.18	0.073	0.065
DCA	3.7	3.1	2.4	1.3	2.6	2.8	0.57	0.90	0.77	0.13	0.060	0.049
CLF	12	12	2.0	0.0093	0.0076	0.028	0.0091	0.0030	0.0026	<0.001	<0.001	<0.001
DCE	6.4	15	42	1.2	1.4	2.0	0.074	0.052	0.083	<0.001	<0.001	<0.001
TCE	4.3	5.3	2.1	0.38	0.40	0.76	0.090	0.058	0.069	<0.001	<0.001	<0.001
Total	34	36	49	6.6	9.2	19	2.6	2.9	2.4	0.31	0.14	0.12
Within 317 HC												
	317151			317181			317221			317452		
Analyte	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE
TCA	48	15	19	5.3	3.6	5.6	0.11	0.37	0.73	<0.001	<0.001	<0.001
DCA	9.9	1.6	3.8	2.5	2.3	3.8	0.22	0.56	0.36	0.0013	0.0038	<0.001
CLF	0.32	0.052	0.21	0.020	0.014	0.048	0.0011	0.003	0.0087	<0.001	<0.001	<0.001
DCE	0.61	0.098	0.17	0.11	0.042	0.39	0.0041	0.0067	0.015	<0.001	<0.001	<0.001
TCE	2.9	2.1	1.6	0.27	0.43	0.72	0.012	0.0054	0.13	<0.001	<0.001	<0.001
Total	62	19	25	8.2	6.4	11	0.35	0.99	1.2	0.0053	0.0078	<0.005
Above and within 319 HC												
				MW007			319171			319261		
Analyte				BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE
TCA				0.015	0.011	0.015	0.24	0.28	0.18	0.0056	0.0058	0.0081
DCA				0.0014	0.0022	0.0011	0.036	0.040	0.015	<0.001	0.0014	0.0013
CLF				<0.001	<0.001	<0.001	0.0017	0.0014	<0.001	<0.001	<0.001	<0.001
DCE				<0.001	<0.001	<0.001	0.0015	0.0016	0.0011	<0.001	<0.001	<0.001
TCE				<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Total				0.019	0.016	0.019	0.28	0.32	0.19	0.010	0.010	0.012

Table 4-6. Mean Tritium Concentration in Ground water (pCi l^{-1})

Well	BSE	MSE	FSE
	Within 319 HC		
319171	10,400	6,600	2,600
319261	3,700	2,000	1,200
Average	7,000	4,300	1,900
	Upgradient 319 HC		
MW007	3,000	2,200	3,100

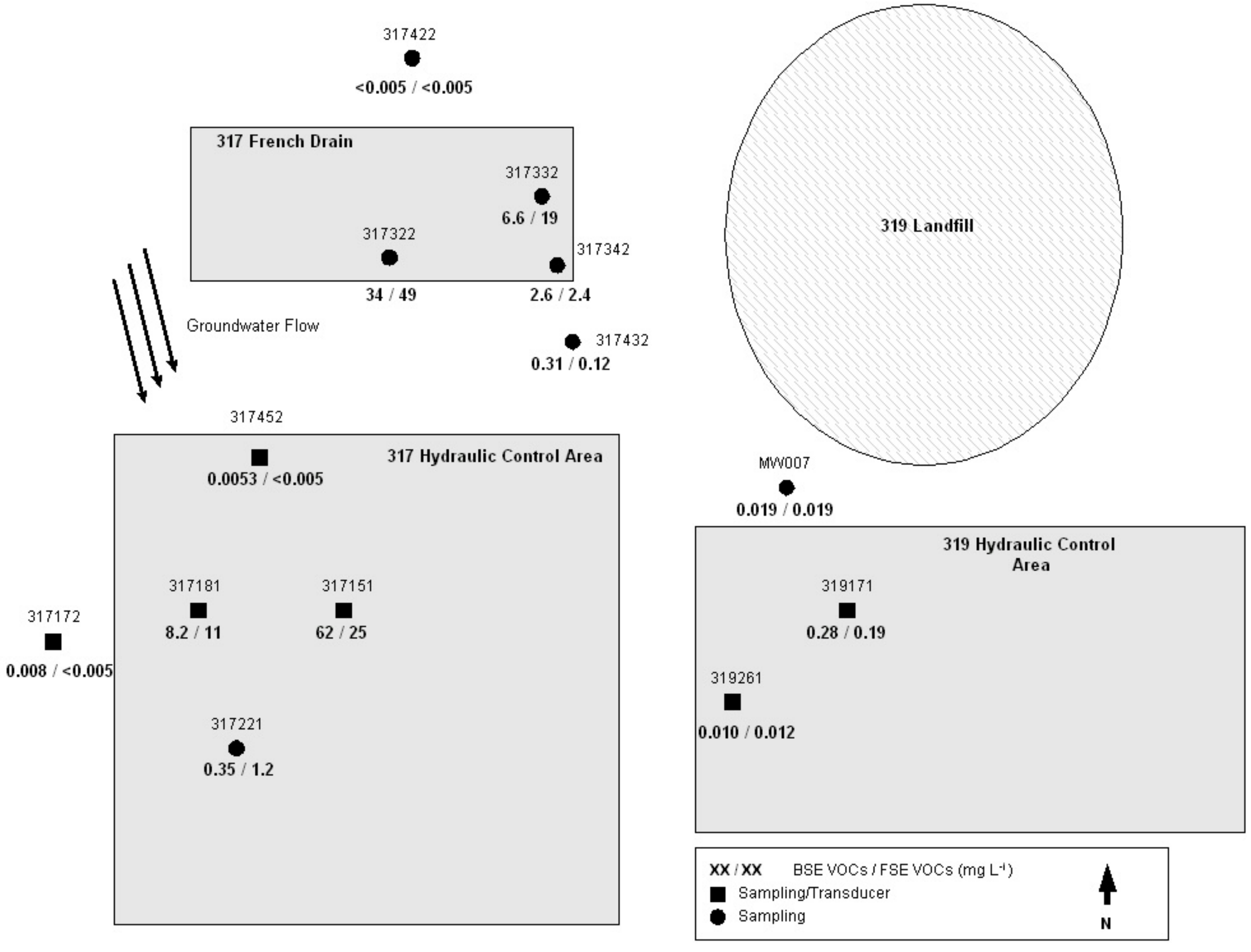

Figure 4-5. Baseline and Final Concentration of Target VOCs

Table 4-7. Water Column Sizes for Sampled Monitoring Wells

Well No.	Well Depth, BTOC (ft)	Avg BSE Water Table, BTOC (ft)	BSE Water Column, (ft)	Avg MSE Water Table, BTOC (ft)	FSE Water Column, (ft)	Avg FSE Water Table, BTOC (ft)	FSE Water Column, (ft)	% Change
317 French Drain								
317322	30.3	20.2	10.1	21.0	9.3	20.1	10.2	1%
317332	36.4	20.2	16.2	22.3	14.1	16.9	19.5	20%
317342	37.9	21.6	16.3	24.0	13.9	19.8	18.1	11%
317432	37.9	20.5	17.4	23.1	14.8	19.4	18.5	6%
317 Hydraulic Control								
317151	31.7	16.9	14.8	18.3	13.4	18.1	13.6	-8%
317181	27.6	19.7	7.9	20.9	6.7	19.3	8.3	5%
317221	36.8	29.3	7.5	29.8	7.0	28.6	8.2	10%
317452	37.0	20.2	16.8		37.0	19.1	17.9	7%
319 Hydraulic Control								
MW007	34.8	22.9	11.9		34.8	23.9	10.9	-8%
319171	28.3	26.8	1.5	27.8	0.5	26.6	1.7	13%
319261	17.0	15.9	1.1	15.1	1.9	13.7	3.3	200%
Above 317 FD and West of 317 HC								
317422	36.9	20.2	16.7		36.9	19.1	17.8	7%
317172	42.5	30.8	11.7		42.5	28.0	14.5	24%

not known specifically, but geochemical and biological indices imply that the analytes may be undergoing dechlorination under weak reducing conditions. Overall, the concentration of total VOCs at monitoring locations within the 317 FD still appears at this stage to be influenced primarily by the elevated analyte levels in the surrounding soils.

Data from monitoring wells within the 317 HC also indicate mixed performance. Locations 317181 and 317221 demonstrate small magnitude gains in all or most individual compounds culminating in significant ($\alpha = 0.10$) total VOC increases of 34% and 240%, respectively. In contrast, 317151 exhibits decreases in all analyte levels with a significant ($\alpha = 0.10$) drop (60%) in total VOCs from 62 mg l^{-1} to 25 mg l^{-1}, although the nature of the attenuation mechanism(s) is unclear. Control well 317172 located upgradient (to the west) of the 317 HC maintained near non-detect VOC levels throughout the demonstration, as anticipated. Location 317452 also maintained near non-detect VOC concentrations. Its placement within the 317 HC in relation to the general direction of groundwater flow makes it likely to receive water from a relatively clean source.

