BIOREMEDIATION OF CHLORINATED SOLVENT CONTAMINATED GROUNDWATER

Prepared for

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by

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NOTICE

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FOREWORD

Environmental concern and interest is growing for bioremediation of chlorinated solvents in groundwater. EPA's Technology Innovation Office (TIO) provided a grant through the National Network for Environmental Management Studies (NNEMS) to prepare a technology assessment report on in situ bioremediation of chlorinated solvents in groundwater. This report was prepared by a senior undergraduate student from Oregon State University during the summer of 1998. It has been reproduced to help provide federal agencies, states, consulting engineering firms, private industries, and technology developers with information on the current status of this technology.

About the National Network for Environmental Management Studies (NNEMS)

NNEMS is a comprehensive fellowship program managed by the Environmental Education Division of EPA. The purpose of the NNEMS Program is to provide students with practical research opportunities and experiences.

Each participating headquarters or regional office develops and sponsors projects for student research. The projects are narrow in scope to allow the student to complete the research by working full-time during the summer or part-time during the school year. Research fellowships are available in Environmental Policy, Regulations, and Law; Environmental Management and Administration; Environmental Science; Public Relations and Communications; and Computer Programming and Development.

NNEMS fellows receive a stipend determined by the student's level of education and the duration of the research project. Fellowships are offered to undergraduate and graduate students. Students must meet certain eligibility criteria.

About this Report

This report is intended to provide a basic summary and current status of in situ treatment technologies for contaminated sediments. It contains information gathered from a range of currently available sources, including project documents, reports, periodicals, Internet searches, and personal communication with involved parties. No attempts were made to independently confirm the resources used.

While the original report included color images, this copy is printed in one color. Readers are directed to the electronic version of this report to view the color images; it is located at **http://clu-in.org.**

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

GLOSSARY OF KEY TERMS

Aerobic - requiring air or oxygen; typically referring to microorganisms that require air or oxygen to live and reproduce

Air- or Biosparging Treatment Systems - the process of injecting pressurized air beneath the water table to promote mass transfer of volatile organic compounds out of the groundwater and mass transfer of oxygen into the groundwater

Anaerobic - requiring an environment devoid of oxygen; typically referring to microorganisms that are able to live and reproduce in the absence of oxygen

Bioaugmentation - addition of exogenous microbes to the subsurface where organisms able to degrade specific contaminants are deficient. Microbes may be "seeded" from populations already present at a site and grown in above-ground reactors, or from specially-cultivated strains of bacteria having known conditions for degrading specific contaminants

Biobarrier - based on a concept of intercepting and treating a contaminant plume as it passes through a permeable barrier. Biobarriers are accomplished by installing wells that deliver substrate in a manner in which microorganisms will grow, and establishing a curtain which extends across the width of a plume as it flows down gradient

Biological Treatment Walls - based on a concept of intercepting and treating a contaminant plume as it passes through a porous barrier. Microorganisms growing on the wall material remove contaminants through biodegradation processes as the groundwater passes through the barrier

Bioremediation - a process by which microorganisms, fungi, and plants degrade pollutant chemicals through use or transformation of the substances

Chlorinated Aliphatic Hydrocarbons (CAHs) - man-made, chlorine-containing organic compounds widely used as solvents and degreasers in various industries. Typical CAHs include tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene, and vinyl chloride (VC). Most CAHs are classified as dense non-aqueous phase liquids (DNAPLs)

Cometabolism - use of a dilute solution of primary substrate (e.g., toluene, methane) that supports breakdown of targeted organic contaminants

Dense non-aqueous phase liquids (DNAPLs) - chlorinated solvents that are minimally soluble in water and are more dense than water. DNAPLs tend to sink and accumulate on the non-permeable layer (aquitard) at the bottom of a confined aquifer

Electron Acceptor - a chemical entity that accepts electrons transferred to it from another compound; an oxidizing agent that, by accepting electrons, is itself reduced. In aerobic metabolism, oxygen is the terminal electron acceptor

Electron Donor - a compound or element that furnishes electrons for reductive reactions

GLOSSARY OF KEY TERMS (continued)

Enhanced Bioremediation - bioremediation of organic contaminants by microbes supplemented by increasing the concentration of electron acceptors, electron donors, and nutrients in groundwater, surface water, and leachate

Exogenous Bacteria - those obtained from a source other than the native site

Facultative - either with or without air or oxygen; typically referring to microorganisms that are able to live and reproduce with or without oxygen

Injection/Extraction Treatment Systems - a closed loop hydraulically contained system, based on a design of down-gradient extraction and up-gradient injections wells; sometimes referred to as a recirculating treatment cell

Nutrients - in addition to carbon, hydrogen, and oxygen, these are the elements required for microbial growth; typical elements include nitrogen and phosphorus

Passive Bioremediation (also known as Natural Attenuation) - use of natural subsurface processes, such as dilution, volatilization, biodegradation, adsorption, and chemical reactions with subsurface materials, which are used to reduce contaminant concentrations

Reductive Dechlorination - sequential reduction of a chlorinated ethene or ethane to ethene or ethane

Substrates - organic compounds used by microbes to carry on biological processes; examples include toluene, lactate, methane, and propane

PURPOSE

The main objective of this report is to present information about recent field applications of enhanced in situ bioremediation for treating groundwater contaminated with chlorinated aliphatic hydrocarbons (CAHs). This report presents information about bioremediation technologies and cost and performance for nine pilot- and full-scale applications. The information in this report also will be used by the U.S. Environmental Protection Agency (EPA), Technology Innovation Office (TIO) as part of a more comprehensive study of bioremediation of CAHs. TIO's study, expected to be published next year, will include detailed descriptions of bioremediation mechanisms as well as detailed analyses of the costs of technology applications. In addition, the Interagency Technology Regulatory Cooperation (ITRC) workgroup is preparing a technical and regulatory document on CAH degradation. This report therefore focuses on available cost and performance information for the nine case studies, and does not include detailed descriptions of mechanisms or an overall analysis of the costs of the technology.

1.0 INTRODUCTION

At approximately 400,000 sites in the United States, soil and groundwater are contaminated with chlorinated solvents (Sutfin 1996). Chlorinated solvents have been widely used as degreasers in various industries for more than 30 years. Past disposal methods and handling practices for chlorinated solvents have contributed to wide spread CAH contamination in soil and groundwater. For example, one practice involved returning spent solvents to a drum. Once the drum was full, it was then closed and buried in a pit with other drums. The drums eventually corroded and their contents leaked onto the soil and subsequently migrated to groundwater aquifers.

In situ bioremediation is used as an alternative to such traditional methods as groundwater pump-and-treat for treating groundwater contaminant plumes. In situ bioremediation was first observed as natural destruction of petroleum hydrocarbons in polluted groundwater aquifers. It later was discovered that microorganisms could also break down CAHs. CAH degradation is typically accomplished through one of the following treatment technologies: injection and extraction, air- or biosparging, and biological reactive walls.

Enhanced vs Passive Bioremediation

Bioremediation is a process by which microorganisms, fungi, and plants degrade pollutant chemicals through utilization or transformation of the substances. The microorganisms most responsible for bioremediation are bacteria. Bacteria are found in all environmental media, including air, water, and soil. When indigenous bacteria degrade compounds under existing subsurface conditions, the degradation is called passive bioremediation or natural attenuation. Natural attenuation is most common in the subsurface, where bacteria are plentiful and where pollutant concentrations are low enough such that the natural degradation is effective in controlling the size of a plume (RTDF 1996).

Enhanced bioremediation involves stimulating indigenous bacteria by adding electron donors (substrates) and/or nutrients to the subsurface to increase bacterial growth yielding faster degradation rates. The compounds injected are determined by the type of bacteria being stimulated to degrade the specific contaminants. The type of bacteria that dominate the subsurface are heterotrophic forms that require organic substrates (carbon based compounds) to serve as a source of energy. Bacteria also are categorized according to the use of oxygen as aerobes, anaerobes, and facultative anaerobes. Aerobes require oxygen, anaerobes require an environment devoid of oxygen, and facultative anaerobes can survive in both aerobic and anaerobic environments (Sutherson 1997).

Enhanced bioremediation also refers to the addition of exogenous microorganisms to a contaminated site (bioaugmentation) specifically for the purpose of bioremediating a polluted area. Bioaugmentation usually is used in conjunction with substrate and nutrient subsurface injection strategies when remediating aquifers contaminated with chlorinated solvents.

Chlorinated Solvents

Since the 1940's, a variety of industries have used chlorinated solvents to degrease machinery. Chlorinated solvents are relatively pure CAHs in the form of chlorinated methanes, ethanes, and ethenes. The majority of chlorinated solvents have the following characteristics: minimally soluble in water, variable vapor pressure, and more dense than water. Therefore, most chlorinated solvents are classified as dense non-aqueous phase liquids (DNAPLs). DNAPLs tend to sink and accumulate on the non-permeable layer (aquitard) at the bottom of a confined aquifer (Sutherson 1997).

