9-2005

A Scientific and Technial Review of the Use of Bioremediation as a Clean Up Technique at the Savannah River Site

Harambee House, Inc.

Mildred McClain

The Community Alliance on the Savannah River Site

HARAMBEE HOUSE, INC.
Project Citizens For Environmental Justice
September 2005

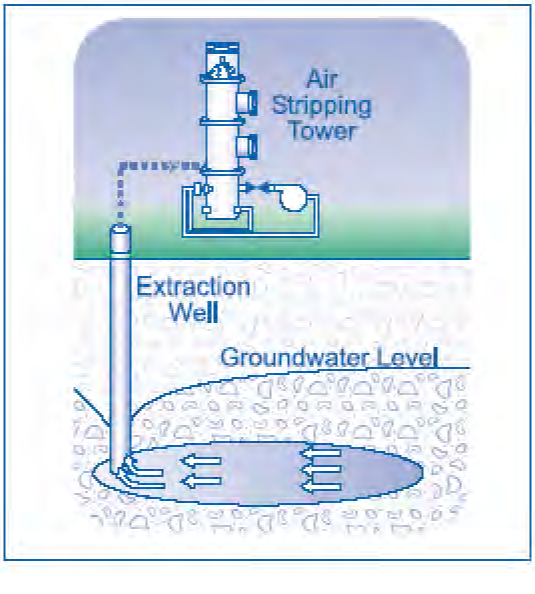
A Scientific and Technical Review of The Use of Bioremediation as a Clean Up Technique At the Savannah River Site

Report Prepared by: Dr. Mildred McClain

Scientific and Technical Analysis Conducted by: Michael Ashby, New York City College
Dr. Kenneth Sajwan, Savannah State University
Dr. Mae Samuel, Benedict College

"Supported by a grant from the Citizens' Monitoring and Technical Assessment Fund"

BIOREMEDIATION



ASSESSMENT OF BIOREMEDIATION AS A CLEAN UP STRATEGY AT SAVANNAH RIVER SITE

TABLE OF CONTENTS

SUMMARY

Halogenated volatile organic compounds (VOCs), including chlorinated aliphatic hydrocarbons (CAHs), are the most frequently occurring type of contaminant in soil and groundwater at Superfund (CERCLA) and other hazardous waste (RCRA) sites in the United States. The U.S. Environmental Protection Agency (EPA) estimates that cleanup of these sites will cost more than $45 billion (1996 dollars) over the next several decades (EPA, 1997). Other evaluations have projected the clean up cost of existing environmental contamination as being more in the region of $1 trillion dollars.

In the early 1980's, little was known about how toxic wastes interact with the hydrosphere. This lack of knowledge was crippling efforts to remediate environmental contamination under the new Superfund legislation---the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Faced with this problem, Congress directed the United States Geological Survey (USGS) to conduct a program to provide this critically needed information. By means of this program, known as the Toxic Substances Hydrology Program (TSHP), the most important categories of wastes were systematically investigated at sites throughout the nation. One of the principal findings of this program was that microorganisms in shallow aquifers affect the fate and transport of virtually all kinds of toxic substances. As a result of these findings, innovative technologies, including *in situ* and *ex situ* bioremediation, are being developed and implemented in an effort to reduce the cost and time required to clean up currently identified sites. For the most part, these technologies involve biogeochemical processes including the concept known as Natural Attenuation.

Natural attenuation may reduce the potential risks posed by site contaminants in one of three ways, depending upon the type of contaminant:

1. Contaminants may be transformed to a less toxic form through destructive processes (e.g., biodegradation, radioactive decay);
2. Potential exposure levels may be reduced by lowering concentration levels (e.g., dilution, dispersion); and
3. Contaminant mobility and bioavailability may be reduced by sorption to the soil or rock matrix.

Several organizations involved in environmental clean-up projects have developed definitions for natural attenuation. The U.S. Environmental Protection Agency (EPA) defines monitored natural attenuation as the "reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These *in-situ* processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; chemical or biological stabilization; transformation; or destruction of contaminants." (EPA, OSWER Directive 9200.4-17P)

The American Society for Testing and Materials (ASTM) defines natural attenuation as the "reduction in mass or concentration of a compound in groundwater over time or distance from the source of constituents of concern due to naturally occurring physical, chemical, and biological processes, such as; biodegradation, dispersion, dilution, adsorption, and volatilization." (ASTM E1943-98, 1998)

The U.S. Air Force Center for Environmental Excellence defines natural attenuation as the processes resulting "from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization." (Wiedemeier, 1999)

The U.S. Army defines natural attenuation as "the reduction of contaminant concentrations in the environment through biological processes (aerobic and anaerobic biodegradation, plant and animal uptake), physical phenomena (advection, dispersion, dilution, diffusion, volatilization, sorption/desorption), and chemical reactions (ion exchange, complexation, abiotic transformation). Terms such as intrinsic remediation or bio-transformation are included within the more general natural attenuation definition." (U.S. Army, 1995)

Natural attenuation processes for reducing organic contaminant levels are currently best documented at petroleum fuel sites. Organisms in the soil and groundwater break down chemicals through biological degradation processes into byproducts that are often nontoxic and harmless. For example, under appropriate field conditions, the compounds benzene, toluene, ethyl benzene, and xylene (known collectively as BTEX) may naturally degrade through microbial activity and ultimately produce non-toxic end products (e.g., Carbon Dioxide (CO_2) and water (H_2O)).

Chlorinated solvents, such as common organic contaminants that may also biodegrade (generally via reductive dechlorination) under certain environmental. Some inorganics, more specifically radionuclides, also “break down” over time. Unlike organic contaminants, radionuclides have a predictable rate of decay. The specific “half-lives” of radionuclides allow for accurate prediction of the time required to reduce their radioactivity to levels that are no longer hazardous. The concentrations of mobile and toxic forms of non-degradable inorganic contaminants may also be effectively reduced by other natural processes.

The movement of metals and radionuclides is attenuated in the subsurface via sorption to mineral surfaces or soil organic matter and occasionally through volatilization. In addition, oxidation/reduction (redox) reactions can transform the valence states of some inorganic contaminants to less soluble, and thus less mobile, forms, or to forms that are less toxic (e.g., hexavalent to trivalent chromium). Contaminant immobilization through natural processes is contaminant and matrix dependent. Some metals/radionuclides often have very little interaction with the matrix and can, consequently, move unretarded through the subsurface. Furthermore, sorption can be reversible depending upon the contaminant and method of attenuation, i.e., it either becomes a permanent fixture within that particular matrix or maintains the potential for re-release. Even though some organic and many inorganic contaminants cannot be destroyed or transformed through natural attenuation processes, they are diluted and/or dispersed as they move through the subsurface. Unlike contaminant destruction or transformation, dilution and dispersion do not lead to a reduction in contaminant mass, but rather a reduction in contaminant concentration. Because of the type and occurrence of VOCs at contaminant sites, biodegradation is one of the more important and utilized processes of those mentioned above.

What is bioremediation?

Biodegradation (biotransformation) is the breakdown of organic contaminants by microbial organisms into smaller compounds. The microbial organisms transform the contaminants through metabolic or enzymatic processes. Biodegradation processes vary greatly, but frequently the final product of the degradation is carbon dioxide or methane and water.

Biodegradation is a key process in the natural attenuation of contaminants at hazardous waste sites. The remediation or clean-up of a contaminate site using biodegradation processes and technology is known as Bioremediation. It allows natural processes to clean up harmful chemicals in the environment. Microscopic “bugs” or microbes that live in soil and groundwater like to eat certain harmful chemicals, such as those found in gasoline and oil spills. When microbes completely digest these chemicals, they change them into water and harmless gases such as carbon dioxide.

As technology improves, ex situ clean-ups are becoming less desirable since they require the removal of contaminated materials (soil or groundwater) to be removed to other locations. This can be cost intensive practice. In situ bioremediation is increasingly being selected to remediate hazardous waste sites because, when compared to other technology approaches (e.g. above-ground technologies), it is usually less expensive, does not require waste extraction or excavation, and is more publicly acceptable as it relies on natural processes to treat contaminants. Over half of bioremediation projects at Superfund remedial action sites (57 percent) are in the operational phase, while 26 percent are in the predesign, design, or installation phases and 17 percent have been completed. Of the 18 completed projects, 14 are ex situ source treatment projects, and 4 are in situ projects for source treatment and groundwater treatment. Since 1991, the percentage of bioremediation projects performed ex situ has decreased while the percentage of projects performed in situ has increased. In 1991, only 35 percent of the Superfund remedial action bioremediation projects were in situ versus 53 percent in 1999. Bioventing is the most commonly implemented in situ treatment technology for source treatment. Land treatment is the most commonly used ex situ source treatment technology (EPA, 2001; FRTR, 2001).
After the initial clean-up of a particular site, it may become necessary to monitor the behavior of the contaminant (plume). This extended oversight has become known as Monitored Natural Attenuation (MNA).

Monitored natural attenuation may be defined as the reliance on natural attenuation processes, within the context of a carefully controlled and monitored site cleanup, to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by more active methods. Monitoring, therefore, is the critical component of any remediation by natural attenuation. Monitoring is imperative to:

- ensure performance objectives are being achieved as expected and
- detect unacceptable migration of contamination so that contingency measures can be implemented to prevent any unacceptable risks to human health and the environment.

How does bioremediation work?

In order for microbes to clean up harmful chemicals, the right temperature, nutrients (fertilizers), and amount of oxygen must be present in the soil and groundwater. These conditions allow the microbes to grow and multiply—and eat more chemicals. When conditions are not right, microbes grow too slowly or die. Or they can create more harmful chemicals. If conditions are not right at a site, EPA works to improve them. One way they improve conditions is to pump air, nutrients, or other substances (such as molasses) underground. Sometimes microbes are added if enough aren’t already there.

The right conditions for bioremediation cannot always be achieved underground. At some sites, the weather is too cold or the soil is too dense. At such sites, EPA might dig up the soil to clean it above ground where heaters and soil mixing help improve conditions. After the soil is dug up, the proper nutrients are added. Oxygen also may be added by stirring the mixture or by forcing air through it. However, some microbes work better without oxygen. With the right temperature and amount of oxygen and nutrients, microbes can do their work to "bioremediate" the harmful chemicals.

Sometimes mixing soil can cause harmful chemicals to evaporate before the microbes can eat them. To prevent these chemicals from polluting the air, EPA mixes the soil inside a special tank or building where chemicals that evaporate can be collected and treated.

Microbes can help clean polluted groundwater as well as soil. To do this, EPA drills wells and pumps some of the groundwater into tanks. Here, the water is mixed with nutrients and air before it is pumped back into the ground. The added nutrients and air help the microbes bioremediate the groundwater. Groundwater can also be mixed underground by pumping nutrients and air into the wells. Once harmful chemicals are cleaned up and microbes have eaten their available "food," the microbes die.

Is bioremediation safe?

Yes. Bioremediation is very safe because it relies on microbes that naturally occur in soil. These microbes are helpful and pose no threat to people at the site or in the community. While the Microbes themselves won't hurt you, it is always good practice never touch polluted soil or groundwater—especially before eating.

No dangerous chemicals are used in bioremediation. The nutrients added to make the microbes grow are fertilizers commonly used on lawns and gardens. Because bioremediation changes the harmful chemicals into water and harmless gases, the harmful chemicals are completely destroyed.

Why use bioremediation?

The EPA estimates that, over the next several decades, site owners will spend billions of dollars to cleanup these sites. New technologies that are less costly and more effective are needed to accomplish hazardous waste site remediation. The selection of bioremediation a clean-up remedy is desirable for several reasons. First and most importantly, once chemical contaminants get into the subsurface, it is virtually impossible to clean them up to pre contamination conditions. Even if there is an attempt to remove all contaminated media.

Secondly, bioremediation or some kind of nature based sustainable process is the only option for cleanup. Bioremediation involves harnessing natural processes. At some sites, natural microbial processes can remove or contain contaminants without human intervention. In these cases where natural attenuation (intrinsic bioremediation) is appropriate, substantial cost savings can be realized. Remediation and Clean-up organizations use intrinsic bioremediation because it takes advantage of natural processes.

Thirdly, it facilitates the treating contamination in place. Most of the cost associated with traditional cleanup technologies is associated with physically removing and disposing of contaminated soils. Because engineered bioremediation can be carried out in place by delivering nutrients to contaminated soils, it does not incur removal-disposal costs. Polluted soil and groundwater can be cleaned at the site without having to move them somewhere else. If the right conditions exist or can be created underground, soil and groundwater can be cleaned without having to dig or pump it up at all. This allows cleanup workers to avoid contact with polluted soil and groundwater. It also prevents the release of harmful gases into the air. Because microbes change the harmful chemicals into water and harmless gases, few if any wastes are created.