In the 319 HC, the concentration of total VOCs in the upgradient well MW007 was unchanged (0.019 mg l^{-1}), as expected. Well 319171 exhibits small declines in each of the target analytes detected combining for a modest drop (32%) in total VOCs from 0.28 mg l^{-1} to 0.19 mg l^{-1}. The attenuation mechanisms are unclear; the geochemical and biological parameters point to the presence of both aerobic and anaerobic conditions (turn to section 4.4.2.2). At 319261 small increases in the analytes detected result in a 20% gain, from 0.010 mg l^{-1} to 0.012 mg l^{-1}. It is suspected that a portion of the difference in baseline/final analyte concentrations at these two monitoring locations can be explained by normal analytical variability.

VOCs: Evaluation of the Project Objective. To evaluate the project objective, SITE examined BSE and FSE data from seven monitoring wells across the 317 FD and HC: 317151, 317181, 317221, 317322, 317332, 317342, and 317432.

Collectively the mean concentration of target VOCs changed only slightly between the BSE (16.3 mg l^{-1}) and FSE (15.2 mg l^{-1}). A statistical test of hypothesis ($\alpha = 0.10$) showed that the suggested SITE reduction target (95%) for the 317 Area ground water was not yet achieved.

Tritium: Evaluation of the Project Objective. To evaluate the project objective, SITE examined BSE and FSE data from the two monitoring wells within the 319 HC, 319171 and 319261. Collectively, the mean concentration of tritium decreased from 7,000 to 1,900 pCi l^{-1}, a 73% reduction. The results were evaluated using a statistical test of hypothesis ($\alpha = 0.10$) that concluded the suggested SITE reduction target (95%) for the 319 HC ground water was not yet achieved.

The mean BSE and FSE data combined with the elapsed time between sampling events (1022 days) yield a tritium half-life of 540 days, according to the following relationship:

$$T_{½} = -0.693\ t / \ln (A_f / A_b) \qquad \textbf{(Eqn. 4-4)}$$

where $T_{½}$ is the half-life (days), t is the elapsed time (days) between activity measurements, A_b is the baseline activity, and A_f is the final activity. When the data sets from 319171 and 318261 are investigated separately, both produce similar half-lives of 510 and 620 days, respectively. These are periods much shorter than the commonly-held standard for tritium of approximately 12.3 years or 4,500 days (Merck, 1989). In contrast, a single check sample (3,100 pCi l^{-1}) collected from MW007, a control well located upgradient of the 319 HC, exhibited essentially no change from the baseline mean (3,000 pCi l^{-1}). These results suggest that tritium is being removed from the system in addition to decreasing by natural decay.

4.4.1.3 Soil Contaminant Removal

Baseline Conditions. Figure 4-6 shows baseline and final TCE concentrations in a way that approximates the layout of the soil bore locations within the 317 FD. For example, SB#01 was physically located near the northwest corner of the 317 FD, and SB#28 was located in the southwest corner. The 317 FD Control Plot (317 FDCP) is a small (unplanted) parcel located just above the northwest corner of the 317 FD. Inspection of figure 4-6 provides the following observations:

- Most TCE detections reside along the borders of the 317 FD from the northwest corner down along the western edge and then across the southern border to the southeast corner.
- The area of heaviest contamination is along a large portion of the southern border, particularly within the subsurface interval from 8 ft to 16 ft (2.4 m - 4.9 m).
- With the exception of some scattered detections, the northern and eastern borders and the central portion of the 317 FD are mostly free of quantifiable amounts of TCE.

Evaluation of the Project Objective. Originally, reductions in TCE soil concentrations were to be evaluated within the context of root density measurements. At the outset of the project it was surmised that meaningful reductions in TCE would be observed only where roots had developed to an extent where (1) roots could contact and uptake TCE entrained in soil-pore water, or (2) conditions for rhizodegradation could be established. However, over the course of the demonstration period, no reliable, standardized procedure could be identified for collecting root density samples at depths to 16 ft (4.9 m) bgs. Therefore, the evaluation of soil contaminant removal, as originally envisioned, could not be performed. Nonetheless, SITE collected FSE samples in order to document changes, if any, in soil TCE concen tration. Results show that the mean concentration of TCE increased 23% between the BSE (3.4 mg kg^{-1}) and FSE (4.2 mg kg^{-1}).

A similar evaluation (non-primary) was performed on PCE, a TCE precursor. Analytical results also demonstrate little movement, with mean baseline and final concentrations of 5.4 and 5.5 mg kg^{-1}, respectively (data not shown).

Control Plot

	SB#29		SB#30	
	BSE	FSE	BSE	FSE
4ft-8ft	56	56	63	56
8ft-12ft	59	59	59	58
12ft-16ft	59	59	61	58

317 Area French Drain

	SB#01		SB#02		SB#03		SB#04		SB#05	
	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE
4ft-8ft	**540**	**360**	**800**	63	58	69	**110**	57	59	55
8ft-12ft	**630**	**1,400**	**4,000**	63	64	58	56	58	64	57
12ft-16ft	**130**	**270**	**12,000**	**77**	61	57	62	61	62	58

	SB#06		SB#07		SB#08		SB#09		SB#10	
	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE
4ft-8ft	**8,600**	**12,000**	63	61	62	61	65	56	59	58
8ft-12ft	**11,000**	**7,500**	61	**4,500**	64	61	66	58	57	56
12ft-16ft	**3,000**	**6,200**	61	**4,200**	66	62	66	65	61	66

	SB#11		SB#12		SB#13		SB#14		SB#15		SB#16	
	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE
4ft-8ft	**110**	**790**	**200**	32	60	63	60	62	**75**	59	58	58
8ft-12ft	**370**	**720**	**1,900**	14	63	63	60	57	59	64	57	59
12ft-16ft	**65**	**360**	**5,400**	**3,100**	**1,100**	**3,800**	**450**	**210**	50	57	**1,500**	**770**

	SB#17		SB#18		SB#19		SB#20		SB#21		SB#22	
	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE
4ft-8ft	**140**	**430**	51	61	50	62	61	63	68	62	58	57
8ft-12ft	**420**	**680**	**73**	**99**	50	57	62	64	60	55	**2,200**	62
12ft-16ft	**120**	**190**	50	4	48	57	**71**	64	59	59	**4,800**	**2,000**

	SB#23		SB#24		SB#25		SB#26		SB#27		SB#28	
	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE	BSE	FSE
4ft-8ft	**3,500**	**2,400**	65	**420**	**18,000**	**840**	**7,000**	**72,000**	**1,300**	**2,600**	**570**	**590**
8ft-12ft	**2,800**	**590**	59	**61,000**	**25,000**	**810**	**40,000**	**60,000**	**21,000**	**17,000**	**620**	**4,000**
12ft-16ft	**2,100**	**3,300**	61	**50,000**	**22,000**	**530**	**47,000**	**20,000**	**31,000**	**6,600**	**240**	59

Units in ug kg^{-1} Figures in bold type are above reporting limit

Figure 4-6. Mean TCE Concentration in 317 French Drain

Nonparametric Test of TCE and PCE Soil Results. The findings of parametric statistical analysis of the results can be influenced by erratic or inhomogeneous measurements. The 317FD TCE and PCE soil measurements for both baseline and final assessment show a relatively large proportion of nondetections together with a relatively small number of measurements at large concentrations. In the parametric statistical analysis, these large measurements can have large effect on sample mean values and standard errors.

A nonparametric, descriptive assessment of the TCE and PCE demonstration measurements is presented. This nonparametric assessment cannot be unduly dominated by a small set of large values. However, it is not a useful approach to estimate the percentage magnitude of pollutant reduction.

For this assessment, samples are paired uniquely across the BSE and FSE episodes by soil bore location and subsurface interval. If both members of the pair are nondetect, then the given sample pair exhibits "no change"; the sample pair exhibits an "increase" if the pollution concentration is larger at the FSE than the BSE; and otherwise, the pair exhibits a "decrease." The respective pair sample counts are displayed in Table 4-8.

For TCE, 37 of the 84 sample pairs showed no change, and there were 23 pairs with an increase in pollutant concentrations and 24 with a decrease. For TCE, these results provide no indication that there is a positive removal on a sample pair basis.

For the 84 PCE measurements, 18 showed no change, 24 showed an increase, and 42 or half the measurements indicated a decrease (data not shown). This lends, at best, a marginal showing that the technology demonstrates a trend of positive removal on an individual sample pair bases, irrespective of the absolute or percentage magnitude of the removals.

Table 4-8. Comparison of Baseline and Final Sample Pairs for French Drain Soils

Sample Count	PCE	TCE
Number sample pairs with no change	18	37
Number of sample pairs with increase	24	23
Number of sample pairs with decrease	42	24
Total number of sample pairs	84	84

4.4.2 Non-primary Objectives

4.4.2.1 <u>Contaminant Uptake and Degradation in Plant Tissue</u>

Plant tissue analyzed for VOCs and their degradation product TCAA show that the willows at the 317 FD started in the 1999 growing season to take up and degrade these contaminants, and continued throughout the three growing seasons at rates that were very specific to each tree analyzed (data not shown). In general, the levels of contaminants and TCAA were consistently and significantly higher than background (as measured in the control trees) in the trees growing at the 317 FD. TCE and PCE were found rarely in the leaf tissue, but consistently in the branch tissue. TCAA in contrast, was found exclusively and consistently in leaf tissue, where it accumulated throughout the summer, typically peaking late in the season, and then reverting to background levels in dead leaves approximately three months from their abscission from the tree. These observations support the hypothesis that contaminants are transported with the ascending sap to the leaves, where they are degraded to TCAA and subsequently mineralized.