The most common chlorinated solvents are 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), carbon tetrachloride, methylene chloride, chloroform, tetrachloroethene (PCE), and trichloroethene (TCE) (Sutherson 1997). In the United States, chlorinated solvents are common contaminants in groundwater with TCE being the most prevalent contaminant. The drinking water standard for both PCE and TCE is 5 micrograms per liter (μg/L) (ToxFAQS 1997).

Enhanced In Situ Groundwater Bioremediation Technologies

There are three main types of in situ groundwater bioremediation technologies that are available to treat contaminated aquifers. The technologies are: injection/extraction systems, air- or biosparging systems, and biological reactive walls. One of the main obstacles to the application of in situ bioremediation is difficulty in transporting the nutrients and substrate to the microbes. Therefore, site characterization must be completed before any in situ bioremediation technology is implemented to ensure that the treatment system can clean up the contaminated site. Site conditions of interest include hydrogeologic characteristics, microbial activity, and aquifer conditions (EPA 1998). Site characterization is not discussed in this report, but further information may be found in *Site Characterization for Subsurface Remediation* (EPA November 1996).

Injection and Extraction Systems

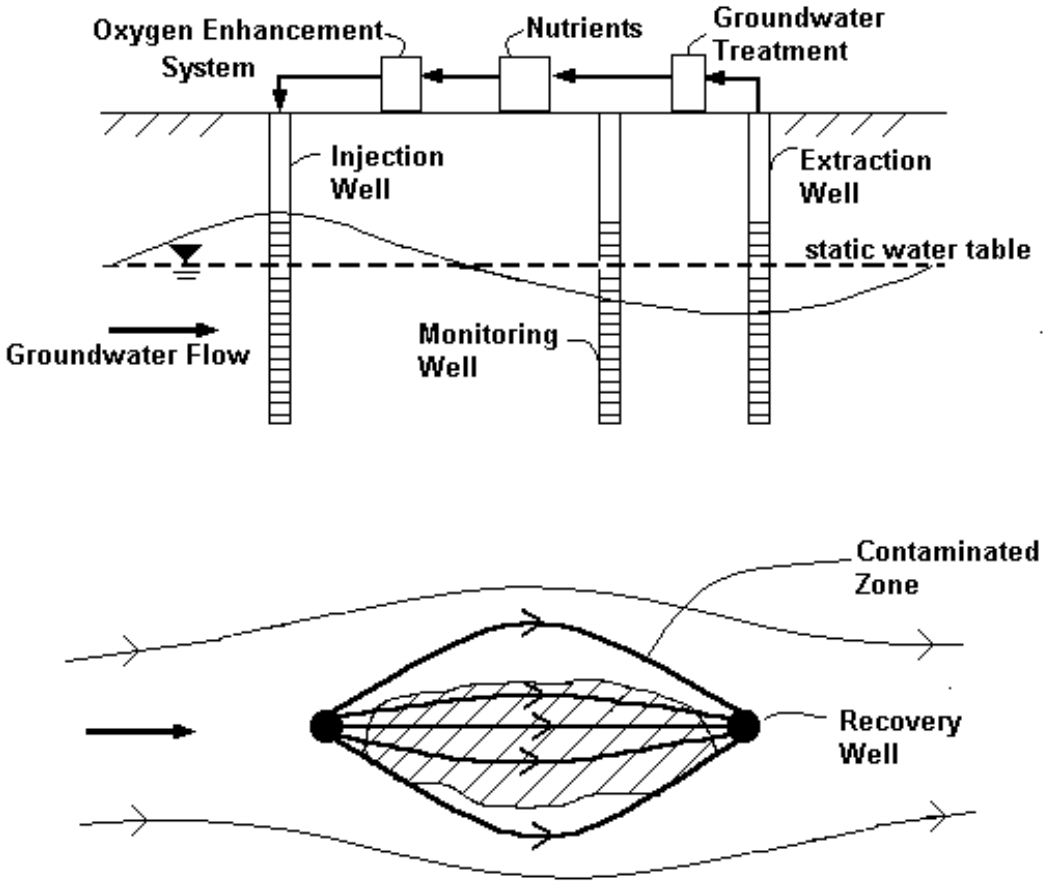
Injection and extraction systems, also known as liquid delivery systems, are used to bioremediate contaminated aquifers in the saturated zone. These systems have been used in the past for treating plumes contaminated with petroleum hydrocarbons, but are also being used for remediating groundwater contaminated with chlorinated solvents.

Injection and extraction bioremediation is a closed-loop hydraulically contained system. The most common design of the treatment system uses down-gradient extraction and up-gradient injections wells, but alternative designs exist including:

- Multiple injection points for enhancing substrate and nutrient distribution and transport
- Infiltration galleries (trenches) rather than injection wells; these are used for more shallow groundwater aquifers
- Horizontal injection wells

The bioremediation system is designed to establish a biological reactive treatment zone (cell) which intercepts and contains the plume in order for contaminant degradation to occur. When water is recirculated through the treatment zone to achieve greater contaminant removal, the zone is referred to as a recirculating groundwater cell. Many injection and extraction systems are based on the Raymond Process (EPA 1995). The Raymond Process consists of: groundwater extraction; above ground treatment of the extracted water; amendment of the water with substrate, electron acceptor (in some cases), and nutrients; and re-injection of the water into a groundwater aquifer, so that the additions reach microorganisms to stimulate their growth. Figure 1 shows a simple Raymond Process configuration.

Figure 1: Description of the Raymond Process



Source: Sutherson, Suthan S. *Remediation Engineering: Design Concepts*

Air- and Biosparging

Air sparging is used to remediate contamination in the saturated zone of a groundwater aquifer, as well as to remediate portions of the unsaturated (vadose) zone. Applicable in circumstances in which volatile and/or aerobically biodegradable organic pollutants contaminate groundwater, air sparging is the process of injecting pressurized air beneath the water table to promote mass transfer of volatile organic compounds (VOCs) out of the groundwater and mass transfer of oxygen into the groundwater (EPA 1998). The mechanisms include: air stripping of VOCs, volatilization of trapped and adsorbed phase contaminants, and aerobic biodegradation. For short-term treatment, aquifer cleanup is accomplished by volatilization; for long-term treatment, aquifer cleanup is accomplished by biodegradation (Sutherson 1997).

A major factor to consider before implementing an air sparging treatment system is the aquifer geology at the site. Air sparging works best if the soil of the aquifer is homogeneous. When significant stratification exists, there is a danger that sparged air could spread laterally below an impervious layer. This in turn would spread pollutants to noncontaminated portions of the aquifer (Norris 1994). Also, high permeability of soil layers may cause a plume to expand. Therefore, it is recommended that air sparging systems be applied when the contamination is in the saturated zone and hydraulic conductivities are less than 10^{-3} centimeters per second (cm/s) (Sutherson 1997).

In most natural aquifer soils, air moves through an aquifer by channels rather than bubbling up through the groundwater. Channeling limits diffusion of VOCs and decreases the efficiency of air sparging systems. Mixing the aquifer by pulse injection of air promotes diffusion of contaminants to the air.

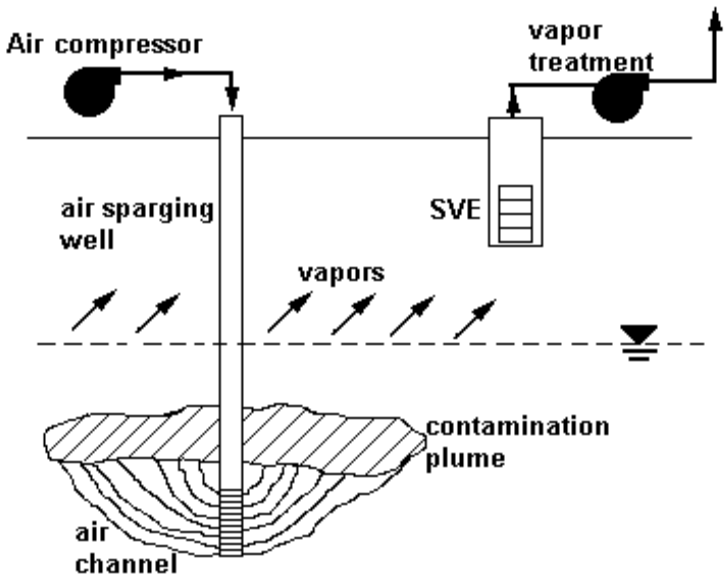
Soil vapor extraction (SVE) is often used in conjunction with air sparging to help control the movement of contaminated vapors. An option to avoid having to use SVE is slow injection of air/oxygen. When air is injected slowly, microorganisms can use the majority of the air being injected thereby promoting biodegradation of the contaminants. Slow injection of air is sometimes referred to as biosparging. Biosparging also refers to injecting gases other than air or oxygen into the subsurface to stimulate microbial activity. Methane (natural gas) is the most common substrate used in biosparging applications. The Savannah River Site case study is an example of biosparging with methane gas and air in conjunction with SVE to remediate a TCE contaminated aquifer.

