IN SITU DECHLORINATION OF SOLVENTS IN SATURATED SOILS

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ABSTRACT

Use of chlorinated solvents has led to extensive soil and groundwater contamination. Current aerobic treatment methods, such as pump-and-treat with carbon sorption or air stripping, are limited and often cost-prohibitive. Researchers have isolated microbial cultures capable of reductively dechlorinating tetrachloroethene (PCE) to ethene (ETH). Field studies have shown reductive dechlorination of chlorinated solvents to be stimulated by the addition of electron donors. Based on these results, this project utilizes indigenous bacteria and added electron donors for degradation of PCE in the field. The approach is designed to achieve a rigorous mass balance on electron donors, electron acceptors, and microbial carbon/energy sources. The effort is aimed at validating reductive dechlorination in a realistic field situation.

1.0 INTRODUCTION

PCE and trichloroethene (TCE), have been used widely since the 1940s. This use, in addition to improper handling and storage, has led to extensive groundwater contamination at both industry and military sites. The U. S. Air Force is responsible for an estimated 1700 chlorinated solvent-contaminated sites which will require some form of cleanup.

Current chlorinated solvent remediation technologies are costly, ineffective, and/or impractical. The use of pump-and-treat technology alone for remediating chlorinated solvent-contaminated aquifers is often unrealistic. Carbon sorption and air stripping are the methods currently used with pump-and-treat. Carbon sorption is a costly nondestructive method. Air stripping merely transfers the contaminant from the water phase to the air phase. In some instances, the contaminated air stream is regulated and requires

treatment. Some chlorinated solvents have been shown to be cometabolically biodegraded *in situ* under aerobic conditions, via methane-oxidizing (1) or phenol-oxidizing (2, 3) microorganisms. However, the successful application of cometabolic aerobic bioremediation may be limited due to competitive inhibition between the cosubstrate and the chlorinated solvent, intermediate product toxicity via chlorinated solvent oxidation, the difficulty of adding poorly soluble cosubstrates such as methane and oxygen to the groundwater, and the relatively high cost of maintaining aerobic conditions *in situ*.

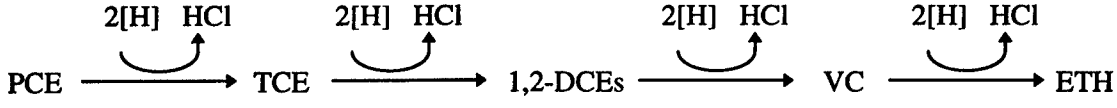
Chloroethenes can be reductively dechlorinated (4-9). Development of a cost-effective *in situ* anaerobic biotreatment technology for groundwater contaminated with chlorinated solvents is urgently needed by the DOD and industry. A microbial culture capable of reductively dechlorinating PCE to ETH with efficient use of electron donors has been isolated at Cornell University (5). In the field, studies with site materials and isolated test plots have shown reductive dechlorination of chlorinated solvents to be stimulated by the addition of electron donors (10-12). Based on these results, this field effort utilizes indigenous bacteria and added electron donors to stimulate the degradation of PCE to ETH in the subsurface at Naval Air Station Fallon, NV (NASF). The study is being conducted through a partnership between the U. S. Air Force Armstrong Laboratory Environics Directorate (AL/EQ), the U. S. Navy, the U. S. Environmental Protection Agency National Risk Management Research Laboratory (NRMRL), Cornell University, and Battelle Memorial Institute.

The objective of this research is to extend positive laboratory results to an *in situ* field demonstration of PCE dechlorination. The field system allows researchers to investigate the addition of various electron donors to enhance the reductive dechlorination already occurring at the site, in addition to investigating dechlorination through natural attenuation and iron electrodes. The field investigation consists of five semi-enclosed treatment lanes, with two outside lanes used for natural attenuation and the iron electrodes. A hydraulic gradient will be applied to all five lanes. Using controls, this approach is designed to achieve a rigorous mass balance on the electron donors, electron acceptors, and microbial carbon/energy sources. A detailed understanding of the dechlorination process will lead to more efficient, cost-effective, and reliable strategies for the bioremediation of PCE and related compounds.