TCE concentrations in branches varied between non-detect and 301 $\mu g\ g^{-1}$ on a dry weight basis. PCE also varied significantly, between non-detect and 600 $\mu g\ g^{-1}$. TCAA was found in the large majority of leaf samples from the contaminated area. For a number of trees a strong, positive correlation was found between TCAA levels in the leaves and TCE and/or PCE in the corresponding branches at least for subsets of time. Many of these trees were spatially related. A few trees showed relatively elevated levels of TCAA, but quite lower levels of parent compounds, and no correlation between them. This points, among other hypotheses, to the potential presence of other contaminants in the soil that are not currently monitored but could degrade to TCAA.

The importance of understanding the kinetics of TCE/PCE metabolism and the quantitative correlation between the TCAA and the parent compounds is fundamental to a correct prediction of contaminant uptake and degradation. However, while the data obtained so far clearly confirm plant uptake and at least partial degradation of the contaminants, more work is needed to determine sufficiently accurate removal rates, and the relationship between kinetics of TCAA formation and further degradation and environmental conditions such as radiant energy, ambient temperature, relative humidity, stomatal conditions, sap velocity, and general plant metabolic rates. For the time being, it is prudent to state that the willows in the 317 FD area are exerting a positive effect on contaminant removal. This effect is expected to be quantitatively more significant as the amounts of contaminated soil-pore water that is taken up and processed by the plants increases with plant size.

4.4.2.2 <u>Geochemical and Microbial Indices of Reductive Dechlorination</u>

Ground water. SITE used geochemical data as indicators of terminal electron acceptor processes occurring in ground water across the study area. The electron acceptor data includes DO, manganese, nitrate, ferric iron, and sulfate. Other measurements such as ORP, specific conductance, pH, and TOC provide additional information concerning biodegradation processes and changes in water chemistry associated with site hydrology. The results are summarized in Table 4-9; Table 4-10 and Figure 4-7 (both adapted from EPA, 1998 and Byl and Williams, 1999) were used in the interpretation of the data. It should be stressed that the criteria contained in table 4-9 and figure 4-7 should be viewed as general guidelines.

317 FD. Because the overall direction of groundwater flow and the general extent of the contaminant plume are known, an attempt was made to identify discrete redox zones along the flow path of the aquifer of interest. The delineation of redox zones, supplemented by analyte chemistry data, was used to infer which VOC reduction process, if any, prevailed along the plume.

Conditions in control well 317422 were aerobic during the study period with moderate levels of DO (2.0 to 2.5 mg l^{-1}) and a positive ORP (4 to 67 mV). Since it is located upgradient of the source area, 317422 contained no detectable levels of the target analytes, as anticipated. The wells located along the flow path downgradient of 317422, sequentially 317332, 317342, and 317432, contained progressively lesser concentrations of DO (1.7 to 0.64 mg l^{-1}, FSE) and total VOCs (19 to 0.12 mg l^{-1}, FSE). ORP measurements between locations fluctuated during the study period, but were within the range of possible reducing mechanisms. The following conclusions can be drawn about the downgradient wells:

- 317332 was consistently aerobic with DO levels above 1.0 mg l^{-1}. Aerobic conditions preclude reductive dechlorination from occurring since oxygen is the preferred electron acceptor. The concentration of total VOCs increased over time, conceivably due to transport from the surrounding soil matrix.
- With DO levels below 1 mg l^{-1}, an ORP between 110 and 130 mV, and a low concentration of nitrate (<0.2 mg l^{-1}), mildly reducing conditions (e.g., nitrate reducing) may be present at 317342. Changes in VOCs were slight, but the movement is consistent with mild reducing conditions in that the concentration of more oxidized species (TCE, TCA, and CLF) decreased, while less oxidized species (DCE, DCA) accumulated.
- As the flow path proceeds downgradient to 317432, the concentration and trend of electron acceptors imply that nitrate reducing conditions may be present. However, the decrease and disappearance of DCA and DCE suggest that other attenuation mechanisms are also acting upon the contaminant plume.

Table 4-9. Mean Groundwater Geochemical Results

	Upgradient 317 FD			**West of 317 HC**		
	317422			317172		
Parameter	BSE	MSE	FSE	BSE	MSE	FSE
DO (mg l^{-1})	2.24	--	--	0.73	--	--
NO_3 (mg l^{-1})	0.163	--	--	0.206	--	--
Fe^{2+} (mg l^{-1})	<0.1	--	--	0.5	--	--
SO_4 (mg l^{-1})	68.4	--	--	94	--	--
Mn (mg l^{-1})	0.13	--	--	0.053	--	--
TOC (mg l^{-1})	<5	--	--	<5	--	--
ORP (mV)	7	--	67	-68	--	-41
S. Cond. (uS cm^{-1})	1200	--	1600	1200	--	1000
pH	6.9	--	6.4	7	--	6.2

Within and downgradient 317 FD

	317322			317332			317342			317432		
	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE
DO	0.90	0.67	0.61	1.8	2.8	1.7	0.57	0.75	0.95	0.52	5.9	0.64
NO_3	0.29	--	<1	--	--	<0.2	--	--	<0.2	0.588	--	<0.2
Fe^{2+}	3.2	--	6.1	--	--	--	--	--	--	<0.1	--	<0.1
SO_4	16	--	2.5	--	--	55	--	--	71	102	--	90
Mn	0.9	--	0.32	--	--	--	--	--	--	0.11	--	0.1
TOC	18	--	41	--	--	4	--	--	3	<5	--	2.1
ORP	-120	--	-410	-43	-18	-3	110	89	130	28	137	74
S. Cond.	2100	2100	2100	1100	1300	1400	1100	1300	1300	1100	1300	1100
pH	7	6.9	7.1	6.9	6.9	6.7	6.9	6.8	6.6	6.9	6.9	6.7

Within 317 HC

	317151			317181			317221			317452		
	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE
DO	0.99	1.22	0.48	0.8	0.58	0.54	--	--	0.46	0.73	--	0.34
NO_3	0.0436	--	1.6	--	--	<0.2	--	--	<0.2	0.298	--	--
Fe^{2+}	<0.1	--	0.2	--	--	--	--	--	--	--	--	--
SO_4	74.9	--	81	--	--	170	--	--	120	80.8	--	--
Mn	0.093	--	0.038	--	--	--	--	--	--	--	--	--
TOC	<5	--	3.3	--	--	3	--	--	2.7	<5	--	--
ORP	100	64	45	-0.9	-7	-21	--	--	-22	-52	--	-36
S. Cond.	1100	1100	890	1300	1300	1300	--	--	940	1100	--	1000
pH	6.9	6.9	6.5	7	6.9	6.5	--	--	6.6	6.9	--	6.8

Upgradient and within 319 HC

	MW007			319171			319261		
	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE
DO	0.51	--	16.4	--	--	--	--	--	--
NO_3	<1	--	--	0.647	--	1.4	0.147	--	0.35

Fe^{2+}	<0.1	--	--	<0.1	--	4.8	<0.1	--	2.1
SO_4	113	--	--	129	--	110	223	--	130
Mn	0.11	--	--	0.046	--	0.2	0.61	--	0.16
TOC	<5	--	--	<5	--	3.4	<5	--	3.9
ORP	-150	--	150	--	--	--	--	--	--
S. Cond.	1100	--	880	--	--	--	--	--	--
pH	6.9	--	6.9	--	--	--	--	--	--

– Data not collected

Table 4-10. Geochemical Indicator Traits

Analyte	Concentration	Interpretation
Dissolved Oxygen	$\leq$1.0 mg l^{-1}	If DO is greater than 1.0 mg l^{-1} (aerobic conditions) reductive dechlorination unlikely; however, cometabolism and direct oxidation are possible.
Nitrate	<1 mg l^{-1}	At higher concentrations, may compete with reductive pathway. Reductive dechlorination of PCE and TCE can occur under these mildly reducing conditions; direct oxidation is also possible.
Soluble manganese (Mn^{2+}) and ferrous iron (Fe^{2+})	Increasing concentrations	Increased concentrations of Mn^{2+} and Fe^{2+} coinciding with low DO levels are indicators that insoluble Mn^{4+} and Fe^{3+} are serving as electron acceptors. Reductive dechlorination of PCE and TCE possible under these mildly reducing conditions.
Sulfate	<20 mg l^{-1}	At higher concentrations, may compete with reductive pathway; however, plumes with high sulfate levels can still support reductive dechlorination. Reductive dechlorination of DCE occurs under these stronger reducing conditions.
TOC	>20 mg l^{-1}	Carbon/energy source, drives dechlorination
Oxidation Reduction Potential (ORP)	<100 mV	Reductive dechlorination possible for highly chlorinated, electron poor compounds under mild reducing conditions (manganese, nitrate, iron); dechlorination of lesser chlorinated compounds requires stronger reducing conditions (sulfate, methanogenesis).
Specific Conductance	Above background	Increase in ionic activity, possibly due to analyte degradation
pH	5<pH<9	Optimal range for reductive pathway.