Fourthly, it reduces environmental stress because bioremediation methods minimize site disturbance compared with conventional cleanup technologies, post-cleanup costs can be substantially reduced. Scientific objectives and technical approaches are based on the hypothesis that among others the most important mass-removal process for natural attenuation is biodegradation. In addition, it can be further hypothesize that a common pattern of biodegradation activity can be found in most groundwater pollution plumes.

There are several different types of computer programs and models that can assist decision makers, regulators, and project managers at contaminated sites and their advisors to be able to forecast natural attenuation for a wide range of pollutants under a variety of site conditions. This will give them, and regulators, greater confidence in including natural attenuation as a viable alternative in their risk-based strategy for site remediation and subsequent management. This will allow resources to be focused on more important environmental and economic objectives at the national levels. Once identify, these zones will have better conditions for biodegradation, and these zones will have more rapid degradation and make a significant contribution to the overall rate of mass loss for the entire plume. Since these areas, once identified, can be modeled prior to actual start up of the clean-up process, there is greater confidence in forecasting the outcome of Natural Attenuation as a risk-based soil or groundwater remediation strategy.

Finally, it reduces clean-up costs by stretching remediation dollars. It has been projected that the cost of remediating contaminated sites to meet the minimal regulatory requirements is likely to run into many billions of dollars. For many States and local communities, remediation of contaminated sites may not be economically or technically feasible with conventional clean-up technologies. Information about the cost of using bioremediation to treat contaminated media was available for 67 sites. Unit costs for bioventing projects ranged from approximately $2 per cubic yard (cy) to more than $300/cy, with most sites less than $40/cy. Unit costs for ex situ bioremediation of soil, such as land treatment or composting systems, ranged from $13/cy to more than $500/cy, with most projects costing less than $300/cy. Simply stated, *in situ* bioremediation can help contain costs (EPA, 2001; FRTR, 2001). As an alternative, a greater emphasis can be placed on risk-based approaches to soil and groundwater resource management. Where remediation objectives at particular contaminated sites are balanced against expected cleanup costs and intended use of the groundwater or land area. Often bioremediation does not require as much equipment or labor as most other methods. Therefore, it is usually cheaper. Few bioremediation Records of Decision (RODs) were signed in the early- to mid-1980s. Beginning in fiscal year (FY) 1988, the number of bioremediation RODs has increased. In general, 8 to 12 bioremediation RODs have been signed per year (EPA, 2001; FRTR, 2001).

How long will bioremediation take?

The time it takes to bioremediate a site varies depending on several factors:

- types and amounts of harmful chemicals present
- size and depth of the polluted area
- type of soil and the conditions present
- whether cleanup occurs above ground or underground

These factors vary from site to site. It can take a few months or even several years for microbes to eat enough of the harmful chemicals to clean up the site. To ensure that bioremediation is working, project managers periodically take and analyze samples of soil and groundwater from the contaminated area.

While Monitored natural attenuation (MNA) has shown that it is a potentially low-cost valuable risk-based remediation strategy for contaminated groundwater, its wider exploitation throughout the nation is still limited by lack of confidence in its application and management, and uncertainty in predicting its performance at many sites.

INTRODUCTION
AND
BACKGROUND

This report provides an overview of the fundamentals and field applications of in situ bioremediation in contaminated soil and groundwater. Bioremediation has been presented to the impacted communities as a technology that is currently being used and tested at the Savannah River Site (SRS). The primary focus this report explain bioremediation as a clean-up technology and analyze what role the technology will play in the new accelerated clean up strategy at SRS as approved by Environmental Management at the U.S. Department of Energy (DOE). The objective is to understand how bioremediation is being used at SRS for clean up. Included is a summary of currently-available information on the mechanisms and technologies used to implement *in situ* bioremediation. Under NEPA (1969), Executive Order 12989 and several EPA statues cleanup managers are required to involve the public so that they can become aware of and participate in activities related to cleanup and environmental management ongoing in their own communities. This report is intended to familiarize affected communities and others involved with hazardous waste site cleanups, including site project managers, contractors, and other technology users, with the dynamics of in situ bioremediation. In addition, the report is intended to present a discussion to community residents and members of the working group to help them to identify and develop the knowledge base of the surrounding community on the Performance Management Plan (PMP) and bioremediation as a remedial technology at SRS.

As such, the level of detail included in this report about bioremediation mechanisms, technologies, and implementation is meant to provide only basic information about the technology, rather than providing an in depth how to manual about *in situ* bioremediation. It will be part of a comprehensive picture of the accelerated clean up plan and the use bioremediation as a clean up technology. The report looks at the use and viability of bioremediation in other locations as part of this review. The report should therefore be used for informational purposes, and should not be used as the sole basis for determining the value and usefulness of this technology at the specific site of concern. It is instructive that such decisions must be made on a case-by-case basis, considering site-specific factors.

This introduction provides background information about *in situ* bioremediation at sites contaminated with various examples of chlorinated aliphatic hydrocarbons (CAHs). This type of contamination is chosen because of the type, number of occurrences and difficulty of clean-up. Because of their nature several of these can be further classified as Persistent Organic Pollutants (POPs). The basic description below includes; identification of typical CAHs and their physical and chemical properties; Processes that transport CAHs through the subsurface environment and biological and chemical mechanisms that can degrade CAHs. More detailed information about the physical and chemical characteristics and the subsurface transport processes of CAHs are beyond the scope of this report but can be found in the references listed below.

BIOREMEDIATION MECHANISMS

Bioremediation has successfully cleaned up many polluted sites and is being used at 50 Superfund sites across the country. The most common type of Superfund remedial action site where bioremediation is used is wood preserving (31 percent), followed by petroleum sites (21 percent). The most common types of contaminants at these sites are polycyclic aromatic hydrocarbons (PAHs) (40 percent); benzene, toluene, ethylbenzene, and xylenes (BTEX) (37 percent); and pesticides and herbicides (27 percent). Available performance data shows that bioremediation is capable of reducing contaminant concentrations in contaminated media. Bioremediation is being used to treat recalcitrant organic compounds, including chlorinated volatile organic compounds (VOCs), PAHs, pesticides and herbicides, and explosives.

For ten projects treating chlorinated VOCs, concentrations of VOCs in treated groundwater ranged from below detection limit (<5 µg/L for tetrachloroethene [PCE], trichloroethene [TCE], and dichloroethene [DCE]) to 1,200 µg/L (for carbon tetrachloride). For seven projects treating PAHs, concentrations of PAHs in treated soil and sludges ranged from 3.3 mg/kg to 795 mg/kg, with some projects showing more than 90% removal. For four projects treating pesticides and herbicides, concentrations of specific pesticides and herbicides in treated soil were less than 10 mg/kg at two projects and less than 200 mg/kg at the other two projects, with some projects showing more than 90% removal. For six projects treating explosives, three showed removals of more than 75% and the others showed removals ranging from little or none to as much as 64% (EPA, 2001; FRTR, 2001).

Chlorinated aliphatic hydrocarbons (CAHs) are manmade organic compounds. They are typically manufactured from naturally occurring hydrocarbon constituents (methane, ethane, and ethene) and chlorine through various processes that substitute one or more hydrogen atoms with a chlorine atom, or selectively dechlorinate chlorinated compounds to a less chlorinated state. As such CAHs are also classified as chlorinated volatile organic compounds (VOCs). They are used in a wide variety of applications, including use as solvents and degreasers and in the manufacturing of raw materials. They include such solvents as tetrachloroethene (PCE), trichloroethene (TCE), carbon tetrachloride ($CCl4$), chloroform (CF), and methylene chloride (MC).

Historical management of wastes containing CAHs has resulted in contamination of soil and groundwater, with CAHs present at many contaminated groundwater sites in the United States. Of these substances, trichloroethene (TCE) is the most prevalent of those contaminants (U.S. Air Force, 1998). In addition to CAHs, their degradation products can include such substances as dichloroethane (DCA), dichloroethene (DCE), and vinyl chloride (VC), which tend to persist in the subsurface.

Physical and Chemical Properties of CAHs

The physical and chemical properties of CAHs govern their transport and fate in the subsurface (underground) environment. The number of substituted chlorine atoms on the CAHs directly affects their physical and chemical behavior. As the number of substituted chlorine atoms increases, the molecular weight and density generally increase, whereas vapor pressure and aqueous solubility generally decrease. A CAH released to the subsurface as a pure organic liquid (commonly referred to as non-aqueous phase liquid [NAPL] in the subsurface) will seek phase equilibrium (a condition in which all acting influences are canceled by others, resulting in a stable, balanced, or unchanging system). The CAH will remain as a NAPL, adsorb to soil, dissolve in groundwater, or volatilize into soil gas to the extent defined by the physical and chemical properties of the individual CAH and the subsurface environment. Partition coefficients, which are related to the hydrophobicity and aqueous solubility of a CAH, define the extent to which a CAH will partition between NAPL, adsorb to soil, and dissolve in groundwater. The vapor pressure of a CAH defines the extent to which it will partition between NAPL or NAPL adsorbed to soil and the soil gas. CAHs dissolved in groundwater will also partition themselves between the dissolved phase and the vapor phase, as defined by their Henry’s Constant. Figure 1 below shows those mechanisms by which CAHs transfer phases in an attempt to reach equilibrium conditions and their related properties.

Non-Aqueous Phase Liquids (NAPLs) are liquids that are sparingly soluble in water. Because they do not mix with water, they form a separate phase. Hydrocarbons, such as oil and gasoline, and chlorinated solvents, such as trichloroethylene, are examples of NAPLs, because they do not mix with water, and oil and water in a glass will separate into two separate phases.

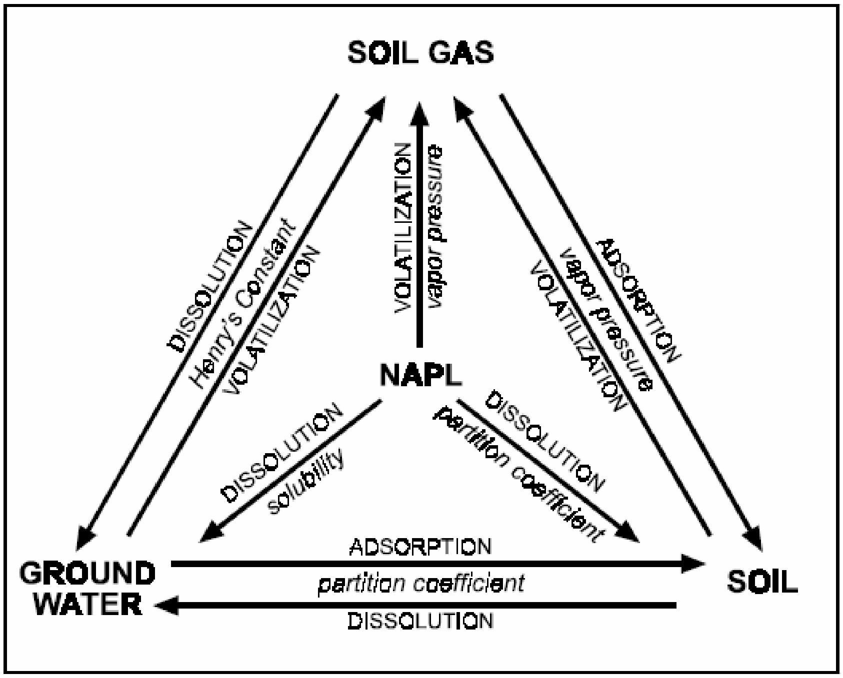


Figure 1: Phase Equilibrium Mechanisms and Defining Properties of CAHs
Source: Modified from Huling and Weaver, 1991

There are two categories of NAPLs. The first type can be lighter than water (LNAPL) while the second group is denser than water (DNAPL). Most of the CAH NAPLs discussed in this report are denser than water. They are generally referred to as dense non-aqueous phase liquids [DNAPLs]). The exceptions are vinyl chloride, chloroethane, and chloromethane, which are gaseous in their pure phase under standard conditions. NAPLs that are less dense than water are generally referred to as light non-aqueous phase liquids [LNAPL]. In addition, capillary forces can trap NAPLs in porous media above or below the water table.

Light Non-Aqueous Phase Liquids (LNAPLs) are liquids that are sparingly soluble in water and less dense than water. They will sink through unsaturated permeable soils and float on the water table, migrating to the lowest water table elevation. Hydrocarbons, such as oil and gasoline, are examples of LNAPLs, oil will "float" on top of water and does not mix. At LNAPL contamination sites, LNAPL can form a pool in the subsurface on top of the water table. The following diagram is a cross sectional view of a hypothetical LNAPL spill.