2.0 BACKGROUND

2.1 REDUCTIVE DECHLORINATION OF CHLOROETHENES IN THE LABORATORY

Cornell University was the first to report complete dechlorination of PCE to ETH, a process of sequential reduction steps with TCE, dichloroethene (DCE), and vinyl chloride (VC) as intermediates (13):



In contrast to hydrocarbons which can be directly biodegraded, reductive dechlorination of chloroethenes requires the addition of electron donors (5). The original focus of the Cornell studies used methanol (MeOH) and developed a culture capable of rapidly dechlorinating high concentrations of PCE to ETH. However, further research revealed that H_2, not MeOH, is the direct electron donor responsible for PCE dechlorination (6). MeOH and other reductants found to support dechlorination merely serve as H_2 precursors.

Electron donors other than MeOH offer several benefits for reductive dechlorination of chloroethenes. Substrates, such as butyrate, lactate, and ethanol-benzoate, are not direct methanogenic substrates. They eliminate competition for the supplied donor itself, as they (unlike MeOH) are not methanogenic. H_2 is a direct fermentation product of these substrates. It is produced slowly at low levels providing for complete

mineralization of PCE, thus favoring dechlorination over competition for the substrates (13). These results suggest that strategies utilizing slow, steady H_2 delivery are best to stimulate and maintain reductive dechlorination.

Gossett and Zinder have evaluated the acclimation, induction, and kinetics of the processes catalyzed by their enrichment to obtain a better understanding of the culture mechanisms. A novel bacterium appears to be solely responsible for the PCE dechlorination. A vitamin solution containing vitamin B_{12} sustains the dechlorination, while fermented yeast extract and sewage sludge supernatant are promising nutrient sources. Insight from these microbial and nutritional studies provides useful information when attempting to harness the reductive dechlorinating capabilities of indigenous bacteria located in PCE-contaminated groundwater.

2.2 PREVIOUS FIELD STUDIES FOR *IN SITU* REDUCTIVE DECHLORINATION

At the DuPont Victoria Plant in Victoria, TX, a test zone in a PCE-contaminated aquifer underlying a former landfill was selected for evaluation. Microbial reductive dechlorination was stimulated by pumping the electron donor benzoate or a sulfate solution into a recirculating groundwater treatment system. After two years of anaerobic treatment, PCE and lesser-chlorinated ethenes were reductively dechlorinated *in situ* to below detection limits (11).

In another study, microcosm studies were conducted with PCE-contaminated core materials collected from the Coast Guard Air Station in Traverse City, MI. Four fatty acids and three alcohols were tested for their ability to act as sources for reducing equivalents for PCE dechlorination (10). Dehalogenation activity was observed as a result of electron donor addition within one week with some amendments while others required two weeks or more. This study indicated that the availability of electron donors is essential for reductive dechlorination of PCE and TCE in the environment (10).

Information gained from these studies and others show the potential for cleanup technologies aimed at stimulating reductive dechlorination of chlorinated ethenes in environments where there is low availability of carbon and energy sources. Results of these studies, in conjunction with the laboratory work performed at Cornell University, are being applied in the field at NASF.

2.3 NASF SOIL MICROCOSM STUDIES

In the laboratory, several electron donors have been demonstrated to stimulate anaerobic fermentation, H_2 production, and reductive dechlorination of PCE using NASF soils (Gossett, 1996). Anaerobic fermentation products and PCE dechlorination capacity of five electron donors [lactate, butyrate, propionate, ethanol (EtOH), and benzoate] and three electron donor mixtures using benzoate plus EtOH have been compared. PCE dechlorination to TCE was observed in the lactate-fed bottles after 150 days of incubation. Low levels of TCE were also detected in butyrate- and benzoate-fed bottles. The addition of nutrients (yeast extract and/or vitamins) appeared to contribute to more rapid PCE dechlorination, as indicated by comparing the rate of PCE removal and TCE production in lactate-fed bottles.

Sulfate reduction in the NASF soil microcosms suppressed H_2 accumulation, methane production, and PCE dechlorination, though the PCE results are inconclusive. More positive results of PCE dechlorination during sulfate reduction were obtained from work done by the EPA NRMRL (Gossett, 1996). The rate of electron donor consumption in the Cornell studies decreased in the following order:

EtOH >> lactate > butyrate and propionate >> benzoate.

EtOH was fermented to a mixture of acetate and propionate, suggesting that EtOH served as both a fast source of H_2 and a slower source of H_2 via propionate production and the subsequent fermentation of propionate to acetate and H_2. If H_2 is the primary electron donor for PCE dechlorination in the NASF microcosms, the Cornell studies suggest that slow release of H_2 is apt to provide the best condition for suppressing methanogenic competition with PCE dehalogenators and enhancing PCE dechlorination (Gossett, 1996).