The design parameters associated with an air sparging groundwater treatment system include:

- Air distribution (zone of influence)
- Depth of air injection
- Air injection pressure and flow rate
- Injection mode (pulse or continuous)
- Injection well construction (Sutherson 1997)

The components that make up an air sparging treatment system include wells, a manifold and compressor system (EPA 1998). Figure 2 shows a process flow diagram for air sparging in conjunction with SVE.

Figure 2: Air Sparging Process Flow Diagram with Soil Vapor Extraction



Adapted from: API Publication 4609, 1995

Design Approaches and Concepts

Both air- or biosparging and injection and extraction well systems can be designed as recirculating treatment cells (zones), biobarriers, or combinations of the two. A recirculating treatment cell is a hydraulically contained system in which the volume of groundwater in the treatment zone is recirculated and treated repeatedly until the treatment goal has been achieved. Such systems are common for treating groundwater contaminated with chlorinated solvents.

A biobarrier intercepts and treats the contaminant plume as it passes through the permeable barrier. Biobarriers are constructed by installing wells that deliver the substrate in such a way that the microorganisms establish a curtain that extends across the width of the plume as it flows downgradient. As the plume crosses the biologically active curtain, the contaminants are degraded similar to the way permeable biological reactive walls work. (See discussion below.)

This report also classifies an injection system that creates a biological treatment zone as a biobarrier. The treatment zone may not extend the full width of the plume, but the design purpose of the system is to treat the source of the contamination without recirculating groundwater to do so.

Bioremediation systems also are designed as a combination of recirculating cells and biobarriers in which a portion of the contaminated water is recirculated and treated repeatedly, while the rest flows out of the system. These systems can be classified as recirculating cells that are not hydraulically contained.

Permeable Biological Reactive Walls

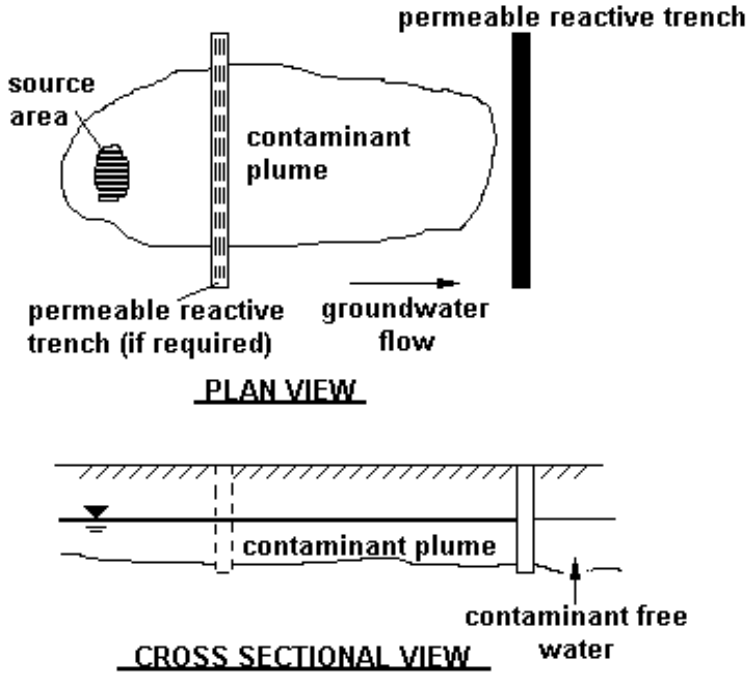
An in situ biological reactive wall consists of a porous barrier that intercepts a groundwater plume. Microorganisms growing on the wall material will remove contaminants through biodegradation processes as the groundwater passes through the barrier. Air sparging and injection and extraction systems also can act as biological barriers when they are aligned to intercept and treat a plume; however, this report does not classify such barriers as biological reactive walls.

One difference between barriers and walls is that walls minimize the need for mechanical systems (Sutherson 1997). Both injection and extraction and air sparging systems require extensive pumping mechanisms to deliver substrates and nutrients to the treatment zone. Biological reactive walls should be equipped with microbial growth medium when installed. However, a method to stimulate more microbial growth, and to unclog the wall if biofouling occurs may be needed. In theory, biological reactive walls would require less operation and maintenance compared to other bioremediation technologies discussed in this report.

The majority of reactive walls used currently to treat groundwater contamination do not do so biologically. However, the types of reactive walls, regardless of their treating mechanism, are relatively similar. The two main types of reactive walls are: permeable reactive trench and funnel-and-gate systems.

Permeable reactive trenches can be designed to span the width of a plume but usually are located downgradient to intercept the entire plume as it passes. The installation of a permeable reactive trench involves digging a trench below the depth of furthest contamination and back filling with permeable material (see Figure 3). As the plume passes through the wall, contaminants can be removed by various mass transfer processes such as air stripping, biodegradation, adsorption, and metal-enhanced dechlorination. Reactive trenches are typically used where the aquifer is less permeable and the contamination is shallow (Sutherson 1997).

Figure 3: Plan and cross-sectional view of a permeable reactive trench



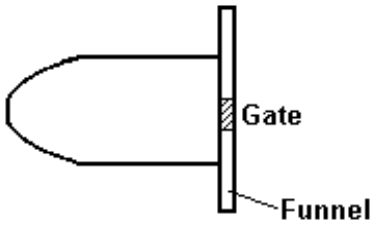
Source: Sutherson, Suthan S. *Remediation Engineering: Design Concepts*

A funnel-and-gate system uses impermeable walls on each side of a permeable reactive gate to direct the flow of contaminated groundwater through the gate. Treatment takes place within the gate (see Figure 4 for a simple funnel-and-gate system). Funnel materials include sheet piles and slurry walls. Different types of permeable media may be used for the gate including pea gravel for air sparging, oyster shells for biodegradation, and reactive materials such as activated carbon or zero-valence iron for treatment through chemical reactions (Sutherson 1997).

The two main types of gates are fully penetrating gate and hanging gate systems. Fully penetrating gates are installed down to the impermeable aquitard or bedrock layer of the aquifer. A fully penetrating gate system rather than hanging gate system would be used for bioremediation of DNAPLs. The hanging gate system does not reach the bedrock of the aquifer, so DNAPL contaminated water could flow under the system.

The gate determines the treatment mechanism to be used. Potentially applicable types of treatment include: volatilization (air stripping), microbial degradation, adsorption (carbon or ion exchange), chemical oxidation, metal-enhanced dechlorination, and metal precipitation. If more than one type of contaminant is to be treated, multiple gates are needed. A specific gate for each contaminant is placed in a series (one gate in front of the next) to remediate the plume. There is an advantage of the funnel-and-gate system over the permeable reactive trench with respect to reactor media replacement or flushing in that replacing a "small" gate would be easier than replacing the entire trench media (Sutherson, 1997).

Figure 4: Simplistic Funnel-and-Gate System



Source: Sutherson, Suthan S. *Remediation Engineering: Design Concepts*

Biological permeable reactive walls require a gate or trench media where attachment of microorganisms will increase the biomass per unit volume of the reactor. Seeding microorganisms into the in situ wall may be required. Before the microbes can be seeded, they should be acclimated to the contaminants present. Once the microbes have been acclimated, they will have a better chance of withstanding the toxic conditions and in turn degrading the contaminants (Sutherson 1997).

The use of biological reactive walls is still in the experimental stage. One study is being conducted at Waterloo Center for Groundwater Research at the University of Waterloo. The Waterloo treatment system is a trench (backfilled with sand) encompassing two injection and one extraction wells. In the

first stage of operation, the water is extracted from the pore spaces of the wall, amended with nutrients and substrate, and reinjected into the wall over a short period of time (a few hours). Once the injected substances are fully delivered in the wall, the pumps are shut off. The passive mode of the wall comes into play for the second stage of operation. The slug of nutrients delivered to the wall is transported out of the wall under natural groundwater flow conditions. This process depends on the flow rate of the aquifer, so transport through the wall may take days, weeks, or even months. Once the slug has been transported out of the wall, the two-stage process is repeated (Devlin and Barker 1994).

As the slug is transported, it mixes with the surrounding groundwater. A zone develops down-gradient of the wall where microorganisms receive a continuous supply of nutrients mixed with contaminants in the groundwater and contaminant degradation takes place (Devlin and Barker 1994).

For the most part, this biological wall application is a passive process. The passive nature of the wall decreases operational costs by reducing power and chemical requirements. Thus far, no full-scale application of a permeable biological wall has been implemented.

2.0 CASE STUDIES

This section presents nine bioremediation treatment case studies from pilot- and full-scale, in situ field applications. The case studies include four bioremediation technologies that promote aerobic degradation mechanisms in the aquifer, one case study that involves anaerobic and aerobic biodegradation, and four case studies that involve anaerobic processes. The technologies that make up the treatment systems are injection and extraction and biosparging. The primary chlorinated solvent treated in the majority of the case studies is TCE.