Dense Non-Aqueous Phase Liquids (DNAPLs) are liquids that are denser than water and do not dissolve or mix easily in water (they are immiscible). DNAPLs will tend to sink through both unsaturated (vadose) and saturated (phreatic) zones of permeable soils until they reach the lowest point on the top of a confining layer of the aquifer or bedrock. This movement is described by some as immiscible transport. In the presence of water it forms a separate phase from the water. Many chlorinated solvents, such as trichloroethylene are DNAPLs.

TRANSPORT PROCESSES

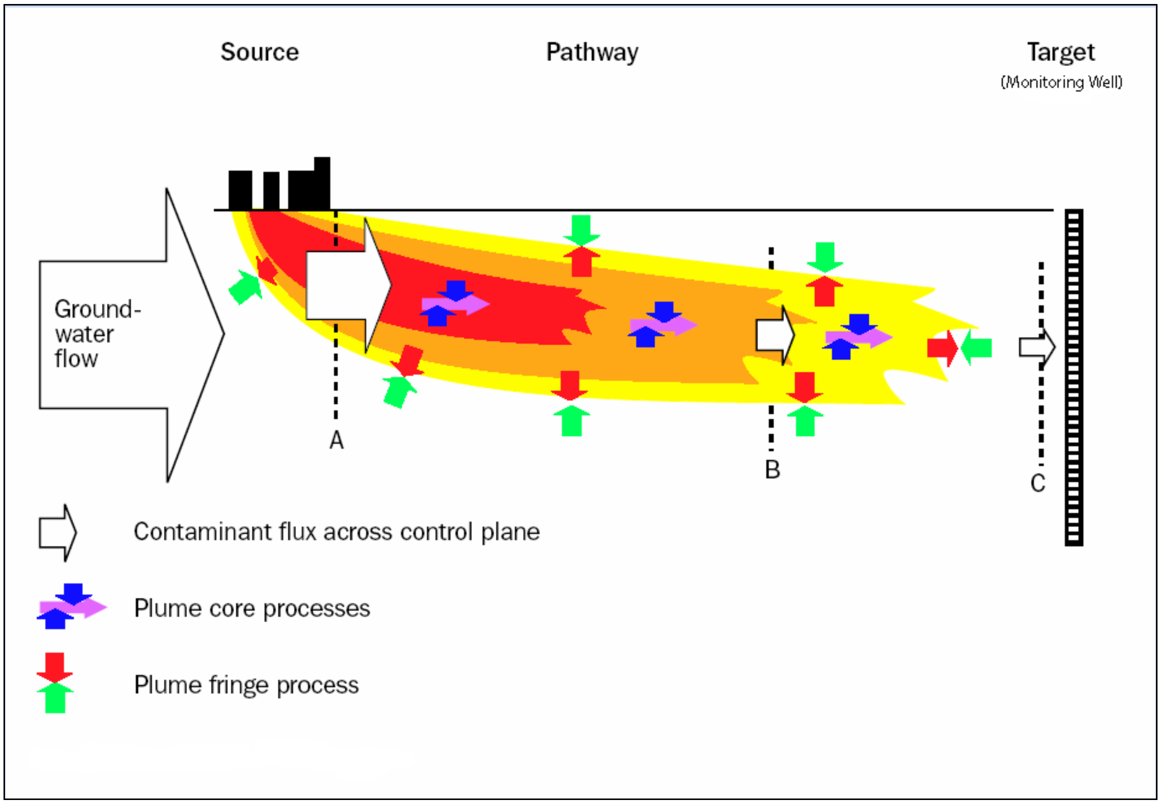


Figure 2: Typically generalized contaminant flow model showing plume dynamics

In addition to transferring phases in an attempt to reach equilibrium conditions (fig. 1), CAHs can migrate in the subsurface in their non-aqueous, aqueous, and vapor phases by both active and passive processes. The active processes, involves such dynamics as advection, dispersion, sorption and relative mobility. CAHs migrate along with the flow of the groundwater or soil gas to which they are partitioned. Passive processes generally involve diffusion and are the result of concentration gradients, which cause the CAH to seek phase and concentration equilibrium with its surrounding environment. The extent of subsurface migration is a function of the volume of CAH released; the area over which the release occurs; the duration of the release; the chemical and physical properties of both the CAH and the subsurface environment. Typically, releases of CAHs to the groundwater result in the formation of a plume (see figure 2 above); releases to soil result in subsurface soil contaminated with CAH constituents. In soil, CAHs typically are transported by the flow of DNAPL or diffusion in soil-gas vapor. In groundwater, advective transport (the movement of contaminants by flowing groundwater) is one of the most important processes that affect the transport of dissolved CAHs. In general, the more soluble the compound, the further it will be transported in the subsurface.
For example, based on solubility data provided in figure , MC and CF would be transported more readily in groundwater that PCE and CT. Figure 3 presents a more detailed example of the subsurface transport processes associated with the dense non-aqueous phase liquid [DNAPL] trichloroethene (TCE), a very prevalent component of those subsurface contamination.

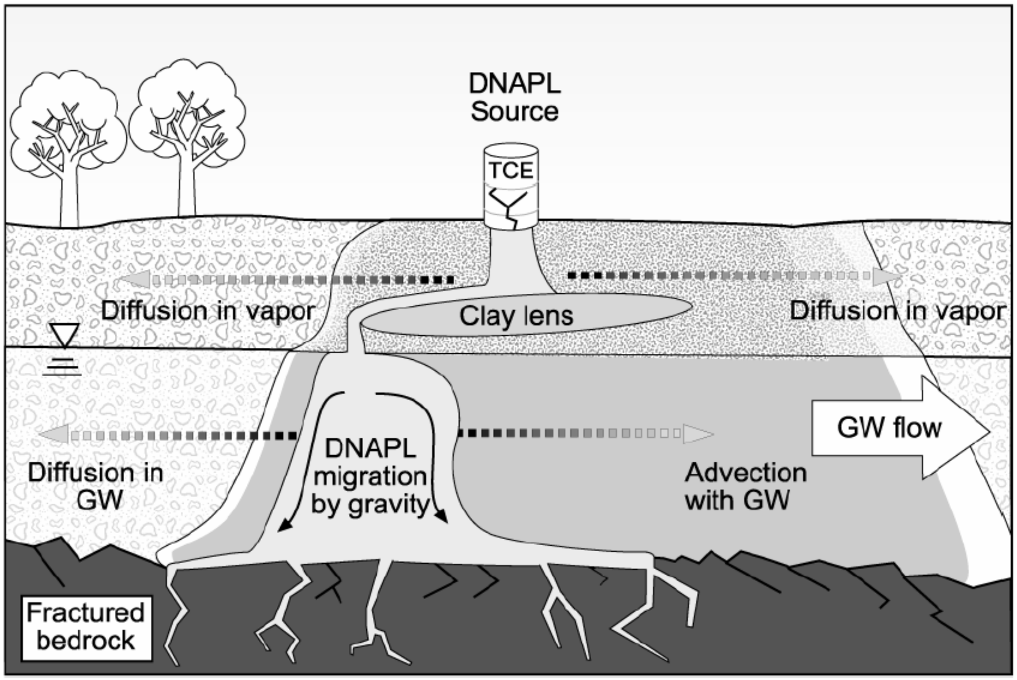


Figure 3: Example CAH Subsurface Transport Processes (DNAPL Source)
Source: Modified from Sims et al., 1992

DEGRADATION MECHANISMS

Bioremediation of CAHs can occur through natural mechanisms (intrinsic bioremediation) or by enhancing the natural mechanisms (enhanced bioremediation). For a few CAHs (for example, 1,1,1-TCA and CCl4), degradation can also occur by abiotic (nonbiological) mechanisms. CAHs can also be degraded or otherwise removed from soil and groundwater by larger organisms (such as trees), in a process referred to as phytoremediation. In most systems, biological degradation tends to dominate, depending on the type of contaminant and the groundwater chemistry (EPA, 1998). A number of biological degradation mechanisms have been identified theoretically and observed on a laboratory scale. The bioremediation mechanisms carried out by bacteria that typically are used for enhanced bioremediation of CAHs generally can be classified into one of the following mechanism two categories:

- Aerobic oxidation (direct and cometabolic)
- Anaerobic reductive dechlorination (direct and cometabolic)

While aerobic oxidation and anaerobic reductive dechlorination can occur naturally under the proper conditions, enhancements such as the addition of electron donors, electron acceptors, or nutrients can help to provide the proper conditions for aerobic oxidation or anaerobic reductive dechlorination to occur. In general, highly chlorinated CAHs degrade primarily through reductive reactions, while less chlorinated compounds degrade primarily through oxidation (Vogel et al., 1987b). Highly chlorinated CAHs are reduced relatively easily because their carbon atoms are highly oxidized. During direct reactions, the microorganism causing the reaction gains energy or grows as the CAH is degraded or oxidized. During cometabolic reactions, the CAH degradation or oxidation is caused by an enzyme or cofactor produced during microbial metabolism of another compound. CAH degradation or oxidation does not yield any energy or growth benefit for the microorganism mediating the cometabolic reaction. Biodegradation involves the production of energy in a redox reaction within a bacterial system.

This includes respiration and other biological functions needed for cell maintenance and reproduction. Ecology involves the different types of bacteria electron acceptor classes, such as oxygen-, nitrate-, manganese-, iron (III)-, sulfate-, or carbon dioxide-reducing, and their corresponding redox potentials. Redox potentials provide an indication of the relative dominance of the electron acceptor classes.

Aerobic Oxidation

In aerobic zones (zones of the subsurface where oxygen is present) of the subsurface, certain CAHs can be oxidized to carbon dioxide, water, and chloride by direct and cometabolic mechanisms (Hartman and DeBont, 1992; McCarty and Semprini, 1994; Malachowsky et al., 1994; Gerritse et al., 1995; Bielefeld et al., 1995; Hopkins and McCarty, 1995). Direct mechanisms are more likely to occur with the less chlorinated CAHs (mono- and di-chlorinates). In general, the more chlorinated CAHs can be oxidized by cometabolic mechanisms, but no energy is provided to the organism. Incidental oxidation is caused by enzymes intended to carry out other metabolic functions. Generally, direct oxidation mechanisms degrade CAHs more rapidly than cometabolic mechanisms (McCarty and Semprini, 1994)

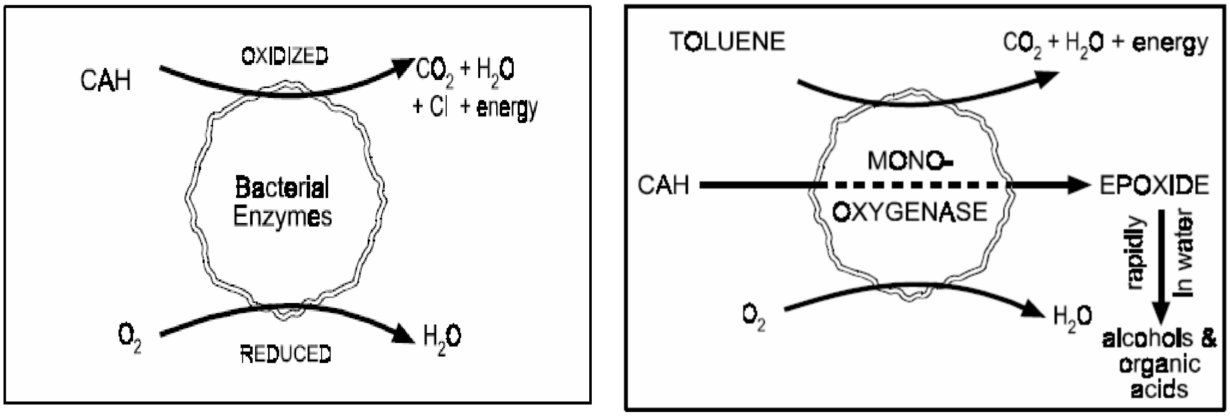


Figure 4: aerobic oxidation (direct) and (cometabolism) of CAH

Aerobic Oxidation (Direct)

Aerobic oxidation (direct) is the microbial breakdown of a compound in which the compound serves as an electron donor and as a primary growth substrate for the micro organism (microbe) mediating the reaction. Electrons that are generated by the oxidation of the compound are transferred to an electron acceptor such as oxygen. In addition, a microorganism can obtain energy for cell maintenance and growth from the oxidized compound (the compound acts as the reductant). In general, only the less chlorinated CAHs (CAHs with one or two chlorines) can be used directly by microorganisms as electron donors. CAHs that can be oxidized directly under aerobic conditions include DCE, DCA, VC, CA, MC, and CM (RTDF, 1997; Bradley, 1998; Harkness et al., 1999). The CAHs are oxidized into carbon dioxide, water, chlorine, and electrons, in conjunction with the reduction of oxygen to water. Figure 4 shows an example of aerobic oxidation (direct) of a CAH.