3.0 FIELD STUDY, NASF

Site 1 at NASF was selected for enhancement of dechlorination by indigenous microbes through the addition of various electron donors. The field system is designed to enhance the reductive dechlorination already occurring at the site. Natural attenuation will serve as the control while reductive dechlorination through the use of an iron electrode will be field-evaluated.

3.1 SITE GEOLOGY

NASF is located 60 miles east of Reno, NV and was established as a military facility in 1942 as part of the Western Defense Program. The Crash Crew Training Area (Site 1) consists of an unlined, earth-bermed burn pit, previously associated with two above ground fuel storage tanks (Figure 1). From the mid-1950s to April 1988, the burn pit was used to conduct fire training for NASF personnel. The pit was reportedly used to burn an estimated 1.1 million gallons of flammable liquids, fuel farms waste products, napalm, lubricants, and solvents. An estimated 99% of the material burned was fuel and lubricants.

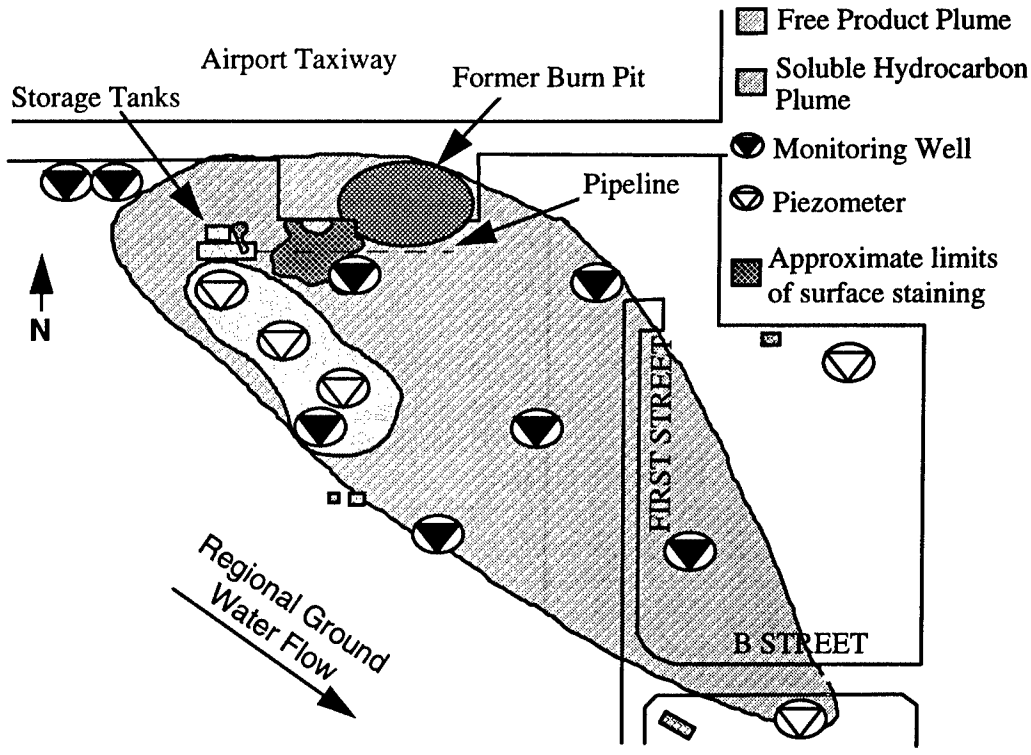


Figure 1. Site area map of Site 1, NAS Fallon, NV.

Sandy soils cover the site at NASF and extends to a depth of approximately 4 ft. Beneath the sandy surface cover is a layer of clay-rich silts and sands, approximately 2 ft thick and appearing to be laterally

continuous across the site. The fine-grained layer and sand layer form an unconfined aquifer which is laterally continuous across the site. At the bottom of the unconfined aquifer is a sandy silt and clay layer which has a thickness in excess of 5 ft. The clay layer is nearly 20 ft thick across most of the site (14).