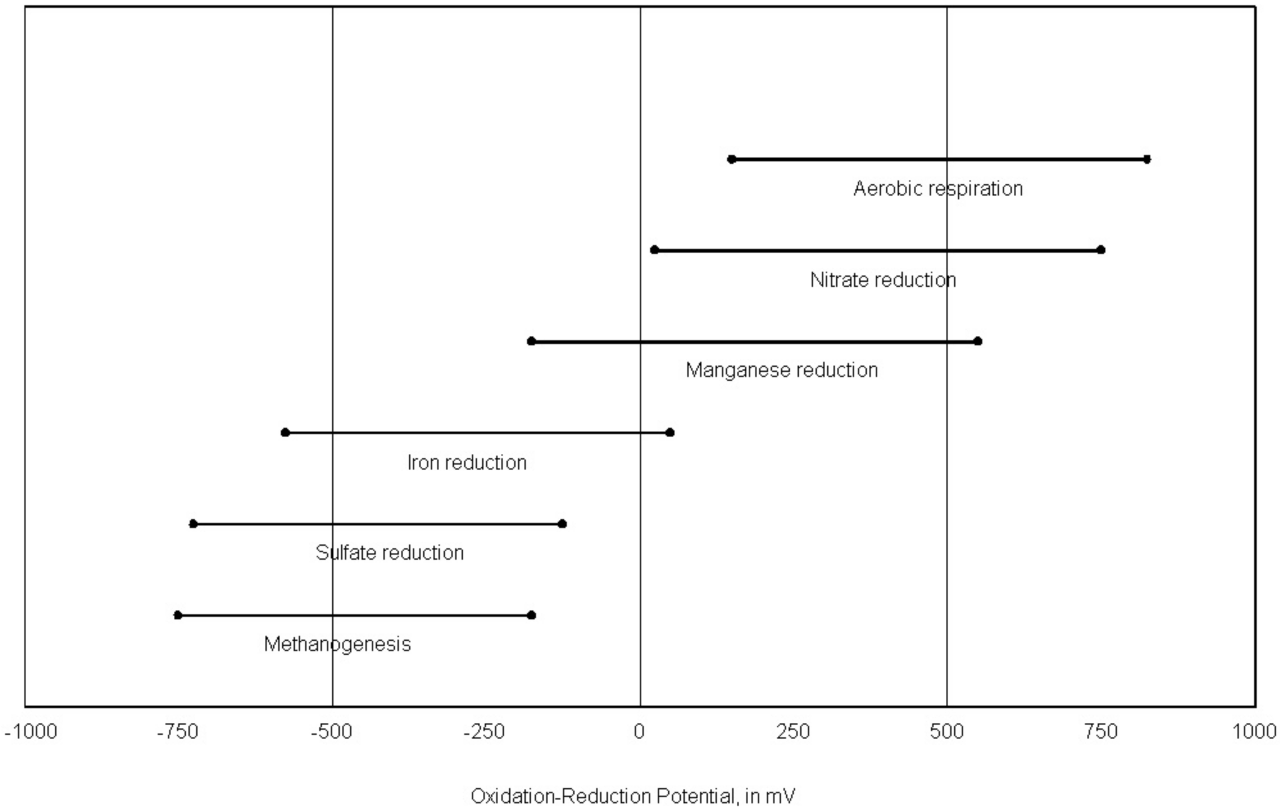

Figure 4-7. ORP Ranges for Various Biochemical Reducing Conditions

- The influence of the planted system on ground water within this group of wells is uncertain. The conditions at each well were largely present at baseline and have not changed appreciably.

Well 317322 is centrally located near the southern edge of the 317 FD. The concentration and trend of electron acceptors were within ranges normally associated with iron or possibly sulfate-reducing conditions. Conditions were strongly anaerobic at baseline and have become even more so during the study period possibly as a consequence of rhizospheric activity, which is expected to have such an effect. It is located in an area with some of the heaviest contamination, which may have helped initiate and promote anaerobic metabolism earlier than other areas. Concentrations for four of the five individual target analytes in samples collected from 317322 decreased over time, including TCA (99.6%), CLF (83%), TCE (52%) and DCA (36%). DCE increased sharply from 6.4 to 42 mg l^{-1}; however, given the presence of strong reducing conditions capable of supporting dechlorination of DCE, it is suspected that the increased DCE is principally the result of transport from the surrounding soil matrix.

317 HC. The monitoring wells within and upgradient of the 317 HC exhibit similar geochemical features. For the most part they are characterized by low DO (0.34 to 0.73 mg l^{-1}), low nitrate (0.30 to <0.20 mg l^{-1}), high sulfate concentrations (81 to 170 mg l^{-1}), a moderately low ORP (45 to -41 mV), and similar specific conductance (890 to 1300 uS/cm). These indices suggest that the environment within this group of wells lies somewhere between nitrate- and iron-reducing conditions. However, the analyte data do not confirm this observation. VOC concentration increases were noted for each analyte over the course of the study period in 317181 and 317221. This includes TCE and TCA, which are normally susceptible to reductive dechlorination under nitrate and iron-reducing conditions. It may be that the absence of dechlorination is a reflection of the lack of TOC to participate in the redox reaction. Well 317151 displayed the opposite performance, with sharp declines in all analytes including DCE (72%) and DCA (62%), compounds which typically require much stronger reducing conditions. Localized dilution does not appear to play a role in the decreases since the water level dropped by 1.2 ft (0.4 m) between the BSE and FSE. The location of the dechlorination process is not clear, but it is possible that the degradation by products were formed near the southern edge of the 317 FD where strong reducing conditions have been observed and transported downgradient to 317151.

319 HC. Well MW007, upgradient of the 319 HC, switched from anaerobic to aerobic conditions during the course of the demonstration, with an increase in DO (0.51 to >1.0 mg l^{-1}) and ORP (-150 to 150 mV). There was no change in the level of total VOCs (0.019 mg l^{-1}). Well 319171, within the 319 HC, exhibits a dual nature. An increase in NO_3^- suggests that the environment is moving away from reducing conditions, while increased concentrations of Mn (0.046 to 0.2 mg l^{-1}) and Fe^{2+} (<0.1 to 4.8 mg l^{-1}) and a decreasing concentration of SO_4^{2-} (130 to 110 mg l^{-1}) are indicative of a reducing environment. (DO data are not available for this monitoring location). The concentration of each detected target VOC (TCE not detected) declined over time with a combined decrease of 32% (0.28 to 0.19 mg l^{-1}).

Product/Byproduct Ratios. Throughout the 317/319 study area decreasing ratios of parent compounds to daughter byproducts offer other indications of where reductive dechlorination is occurring. Under reducing conditions compounds such as TCE and TCA degrade more readily than their respective byproducts DCE and DCA, which results in decreasing ratios of TCE/DCE and TCA/DCA. In several cases increases in DCE and DCA were accompanied by increases in TCE and TCA. These movements are more likely the consequence of transport processes and not reductive dechlorination. Table 4-11 summarizes the results across the study area where decreases in TCE and TCA have occurred. Consistent, decreasing ratios are seen at locations were reducing conditions are suspected (317322 and 317342). Where conditions are less apparent (317432, 317151, 319171), ratios are either unchanged or increasing.

Biological Indicators**.** The geochemical information helps determine if conditions are suitable for biodegradation. Bacterial identification and quantification strengthens the interpretation of the geochemical data.

Analysis of PLFA has been demonstrated useful in providing information on the amount and types of bacteria present in a system and how they are reacting to environmental factors (White et al., 1997). Specifically, PLFA gives quantitative insight into two main areas of microbial communities: viable biomass and community structure. Phospholipid fatty acids are found in the membranes of all living cells, but decompose rapidly upon cell death through enzymatic hydrolysis. Thus, measuring the total PLFA content provides a gauge of viable microbial biomass. Categorizing and quantifying the different fatty acid species creates profiles that can be used to distinguish the community composition among different samples.

PLFA results are summarized in Table 4-12. Overall, the lab reported that the concentration of biomass was much lower than that found in soil, with a median concentration of 0.4 pmol PLFA ml^{-1} water versus 145 pmol PLFA g^{-1} soil. There were notable differences among the fatty acid profiles in groundwater samples, although most contained moderately diverse community structures (data not shown). In general, the lipid makeup of groundwater samples was more varied and different than soil samples, even for water samples collected near soil bores. For example, the community structure of well 317342 did not correspond to the community structure of the soil sample SB28; the same is true for 317332 and SB16 and 317322 and SB26. These differences are expected to diminish over time as the plantations mature and exert a dominant influence within the subsurface environment.