Aerobic Oxidation (Cometabolic)

Aerobic oxidation (cometabolic) is the microbial breakdown of a contaminant in which the contaminant is oxidized incidentally by an enzyme or cofactor produced during microbial metabolism of another compound. In such a case, the oxidation of the contaminant does not yield any energy or growth benefit for the microorganism involved in the reaction.

The CAHs that have been observed to be oxidized cometabolically under aerobic conditions include TCE, DCE, VC, TCA, DCA, CF, and MC (Edwards and Cox, 1997; McCarty, 1997a; Munakata-Marr, 1997; RTDF, 1997; Travis and Rosenberg, 1997; Bradley and Chapelle, 1998; McCarty et al., 1998). The electron donors observed in aerobic oxidation (cometabolic) include methane, ethane, ethene, propane, butane, aromatic hydrocarbons (such as toluene and phenol), and ammonia. Under aerobic conditions, a monooxygenase (methane monooxygenase in the case of methanotrophic bacteria) enzyme mediates the electron donation reaction. That reaction has the tendency to convert CAHs into unstable epoxides (Anderson and Lovley, 1997). Unstable epoxides degrade rapidly in water to alcohols and fatty acids, which are readily degradable. Figure 4 above also shows an example of aerobic oxidation (cometabolic) of a CAH.

Wilson and Wilson (1985) were the first to observe that the simultaneous addition of methane and oxygen can stimulate biodegradation by aerobic oxidation (cometabolic) of TCE in aquifer material. Subsequently, that approach was tested in the field at Naval Air Station (NAS) Moffett Field, California. Intermittent pulses of oxygen and methane were provided to the subsurface, bringing about the in situ stimulation of biodegradation of TCE, c-DCE, and VC in a contaminated aquifer (Semprini et al., 1990). The strategy has been applied successfully to biodegradation of CAHs at a variety of other sites (McCarty et al., 1991; Travis and Rosenberg, 1997). Although the studies have demonstrated that addition of methane is an effective means of stimulating cometabolic biodegradation of CAHs, additional field studies at the Moffett test site have shown that toluene and phenol can be more effective electron donors than methane in the stimulation of cometabolic biodegradation of TCE, c-DCE, and VC in groundwater (Hopkins et al., 1993; Hopkins and McCarty, 1995).

Anaerobic Reductive Dechlorination

Under anaerobic conditions, reductive dechlorination mechanisms can effectively biodegrade CAHs. Reductive dechlorination generally involves the sequential replacement of a chlorine atom on a CAH with a hydrogen atom (that is, converting PCE to TCE to DCE, and so on) and has been observed to occur both directly and co-metabolically. In anaerobic reductive dechlorination (direct), the mediating bacteria use the CAH directly as an electron acceptor in energy-producing redox reactions. Anaerobic reductive dechlorination (cometabolic) occurs when bacteria incidentally dechlorinate a CAH in the process of using another electron acceptor to generate energy. Reductive dechlorination theoretically is expected to occur under most anaerobic conditions, but has been observed to be most effective under sulfate-reducing and methanogenic conditions (EPA 1998). As in the case of aerobic oxidation, the direct mechanisms may biodegrade CAHs faster than co-metabolic mechanisms (McCarty and Semprini, 1994)

Anaerobic Reductive Dechlorination (Direct)

Anaerobic reductive dechlorination (direct) is a biodegradation reaction in which bacteria gain energy and grow as one or more chlorine atoms on a chlorinated hydrocarbon are replaced with hydrogen (Fennel et al., 1997; McCarty, 1997b; Mayo-Gatell et al., 1997; Gerritse et al., 1999). In that reaction, the chlorinated compound serves as the electron acceptor, and hydrogen serves as the direct electron donor (Fennel et al., 1997). Hydrogen used in the reaction typically is supplied indirectly through the fermentation of organic substrates. The reaction is also referred to as halorespiration or dehalorespiration (Gossett and Zinder, 1997).

Anaerobic reductive dechlorination (direct) has been observed in anaerobic systems in which PCE, TCE, DCE, VC, and DCA are used directly by a microorganism as an electron acceptor in their energy producing redox reactions (Freedman and Gossett, 1989; Major et al., 1991; DeBruin et al., 1992; Hollinger, 1993; Hollinger and Schumacher, 1994; Neumann et al., 1994; Tandol, 1994; Yagi et al., 1994; Scholz-Muramatsu et al., 1995; Gerritse et al., 1996; Gossett and Zinder, 1996; Sharma and McCarty, 1996; Smatlak, 1996; McCarty, 1997b; Maymo-Gatell et al., 1997; Yager et al., 1997). The mechanism generally results in the sequential reduction of a chlorinated ethene or chlorinated ethane to ethene or ethane. Figure 5 shows the step-by-step dechlorination of PCE.

The anaerobic reductive dechlorination of the more chlorinated CAHs (PCE and TCE) occurs more readily than the dechlorination of CAHs that already are somewhat reduced (DCE and VC); for that reason, DCE and VC may accumulate in anaerobic environments. It also has been observed that, while VC can be effectively dechlorinated, the presence of PCE in groundwater may inhibit the anaerobic reductive dechlorination of VC (Tandol and others, 1994). VC is more commonly remediated using aerobic mechanisms than anaerobic mechanisms. In anaerobic environments in which VC accumulates, enhanced aerobic bioremediation can be implemented to degrade the VC. Recent studies have demonstrated significant anaerobic oxidation of VC to carbon dioxide under Fe(III)-reducing conditions (Bradley and Chapelle 1998b) and of DCE to VC and VC to carbon dioxide under humic acid-reducing conditions (Bradley and Chapelle 1998a). These studies suggest the possibility of alternative biotransformation mechanisms under anaerobic conditions.

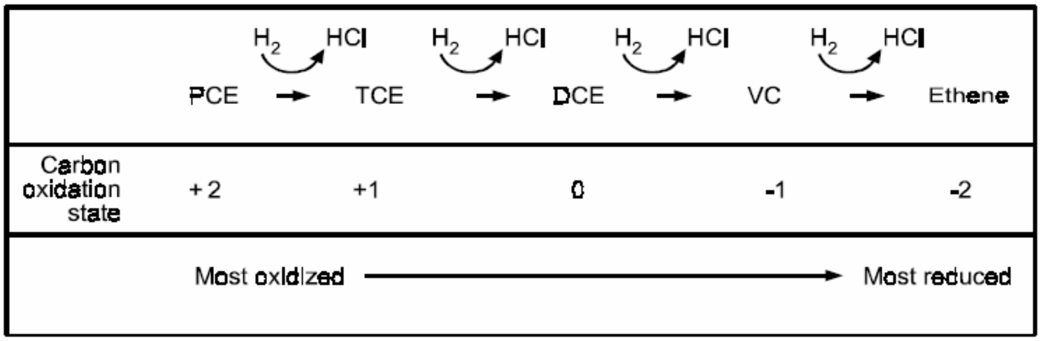


Figure 5: diagram shows the step-by-step dechlorination of PCE.

Hydrogen has been observed to be an important electron donor in anaerobic reductive dechlorination (Fennell et al., 1997). The presence of hydrogen establishes a competition between the bacteria that mediate the anaerobic reductive dechlorination (such as Dehalococcus ethenogenes and Dehalospirillium multivorans) and methanogenic bacteria that also use hydrogen as an electron donor (ITRC 2000).

However, it has been observed that the dechlorinating bacteria can survive at a partial pressure of hydrogen ten times lower than that at which the methanogenic bacteria can survive (Smatlak et al., 1996), thus providing an opportunity to support the dechlorinating bacteria by providing hydrogen at a slow rate. Hydrogen addition at a slow rate has been demonstrated with the fermentation of butyric or propanoic acid (Fennell et al., 1997). In addition, in some subsurface environments, competition from nitrate or sulfate-reducing bacteria may limit both methanogenic activity and the extent of anaerobic reductive dechlorination (RTDF, 1997).

Past studies have shown that anaerobic reduction of CAHs can occur by reductive dechlorination in a variety of environmental conditions (Beeman et al., 1994; Semprini et al., 1995). A review of the transformation of halogenated compounds has shown that the theoretical maximum redox potential for transformation of PCE to TCE is +580 millivolts and for TCE to DCE is +490 millivolts (Vogel et al., 1987). Therefore, the anaerobic reductive dechlorination of the compounds is thermodynamically possible under manganese- or iron-reducing conditions. No peer-reviewed reports of the transformation of PCE to TCE under aerobic conditions were identified. However, the efficiency of the anaerobic dechlorination processes at high redox potential values is limited; efficiency improves as the redox potential decreases. Figure 6 shows the possible reduction/oxidation (REDOX) zones associated with a petroleum plume in an aerobic aquifer.

Pilot studies have been conducted at a variety of sites to examine the feasibility of stimulating *in situ* anaerobic reductive dechlorination by providing to the subsurface simple organic substrates, such as lactate, butyrate, methanol, ethanol, and benzoate (Freedman and Gossett, 1989; Gibson and Sewell, 1992; Becvar et al., 1997; Buchanan et al., 1997; Litherland and Anderson, 1997; Spuij et al., 1997; Sewell et al., 1998; Harkness et al., 1999).

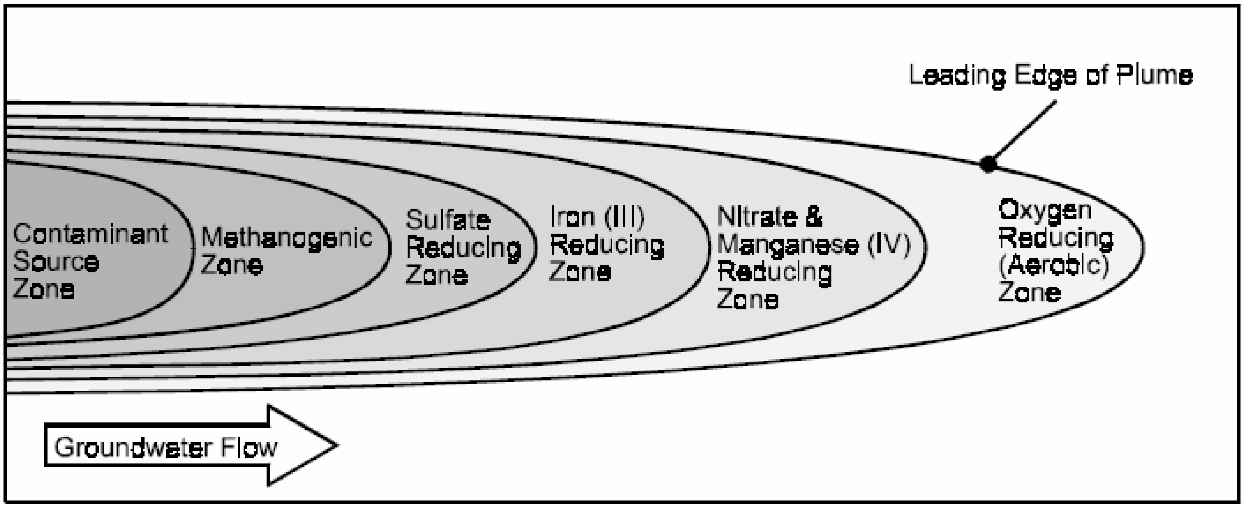


Figure 6: Redox Zones of a Typical Petroleum Plume in an Aerobic Aquifer (Areal View)
Source: Modified from Anderson and Lovley, 1997

Anaerobic Reductive Dechlorination (Cometabolic)

Anaerobic reductive dechlorination (cometabolic) is a biodegradation reaction in which a chlorinated hydrocarbon is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound. In such a case, biodegradation of the chlorinated compound does not appear to yield any energy or growth benefit for the microorganism mediating the reaction (Gossett and Zinder, 1997).

Several CAHs have been observed to be reductively dechlorinated by co-metabolic mechanisms. In those instances, the enzymes that are intended to mediate the electron-accepting reaction “accidentally” reduce and dehalogenate the CAH. Anaerobic reductive dechlorination (co-metabolic) has been observed for PCE, TCE, DCE, VC, DCA, and CT under anaerobic conditions (Fathepure, 1987; Workman, 1997; Yager et al., 1997).