2.1 Methane Enhanced Bioremediation and Soil Vapor Extraction (Savannah River Site)

A pilot-scale bioremediation study was conducted at the U.S. Department of Energy's (DOE) Savannah River site (SRS) located in Aiken County, South Carolina. The principle investigator at this site was Dr. Terry Hazen in association with Westinghouse Savannah River Company. The SRS facility generated nuclear textiles for defense operations for over twenty years. Solvents used in degreasing operations were disposed of in seepage basins and discharged into a leaky sewer line resulting in TCE and PCE groundwater contamination in area M of the 300 square mile site. The solvents migrated into the groundwater producing a TCE and PCE plume.

The contaminated aquifer lies in a tan clay zone, 30 to 47 meters (m) below ground surface (bgs). The water table is located 36.5 m bgs. Methane enhanced bioremediation (MEBR) or biosparging using horizontal wells was the innovative technology tested at this site.

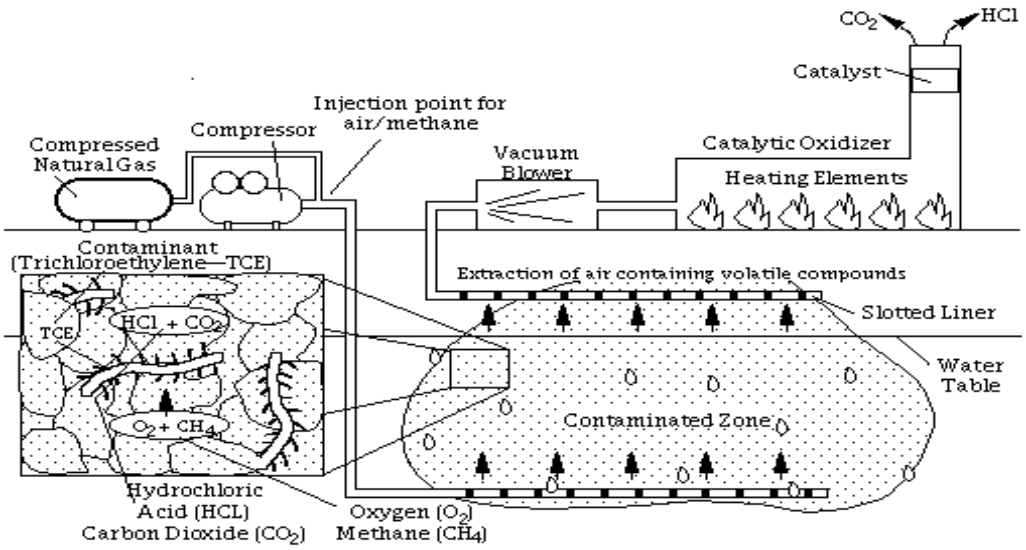
The aerobic MEBR consisted of two horizontal wells, a lower injection well and an upper extraction well. The lower horizontal well was constructed in the aquifer 50.3 m bgs and was used to inject gas, nutrients, and air into the contaminated zone of the aquifer. The methane-air mixture as well as nutrients (nitrogen and phosphorus) were introduced to stimulate the growth of methanotrophs which produce the enzyme monooxygenase (MMO). Nitrogen and phosphorus were added in the form of nitrous oxide and triethyl phosphate, respectively. Following the addition of methane, nutrients, and air, the population of MMO generating microorganisms increased to five times its original concentration after two months, then remained constant.

An upper horizontal extraction well, located in the unsaturated zone of the aquifer, 23 m bgs, was used to extract air containing VOCs that had not been oxidized. The extracted air plus VOCs were treated further in a catalytic oxidizing furnace (CatOx system). Carbon dioxide and hydrochloric acid (HCl) were released into the atmosphere. (See Figure 5 below for a schematic of the process.)

The system was operated for 429 days. A monitoring system composed of 13 wells was sampled bimonthly throughout the duration of the demonstration. By the end of the demonstration, the concentration of TCE and PCE had been reduced to 2 μg/L. The final concentrations were below the drinking water standard of 5 μg/L for both TCE and PCE. It is important to note that PCE is not biodegraded aerobically. However, PCE degradation can be enhanced by nearby methanotrophic activity (Enzien 1995). Most of the PCE was assumed to have volatilized and been captured in the vapor extraction well.

The initial cost for the system including set up and assembly was approximately $150,000. An estimated 200 hours were required for site preparation. The operation and maintenance of the site required only one technician 25 percent of the time (10 hours per week). The operational costs included: the electricity required to run the system, natural gas (methane) and nutrients, and equipment maintenance. The total cost of the MEBR system, which removed 16,934 lbs of VOCs, was about $354,000. Therefore, the estimated cost per pound of VOC remediated was $21.

Figure 5: Methane Enhanced Bioremediation (MEBR)



Source: Westinghouse Savannah River Company-
<http://www.nttc.edu/env/Catalog/Tech_Cat_chap5_14.html

The addition of methane substrate promoting bioremediation of contaminants has been demonstrated to enhance performance and efficiency of in situ air stripping by destroying 40% more VOC. This cleanup method is best where methanotrophic microbes are indigenous to the area. A concern exists as to the possible lateral spread of the contaminant plume in areas where geology constricts vertical flow, when using horizontal wells. However, the horizontal wells improve methane and nutrient distribution which increases contact efficiency and helps reduce clogging potential. DOE received a patent for MEBR technology in December 1987.

The primary objective of this 1994 pilot-scale aerobic bioremediation demonstration at SRS was to gain knowledge for optimizing an injection schedule. The addition of nitrogen and phosphate nutrients in conjunction with 4% pulsed methane injection was found to be the best schedule. The pilot study showed that the MEBR technology could reduce concentrations of PCE and TCE to below drinking water standards.

2.2 Methane Treatment Technology (MTT) (rural Virginia)

A natural gas pipeline compressor station in rural Virginia is contaminated with chlorinated solvents and hydrocarbons. In 1997 a bioremediation technology known as methane treatment technology (MTT),

developed by the Gas Research Institute (GRI), was employed on a pilot-scale basis to clean up groundwater contamination in situ at this site. GRI and the gas transmission company responsible for the site contracted with Radian International LLC to characterize the site and implement the treatment system.

MTT involves injecting air, methane, and nutrients into the subsurface through injection wells to stimulate growth of methanotrophic bacteria. These microorganisms produce the enzyme MMO which degrades TCE.

The main chlorinated VOCs at the site are PCE and TCE. The groundwater table varies in depth between 8 and 10 ft, with an average groundwater velocity and hydraulic conductivity of 1.2 centimeters per day (cm/d) and $3x10^{-4}$ cm/s, respectively. The aquifer is composed of saprolitic overburden above bedrock. The groundwater contaminant plume covers an area of about one acre, with the pH averaging between 5.4 and 6.6.

A pilot-scale MTT system was in operation for four-and-a-half months. The treatment system included one standard vertical injection well, six existing monitoring wells, four additional observation wells, and two vapor sampling points. Two of the observation wells (OW-1 and OW-4) were installed based on a calculated radius of influence of 20 ft in the direction of groundwater flow (actual radius of influence was 30 ft). The gas mixture introduced into the aquifer consisted of air, methane, nitrous oxide (N_2O) and triethylphosphate (TEP) (nitrogen and phosphorus nutrient sources). The airflow rate was increased from 0.85 cubic feet per minute (cfm) to 1.24 cfm. The methane gas and N_2O flow rates were 4% and 0.02%, respectively, and TEP flow rate remained constant at approximately 0.24 mL of gas per minute. The methane was fed at a constant rate for the first five weeks. Once an abundant population of methanotrophs had been established (an increase of six orders of magnitude from the original concentration), methane was injected on a pulse schedule, 8 hours on and 16 hours off. Pulsing helped reduce the clogging of the injection well.

Over 139 days of operation, methane levels detected in the vapor points declined to between 2 and 20 parts per million by volume (ppmV). However, the most significant degradation of PCE and TCE occurred during the first three weeks of operation. The decreases in concentrations were as follows: TCE from approximately 2000 μg/L to 150 μg/L, and PCE from 50 μg/L to nondetectable (ND). PCE is not known to degrade by aerobic metabolism or cometabolism, but its degradation is enhanced by nearby methanotrophic activity (Enzien 1995). Trans-1,2 DCE decreased from 25 μg/L to ND within two-and-a-

half months of operation, and DCA decreased from 120 μg/L to 15 μg/L over the duration of the test. Cis-1,2-DCE fluctuated, but no decline in concentration was observed.

The objective of this project was to demonstrate a significant decrease in TCE concentration within a short period of time (a few months). A full-scale operation is currently underway. Modifications to the existing system included the addition of two injection wells and two observation wells. Additionally, some of the injection equipment was upgraded to support the increase in airflow and gas flow rates up to 5.3 cfm. The expanded pilot-scale system was designed to remediate the entire plume.

2.3 Bioremediation of TCE through Toluene Injection (Edwards Air Force Base, California)

A full-scale aerobic cometabolic degradation field demonstration was conducted at Edwards Air Force Base (AFB) in California. Dr. Perry McCarty and bioremediation specialists conducted this bioremediation operation and reported the findings in the 1998 edition of *Environmental Science & Technology*.