Within the 317 HC, well 317322 showed a substantial increase (32%) in gram-negative monoenoic bacteria. These bacteria are of particular interest due to their ability to use a wide range of carbon sources and adapt quickly to environmental conditions. Biomarkers for obligate iron and sulfate-reducing anaerobic bacteria, absent at baseline, were detected (1.9% of PLFA) in a sample collected during the FSE. The implication is that groundwater in the vicinity of

Table 4-11. Groundwater Product / Byproduct Ratios

	Within and below 317 FD								
	317322			317342			317432		
Analytes	BSE	MSE	FSE	BSE	MSE	FSE	BSE	MSE	FSE
TCA/DCA	2.3	0.2	0.01	2.9	1.8	4.7	3.2	2.1	1.9
TCE/DCE	0.7	0.4	0.05	0.3	0.3	0.4	N/C	N/C	N/C

	Within 317 HC		
	317151		
Analytes	BSE	MSE	FSE
TCA/DCA	4.8	9.4	5.0
TCE/DCE	4.7	21.4	9.0

	Within 319 HC		
	319171		
Analytes	BSE	MSE	FSE
TCA/DCA	6.6	7.0	12
TCE/DCE	N/C	N/C	N/C

N/C= Not calculable

Table 4-12. Selected Groundwater PLFA Results

	% of Total PLFA								pmol PLFA ml^{-1}	
Well No.	Monoenoic, Gram-negative bacteria		Obligate anaerobes: Iron reducers and Desulfovibrio-like sulfate reducers		Desulfobacter-like sulfate reducers and facultative anaerobes: 10me16:0		Actinomycetes (obligate and facultative aerobes): 10me18:0		Bacterial Biomass	
	Baseline	Final	Baseline	Final	Baseline	Final	Baseline	Final	Baseline	Final
	Upgradient, within, and downgradient of 317 FD									
317322	46.0	60.7	0.0	**1.9**	1.8	1.2	0.1	0.0	**18**	7
317332	---	40.2	---	0.0	---	6.4	---	0.0	---	0.4
317342	---	69.8	---	0.0	---	1.2	---	0.0	---	0.4
317422	29.9	Lost	0.0	Lost	1.7	Lost	1.3	Lost	1	Lost
317432	43.0	24.8	0.0	0.0	0.0	0.0	0.0	0.0	0.2	**0.3**
	Upgradient and within 317 HC									
317151	Lost	42.7	Lost	0.0	Lost	3.1	Lost	0.0	Lost	0.4
317172	21.0	---	0.0	---	1.3	---	1.2	---	1	---
317181	---	48.2	---	0.0	---	3.4	---	0.0	---	0.2
317221	---	87.6	---	0.0	---	0.0	---	0.0	---	0.6
317452	54.7	---	0.0	---	4.2	---	0.0	---	4	---
	Upgradient and within 319 HC									
319171	43.0	**78.8**	0.0	**0.4**	**3.5**	0.1	2.0	0.1	4	**107**
319261	**59.9**	24.1	0.0	**0.6**	**1.7**	0.3	0.3	0.3	15	**35**
MW007	40.7	---	0.0	---	0.0	---	0.0	---	1	---

Bold values under Final column represent increases of 50% or more over Baseline; bold values under Baseline column indicate sampling points were Final values declined 50% or more.

– Data not collected

317322 is shifting in nature from aerobic to anaerobic. There was a decrease in the fatty acid indicator for the Desulfobacter-like sulfate reducing bacteria, which suggests that the *Desulfobacterium sp.* may not be primarily responsible for reductive dechlorination. The decrease in total biomass (18 to 7 pmol ml^{-1}) is not unexpected since it is well known that anaerobic metabolism is generally less efficient and therefore produces less biomass than aerobic metabolism. These data corroborate the general perception that conditions at 317322 are strongly anaerobic and can support bacteria capable of dechlorinating all of the target VOCs.

Within the 319 HC, well 319171 showed a substantial increase (83%) in gram-negative monoenoic bacteria. This was accompanied by an increase of more than 25-fold in total biomass (4 to 107 pmol ml^{-1}). Given the relatively low level of available food as measured by TOC (3.4 mg l^{-1}), the large build-up of bacteria and biomass suggest the presence of aerobic respiration since it is much more growth-efficient (capable of growing larger on a given measure of food) than anaerobic metabolism. However, the development of iron and sulfate-reducing anaerobic bacteria during the same period implies a trend toward anaerobiosis. Thus 319171 exhibits both aerobic and anaerobic traits, a conclusion in agreement with the trends of the geochemical data for this location.

Soil. Geochemical data were used as indicators of the capability of the soil within the 317 FD to support a reducing environment. Data includes surveillance of terminal electron acceptors (manganese and iron) and available food sources (TOC). It is assumed that a portion of the manganese and iron are in insoluble forms (Mn^{4+} and Fe^{3+}) and that anaerobic conditions will favor the bacterial reduction of these oxidized metals into more soluble (reduced) species(Mn^{2+} and Fe^{2+}) with an accompanying decrease in the soil-bound concentration of total manganese and iron. The level of TOC is expected to increase in response to expression of root exudates and decaying root matter.

The data are summarized in Figure 4–8, which is a simplified representation of the 317 FD and FDCP, and Table 4-13. Across the study area, there were measurable but insignificant changes in the concentration of iron and manganese. There was a large increase of nearly 8-fold in the average concentration of TOC (2,700 to 21,000 mg kg^{-1}). Increases were observed at all sampling locations across the 317 FD and viewed initially as a natural response to root growth and influence permeating the soil volume. However, this interpretation is less certain since the (unplanted) 317 FDCP also exhibited a similar growth in TOC.

It was noted earlier that the areas of heaviest contamination occur along the western and southern borders of the 317 FD. Soil bores SB06, SB24, and SB26 lie along these borders. These locations exhibited decreases in manganese and iron and increases in TOC well above either the site-wide average or that observed in the 317 FDCP. It is suspected that these trends, which run counter to the trends of the other soil bore locations, have been induced by a shift in the subsurface environment toward anaerobiosis. Well 317322, which is located just west of SB26, was described previously as exhibiting geochemical and biological characteristics of strongly reducing conditions. These observations lend support for the association of anaerobic conditions and areas of elevated contamination within the 317 FD.

Biological Indicators. PLFA results are summarized in Table 4-14. Overall, the mean concentration of biomass and monoenoic gram-negative bacteria exhibited no significant changes. During the course of the study, the lipid make of soil samples varied less as the community structures of some locations changed to resemble other locations. For example, samples SB14, SB16 and SB28 changed to resemble SB22; and SB02 and SB08 changed to resemble SB20.

In general, the PLFA profiles among soil samples varied less than water samples. This convergence of biomarkers is seen as an indication that the root system is encouraging the development of similar microbial communities.

Obligate anaerobic, iron and sulfate-reducing bacteria were absent from all samples collected at baseline. This was an expected consequence of planting activities. Boreholes were drilled to depths of 10 ft (3 m) bgs at 200 locations across the 317 FD. This likely resulted in localized aeration of the soil volume, perhaps including, perhaps, the 317 FDCP, which is located 15 ft (4 m) north of the 317 FD. Obligate anaerobes were detected in all samples collected at the end of the

Figure 4-8. Mean Soil Geochemical Results

Results in mg kg^{-1}, except pH.
– Data not collected

Control Plot

	SB#29		SB#30		SB#31	
			BSE	FSE		
Fe	---	--	17,000	25,000	---	--
Mn	---	--	440	550	---	--
TOC	---	--	2,400	16,000	---	--
pH	---	--	7.5	7.9	---	--

317 Area French Drain

	SB#01		SB#02		SB#03		SB#04		SB#05	
			BSE	FSE			BSE	FSE		
Fe	---	---	15,000	32,000	---	—	19,000	17,000	---	---
Mn	---	—	280	450	---	---	500	320	---	—
TOC	---	---	5,200	26,000	---	—	3,200	24,000	---	---
pH	---	—	7.6	8.1	---	---	7.8	8.6	---	—

	SB#06		SB#07		SB#08		SB#09		SB#10	
	BSE	FSE			BSE	FSE			BSE	FSE
Fe	22,000	14,000	---	---	27,000	44,000	---	—	15,000	19,000
Mn	710	480	---	---	390	550	---	—	430	350
TOC	<90	30,000	---	---	3,400	23,000	---	—	2,200	22,000
pH	7.6	8.6	---	---	7.6	7.8	---	—	7.7	8.2

	SB#11		SB#12		SB#13		SB#14		SB#15		SB#16	
			BSE	FSE			BSE	FSE			BSE	FSE
Fe	---	---	20,000	26,000	---	—	25,000	31,000	---	---	19,000	17,000
Mn	---	—	360	420	---	---	420	450	---	—	340	340
TOC	---	---	2,900	21,000	---	—	4,100	26,000	---	---	1,500	24,000
pH	---	—	7.8	8.3	---	---	7.6	7.9	---	—	8.0	8.6