Combined Aerobic Oxidation and Anaerobic Reductive Dechlorination

Several investigators have suggested that the most efficient bioremediation of CAHs will occur in aquifers that are characterized by an upgradient anaerobic zone and a downgradient aerobic zone (Fathepure et al., 1987; Carter and Jewell, 1993; Bouwer, 1994; Gerritse et al., 1995). In the upgradient aerobic zone, anaerobic reductive dechlorination of PCE might degrade to TCE, and eventually to VC. VC could then be degraded by aerobic oxidation (direct) downgradient in the aerobic zone of the CAH plume (the leading-edge fringe of the plume). Stratified redox conditions in the field may provide the best opportunities, other than engineered remedies, for intrinsic biodegradation of CAHs.

Generally, the substrate requirement for direct metabolism is relatively less than that for co-metabolism. In co-metabolism, often the amount of primary substrate required is a factor of 100 to 1,000 times the amount of the CAH. In direct metabolism (respiration with only the chlorinated solvent as the electron acceptor), the stoichiometry is much more favorable, and a much smaller amount of supplemental chemical is required (Bouwer, 1994).

Abiotic Degradation Mechanisms

Abiotic degradation mechanisms involve chemical reactions to treat CAHs without biological processes. These mechanisms include hydrolysis, elimination, and abiotic reductive dechlorination. In general, the rates of abiotic degradation may be slow relative to biological mechanisms. However, the abiotic mechanisms may play a significant role in the overall remediation of a site at which CAH contamination is present, depending on the specific site conditions (for example, a site at which the contaminant plume is moving slowly) (EPA, 1998). Hydrolysis and elimination reactions are generally independent of redox conditions, while abiotic reductive dechlorination is highly dependent on redox conditions.

Hydrolysis is a substitution reaction in which a CAH may react with water to substitute a chlorine atom with a hydroxyl group, producing organic alcohols, acids, or diols, such as the formation of acetic acid from 1,1,1-TCA equation (1). Generally, less chlorinated CAHs are more susceptible to degradation by hydrolysis. Hydrolysis rates have been reported that have half-lives ranging from days for monochlorinated alkanes to thousands of years for tetrachloromethane.

$$\underset{\text{1,1,1-TCA}}{Cl_3C\text{-}CH_3} + 2H_2O \rightarrow \underset{\text{Acetic Acid}}{H_3C\text{-}COOH} + 3HCl \qquad (1)$$

Hydrolysis is a common transformation mechanism for 1,1,1-TCA, chloroethane, and chloromethane, producing acetate, ethanol, and methanol, respectively (Vogel and McCarty, 1987). Elimination reactions involve the removal of a hydrogen and a chlorine atom (sometimes referred to as dehydrohalogenation) from a chlorinated alkane, with the formation of the corresponding alkane equation (2). In contrast to hydrolysis reactions, elimination reactions become more effective as the CAHs become more chlorinated. Assuming that elimination rates for monochlorinated CAHs are negligible, the abiotic conversion of TCA to DCE at 20oC has been reported to exhibit relatively rapid first-order kinetics, with a rate constant of approximately 0.04 ± 0.003 year-1 (Vogel and McCarty, 1987).

$$\underset{\text{1,1,1-TCA}}{Cl_3C\text{-}CH_3} \rightarrow \underset{\text{1,1-DCE}}{Cl_2 = CH_2} + HCl \qquad (2)$$

Abiotic reductive dechlorination of several CAHs also has been observed (Reinhard et al., 1990; Gillham and O'Hannesin, 1994; Workman et al., 1997). Abiotic reductive dechlorination occurs in the presence of an extremely strong reductant (for example, zero-valent iron or reduced vitamin B12). When the reductant present is sufficiently strong, the more chlorinated (and, therefore, more oxidized) of the CAHs (PCE, TCE, CT, and CF) can be reduced to less chlorinated species without the mediation of bacteria.

	CCH_4	+	2Fe0	→	MC	+	$2Fe^{2+}$	(3)
	Carbon tetrachloride		zero-valent iron		methylene chloride		ferrous iron	
Iron oxidation state			0	→			+2	
Carbon oxidation state	+4			→	0			

As in the case of biologically mediated reductive dechlorination, abiotic reductive dechlorination becomes less effective or ineffective for the less chlorinated CAHs which are already somewhat reduced. Equation (3) shows the general mechanism of abiotic reductive dechlorination (using zero-valent iron as the reducing agent).

BIOREMEDIATION TECHNOLOGIES

In Situ Source Treatment Processes

In situ bioremediation technologies are used to enhance the mechanisms that degrade CAHs in contaminated soil and groundwater. Technologies include bioaugmentation and the addition of nutrients, electron donors (substrates such as toluene, propane, and methane), and electron acceptors (such as oxygen). Design configurations of in situ bioremediation systems include direct injection, groundwater recirculation, installation of permeable reactive barriers (PRBs), and bioventing.

Generally, in situ bioremediation technologies employ engineered systems to heighten the effects of naturally occurring degradation mechanisms. The engineered systems are designed to include one or more of the following general classes of technologies: the addition of bacteria (bioaugmentation), the addition of nutrients, the addition of electron donors, or the addition of electron acceptors. Each of the technologies is discussed below in a little more detail. The discussion presents a summary of information about each technology, including an example of how each may be applied, a discussion of the biodegradation mechanisms generally supported by each, a discussion of the typical CAHs targeted through the use of each technology, and a summary of how the enhancement technologies have been applied at the case study sites. (For a more detailed summaries of these studies refer to Grindstaff, 1998; EPA/540/R-95/532).

Bioaugmentation – involves the addition of supplemental microbes to the subsurface where organisms that are able to degrade specific contaminants are deficient. Microbes may be "seeded" from populations already present at a site and grown in aboveground reactors or from specially cultivated strains of bacteria known to degrade specific contaminants. The application of bioaugmentation technology is highly site-specific and highly dependent on the microbial ecology and physiology of the subsurface (EPA, 1998). This methodology has been used at Dover Area 6,

Nutrient addition – involves the addition of key biological building blocks, such as nitrogen and phosphorus and other trace nutrients necessary for cell growth. Addition of nutrients generally is applied as a supplement to bioaugmentation or addition of electron donors or electron acceptors, so that concentrations of nutrients in the subsurface do not become a limiting factor for an in situ bioremediation application. This technique has been used in the past at SRS, Texas Gulf Coast, Watertown, and Dover Area 6.

Electron donor addition – involves the addition of a substrate that acts as a reductant in the redox reaction used by the CAH-degrading microbe to produce energy. A substrate such as toluene, propane, or methane may be added to act as a co-metabolic oxidant, when the CAH also is oxidized. A substrate such as hydrogen, a source of hydrogen, or a hydrogen release compound may be added to act as a direct reductant, when the CAH is reduced. Addition of electron donors, such as toluene, propane, or methane, and an electron acceptor (oxygen) for aerobic co-metabolic oxidation were used at the following five sites: Moffett Field, Edwards AFB, SRS, Watertown, and Dover Building 719. Addition of an electron donor in the form of a hydrogen source, such as methanol, molasses, or lactate, for anaerobic reductive dechlorination was used at the following five sites: Texas Gulf Coast, Avco Lycoming, Emeryville, Watertown, and Dover Area 6.

Electron acceptor addition – involves the addition of oxygen (for aerobic mechanisms) or an anaerobic oxidant such as nitrate (for anaerobic mechanisms), which is used by the CAH-degrading microbes present in the subsurface. One method to identify different biogeochemical zones is to monitor the concentration of certain chemicals and minerals, those that are involved in biogeochemical processes, in groundwater and in aquifers. Electron acceptors are minerals or chemicals that can occur naturally in aquifer solids or ground water, such as iron oxides in the sediments or sulfate dissolved in ground water. These chemicals are called electron acceptors because microorganisms transfer electrons to them during respiration, which is part of the process the microorganisms use to obtain energy. During respiration, an electron is transferred from an electron donor, such as an organic contaminant compound, to an electron acceptor. This electron transfer occurs when microorganisms break down organic contaminant compounds. The availability of electron acceptors in an aquifer is therefore an important factor for evaluating the effectiveness and sustainability of natural attenuation in contaminated aquifers.

Ex Situ Source Treatment Processes

Below are several examples of *ex situ* treatment processes used to remove contaminants. Since *ex situ* processes require more human intervention and are generally more costly they are only mentioned here but discussion of their details is outside the intended scope of this discussion. Their reference is mainly establishing a comparison and gives a better idea of what is involved in *in situ* projects.

Land Treatment - Contaminated soil, sediment, or sludge is excavated, applied to lined beds, and periodically turned over or tilled to aerate the contaminated media. Amendments can be added to the contaminated media in the beds.

Composting - Contaminated soil is excavated and mixed with bulking agents such as wood chips and organic amendments such as hay, manure, and vegetable wastes. The types of amendments used depend on the porosity of the soil and the balance of carbon and nitrogen needed to promote microbial activity.

Biopiles - Excavated soils are mixed with soil amendments and placed in aboveground enclosures. The process occurs in an aerated static pile in which compost is formed into piles and aerated with blowers or vacuum pumps.

Slurry-Phase Treatment - An aqueous slurry is created by combining soil, sediment, or sludge with water and other additives. The slurry is mixed to keep solids suspended and microorganisms in contact with the contaminants. Treatment usually occurs in a series of tanks.

TECHNOLOGY DESIGN APPROACHES

The components of *in situ* bioremediation technologies components described above can be implemented in several different general configurations: direct injection, groundwater recirculation, permeable reactive barriers (PRBs), and bioventing. In addition, *in situ* bioremediation may occur naturally, without the application of enhancement technologies. The latter approach is one component of the approach EPA refers to as monitored natural attenuation (MNA) (EPA, 1998). Because MNA does not use enhancement technologies, it is not discussed in detail in this report. This report includes a summary of the purpose, advantages, and potential limitations of direct injection, groundwater recirculation, PRB, and bioventing systems, described below, and reference to several projects sites at which the chosen configuration was used.

As mentioned previously, there is a conceptual model for flow within the subsurface (see fig. 2). Figure 3 and figures 7 through 11 are variation of that general idea with relevant technology design. Figure 7 shows the general layouts of the configurations, often referred to as amendment delivery systems. The configurations include use of vertical wells, horizontal wells, and trenches for both injection and extraction of groundwater, or for injection of amendments. Biological, nutrient, electron donor, or electron acceptor amendments are injected in a liquid or a gaseous phase.

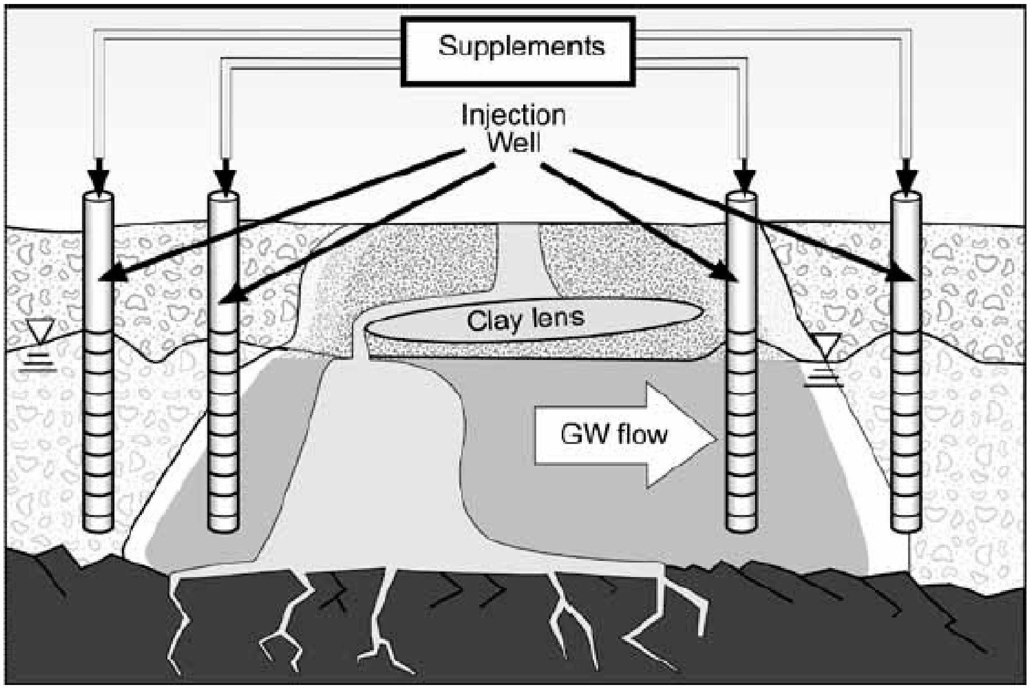


Figure 7: In Situ Bioremediation System Configurations (Direct Injection)

Direct injection system - degradation of contaminants is enhanced through the addition of microbes, nutrients, oxidants, or reductants directly into the aquifer at injection points or directly into the soil. The natural flow of the groundwater generally is not impeded, but is monitored to determine that the degradation of the contaminants and their daughter products is completed within an acceptable distance from the source. Figure 4 above depicts a generalized diagram of what a direct injection system using four wells would look like.