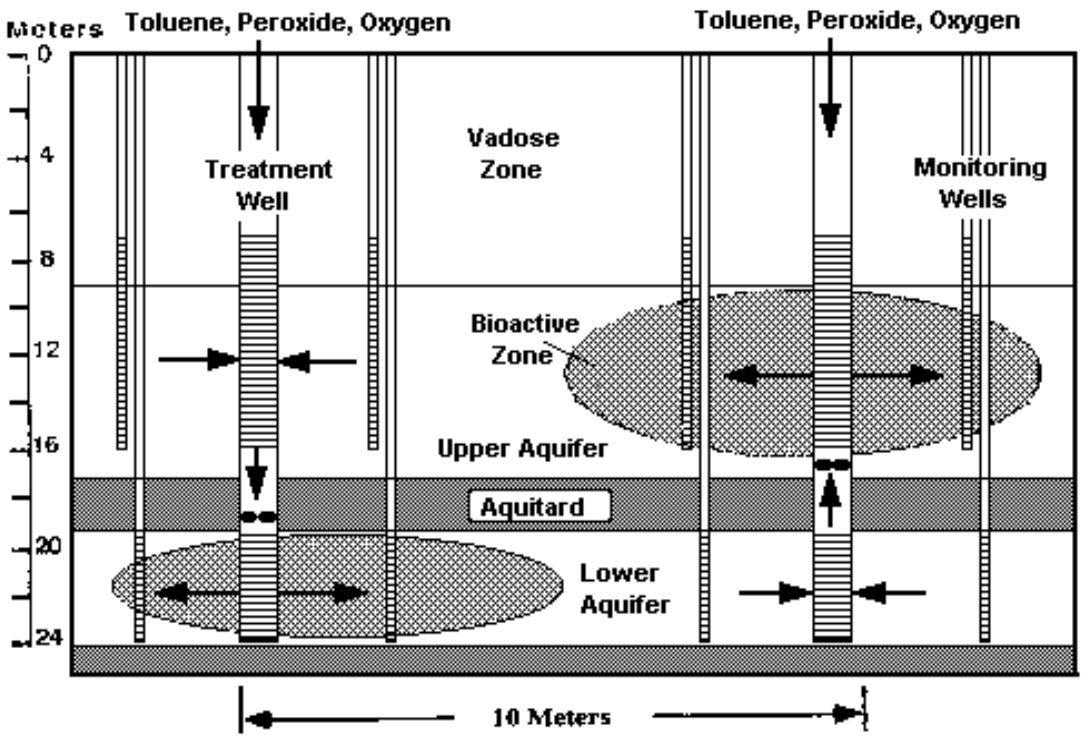
The chlorinated solvent contaminated site is located on the western portion of the Mojave Desert, approximately 60 miles north of Los Angeles. The site itself covers an area of 53 acres and is commonly referred to as site 19. From 1958 to 1967, X-15 rocket plane engines were maintained at Edwards AFB. Approximately one 55-gallon drum of TCE was used each month to clean the engines. The used TCE was then discarded in the nearby desert. This disposal method resulted in a large groundwater contamination plume. The concentration of TCE in the groundwater plume varies between 500 and 1200 μg/L.

There are two aquifers at Site 19. The upper, unconfined aquifer is 8 m thick, and is separated by a 2 m aquitard from the lower confined aquifer. The lower aquifer is approximately 5 m thick and lies above weathered bedrock. The aquifers consist of medium sized sand mixed with some silt. The groundwater table is 9 m bgs. The groundwater within the aquifer is moving at an estimated velocity of 6.9 cm/d to the east southeast. The average TCE concentrations in the upper and lower aquifers are 680 and 750 μg/L, respectively.

In 1995 a full-scale in situ bioremediation treatment system was installed at the site. The treatment system consisted of two 8-in diameter, polyvinyl chloride (PVC) treatment wells approximately 24 m deep and spaced 10 m apart. Each treatment well was screened at two depths - one in the upper aquifer

and one in the lower aquifer. The initial flow rate for the wells were 38 liters per minute (L/min) based on aquifer testing and modeling. A submersible pump was located within each well and used to draw contaminated water into the well where toluene (primary substrate) and oxygen were introduced by feedlines. Groundwater was never pumped to the surface. The groundwater, containing TCE, toluene, and oxygen, was discharged into the aquifer, where an in situ bioactive treatment zone developed around the discharge screen of each well. Water flowed into the system through the screen in the upper aquifer of treatment well 1 (T1) and discharged through the screen in the lower aquifer; the same mechanism occurred in treatment well 2 (T2), but in reverse. This process recirculated the water between the two aquifers, creating a bioreactive treatment cell (see Figure 6).

Figure 6: Cross-section of two-well cometabolic TCE biodegradation treatment system spanning two separate aquifers



Source: McCarty, Perry L et al. *Environmental Science & Technology*, 1998.

The system was operated for 410 days. An area of 480 square meters (m^2) (0.12 acre) was monitored by 14 monitoring wells. Twelve of the fourteen monitoring wells surrounded T1 and T2 in a diamond formation, and the remaining two wells were nested between the treatment wells. Continuous monitoring

was performed with 30 samples taken per day. By the final stage of the operation, starting at day 284, the TCE removal efficiencies were 83% in the lower aquifer and 86% in the upper aquifer for water circulating once through the treatment cell. However, a portion of the water in the aquifer was recirculated through the treatment cell more than once. The treatment system inherently recycled groundwater in the aquifers, 91.5% of flow in T1 and 85% of the flow in T2 was recycled. Therefore, this system had an overall removal efficiency of 97.6%. The concentration of TCE decreased from 1000 μg/L to 24 μg/L. In addition, 99.98% of the toluene added to the system was removed within the first 2.5 m of travel from each of the treatment wells.

Clogging of wells has been found to be the major disadvantage of this in situ treatment. The degree of clogging depends upon the characteristics of the aquifer; the coarser the material, the less likely it is to clog.

In addition to operational costs associated with preventing clogging of wells or well regeneration, another major cost contributor was monitoring costs. An extensive monitoring system was installed to evaluate the treatment system's performance. Table 1 presents the total cost of the Edward's bioremediation treatment system including capital, monitoring, and operation and maintenance costs.

Table 1: Capital and Operation Costs for Aerobic In Situ Bioremediation at Edwards AFB

CAPITAL COSTS ($)	
Total treatment costs (treatment wells, mixers, pumps, deionized water system, etc.)	62,707
Total monitoring costs (19 monitoring wells, pumps, tubes & connectors, valves & fittings)	260,746
Total Capital Costs	**323,453**
ANNUAL OPERATING COSTS ($)	
Well redevelopment ($/well-year) x 2 wells	8,000
Hydrogen peroxide, 30%	4,633
Toluene	47
Oxygen	1,674
Total Annual Operating Costs	**14,354**

Source: Adapted from: Rowans, Patricia. June, 1998.

The objectives of the demonstration conducted at Edwards AFB were to demonstrate that a full-scale in situ bioremediation process was viable for remediating a TCE contaminated groundwater plume, and to show that bioremediation through toluene injection is well enough understood, scientifically, to make predictions as to the performance of the actual system. Many calculations were performed to predict recycle flow rates, removal efficiencies, rates of microbial growth, and other factors which provided good approximations of the performance of the full-scale project. The groundwater plume was not cleaned to drinking water standards (TCE concentration of 5 μg/L), but the objective of the demonstration was accomplished.

2.4 Bioremediation Using Methanol Injection Trenches (Texas Gulf Coast)

A full-scale in situ anaerobic biodegradation system was installed to remediate a TCE contaminated groundwater site along the Gulf Coast of Texas. The manufacturing facility causing the pollution discontinued TCE use around 1978, after approximately 25 years. An area of 420,000 square feet (9.64 acres) was left to cleanup. Monitoring at the site between 1986 and 1995 demonstrated a decrease in TCE concentration from 50 mg/L to 22 mg/L due to natural attenuation; however, the removal rate had slowed over time. A bioremediation treatment system was implemented to stimulate naturally occurring biological activity. The following bioremediation application was presented by Roy F. Weston, Inc. at the Fourth International In Situ and On-Site Bioremediation Symposium held in New Orleans in 1997.

The Texas Gulf Coast site consists of three water-bearing zones, a shallow, a main, and a deep zone. No TCE contamination has been found in the deep zone located at 30 ft bgs. The shallow and main water bearing zones contain TCE and are separated by a 15-ft thick clay layer. The main water bearing zone is located 12 ft bgs. This unconsolidated zone continues approximately 8 ft deeper to a depth of 20 ft bgs. The hydraulic conductivity and seepage velocity of the main zone are in the range of $1x10^{-4}$ to $4x10^{-4}$ cm/sec and 4 to 8 feet per year (ft/yr), respectively.

During the summer of 1995, an in situ full-scale system was installed to increase anaerobic degradation rates. The treatment system consists of an alternating series of seven injection and extraction trenches used to introduce and circulate the primary substrate and nutrients with the groundwater. The extraction and injection trenches are 1800 and 1100 linear feet (LF), respectively. The trenches were dug 100 ft apart down to a depth of 20-22 ft bgs, at least 1 ft into the bottom clay layer. A perforated pipe was installed in each trench to provide an open path way to the sump located at the downward sloping end of each extraction trench. The sump pumps the water to a control room where nutrients and methanol are

added. The amended water then flows into a wet well before being released into the injection trenches. The water flows through the system at a rate of 12 gallons per minute (gpm).