The water table surface in the Fallon area experiences seasonal and daily fluctuations due to irrigation and rainfall influences. Groundwater at the site is perched on a regional lake bed clay layer at a depth of 8 to 10 ft. The regional clay layer acts to impede contaminant movement from the local aquifer to deeper aquifers. The groundwater flow direction is to the south in the northern half of the site and to the southeast in the southern half of the site. The average hydraulic gradient is 4.0×10^{-4} ft/ft (14).

3.2 SITE CONTAMINATION AND GENERAL GROUNDWATER CHEMISTRY

Primary contaminants reported at Site 1 include chlorinated solvents, JP-5, gasoline, and waste oil. Most chlorinated solvent contamination at Site 1 is associated with free product on the water table with lower concentrations in the groundwater. The dissolved-phase plume at Site 1 contains both fuel and chloroethene related constituents (Table 1). Maximum concentrations for all constituents were found immediately adjacent to the burn pit, approximately 50 m from the test site (Figure 1). The maximum PCE and TCE concentrations reported were 680 and 340 µg/L (14), respectively. 1,2-*cis*-DCE is a known metabolite of TCE dechlorination, and its presence suggests biological reductive dechlorination of PCE at Site 1.

TABLE 1. CONTAMINANT CONCENTRATION AND GENERAL GROUNDWATER CHEMISTRY

Contaminant	Concentration (µg/L)	General Water Chemistry	Concentration
PCE	2.6 - 680	pH	7.60 - 9.11
TCE	9.9 - 340	Conductivity	48,900 - 3,750 µmhos
1,1-DCE	1.5 - 8.0	Total Alkalinity	569 - 701 mg/L
t-DCE	1.0 - 101	O-P	0.74 - 3.08 mg/L
c-DCE	1.5 - 609	Cl^-	661 - 15,100 mg/L
VC	1.1 - 2.9	SO_4^{-2}	386 - 8,650 mg/L
toluene	1.3 - 18	NO^-_2 (N)	< 0.20 mg/L
benzene	1.2 - 242	NO^-_3 (N)	< 2.68 mg/L
ethylbenzene	2.0 - 152	NH_3 (N)	< 0.23 mg/L
xylenes	1.2 - 450		

3.3 FIELD TEST TREATMENT SCENARIO

This field study involves the use of five semi-enclosed treatment lanes separated by four high-density polyethylene (HDPE) sheetpiles. Each lane represents a unique treatment scenario using different electron donors and nutrient additions. An artificial hydraulic gradient is being imposed in each lane and controlled via groundwater pumping from influent injection and effluent extraction wells. Each treatment lane is scheduled to receive different nutrient and electron donor additions (Table 2). Two of the three inside lanes will receive organic electron donors (lactate or EtOH plus benzoate) and nutrients (vitamins plus yeast extract). The third inside lane will receive high yeast extract concentrations plus vitamins, with yeast extract acting as the electron donor. One of the outside lanes will be a control lane operated without adding electron donors, vitamins, or yeast extract to monitor nonbiological losses and losses due to intrinsic PCE biotransformation. The second outside lane will not be fed an electron donor, vitamins, or yeast extract. An iron electrode will be installed *in situ*, downstream of the injection well, to produce H_2 via iron oxidation and the reduction of H^+ ions in water to H_2.

TABLE 2. FEED SCHEDULE FOR ELECTRON DONORS, VITAMINS, AND YEAST EXTRACT

Lane	Treatment Amendments
A (outside)	Control (natural attenuation)
B (inside)	Ethanol plus benzoate, vitamin solution, and yeast extract
C (inside)	Lactate plus vitamin solution and yeast extract
D (inside)	High yeast extract plus vitamin solution
E (outside)	Electrode potential with iron (no vitamin solution or yeast extract added)

Initial electron donor concentrations are shown in Table 3 and are to be modified as needed. The concentrations are based on the NASF soil microcosm studies performed at Cornell. Over 16 g/L lactate, 8 g/L benzoate, or 8 g/L EtOH would be required to satisfy the total sulfate burden in each lane. Because cost and the potential for clogging the aquifer render such high electron donor concentrations prohibitive, the added electron donors are not expected to satisfy the electron donor-demand for sulfate reduction. Vitamin and yeast extract concentrations are shown in Table 4. The high yeast extract concentration (200 mg/L) is applied to Lane D.