The case study sites at which direct injection into groundwater was used in the past are SRS, Avco Lycoming, and Emeryville. At SRS, methane (gas) and air were injected below the water table using a “lower” horizontal well located at a depth of 175 ft below ground surface (bgs). An “upper” horizontal well, located at a depth of 80 ft bgs, was used to extract air and contaminated vapors from the vadose zone. At Avco Lycoming, a molasses solution was injected through 20 four-inch diameter wells completed in the overburden. Molasses was added twice each day at various concentrations and rates, as the results of monitoring the system indicated were appropriate.

Groundwater recirculation - extracts contaminated groundwater from the site, adding to or amending the extracted water ex situ, and reinjecting the “activated” water to the subsurface, generally upgradient of the contaminated zone (fig. 8). As an alternative, extraction and injection are performed at different elevations in a single well, creating vertical circulation. A groundwater recirculation configuration may be used to provide containment of a plume or to allow the addition of amendments in a more controlled environment.

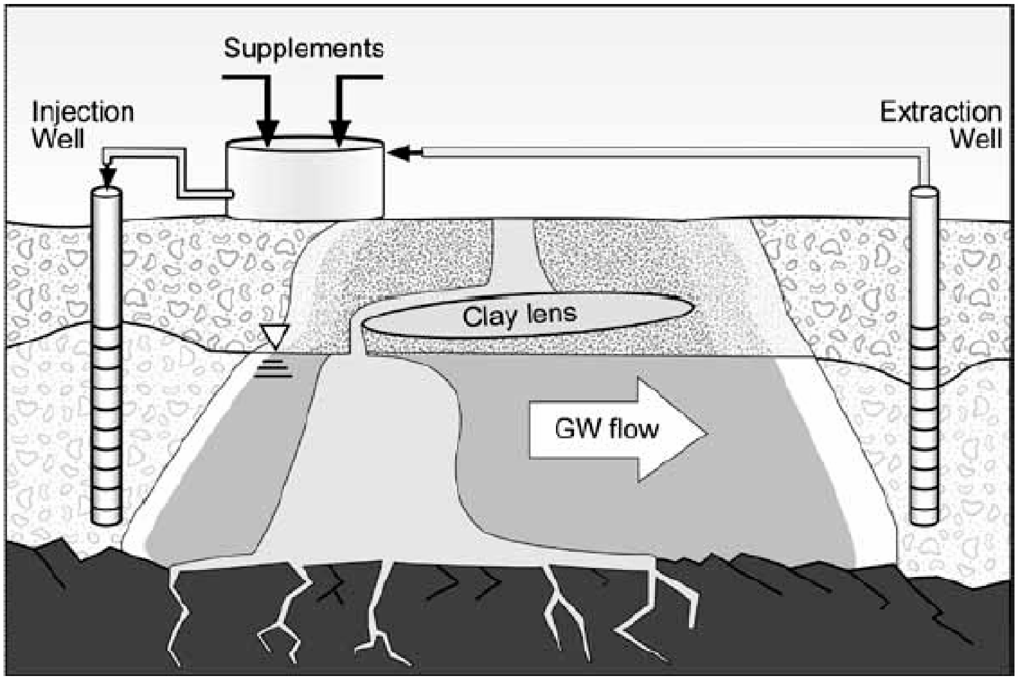


Figure 8: In Situ Bioremediation System Configurations (Groundwater Recirculation)

The case study sites at which groundwater recirculation was used are Moffett Field, Edwards AFB, Texas Gulf Coast, Watertown, and Dover Area 6. The project at Moffett Field was one of the earliest field demonstrations of *in situ* bioremediation, the Edwards AFB project was conducted by the group of researchers who had conducted the Moffett Field demonstration, who built upon the results obtained from the earlier project. A further discussion of these two demonstrations is included later in this report

Permeable Reactive barrier (PRBs) - an active bioremediation zone is created by such methods as backfilling a trench with nutrient-, oxidant-, or reductant-rich materials, or by creating a curtain of active bioremediation zone through direct injection or groundwater recirculation at the toe of a plume. PRBs contain a contaminant plume by treating only groundwater that passes through it. PRBs are an emerging design approach for use of in situ bioremediation. To date, application of PRBs to in situ bioremediation of CAHs has been limited to demonstration tests (ITRC, 1997). Two conceptual designs of PRBs are shown in Figures 9 and 10 below.

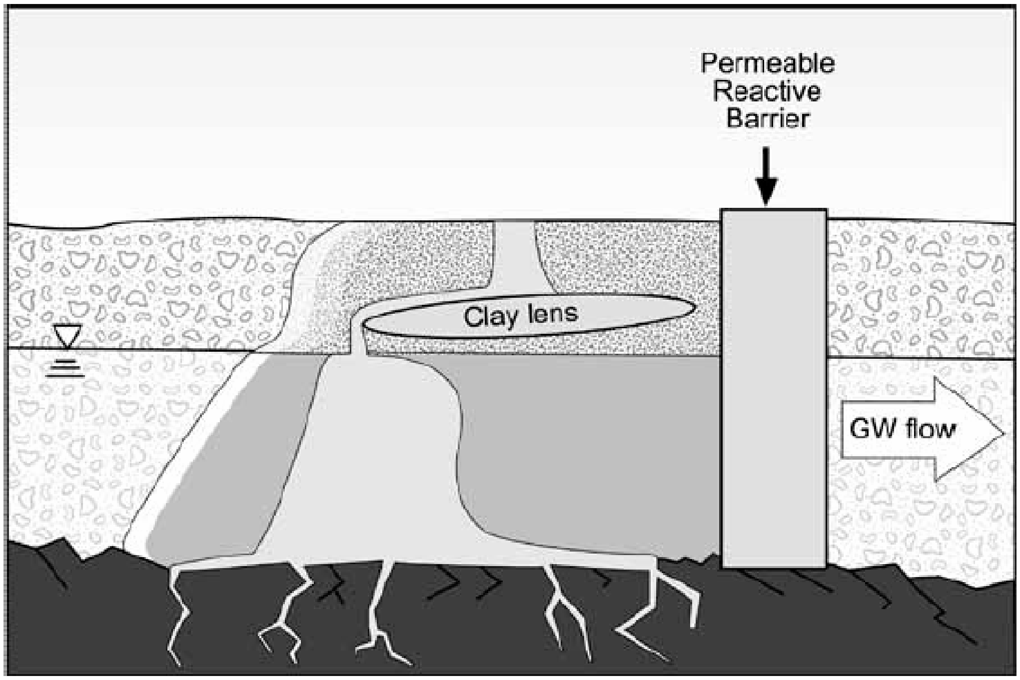


Figure 9: In Situ Bioremediation System Configurations (Permeable Reactive barrier [PRB])

At the Waterloo Center for Groundwater Research at the University of Waterloo, in Ontario, Canada, a treatment system consisting of a trench (backfilled with sand) was used in a demonstration test at a site with groundwater contaminated with CAHs.

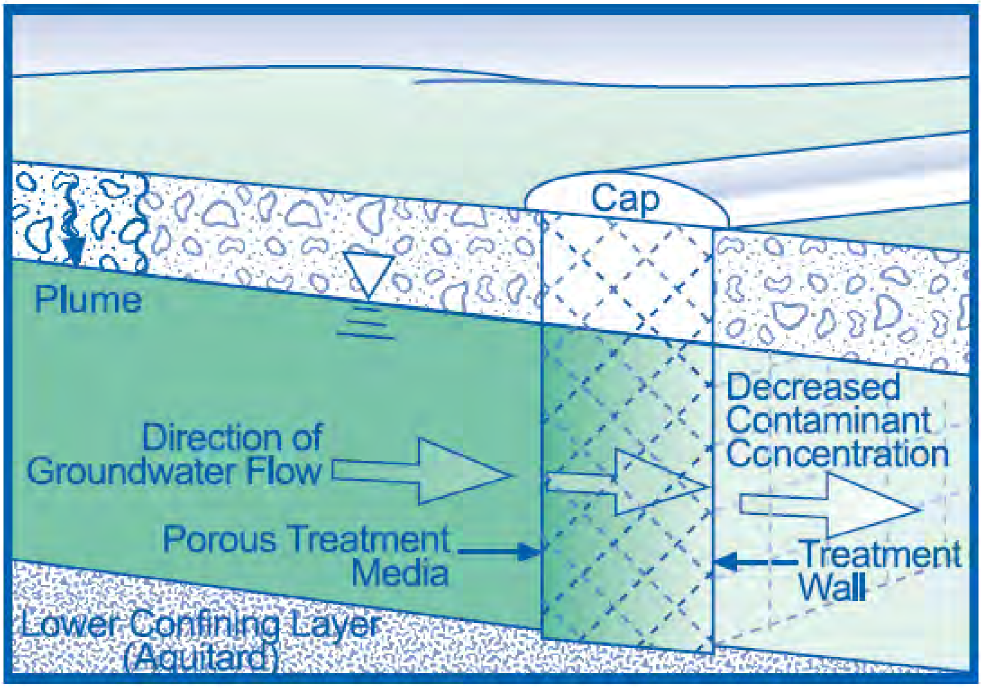


Figure 10: Model of a Permeable Reactive Barrier (EPA/542/R-01/022)

In that system, water was 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). After reinjection had been completed, the pumps were shut off, and the nutrients were transported out of the wall under natural groundwater flow conditions (as a "slug"). The slug of amended groundwater mixed with surrounding groundwater, and a zone developed in which microorganisms received a continuous supply of the nutrients required to support biodegradation (Devlin and Barker, 1994).

Bioventing - the process of aerating soils to stimulate in situ biological activity and promote bioremediation. In this process, oxygen is delivered to unsaturated soils by forced air movement (either extraction or injection of air) to increase oxygen concentrations and stimulate biodegradation. Bioventing uses low air flow rates to provide only enough oxygen to sustain microbial activity, with oxygen most commonly supplied through direct air injection.

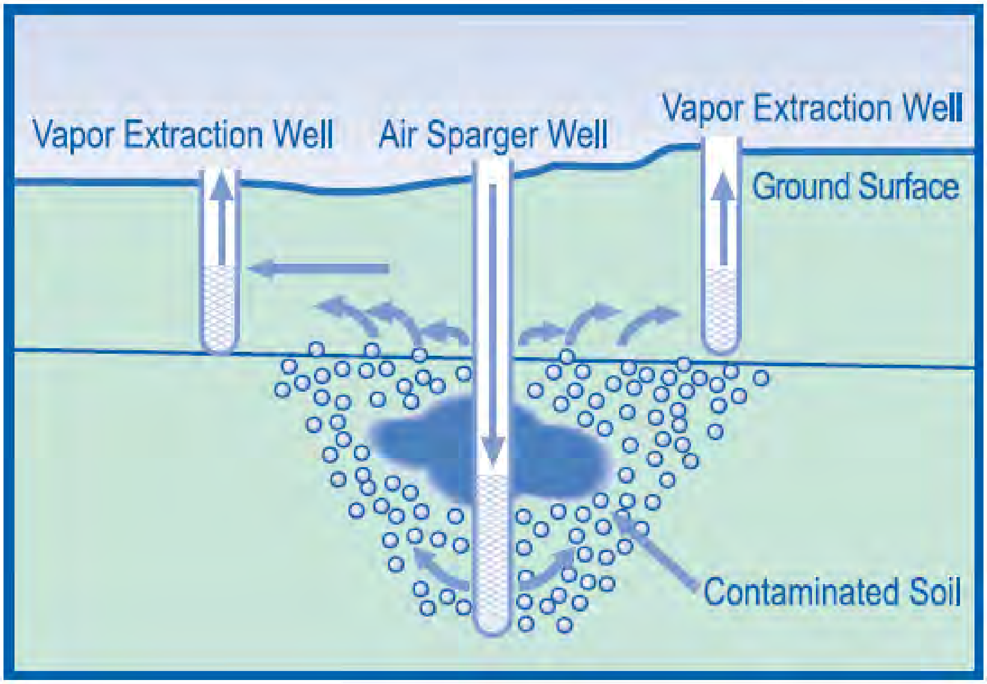


Figure 11: Model of an Air Sparging System (EPA, 2004)

Bioventing is commonly used for treatment of fuel-contamination in the vadose zone (EPA, 1995). At Dover Building 719, an air-sparge blower (shown in fig. 11) was used to inject a mixture of air and propane through three injection wells screened to a depth of 10 ft bgs. The Dover Building 719 site is a field demonstration of bioventing, at which treatment is limited to the soil above the water table.