Operation of the system began in September 1995 with the addition of nitrogen and phosphate nutrients only. Nitrogen was added in the form of potassium nitrate, and phosphate added as potassium tripolyphosphate. An initial decrease occurred in TCE concentration, but the degradation rate remained very slow. In June of 1996 methanol was added to the system to serve as the primary substrate reducing dissolved oxygen (DO) and oxidation-reduction potential levels, to favor anaerobic degradation. Methanol was injected continuously until an increase in microbial activity was observed. Later, pulsed injection was used to limit biofouling. The concentrations of nutrients and methanol added were established by mass balance concentrations required in the subsurface. The reinjection concentrations of nitrogen and phosphate are 9 mg/L each, and methanol 80 mg/L. As of October 1996, recirculation rates had slowed to 10 gpm and a total of 5.2×10^6 gallons had been recirculated through the system.

The performance of the system was difficult to determine because in the beginning, the treatment area was not well mixed; it took about a year of operation to establish a well-mixed system. In addition, only a limited number of monitoring locations were established and the treatment facility was an open system that was exposed to rain infiltration. In June 1995 TCE concentration ranged from 2.0 to 88 mg/L. By May 1996 (only nutrients had been added) TCE concentration had dropped to 5.4 to 65 mg/L. After five months of full operation (methanol and nutrients injected) TCE levels dropped to 0.7 to 16 mg/L with all but two monitoring locations between 3.3 and 5.0 mg/L, indicating a 51% decrease from May.

2.5 Anaerobic and Aerobic Biodegradation of PCE and TCE (Watertown, Massachusetts)

A pilot-scale bioremediation effort is being conducted at Watertown Industrial Site in Watertown, Massachusetts. The objective of the study is to test the ability of the treatment facility to break down groundwater contaminants, first under anaerobic conditions then under aerobic conditions. Gas manufacturing plant, textile manufacturing, dry cleaning, and metal plating facilities were located at the site and in the surrounding area. The metal plating facility operated until 1990, and its degreasing shed is the probable source of the groundwater contamination. The contaminants of interest at this site are PCE and TCE. ABB Environmental Services is conducting the pilot study of anaerobic followed by aerobic in situ degradation. Bench-scale treatability tests were completed in 1994 confirming that natural attenuation by means of cometabolic reductive dehalogenation is ongoing at the site.

The site lithology is composed of three layers. The upper layer is 13 ft of sand and gravel, the following layer is 7 ft of silty sand, and the last layer, before Cambridge Argillite bedrock, is 5 ft of glacial till which acts as an aquitard. The groundwater table occurs at 8 ft bgs. Groundwater runs into the Charles River, located 200 ft downgradient from the site.

In November 1996, a pilot-scale treatment study began. The treatment design includes recirculating groundwater through a confined treatment cell. Groundwater is extracted from three downgradient wells to the surface where nutrients, nitrogen and phosphorus in the form of ammonium chloride and potassium phosphate at concentrations of 25 mg/L each, and lactic acid are added. The enhanced groundwater is then reinjected into three upgradient injection wells. The extraction and injection wells (EW and IW) were constructed of 4-in PVC pipe and screened in the silty sand layer 13-20 ft bgs. The treatment cell covers an area of 400 ft^2 with a flow rate of 0.25 gpm, close to the normal groundwater flow. Five monitoring wells (EPA 1 through 5) are located within the treatment area. Groundwater samples are taken from those wells twice per month.

The injection strategy began with continuous injection from the beginning of operation, mid-November 1996, until April 11, 1997. From April 11 to October 1997 pulse injection was used. A 375 mg/L concentration of lactic acid pulsed through the system was demonstrated to be the most effective. The treatment system remained anaerobic until late July 1997. The average initial concentrations of PCE, TCE and daughter product vinyl chloride (VC) were 1,300 μg/L, 12,000 μg/L, and 3,200 μg/L, respectively. The above concentrations were averaged from five wells: EPA 1, 2 and 3; IW 2; and EW 2. Those five wells are aligned through the center of the treatment area. After eight months of anaerobic operation the average concentrations of the above contaminants decreased to: TCE, 1,100 μg/L, PCE, 1,000 μg/L, and VC, 3,500 μg/L.

In late July 1997, the system was converted to operate under aerobic conditions in order to degrade TCE daughter products, DCE and VC. Oxygen was added by inserting oxygen releasing compound (ORC) socks into each of the injection wells. Methane was added through the injection wells and acts as the electron donor for aerobic cometabolic degradation. The aerobic portion of the Watertown treatment operation is currently operating; data are not yet available to evaluate the performance of the system under these conditions.

The objective of the Watertown pilot study was to test the two stage, anaerobic/aerobic, process. During the anaerobic phase, the concentrations of TCE and PCE were not degraded to levels below drinking water standards.

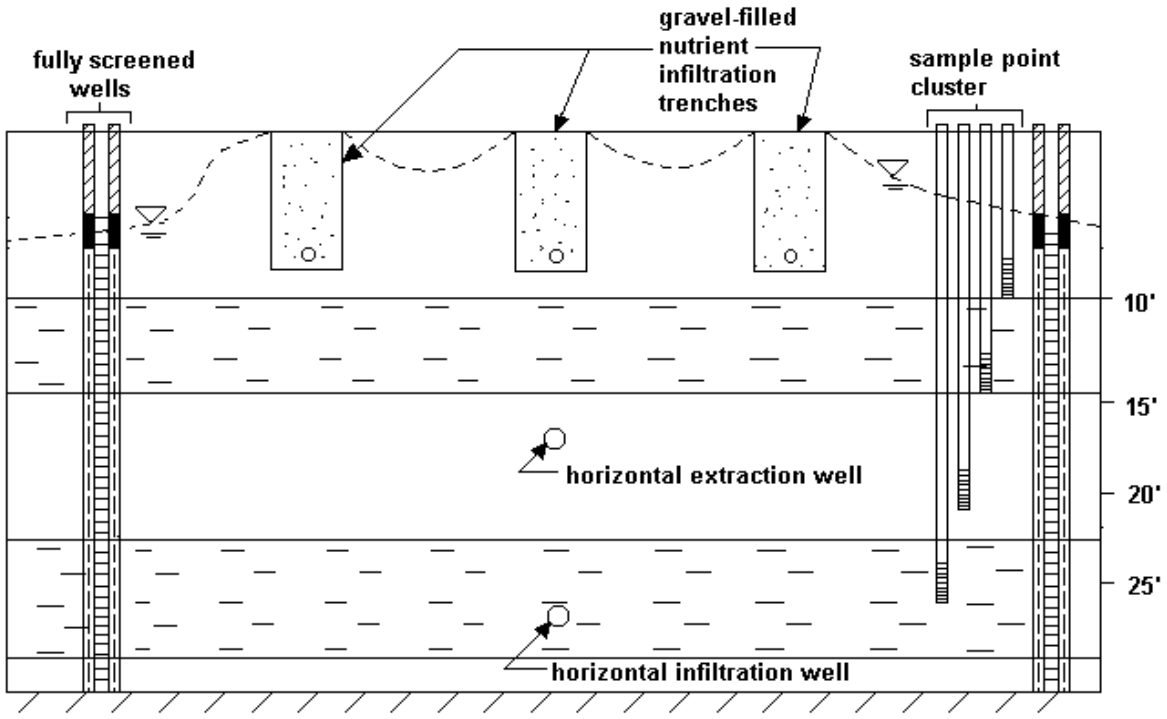
2.6 Anaerobic Biodegradation of Chlorinated Solvents at Pinellas Science, Technology, and Research (STAR) (Largo, FL)

An in situ anaerobic bioremediation demonstration was completed in July of 1997 for a portion of the groundwater plume at the former DOE's Pinellas Plant in Largo, Florida, now known as Pinellas STAR Center. From 1956 to 1994, nuclear generators and components for nuclear weapons were manufactured at the Pinellas Plant. One area of the site is contaminated with chlorinated solvents as a result of past waste storage and disposal practices. The following case study is a condensed version of the *Cost and Performance Report: In Situ Anaerobic Bioremediation Pinellas Northeast Site Largo, Florida* published in April 1998.

A pilot-scale bioremediation demonstration was conducted to remediate moderate levels of chlorinated solvent contamination. The main chlorinated solvents present in the water include TCE, cis-DCE, VC and methylene chloride. Contaminant concentrations ranged from 10 to 400 mg/L in the groundwater, but one monitoring well exceeding 2900 mg/L.