	SB#17		SB#18		SB#19		SB#20		SB#21		SB#22	
			BSE	FSE			BSE	FSE			BSE	FSE
Fe	---	—	16,000	16,000	---	---	28,000	32,000	---	—	16,000	27,000
Mn	---	—	380	270	---	---	460	480	---	—	660	430
TOC	---	—	1,800	15,000	---	---	3,600	17,000	---	—	5,200	8,600
pH	---	—	7.7	8.3	---	---	7.5	7.7	---	—	7.8	8.2

	SB#23		SB#24		SB#25		SB#26		SB#27		SB#28	
			BSE	FSE			BSE	FSE			BSE	FSE
Iron	---	---	24,000	17,000	---	—	21,000	20,000	---	---	15,000	19,000
Mn	---	—	410	310	---	---	380	350	---	—	330	370
TOC	---	---	1,800	29,000	---	—	<90	17,000	---	---	3,000	21,000
pH	---	—	7.5	8.2	---	---	7.1	7.8	---	—	7.9	8.1

Table 4-13. Summary of Soil Geochemical Data

Analyte	Mean BSE	BSE Range	Mean FSE	FSE Range
Fe	20,000	15,000 - 28,000	24,000	14,000 - 44,000
Mn	430	280 - 710	410	270 - 550
TOC	2,700	<90 - 5,300	21,000	8,600 - 30,000
pH	7.6	7.1 - 8.6	8.2	7.7 - 8.6

Table 4-14. Summary of Soil PLFA Results

	% of Total PLFA								pmol PLFA g^{-1}	
	Monoenoic, Gram-negative bacteria		Obligate anaerobes: Iron reducers and Desulfovibrio-like sulfate reducers		Desulfobacter-like sulfate reducers and facultative anaerobes: 10me16:0		Actinomycetes (obligate and facultative aerobes): 10me18:0		Bacterial Biomass	
	Baseline	Final	Baseline	Final	Baseline	Final	Baseline	Final	Baseline	Final
SB02	22.8	30.9	0.0	**3.5**	**11.9**	3.1	**1.4**	0.7	176	**1,298**
SB04	27.9	22.2	0.0	**2.4**	12.5	12.3	**2.7**	0.9	**519**	76
SB06	35.5	30.3	0.0	**4.1**	2.5	**8.4**	1.4	1.3	229	185
SB08	41.5	23.8	0.0	**2.8**	**7.0**	2.7	**2.1**	0.7	**1,069**	375
SB10	36.6	22.0	0.0	**1.6**	10.3	10.8	**4.6**	1.0	**296**	128
SB12	23.2	19.9	0.0	**4.2**	7.1	5.4	2.0	2.0	299	**1,011**
SB14	18.0	26.1	0.0	**1.9**	1.7	2.5	0.3	0.4	215	**322**
SB16	25.3	24.0	0.0	**2.3**	6.6	7.9	**1.8**	0.8	184	96
SB18	24.4	23.0	0.0	**4.3**	7.3	**14.0**	2.1	1.4	189	108
SB20	25.2	19.1	0.0	**3.0**	**7.9**	2.4	**1.9**	0.5	233	**382**
SB22	21.6	30.4	0.0	**4.1**	5.6	4.6	1.0	0.7	106	145
SB24	17.4	25.0	0.0	**5.5**	2.4	**6.8**	0.1	**0.3**	230	137
SB26	15.3	14.6	0.0	**2.8**	2.9	**4.6**	1.7	1.1	180	105
SB28	27.3	24.2	0.0	**7.8**	5.6	5.1	**2.5**	1.1	103	113
SB30	35.7	25.7	0.0	**3.2**	7.0	3.8	**2.8**	0.7	613	879
Average	26.5	24.1	0.0	**3.6**	6.5	6.3	**1.9**	0.9	309	357

study period. While, perhaps, not a direct reflection of the action of the trees (these anaerobes were detected in the control plot as well), it does suggest that available oxygen is being used up by biotic and/or abiotic processes.

4.4.2.3 Modeling and Confirming Water Use and Hydraulic Control

Continuous groundwater elevations were evaluated over the period covering November 1999 through December 2001. Its analysis informs on important aspects of the site's hydrogeology and the affect of the young plantation on water levels. A clear response to precipitation was observed, with hydraulic heads rising within one hour of the onset of precipitation. The magnitude of the water level response is roughly correlated with the amount of rainfall, though smaller wintertime precipitation events may create significant head increases because of concurrent snowmelt.

Additional examination of the continuous head data reveals additional details about the effect of the phytotechnology system on the nearby water levels. The 809 trees, including more than 500 TreeWells® targeting a confined aquifer, were planted in summer 1999. The TreeWells® were planted deep ("up to their shoulders") in order to maximize their initial root depth within their lined boreholes, and they were pruned heavily in order to reduce stress during their hot-weather planting. In 2000, the growing season was cool. The height of the growing season (June - August) registered only 570 CDD as compared to an average of 628 CDD for the area, and 32°C (90°F) was not reached until September (data not shown). During that summer, the trees did not exhibit significant above ground growth; instead, the cool weather seemed to give them time to establish themselves. The data from the cool 2000 growing season shows no obvious impact of the trees on water levels. However, in September 2000, during a brief warming period, the plantation began exhibiting diurnal fluctuations (data not shown). These fluctuations, which are up to 7 cm (0.25 ft) in well 317151, were present to a lesser degree at 317172, 317452, and 317181. Diurnal fluctuations were not present at 317391, which is upgradient of the phytotechnology system, or at the two 319 Area wells 319261 or 319171. The water levels in the 319 Area wells may not be responding due to different hydrologic conditions or a smaller plantation.

The diurnal fluctuations continued during the 2001 growing season and varied in amplitude with the amount of daily solar radiation. What is noteworthy of the 2001 data is that the water levels, such as in well 317151, exhibit a gradual downward trend during days of high sunlight and strong diurnal fluctuations, with gradual recovery of water level during cloudy days that lack strong fluctuations (Figure 4-9). For this young plantation, this is an early indication of what is expected in the upcoming years, namely that the maturing poplars will exert an increasing effect on the site's hydrology and ultimately result in hydraulic containment. This anticipated containment has been evaluated through groundwater modeling that incorporated the best estimate of water use by the TreeWells® through each month (Quinn et al. 2001). Results suggest that despite leaf-off winter periods, the plantation will provide full containment on the larger western (317 Area) side of the plantation, and a strong degree of containment on the eastern (319 Area) side.

4.4.2.4 Health and Growth of the Planted System

During their first year from planting, the trees developed, although at a slower rate than their potential, and successfully established themselves at the site, both at the source area and at the hydraulic control areas. While some of the initial trees had to be replanted, as they did not survive the transplant shock (the trees were planted in an extremely hot and dry weather), the health of those that overcame the transplant (the majority) was more than satisfactory. It is believed that the non-optimal climatic conditions at the time of transplant and throughout the first summer caused the trees to go into a "survival" mode (rather than a fast growth mode), and that a cooler than expected growing season of 2000 slowed down the trees' growth compared to their potential.

The 2001 growing season was overall was more favorable to plant growth than the 2000 season. In the summer of 2001, a number of the poplars started to show the large apical leaves that are a sign of unrestricted water availability. Poplars grew and average of 10 mm in diameter and 109 cm in height. Poplars grew 2.8 more times in height and 1.6 times more in diameter in 2001 compared to 2000. On average, during the 2001 summer, willows increased 7 mm in diameter and 20 cm in height. Compared to the year 2000 growing season, willows grew 2.6 times more in height, while growing at about the same pace in diameter (in 2000 the willows grew substantially more in diameter than in height).

The groundcover species sowed at the site grew according to expectations and were able, by the summer of 2000, to establish themselves as a ground cover and minimize risks of erosion and runoff. In some areas, local vegetation composes a significant portion of the final plant cover, without decreasing the groundcover effectiveness.