SELECTION AND IMPLEMENTATION OF BIOREMEDIATION

The steps typically followed in the selection and implementation of an *in situ* bioremediation system, at a site contaminated with CAHs, are generally the same as the steps taken to implement other types of remedial systems. However, special attention is typically given to identifying the degradation mechanisms that may be used to remediate the site and the enhancement technologies that could be beneficial for use at the site. Figure 9 shows the typical steps in selection and implementation of in situ bioremediation, which are:

- Evaluate site characteristics
- Identify general site conditions and engineering solutions
- Identify primary reactants and possible additives
- Perform treatability (bench-scale) testing
- Perform system design, field testing, and implementation

Site Characteristics - Site characteristics relevant to in situ bioremediation of include physical, chemical, and biological parameters. Figure 12 summarizes the parameters that are commonly evaluated for a site where in situ bioremediation of CAHs is being considered. These parameters are also relevant to the design and implementation of the technology, as discussed later.

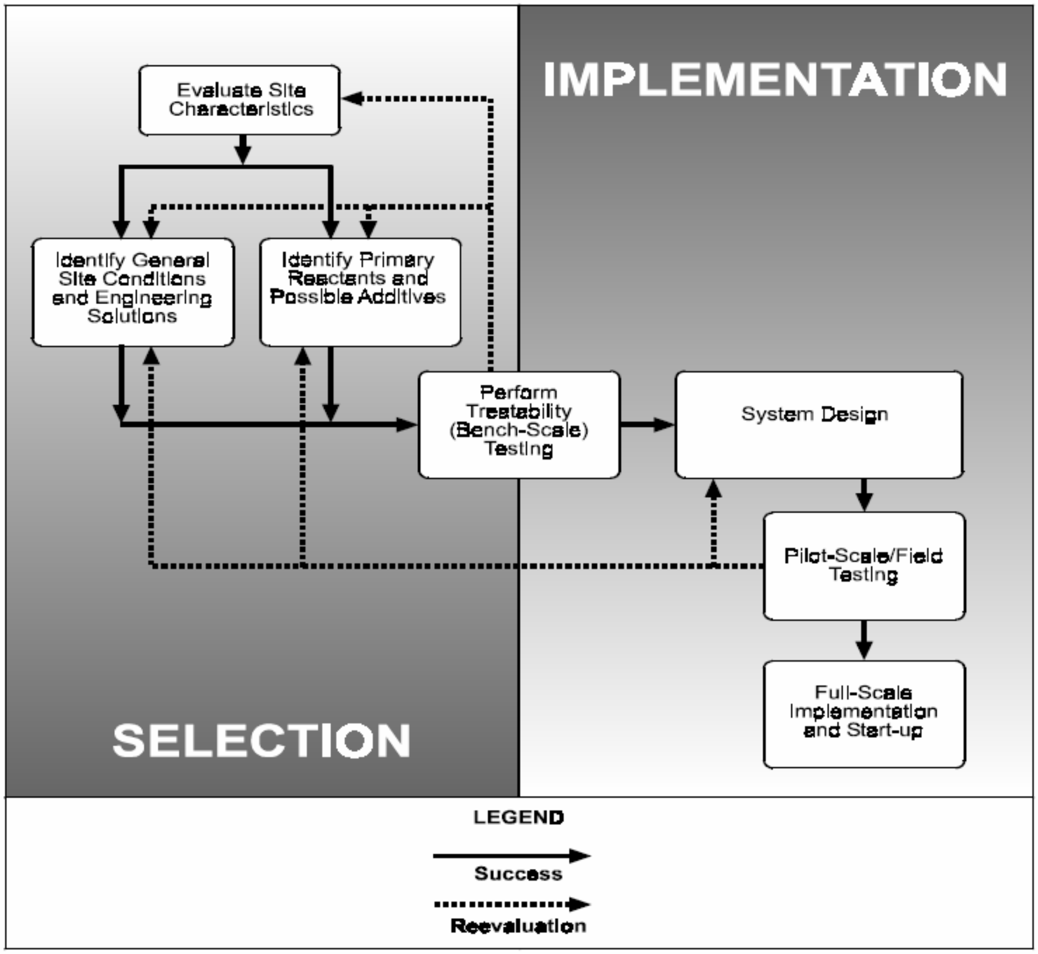


Figure 12: Typical Selection and Implementation Steps for In Situ Bioremediation
Source EPA 542-R-00-008 July 2000 (revised)

Physical Parameters - Physical parameters determine how and at what rate liquids and gases move through soils, aquifers, and other geologic units. Common physical parameters that are relevant to in situ bioremediation include porosity, hydraulic conductivity, and hydraulic gradient of the geologic unit, and the organic and moisture content of the soil. Because these parameters affect the flow rate of fluids, they also are considered in determining the delivery method for any amendments that are used.

Hydrogeologic studies help determine information about several physical parameters such as groundwater flow, and contaminant fate and transport, and might include aquifer parameter testing, tracer tests and hydrogeologic flow and transport modeling. Aquifer parameter tests include either slug tests or downhole velocity measurements. Tracer tests have been conducted using constituents such as sodium bromide, added at 100 times its detection limits. According to ITRC, the most commonly used flow model is the U.S. Geological Survey model MODFLOW, which is often coupled with transport models such as RT3D or MT3D, and a particle tracking module such as MODPATH. (ITRC, 1998)

Chemical Parameters - Chemical parameters, along with biological parameters, affect the type of degradation mechanisms that are likely to occur and the rate of degradation. Common chemical parameters that are relevant to in situ bioremediation include concentrations of CAHs and daughter products, oxygen content, pH, redox potential, concentrations of electron donors and acceptors, and nutrient concentrations. Such parameters provide information about the baseline contamination at the site, whether the natural conditions at the site are aerobic or anaerobic, whether sufficient electron donors and acceptors are present to support biodegradation, and whether and how much intrinsic biodegradation (without enhancements) may be occurring at the site. Several of these parameters are discussed in more detail below.

CAH concentrations affect the specific degradation mechanisms that may be occurring at the site and the substrate levels for direct degradation. In addition, the presence of co-contaminants may affect biodegradation. For example, organic compounds such as toluene, methane, or phenol may augment the performance by providing a substrate for oxygen depletion or for co-metabolic degradation. Alternatively, biodegradation may be limited by high concentrations of metals or other toxic compounds that may inhibit microbial activity.

GEOCHENICAL TRANSPORT MODELS

Modeling Contaminant Transport and Biodegradation

Numerical models that simulate transport and biodegradation processes are useful for integrating information collected in the field and for studying the relative importance of simultaneously occurring processes. It is difficult to develop an accurate mass balance for a contaminant, and thus to distinguish the amount and rate of removal by biodegradation, dilution, and sorption. If sufficient data are available, a numerical model can be used to help explore these questions, simulate the evolution of the plume, and evaluate factors limiting biodegradation.
A two-dimensional, multispecies solute-transport model including multiple substrate uptake, sequential terminal electron acceptor use, and cellular nutrient limitation of biomass growth (BIOMOC, Essaid and Bekins, 1997) was developed to analyze the evolution of the ground-water contaminant plume at the Bemidji site (Essaid and others, 1995).

Simulations included the biodegradation of volatile (VDOC) and non-volatile dissolved organic carbon (NVDOC) fractions of DOC by aerobic processes, Mn/Fe reduction, and methanogenesis. Geochemical evidence indicates that these processes are important in degrading the oil. Model parameter estimates were constrained by published Monod kinetic parameters, theoretical yield estimates, and field biomass measurements. Despite considerable uncertainty in the model parameter estimates, results of simulations reproduced the general features of the measured ground-water plume (fig. 19) and the measured constituent concentrations (fig. 13). For the simulation shown in figure 13, 46 percent of the TDOC introduced into the aquifer was degraded after 13 years. Aerobic degradation accounted for 40 percent of the TDOC degraded and anaerobic processes accounted for 60 percent: 5 percent by Mn reduction, 19 percent by Fe reduction, and 36 percent by methanogenesis. The model results indicate that anaerobic processes account for more than one-half of the removal of DOC at this site, consistent with the geochemical evidence.

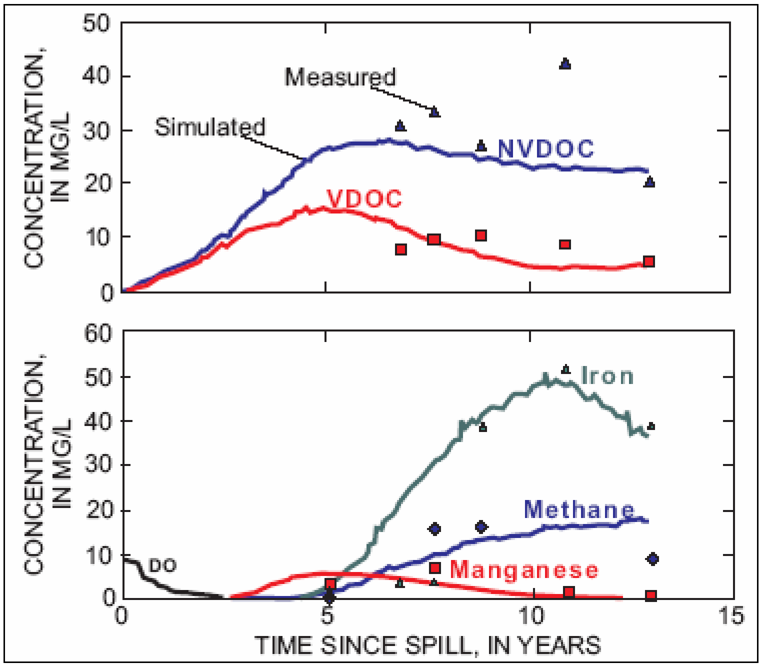


Figure 13: Simulated and measured concentrations of selected constituents 36 meters downgradient from the center of the oil body. (USGS Fact Sheet 084-98)

Microbial Distributions - In 1994, water and sediment samples were collected from a background location and six locations downgradient from the oil body for microbial biomass determinations (Essaid and others, 1995). The Most Probable Number method was used to enumerate microorganisms capable of degradation under differing redox conditions. In the background location, aerobes and fermenters were the only significant microbes detected. Within the plume the microorganism counts are consistent with the conceptual model of sequential aerobic, Mn/Fe reduction, and methanogenesis degradation sequence. There are 104-105 iron-reducers per gram in the contaminated aquifer compared to none detected in the uncontaminated background area. Similarly there are 102 methanogens per gram in the plume and none detected in the background area. This result is similar to that of Godsy and others (1992) who reported a 100-fold increase in methanogens within a creosote plume. In general, greater numbers of microorganisms were found closer to the oil body and in the upper half of the plume. Denitrifiers and sulfate reducers are present in lower numbers than all other types of microbes, in accordance with the low availability of nitrate and sulfate in the ground water. The data were used to formulate a model of biodegradation of the contaminants coupled to growth of the microbial population.

Bioremediation technologies also include predictive modeling of coupled hydraulic-geochemical-microbial processes in surface and subsurface environment. Geochemical and 1-, 2-, and 3-D flow programs (e.g. PhreeQC, USGS) can be used to model multimedia fate and transport of contaminants.

Aerobic Biodegradation of Xylene with Biomass Increase - Biodegradation relies on the catalyzing action of enzymes produced by microbes. Therefore, the maximal rate depends on the concentration of the enzymes or the bacteria. The variable kmax in the Monod rate equation (see eqn (7) in the phenol example below) can be rewritten to account explicitly for the concentration of bacteria:

$$\frac{dS}{dt} = R_{Monod} = -\left(\mu_{\max}\frac{B}{Y}\right)\frac{S}{k_{1/2}+S} \quad (4)$$

where:
μmax is the specific bacterial growth rate (S-1)
B is biomass (mol C/ L-1)
Y is the yield factor (mol biomass-C / mol substrate-C)

Y expresses how much of substrate in converted into biomass. As substrate is degraded and transformed into energy and organic molecules which can be used for biosynthesis, the number of microorganisms (bacteria) increase by:

$$\frac{dB}{dt} = -Y\frac{dS}{dt} \quad (5)$$

equations (4) and (5) are coupled reactions. Biodegradation augments when the bacteria increase in number, and more biodegradation produces more bacteria. In figure 14 below the decrease of substrate concentration first becomes notable when sufficient microbes are present, and the process stops when all the substrate has been consumed. Schirmer et al. (1999) measured aerobic breakdown of xylene, a component in BTEX, in a batch experiment with pristine aquifer sediment in which the microbes had to adapt and grow before they could digest their new food.