TABLE 3. INFLUENT ELECTRON DONOR CONCENTRATIONS FOR LANES B AND C

Lane	Electron Donor	Electron Donor Concentration (mg/L)
B	Lactate	540
C	Ethanol	140
	Benzoate	170

TABLE 4. INFLUENT AND YEAST EXTRACT CONCENTRATIONS

Vitamin/Yeast Extract	Concentration (mg/L)
d-biotin	0.01
folic acid	0.01
pyridoxine hydrochloride	0.05
thiamin hydrochloride	0.025
riboflavin	0.025
nicotinic acid	0.025
DL-calcium pantothenate	0.025
vitamin B_{12}	0.025
p-aminobenzoic acid	0.025
lipoic acid	0.025
yeast extract amendment	20
high yeast extract	200

3.4 TREATMENT LANE CONFIGURATION

Figure 2 shows the plan view of the five treatment lanes. The treatment lanes are oriented in the direction of the groundwater flow. Each lane is dependent on one extraction well located upgradient from the treatment area and a cluster of three injection wells at different depths in each lane. The injection and extraction wells are separated by 17.5 ft. Injection and extraction flowrates are established to induce an artificial hydraulic gradient without allowing cross-contamination between lanes. Influent groundwater is pumped into the injection wells at a rate of 60 gallons per day (gpd), split between the three levels at 8 ft, 10 ft, and 12 ft below ground surface (bgs). Effluent groundwater is pumped from the

extraction wells at 200 gpd. The nutrient feed solutions are blended with the influent water immediately upstream of the injection wells.

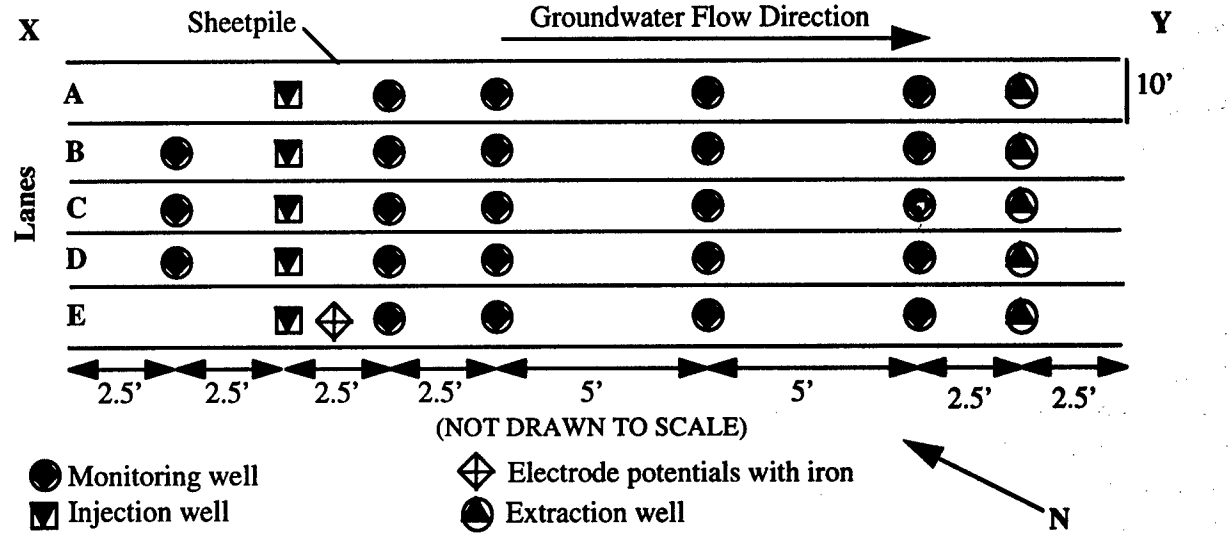


Figure 2. Plan view of the five treatment lanes (Lanes A through E).

A cross section of a typical inside lane is shown in Figure 3. There are four bi-level groundwater monitoring well clusters between each pair of injection and extraction wells, located along the centerline axis of each lane. Each bi-level monitoring well cluster has well screens at 8 ft and 12 ft bgs.