4.5 Discussion

The phytotechnologies deployed at ANL-E sites are supplementary to and intended to eventually replace an existing pump-and-treat system. As the trees completed their third growing season in the field (2001), a significant amount of information had been collected to assess their performance at achieving the remedial objectives. From this data, the

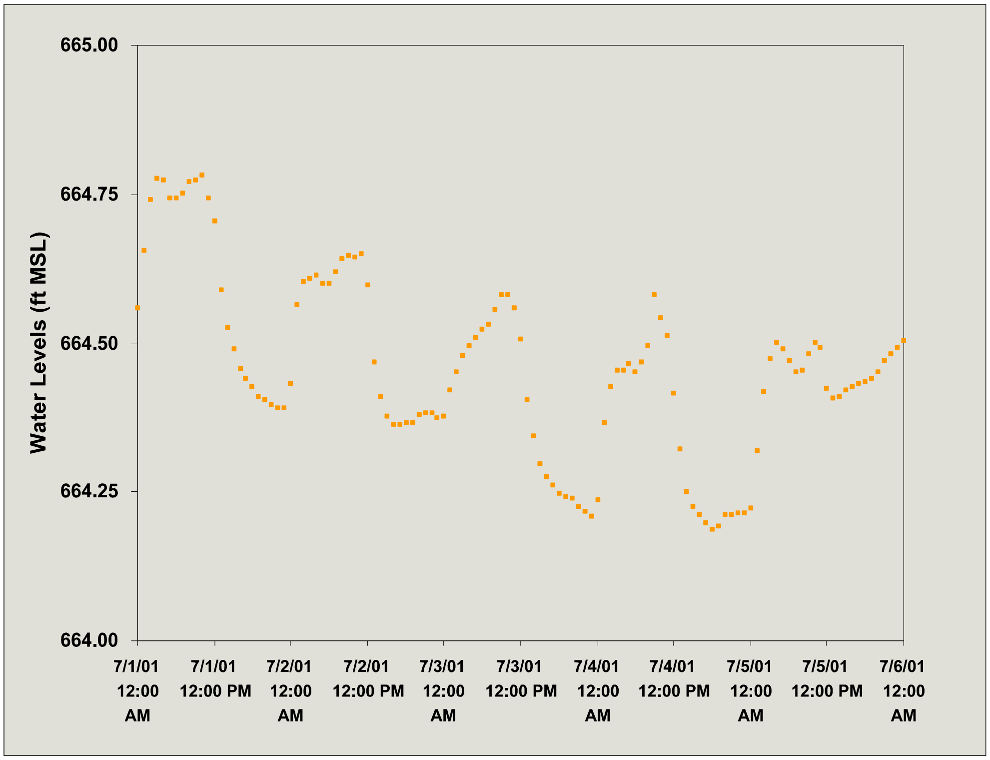

Figure 4-9. Well 317151 Water Levels, July 1-5, 2001

young plantations appear to have begun to influence the cleanup area. The deep-planted trees have tapped into the lower saturated zone and are consuming contaminated water. Degradation of volatile organics from the source area soil is occurring in the plants, and the rhizosphere is moving toward conditions that are capable of supporting reductive dechlorination. In ground water, pollutants are being removed (tritium) or degraded (VOCs) in some areas of the contaminated groundwater plumes. Overall, less contamination is reaching the extraction well system than before the plants were installed.

Probably the key remediation mechanism of this planted system is the interception and removal of water from the impacted aquifer (i.e. phytostabilization). Consequently, the magnitude of transpiration is one of the most important monitoring parameters: transpiration rates for the trees at the site provide information for evaluating current water removal as well as predicting future water usage. Quantified sapflow rates were used to estimate transpiration. Data show that maximum sapflow rates determined during the 2001 growing season are still below the plants' potential as estimated by the hydraulic flux at baseline. However, the year-to-year increase in rates suggests that across the plantation water use is closing the gap. These data complement others derived from the recording of continuous groundwater elevation at the site, which shows diurnal fluctuations of hydraulic heads in correspondence with elevated daily solar radiation (transpiration) during the vegetative season.

Multiple lines of evidence are often needed to demonstrate biodegradation processes at contaminated sites (EPA, 1998). The lines of evidence used to examine biodegradation for this project include (1) detection of TCE and its degradation products in tree tissue in the 317 FD; (2) groundwater chemical data that indicate decreasing concentrations of target VOCs and increasing concentrations of degradation byproducts (3) geochemical data that indicate depletion of electron donors and acceptors; and (4) laboratory microbiological data that indicate the bacteria present at a site can degrade contaminants.

Tissue analysis of willows growing at the contaminated source area indicate that TCE and PCE are taken up by the trees in measurable amounts, and that at least a portion of the transported contaminants is degraded in the leaf. The intermediate degradation product, TCAA, appears to be subsequently degraded further in the leaf litter to background levels.

TCE and TCA and their degradation byproducts are seen at nearly all groundwater wells throughout the study area, implying that microbial attenuation of some form has occurred. In a number of cases monitoring data are unclear about where or how degradation byproducts were formed, and at other locations VOC, geochemical, and biological indicators suggest that reductive dechlorination is ongoing.

Source area soils, which may have been aerated as a result of plant installation, have lost much of their initial aerobic nature. Obligate-anaerobic, iron and sulfate-reducing bacteria have established colonies across the 317 FD, and there appears to be a particularly strong anaerobic character building in segments of the source area where contaminant levels are greatest.

After enduring a transplant shock and below-optimal growth conditions during the first two years in the field, the trees grew at faster rates in 2001. Their increased size is reflected in increased transpiration rates, and presumably larger/longer root systems and enhanced rhizosphere to better influence contaminant reduction and hydraulic control. Modeling based on data collected during the first three years of the project predicts full containment of the 317 plume, and significant containment of the 319 plume.

Phytotechnologies are by definition dependant on weather and are equally difficult to predict specifically. The timing of tree growth is as variable as sunshine and cloud patterns, but equally reliable on the average in the long term. For a variety of reasons these planting did not develop as quickly as expected. The question of when trees will be effective is not answered in this demonstration, and that uncertainty must be built into regulatory acceptance and financial considerations of similar applications.

4.6 Data Quality Summary

A review of the primary sample data and associated QC analyses was performed to determine whether the data collected were of adequate quality to provide proper evaluation of the project’s technical objectives. Three primary parameters were validated:

1. TCE in soil
2. Target VOCs in ground water (see section 4.3.1.2 for a list of target VOCs)
3. Tritium in ground water

The results of the measurements designed to assess the data quality objectives are summarized below. A detailed description of project quality assurance can be found in the companion Technology Evaluation Report for this project.

4.6.1 TCE in Soil

Accuracy objectives for soil TCE were assessed by the evaluation of 5 spiked samples analyzed in accordance with standard procedures in the same manner as the samples. Recovery values for TCE were well within objectives specified in the project Quality Assurance Project Plan.

Recovery for trichloroethylene averaged 97.2% and for tetrachloroethene (non-primary) the average recovery was 97.5%, giving an overall percent recovery of 97.4% for the critical organics.

Precision was assessed through the analysis of 5 duplicate spikes. Data quality objectives for precision, established as RPD values less than 25% , were met.

Detection limits were established so as to be sufficiently below the concentration of interest for TCE. The program required detection limit was established at 50 ppb. Due to the laboratory sample preparation of field methanol extracted samples, this required a method detection limit (MDL) of 1 ppb. The MDL was successfully achieved.

Comparability was achieved through the use of a QAPP, approved EPA protocols, and verified by the validation of analytical data, which indicated that the QAPP and method-specified criteria were met.

Completeness The number of samples for the baseline analysis required to meet completeness was estimated to be 84 samples. Eighty-four samples were collected in the field and successfully analyzed by the laboratory during both the baseline and final sampling events.

Representativeness refers to the degree with which a sample exhibits average properties of the waste stream at the particular time being evaluated. For soil samples, this is assessed in part, by the analysis of split samples spiked in the field with trichloroethene, which also provide insight into the homogeneity, or heterogeneity, of the matrix. Spiked split samples have, inherent in the result, combined field and analytical variability. The spiked split samples indicated reasonable agreement in results, with RPD values for the baseline spiked duplicates averaging 18.3 % with a maximum of 38.4 %, final spiked duplicates averaged 19.7 % with a maximum of 50 %, and a goal of ≤35 % RPD.

4.6.2 Target VOCs in Ground water

Accuracy objectives for groundwater target VOCs were assessed by the evaluation of 5 spiked samples during the baseline sampling event, 2 spiked samples during the midterm sampling event, and 6 spiked samples during the final sampling event. The spiked samples were analyzed in accordance with standard procedures in the same manner as the samples. Recovery values for the critical compounds were well within objectives specified in the QAPP, except for one cis-1,2-dichlorethene result during the baseline sampling event, and one sample during the final event. The sample during the final event with high % R (up to 135 %) had sample concentrations up to 79 % of the spike concentration. The highest spike recovery on other samples during the final event was 118%. (The QAPP actually required that the % R be achieved only for trichloroethene.) Overall recovery averaged 104 % for the target VOCs.

Precision was assessed through the analysis of 5 spiked duplicates during the baseline sampling event, 2 spiked duplicates during the midterm sampling event, and 6 spiked duplicates during the final sampling event. Data quality objectives for precision, established as RPD values less than 20 %, were met.

Detection limits achievable by the laboratory method were sufficiently below the concentration of interest for the groundwater target VOCs. The program therefore utilized the pre-established detection limit of 1 ppb.

Comparability was achieved through the use of a QAPP, approved EPA protocols, and verified by the validation of analytical data, which indicated that the QAPP and method-specified criteria were met.

Completeness The number of samples for the baseline analysis required to meet completeness was estimated to be 47 results per volatile organic. Forty-eight baseline samples were collected in the field and analyzed by the laboratory. These samples were collected from eight wells at a rate of one per day for six days. During data validation, one sample was qualified as "R", rejected do not use for any reason, leaving 47 valid analyses. Well 317452 had "less than" results for all analyses on all days, this well was not sampled as a "primary" well during the final sampling event. Forty-two samples (seven wells at one sample per well per six days) were collected in the field and analyzed by the laboratory.