The groundwater plume covers an area from three to four acres. The area is composed of a shallow, sandy aquifer with horizontal and vertical hydraulic conductivity ranging from 0.2 to 6.6 ft/day and 0.003 to 0.3 ft/day, respectively. The pH of the aquifer varies between 5.5 and 7.2 depending on location, with neutral (7.0) pH as the mean. The bioremediation system covered an area of approximately 2,025 square feet down to a depth of 30 ft bgs, where a confining clay layer acts as an impermeable barrier. A pilot-scale in situ bioremediation treatment system operated for six months. The treatment system was composed of three 8-ft deep, 30-ft long and 2-ft wide, gravel-filled, surface infiltration trenches, and, two 240-ft long horizontal wells with 30-ft of screen placed in intervals. The gravel trenches were designed for efficient delivery of nutrients. The horizontal wells were installed through the center of the treatment zone. The extraction well was located 17 ft bgs and the infiltration well was placed directly under the extraction well at 26 ft bgs (see Figure 7). The most effective pumping rate for the extraction well was found to be 1.5 gpm. Biofouling, resulting from continuous nutrient injection, caused clogging in the horizontal extraction well. The extraction well had to be redeveloped eight times, however, the infiltration well had to be redeveloped only once.

Figure 7: Cross Section of Treatment Area



Source: Cost and Performance Report - Pinellas In Situ Anaerobic Bioremediation

There were 16 monitoring locations within the treatment zone. Each location consisted of four sampling points. Each point was at a different depth below the ground surface: 8 to 10 ft bgs, 12 to 14 ft bgs, 18 to 20 ft bgs, and 22 to 24 ft bgs. In addition, four monitoring wells were installed around the perimeter, one in each corner of the treatment area. Monitoring for substrate and contaminant concentrations were performed semimonthly, while bromide tracer studies were conducted weekly.

Electron donors (substrates) were added continuously to the system from February 7 to June 30, 1997. The substrates used were sodium benzoate (rapidly reducing to acetate), sodium lactate and methanol at concentrations of 120 mg/L, 180 mg/L and 60 mg/L, respectively. The average initial concentration of each contaminant was as follows: TCE, 46.6 mg/L, cis-1,2-DCE, 45.6 mg/L, methylene chloride, 19.2 mg/L, and VC, 9.5 mg/L. Most of the biodegradation took place in the first four to eight weeks after

substrate arrival. The concentration of TCE was reduced by 94%; the other contaminants were reduced 55 to 60%. However, by the end of the cleanup action 90 to 95% of all the contaminants had been reduced through groundwater recirculation in the treatment cell.

A full-scale treatment system is planned to cleanup the entire groundwater plume which spans an area of approximately 3.5 acres. The total cost of the pilot system was $397,074. Table 2 presents a breakdown of costs. The cost of scaling the pilot-system to a full-scale treatment facility was estimated as $3 to 4 million for construction. It was estimated that an additional $600K and $750K per year would be required for system operation and nutrient addition, respectively. The cost for the full-scale system is only approximate because much of the Northeast site has lower contaminant levels (less than 200 mg/L) than those treated with the pilot-scale system. For areas where contaminant levels are greater than 200 mg/L, a more aggressive technology will be implemented. Operation and maintenance costs may increase with the full-scale system due to required well redevelopment because of biofouling. These estimates suggest that a full-scale bioremediation system with horizontal recirculation design would cost $4.5 to 5.5 million to construct and operate for 2 to 3 years.

The objectives of this pilot study were to deliver sodium benzoate, sodium lactate, and methanol throughout the heterogeneous aquifer within six months, and construct a closed loop groundwater recirculation treatment system without a need for groundwater disposal. The pilot study demonstrated an aquifer must have favorable geochemical, microbial, hydraulic, and hydrological characteristics for an in situ bioremediation treatment facility to be implemented successfully. All objectives have been met; therefore a full-scale cleanup effort using in situ anaerobic bioremediation is planned for treating the moderately contaminated portion of the groundwater plume at the Pinellas site.

Table 2: Pilot-Scale Treatment System Costs

Cost Element	Cost ($)
Mobilization and preparatory work	35,000
Monitoring, sampling, testing, and analysis	238,310
Groundwater collection and control	87,53

Biological Treatment	23,748
Project management and engineering	12,480
TOTAL	397,074

Source: Cost and Performance Report - Pinellas In-Situ Anaerobic Bioremediation

2.7 In-situ Anaerobic Bioremediation Pilot Study with Bioaugmentation (Dover Air Force Base, Delaware)

A pilot-scale in-situ enhanced anaerobic biodegradation study is coming to a close at Dover Air Force Base, Delaware. Chlorinated solvents, PCE, TCE, cis-DCE, and VC, contaminate the aquifer in Area 6 of the base. Historically, spent solvents were disposed of in a pit. Once the pit was full, the contents were burned and chlorinated solvents seeped through the subsurface into groundwater.

The cleanup strategy employed to remedy the site is enhanced biodegradation with substrate injection into the aquifer to stimulate reductive dechlorination. The project at Dover AFB was sponsored by the companies involved with the Chlorinated Solvents Consortium, an action team within the Remediation Technologies Development Forum (RTDF).

Hydrogeologic testing and sampling were performed to characterize the test site. The concentrations of the contaminants at the Dover site are as follows: PCE, 50 μg/L, TCE, 5,000 to 10,000 μg/L, cis-DCE, 1,000 to 2,000 μg/L, and VC, 20 μg/L. The aquifer is composed of silty sand, relatively homogeneous soil down to a clay aquitard at about 50 ft bgs. The groundwater table occurs at 10 to 12 ft bgs, and the existing hydraulic conductivity is 0.021 cm/s (60 ft/day). The pilot system covered an area of 40 ft x 60 ft down to the confining clay layer. The groundwater flows south at a gradient of 0.001 with a velocity of about 0.5 ft/day.

The anaerobic bioremediation pilot treatment system designed for the site began operating in September 1996. The system consisted of three injection and three extraction wells installed vertically, forming a contained treatment cell within the aquifer. Groundwater travels 60 ft from injection to extraction with a residence time of 90 days. The wells were designed vertically to distribute the substrate to the point of interest within the aquifer, about 36 ft bgs, where the highest concentration of contaminants occur. The injection and extraction wells were designed for a total flow rate of 3.6 gpm, 1.2 gpm for each well.

However, clogging of the injection wells has been a significant problem, and therefore the average flow rate of the system throughout the study has been around 2.4 gpm (Ed Lutz, personal communication).

Several different remedies for the clogging problem were tried, including redevelopment, weekly brush and pump treatment, peroxide cleaning, and changing the substrate from sodium lactate to lactic acid for a month. Each of the alternatives worked well for a while, but none prevented clogging for an extended period of time.

The clogging of the injection wells is attributed to high concentrations of bacterial growth around the well opening. Bacteria have a tendency to accumulate near the opening of the well due to the injection of substrate and nutrient enhanced groundwater. Sodium lactate was used as the substrate in the Dover pilot, and injected nutrients were nitrogen and phosphorus containing compounds. The concentration of 60% sodium lactate solution added to the extracted groundwater was 100 mg/L, as carbon, and the nutrient feed concentration injected was 5 mg/L. Both substrate and nutrients were pulse injected in a continuous cycle. The injection schedule is as follows: the substrate enhanced groundwater is injected for 3.75 days, then unamended groundwater is circulated for a half day, next nutrients are injected along with the groundwater for 2.75 days, then unamended groundwater is circulated for a half day.

The indigenous microbial flora that used the substrate and nutrients to cometabolically reduce TCE to cis-DCE at Dover were unable to further degrade DCE or VC. Bioaugmentation was implemented to reduce the TCE daughter products to ethene. Microorganisms from the Pinellas STAR Center were cultured, then 370 liters (L) were injected at a concentration of 10^8 cells per milliliter into the aquifer at the Dover site.

Following bioaugmentation with the Pinellas culture, DCE and VC were observed to degrade to ethene. The treatment system had a 99% removal efficiency for TCE and PCE, reducing the concentrations to below drinking water standards (5 μg/L). The removal efficiency for DCE and VC is approaching 99%, but it is not yet known whether VC concentrations meet drinking water standards (2 μg/L), because the lowest concentration that currently can be measured is 5 μg/L. VC concentrations are dropping below that level, but, the extent of decline is uncertain.

The capital cost of the pilot-system was $360,000. The operation and maintenance costs, excluding analytical costs, were approximately $125,000. Because the original volume of water in the system was recirculated for 18 months, the unit cost was calculated to be $1,860 per one thousand gallons of

groundwater treated. This unit cost is projected to drop for the full-scale single pass treatment facility being designed to treat the source of the plume at the Dover site (Ed Lutz, personal communication).

The objective of the pilot bioremediation study has been achieved. The treatment system demonstrated accelerated destruction of TCE; transformation occurred by means of reductive dechlorination. Because of the success with the pilot, a full-scale treatment system is being designed to treat the source of this contaminated groundwater plume. The full-scale design will be a single pass system with a long enough residence time for degradation to occur. Design and installation of the full-scale treatment facility is scheduled to be accomplished in fiscal year 1999, with startup planned for spring.