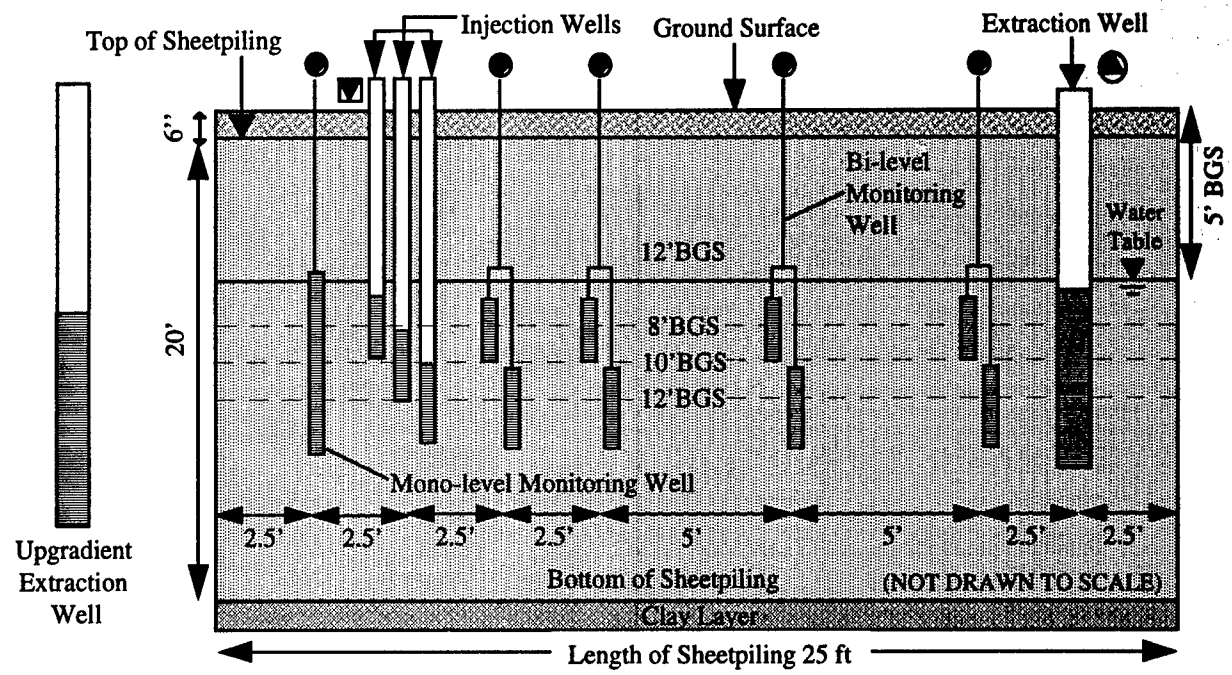


Figure 3. Cross section of a typical inside lane

A cross section of a typical outside lane is shown in Figure 4. There are four mono-level groundwater monitoring well clusters between each pair of injection and extraction wells, located along the centerline

axis of each lane. Monitoring well screens are at 10 ft bgs. Table 5 shows depth and screened intervals for injection and monitoring wells.