Representativeness refers to the degree with which a sample exhibits average properties of the waste stream at the particular time being evaluated. This is assessed in part by the analysis of field triplicates (duplicates are frequently utilized), which also provide insight into the homogeneity, or heterogeneity, of the matrix. Field triplicate samples have, inherent in the result, combined field and analytical variability. Results for calculating RSDs are used only when sample and triplicate results are all at least 2 times the MDL for a given target VOC. The triplicates indicated reasonable agreement in results, with RSD values for the triplicates averaging 5.4 % with a goal of ≤20 % RSD.

4.6.3 Tritium in Ground Water

Accuracy objectives for tritium were assessed by the evaluation of 1 spiked sample during the baseline sampling event, 2 spiked samples during the midterm sampling event, and 2 spiked samples during the final sampling event. The spiked samples were analyzed in accordance with standard procedures in the same manner as the samples. Recovery values for tritium were well within objectives specified in the QAPP. Overall recovery averaged 103 % for tritium.

Precision was assessed through the analysis of 1 sample duplicate during the baseline sampling event, 2 sample duplicates during the midterm sampling event, and 1 sample duplicate during the final sampling event. Results for calculating RPDs are used only when both the sample and duplicate result are all at least 2 times the MDL. Data quality objectives for precision, established as RPD values less than 15 %, were met.

Detection limits achievable by the laboratory method were 500 pCi/L for tritium. This concentration is sufficiently below the concentration of interest; therefore, the project utilized the laboratory pre-established detection limit.

Comparability was achieved through the use of a QAPP, approved EPA protocols, and verified by the validation of analytical data, which indicated that the QAPP and method-specified criteria were met.

Completeness The number of samples for the baseline analysis required to meet completeness was unable to be statistically determined due to the minimal (two) number of analyses previously collected. The intent of the project (and QAPP) was to collect samples over six days from three different wells within the tritium plume, yielding 18 samples. Due to field conditions and placement of the wells, only two wells were available for sampling within the suspected tritium plume. Each of the two wells were sampled over six days for a total of 12 samples during both the baseline and final sampling events.

Representativeness refers to the degree with which a sample exhibits average properties of the waste stream, at the particular time being evaluated. This is assessed in part by the analysis of field triplicates (duplicates are frequently utilized), which also provide insight into the homogeneity, or heterogeneity, of the matrix. Field triplicate samples have, inherent in the result, combined field and analytical variability. For tritium, the primary sample, duplicate, and triplicate were collected immediately after each other. Results for calculating RSDs are used only when sample and triplicate results are all at least 2 times the MDL. The field triplicates indicated reasonable agreement in results, with RSD values for the field triplicates averaging 4.4 % with a goal of ≤15 % RSD. A sample duplicate was collected during the midterm sampling event.

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SECTION 5
OTHER TECHNOLOGY REQUIREMENTS

5.1 Environmental Regulation Requirements

The deployment of phytotechnology at ANL-E is being conducted under the jurisdiction of the IEPA. Similar phytotechnology efforts conducted outside of the state of Illinois will likely be subject to alternate federal, state and/or local regulations consistent with the change in jurisdiction. Governing agencies may require permits prior to implementing a phytotechnology system of a similar size and purpose. Section 2 of this report further discusses the environmental regulations that may apply to this or similar phytotechnology applications.

5.2 Personnel Issues

The number of personnel required to implement a particular phytosystem is largely dependent on the size of the area to be treated. Large sites requiring extensive site preparation, tree planting, and other support items may require several individuals (inclusive of contractors), especially if there are constraints on time. The size of the 317/319 area at ANL-E covers approximately 2 hectares (5 acres) of which about 11,000 m^2 (120,000 ft^2) consists of the tree plantings. During1999, the year in which the site preparation and tree installation took place, ANL-E utilized three full-time personnel in addition to contracted services. Estimated labor requirements for the ANL-E site are discussed in Section 3 of this report.

For complex sites, there may be a need for specialized engineering and/or scientific services. For example, at the ANL-E site the physical effects of the tree plantings on the groundwater was modeled using the specialized hydrologic software program MODFLOW. Also, there was a need for generating engineering specifications, drawings, and installation details so that the state regulatory agency could review the system design. Radiological sites, such as the 317/319 Area, further require specialized training for personnel. Also, health physicists were routinely required to monitor activities and scan vehicles, samples, and equipment prior to leaving the site.

The site owner, or other responsible party desiring the installation of a phytotechnology system may need to out source certain tasks. Potential out sourcing may involve a landscaping, construction firm, or well drilling firm equipped to perform the work. For example, the hybrid poplars used at ANL-E were initially grown at a tree farm owned by ANS. The hybrid poplars were grown and nurtured for about two years at that company’s nursery and were then shipped to ANL-E and planted using the TreeWell® system patented by ANS.

Sampling events also require the services of several personnel, whether acquired in house or contracted. During the demonstration soil sampling events at ANL-E, a two-person Geoprobe® crew and a geologist were required to collect soil samples. Groundwater sampling additionally required one or two 2-person crews to sample selected wells and prepare those samples for off-site shipment.

Personnel present during sample collection activities at a CERCLA or RCRA waste site must have current OSHA health and safety certification and annual medical surveillance.

Certain sites may require training above and beyond OSHA certification. For instance, the ANL-E site required all contractor personnel to attend a contractor orientation class and complete a Radiological Worker 1 training course.

For most sites, the personnel protective equipment (PPE) for workers will include steel-toed shoes or boots, safety glasses, hard hats, and chemical resistant gloves. Depending on contaminant types, additional PPE (such as respirators) may be required. Noise levels would usually not be a concern for a phytotechnology technology. However some equipment used for vegetative clearing and regrading (e.g., mowers, chain saws, etc.), tree planting (e.g., trenching or drilling equipment) and maintenance activities (e.g., mowers and loaders for moving and spreading fertilizer) could create appreciable noise during short time periods. Thus, noise levels should be monitored for such equipment to ensure that workers are not exposed to noise levels above the time weighted average of 85 db over an 8-hr day. If this level is exceeded and cannot be reduced, workers would be required to wear hearing protection.

5.3 Community Acceptance

Phytotechnology approaches have received higher public acceptance than most conventional remedial options. Because phytotechnology is a solar-energy driven, passive technique, there are few environmental disturbances associated with the process. Phytotechnology systems are low maintenance and produce virtually no process residuals. They can be used along with, or in some cases, in place of intrusive mechanical cleanup methods. No appreciable noise beyond that generated by the short term use of installation equipment is anticipated for the majority of the treatment time. A fence may be desirable to keep unauthorized visitors from entering the site.

Potential hazards to a surrounding community may include exposure to particulate matter that becomes airborne during drilling or trenching operations used to plant rows of trees. Air emissions of VOCs are possible if volatile contaminants, such as TCE, are present in the soil (as was the case at ANL-E). Particulate air emissions from installation activities can be controlled by dust suppression measures.

SECTION 6
TECHNOLOGY STATUS

6.1 Previous Experience

Continued research is needed to better understand the advantages and limitations of the phytoremediation, particularly in the area of contaminant transport. A number of studies have been conducted to determine if organic contaminants simply pass through the trees and are released to the atmosphere via leaf stomata during evapotranspiration. Research in this area has produced mixed results and is not close to quantifying the amounts of organics released. Although rhizopheric biodegradation and breakdown of chemicals through metabolic activities within plant tissue are components of phytoremediation, these processes as they relate to this technology are not well understood.

While most phytoremediation systems are limited to the upper three meters of the soil column, new methods may be effective to greater depths. Researchers and companies that offer phytoremediation services have developed and employed specialized (often proprietary) techniques that train the tree roots to penetrate to greater depths or herd them into deeper contamination zones via subsurface drip irrigation.

ANS reports on their web site (www.treemediation.com) to have project sites including government and commercial operations affected by landfills, sludge lagoons and spills. ANS also claims to have the distinction of being the first company to obtain regulatory approval for groundwater phyto-projects in the states of New York, New Jersey, Michigan, Maryland, Wisconsin, Illinois, North Carolina, Louisiana and Ohio.

6.2 Ability to Scale Up

Phytoremediation has been described as being well suited for use at very large field sites, where other methods of remediation are not cost effective or practical (EPA, 2001). The type of phytoremediation system that was installed at ANL-E is an evolving and adaptive process that can be adjusted to different sized sites having various site conditions. That particular system involves treatment of VOCs and tritium in groundwater in the uppermost aquifer, having a depth to top of unit ranging from 6.7 m -10.4 m (22 ft - 34 ft) bgs.

ANS has reported additional projects in which the impact of TreeMediation® is being evaluated on soil as deep as 6 m (20 ft) and groundwater up to 15 m (50 ft) bgs for the cleanup of organic compounds, primarily VOCs (TCE, PCE & BTEX), and inorganic compounds, including heavy metals. With regards to non-volatile organics, ANS has reported that soils contaminated with pesticides (Alachlor and Atrazine, and other agricultural compounds) and petroleum hydrocarbons have been successfully treated.

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