2.8 Reductive Dechlorination Using Molasses Injection (Eastern Pennsylvania)

Anaerobic biodegradation of CAHs is being explored as a viable way to cleanup contaminated aquifers at numerous sites around the country. ARCADIS Geraghty & Miller is influencing the biodegradation process by injecting a molasses and water mixture into the aquifer as the primary substrate for microorganisms. The basis for injecting molasses is its use as a carbon/energy source for indigenous microorganisms. The microbes readily degrade the primary substrate by utilizing available dissolved oxygen (DO) creating an anaerobic or reduced state in the system. In this reduced state hexavalent chromium can precipitate out of the aquifer and TCE can be degraded.

Evan Nyer and colleagues from ARCADIS Geraghty & Miller have recently published in the journal *Ground Water Monitoring and Remediation* an ongoing in-situ reductive dechlorination pilot demonstration at a manufacturing facility. The facility is located in eastern Pennsylvania on 16 paved acres. The facility was used for metal plating, textile operations and assembling of machinery. The aquifer beneath the industrial facility site was contaminated through the disposal of metal plating wastes and process water being dumped into deep bedrock injection wells for over 30 years until the early 1980s, when Pennsylvania Department of Environmental Protection (PADEP) put a stop to this practice. From 1982 until March 1997, when ARCADIS became involved, pump-and-treat was applied to reduce TCE and hexavalent chromium concentrations. The pump-and-treat system was operated for approximately 15 years, to a point where it was no longer efficient in removing significant contaminant mass.

In March 1997, the concentration of TCE in the aquifer was about 100 parts per billion (ppb). The aquifer geology consists of limestone and dolostones located 15 ft bgs. The majority of the groundwater is in the limestone aquifer.

Before initiating the pilot field application, testing was conducted to evaluate the natural biodegradation mechanisms at the site. Elevated concentrations of ethene, ethane and carbon dioxide were detected from the source area wells indicating that reductive dechlorination is taking place at the site, but at very slow rates. A pilot application was initiated in May 1997.

The pilot treatment facility established high reducing conditions in the aquifer to degrade TCE and precipitate out hexavalent chromium at a much faster rate. The means by which ARCADIS did this was by using the established boreholes from previous waste disposal practices In order to deliver substrates to the source of the contamination, PVC drop pipes were installed. A 1:50 molasses and water solution was injected on a weekly basis beginning in May 1997. Monitoring was performed every three months thereafter.

The objective of the demonstration was to reduce contaminant concentrations in the aquifer. Monitoring indicated that a large reactive zone had been established within the groundwater aquifer favoring strong reducing conditions. By September 1997, the TCE concentration had decreased by 60 to 84 percent throughout the monitoring field. Hexavalent chromium concentrations had dropped to non-detectable levels at the source area within the first three weeks of operation.

2.9 Reductive Dechlorination and Chromium Reduction at the Lycoming Superfund Site (Pennsylvania)

In the mid-1980s, moderate concentrations of CAHs were found in the alternate water supply near Williamsport, Pennsylvania. The alternate water supply is located approximately 3,000 feet downgradient from the Lycoming Superfund Site, an operating aircraft manufacturing facility. The contamination at the aircraft manufacturing facility extends over 28 acres, including surrounding residential neighborhoods. The contaminants of concern at the site were hexavalent chromium (Cr(VI)), cadmium (Cd), and CAHs (specifically TCE and daughter products 1,2-DCE and VC). The maximum concentrations of the contaminants at the site were Cr(VI), 3 mg/L, cadmium, 0.8 mg/L, and TCE, 0.7 mg/L. The geology of the contaminated aquifer consists of sandy silt overburden overlying weathered

bedrock and fractured limestone. The target area for treatment was the shallow overburden to 25 ft bgs covering an area of 2 acres. This site was placed on the National Priorities List (NPL) in 1988.

The article "In Situ Reactive Zones: Dehalogenation of Chlorinated Hydrocarbons" by Evan Nyer and colleagues from ARCADIS Geraghty & Miller describes the steps used to remediate the Lycoming Superfund Site. In 1995, ARCADIS Geraghty & Miller, consultants at the site, installed a pilot system to remediate the Cr(VI) and Cd groundwater plumes. The treatment system consisted of 20 4-inch diameter injection wells. Each well was connected to the 10 x 10 square-foot treatment building by means of a 3/4-inch pipe. The treatment building includes a molasses storage tank, a mixing tank, feed pumps, a control panel, and a solenoid valve nest. "A programmable logic controller monitors and controls the feed rate and frequency of the molasses feed and solution feed pumps, as well as the timing of the solenoid valve network that controls the metered flow to the injection wells" (Nyer et al, 1998). Molasses injections occur twice daily at various rates, with concentrations based on monitoring results.

In 1995, ARCADIS Geraghty & Miller began a pilot test at the site of their treatment technology known as in situ reactive zone technology, which uses molasses injection. The objective in molasses injection was to create reducing conditions in the subsurface so that microbial reduction of Cr(VI) to Cr(III) can occur. "The mechanisms of Cr(VI) reduction to Cr(III), under the induced reducing conditions can be likely a microbial reduction process involving Cr(VI) as the terminal electron acceptor for the metabolism of carbohydrates, by species such as *Bacillus subtilis*" (Nyer and Sutherson, 1996). The end product of the Cr(VI) reduction is the formation of chromium hydroxide ($Cr(OH)_3$) precipitate from Cr(III) in alkaline to moderately acidic conditions. The stable precipitate is primarily insoluble and immobilized in the soil matrix of the aquifer (Palmer and Puls, 1994).

The pilot study ran for six months in which the system was found to reduce chromium from 7 mg/L in the test zone down to below 0.05 mg/L. Further, it was found that the reactive zone treatment technology established appropriate conditions in the aquifer to reduce concentrations of CAHs through reductive dechlorination.

In the summer of 1996, the ROD was revised to include reactive zone technology and an AS/SVE curtain for the containment of CAHs as well as Cr(VI) and Cd. The full-scale treatment system was designed and constructed in the summer through winter of 1996, and began operation in January 1997.

Intensive groundwater monitoring was conducted to monitor the performance of the full-scale system, and eight additional monitoring wells were added. The majority of the wells were added as regulatory requirements since the Lycoming Superfund site was the first Superfund application to use molasses enhanced reactive zone treatment technology. Monthly to quarterly sampling has been underway for constituents such as redox potential, pH, Cr(VI), Cd, and CAHs.

The following results have been found after eight months of treatment. Cr(VI) concentration in "hot spots" decreased from 2-3 mg/L to 0.5 mg/L. In other portions of the plume, chromium levels were reduced from 1.5 to 0.005 mg/L, and the plume itself shrank to one-third of its original aerial extent. The results of monitoring well 3 from January to October 1997 showed a major decrease in CAH concentration. The TCE concentration was reduced from about 330 μg/L to approximately 40 μg/L; the DCE concentration was reduced from 670 to 180 μg/L; and the VC concentration was reduced from 20 μg/L to ND levels.

3. SUMMARY

Performance

The principal contaminant treated in the majority of the case studies was TCE. Recirculating cell treatment systems removed up to 99% of TCE in moderately contaminated groundwater, with an average removal rate of approximately 90%. Moderately contaminated groundwater is on the order of 1 mg/L of TCE. In general, TCE was degraded under both aerobic and anaerobic conditions. Daughter products from anaerobic reductive dechlorination of TCE persist longer in the aquifer. In two case studies, "In-Situ Anaerobic Bioremediation Pilot Study with Bioaugmentation (Dover AFB)" and "Anaerobic/Aerobic Biodegradation of PCE and TCE (Watertown, MA)", methods were established to accelerate degradation of the daughter products.

The biobarrier treatment used at the SRS was biosparging in conjunction with SVE. Higher TCE removal efficiencies were achieved due to SVE accompanying biosparging. The MTT technology employed in rural Virginia established a treatment zone with an injection well and monitoring well, but no extraction well was used. This system could be considered a biobarrier. Its removal efficiency was approximately 92%. One biobarrier application is not sufficient for inferring a general treatment efficiency for biobarriers. Plus, removal using biobarriers, like most bioremediation applications, is site specific.

Future Needs

There is a need for additional research into bioremediation of CAHs, including further investigation of techniques that have been established to alter intrinsic environmental conditions and to enhance the mechanisms in which cometabolic bioremediation will work. For example, procedures have been implemented to force an aquifer more aerobic or anaerobic depending on the degradation mechanism, and hydraulic containment of groundwater has been achieved to recirculate the water for more efficient removal.

Additional areas of research for bioremediating CAHs include:

- Scale-up of pilot study results to full-scale systems
- Evaluation of suitable habitats, nutritional requirements, lag times, and degradation rates (in the field) for various chlorinated contaminants
- Optimization of environmental conditions, and stimulation of favorable growth conditions under site-specific variations
- In situ methods for monitoring process efficiency
- Mass balance of electron donors and acceptors within a given system
- Impact on aquifer permeability due to enhanced bioremediation
- Enhancing bioremediation in low permeability environments
- Understanding bioaugmentation, including which organisms degrade specific chlorinated compounds and how
- Hydraulic field effects on microbial activity
- Techniques to minimize well fouling

Source: Adapted from Suthersan, Suthan S. *Remediation Engineering: Design Concepts*

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