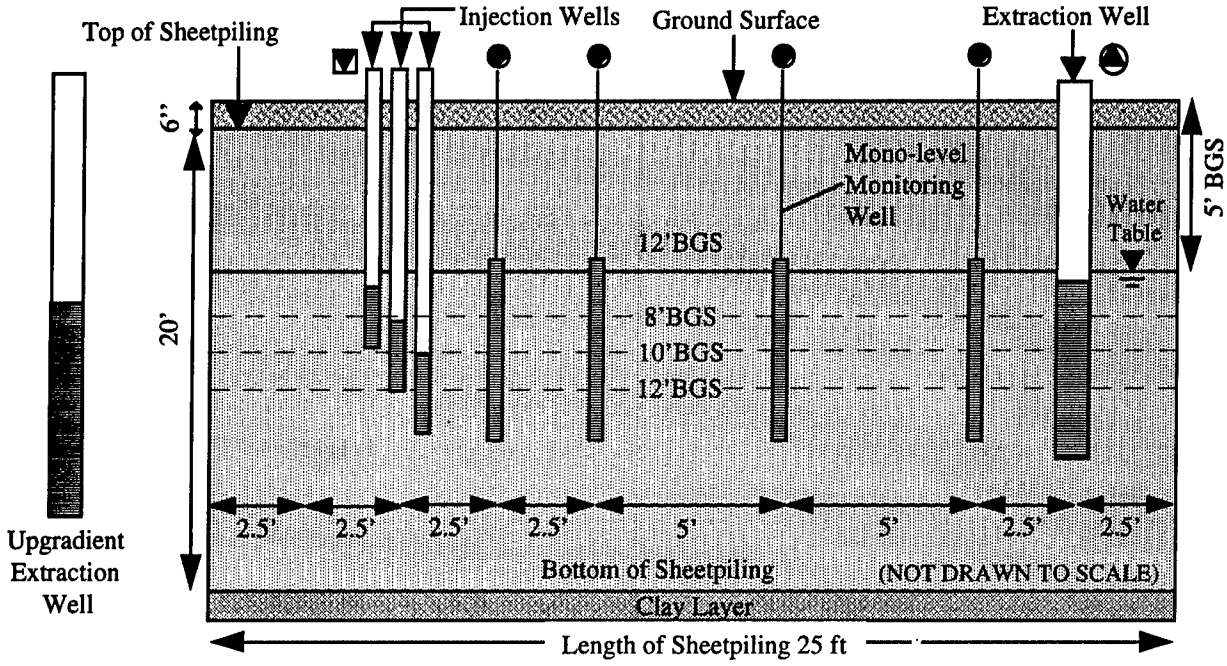


Figure 4. Cross section of a typical outside lane

TABLE 5. WELL DEPTHS AND SCREENED INTERVALS

Lane	Well	Depth (ft)	Screened Interval (ft)
A - E	Tri-level injection wells	8	6 to 8
		10	8 to 10
		12	10 to 12
A - E	Extraction wells	10	5 to 10
A - E	Mono-level monitoring wells	8	6 to 8
B - D	Bi-level monitoring wells	8	6 to 8
		12	10 to 12

Four sheetpiles, installed at a depth of 20 ft, separate the five treatment lanes. The sheetpiles are installed approximately 4 ft into the clay layer which separates the surface aquifer from the deeper, confined aquifer. The sheet piles are 25 ft long, extending 5 ft upstream of the injection wells and 2.5 ft downstream of the extraction wells. Each treatment lane is 10 ft wide.

An iron electrode will be installed in Lane E. The iron acts as an anode, giving off electrons which go toward the reduction of hydrogen ions (H^+) to dissolved H_2 gas. The iron anode is electrically connected to another metal other than iron (i.e., zinc), which acts as the cathode in an *in situ* galvanic cell. H_2 is expected to contribute to the reductive dechlorination of PCE. H_2 which does not contribute to PCE dechlorination will be consumed by lithotrophic bacteria or volatilize to the atmosphere.

3.5 SAMPLING SCHEDULE

The sampling schedule is shown in Table 5. Organic analyses include PCE, dechlorination byproducts (TCE, DCE, and VC), and electron donor concentrations. Dissolved gas analyses include CH_4, H_2S, and CO_2. Inorganic analyses include sulfate, nitrate, iron, DO, pH, alkalinity, and conductivity.

Dissolved gas is scheduled for analysis less frequently than the organic and inorganic analytes. Influent lines and the first two bi-level groundwater monitoring wells will be tested during the first months of the test to determine the extent of anaerobic production of methane and sulfide gasses. Once anaerobic activity is established and confirmed analytically, changes to the dissolved gas monitoring will be evaluated. In addition to the analyses described in Table 5, the following groundwater analyses will be performed for each monitoring well sample point: pH, temperature, conductivity, redox potential, and DO concentration.

TABLE 6. SAMPLING FREQUENCY

Sampling Events	Organic Analyses	Dissolved Gas Analyses	Inorganic Analyses	Field Analyses
First Month	50 per week	10 per week	50 per week	50 per week
Months 2 to 12	50 per month	20 per month	50 per month	50 per month

CONCLUSIONS

To date, data collection has been limited to microcosm studies performed at Cornell. This effort is aimed at validating the technology of enhanced *in situ* reductive dechlorination in a field situation. A detailed understanding of *in situ* dechlorination will lead to more efficient, cost-effective, and reliable strategies for bioremediation of PCE and related compounds. Insight from this study will be useful in modeling the fate of compounds and predicting the success of natural attenuation of chlorinated solvents. Understanding the microbiology will enable researchers to understand and control processes which remove chloroethenes from the environment. The information will directly feed into the development of a protocol to serve in the assessment of successful application of enhanced *in situ* reductive dechlorination.

ACKNOWLEDGMENTS

This field effort marks the transition of 16 years of investment by AL/EQ and Cornell University in the remediation of chlorinated solvents from the laboratory to the field. Through the combined financial, technical, and consultant efforts of the group involved in the effort at NASF a highly successful laboratory program is being realized in the field.

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