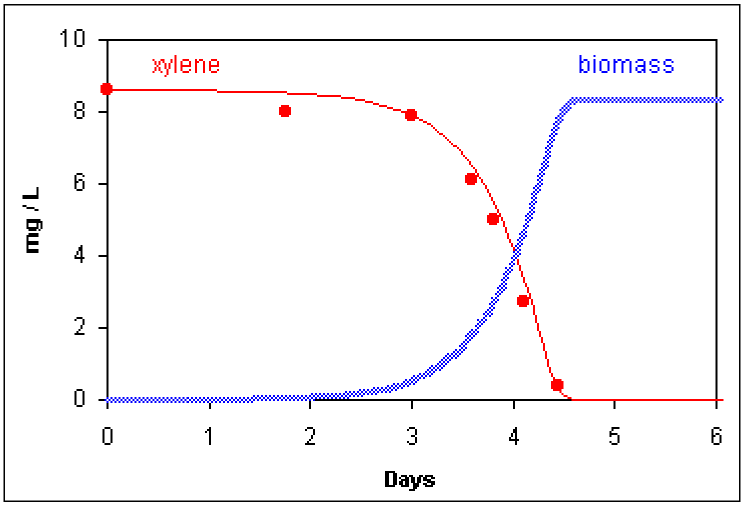


Figure 14: The decrease of substrate concentration first becomes notable when sufficient microbes are present, and the process stops when all the substrate has been consumed

The geochemical program PHREEQC is used to calculate the above equations and plot the lines in the graph, the data points are from Schirmer et al. (1999). Quite conspicuous is the delay of xylene breakdown that occurs because the microbes which degrade the substance first must grow and increase in number. When the biomass is sufficient, xylene is quickly consumed. Note that the xylene concentration in Schirmer's experiment indicates only part of total xylene. Other biodegradable forms comprise xylene that is sorbed to the sediment and gaseous in the headspace. These are mimicked with a retardation factor R, but they can be included as process-dependent entities in the model. The yield factor was found to be 0.305 mol biomass-C/xylene-C. Thus, the actual increase in biomass can be calculated. In the above example the biomass growth is calculated as:

$$\left(\frac{8.6\,mg\;xylene\,L^{-1}}{106\,g\;mol^{-1}\;xylene}\right)\times(8\,mol\,C\,/\,mol\;xylene)(R)(Y)(22.6\,g\,/\,mol\,CH_{1.4}O_{0.4}N_{0.2}) \tag{6}$$

In the above calculation, the retardation factor (R) = 1.86 and the yield factor (Y) = 0.305. CH1.4O0.4N0.2 is the formula used for calculating the molar weight of dry biomass. This produces a result of 8.32 mg biomass L-1.

Methanogenic Biodegradation of Phenol - Similarly, it can be calculated that the anaerobic degradation of 40 mg phenol produces 2.9 mg biomass using the above yield factor, for methanogenic conditions, Y usually is small, about 0.05. This is about the increase shown in fig 15 (blue line) for the phenol calculation. Accordingly, the biomass can be considered constant in the phenol model and therefore included in the value of kmax. The concentrations of phenol and biomass during methanogenic degradation in this laboratory experiment are shown In Figure 15 (Bekins et al., 1998). The phenol concentration decreases linearly with time (characteristic for a zeroth order degradation rate), but the degradation declines at very small concentrations.

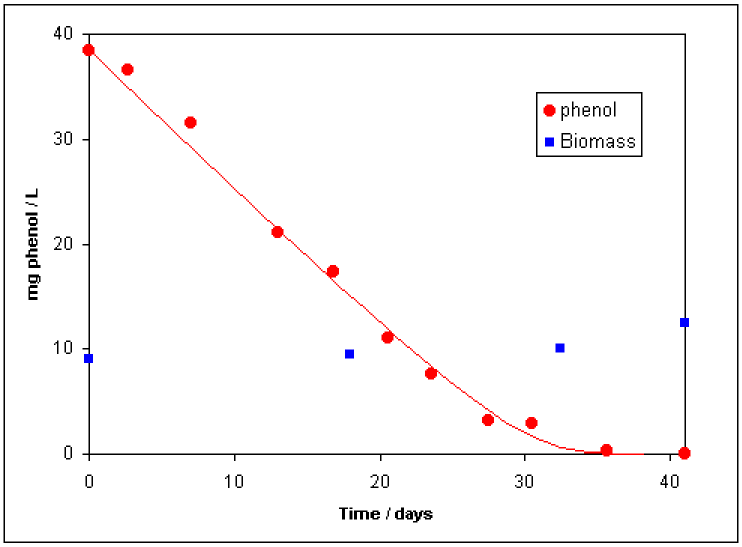


Figure 15: the concentrations of phenol and biomass during methanogenic degradation in a laboratory experiment are shown in the figure (Bekins et al., 1998). The phenol concentration decreases linearly with time (characteristic for a zeroth order degradation rate), but the degradation declines at very small concentrations.

The breakdown is modeled with the Monod kinetic rate equation:

$$\frac{dS}{dt} = R_{Monod} = k_{\max} \frac{S}{k_{1/2} + S} \qquad (7)$$

where:
S is the concentration of phenol (mg L-1)
t is time (sec)
kmax is the maximal rate (mg L-1s-1)
k½ is the half-saturation constant (mg L-1).

In fig. 15 the rate is zero order when the phenol concentration is above 5 mg L-1 (about 3 times higher than k½, the slope dS/dt is constant), but that it becomes first order with respect to phenol (S) at lower concentrations.

ENVIRONMENTAL PROJECTS USING BIOREMEDIATION TECHNOLOGIES

The following discussion takes a brief look at several case studies prepared by EPA and USGS of sites which have used, or are in the process of using, in situ bioremediation for treatment of CAHs in contaminated soil and groundwater. In addition, summary information about other full-scale and pilot-scale applications of in situ bioremediation based on information from the proceedings of the Fifth International and On-Site Bioremediation Symposium and from the Bioremediation the Field Search System (BFSS) is included.

Ground-water contaminated with crude oil

Ground-water contamination by crude oil, and other petroleum-based liquids, is a widespread problem. An average of 83 crude-oil spills occurred per year during 1994-96 in the United States, each spilling about 50,000 barrels of crude oil (U.S. Office of Pipeline Safety, electronic commun., 1997). An understanding of the fate of organic contaminants (such as oil and gasoline) in the subsurface is needed to design innovative and cost-effective remedial solutions at contaminated sites.

The problem ground-water contamination by crude oil and other petroleum-based liquids started in Hanahan, South Carolina, a quiet suburb of Charleston. In 1975, a massive leak from a military fuel storage facility released about 80,000 gallons of kerosine-based jet fuel. Immediate and extensive recovery measures managed to contain the spill, but could not prevent some fuel from soaking into the permeable sandy soil and reaching the underlying water table. Soon, ground water was leaching such toxic chemicals as benzene from the fuel-saturated soils and carrying them toward a nearby residential area.

By 1985, a contaminant plume had reached the residential area, and the facility was faced with a serious environmental problem. At the time, removing the contaminated soils was technically impractical, and removing contaminated groundwater did not address the source of the contaminants. The underlying question was, how could contaminated ground water be kept from seeping toward the residential area in the future?

One possible solution was a new technology called bioremediation. Studies by the U.S. Geological Survey (USGS) had shown that microorganisms naturally present in the soils were actively consuming fuel-derived toxic compounds and transforming them into harmless carbon dioxide. Furthermore, these studies had shown that the rate of these biotransformations could be greatly increased by the addition of nutrients. By "stimulating" the natural microbial community through nutrient addition, it was theoretically possible to increase rates of biodegradation and thereby shield the residential area from further contamination.

In 1992, this theory was put into practice by USGS scientists. Nutrients were delivered to contaminated soils through infiltration galleries, contaminated ground water was removed by a series of extraction wells, and the arduous task of monitoring contamination levels began. By the end of 1993, contamination in the residential area had been reduced by 75 percent. Nearer to the infiltration galleries (the source of the nutrients), the results were even better. Groundwater that once had contained more than 5,000 parts per billion (ppb) toluene now contained no detectable contamination. Bioremediation had worked!

Similarly, a long-term, interdisciplinary research project sponsored by the USGS' Toxic Substances Hydrology Program began in 1983 at a crude-oil spill site near Bemidji, Minnesota (fig. 16). The project involves research by scientists from the USGS and several academic institutions. This research is directed toward understanding the physical, chemical, and biological processes controlling the migration and fate of hydrocarbon contaminants in the subsurface.

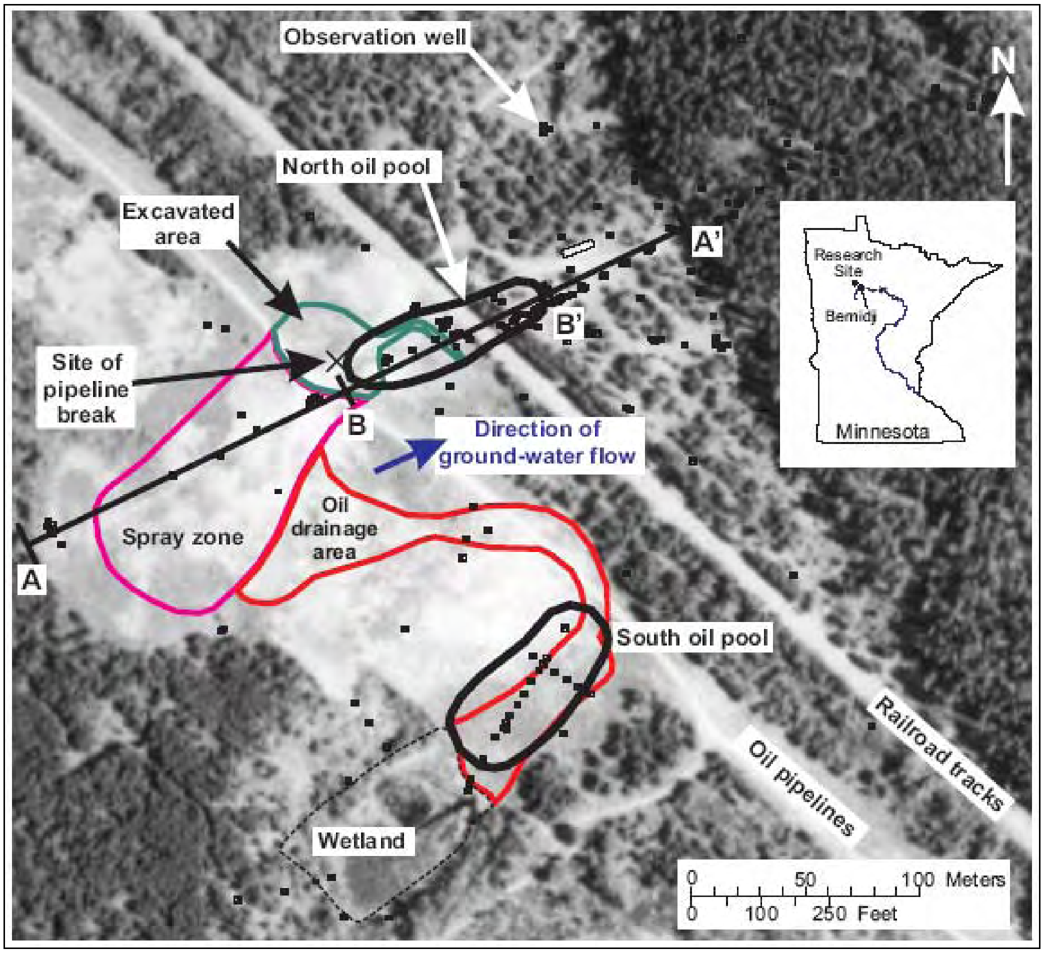


Figure 16: Features of the Bemidji, Minnesota crude-oil spill research site superimposed on a 1991 aerial photograph. (Adapted from USGS Fact Sheet 084-98)

A buried crude oil pipeline located in a glacial outwash plain near Bemidji, Minnesota, ruptured in 1979, spilling about 1.7x106 liters (11,000 barrels) of crude oil contaminating the underlying aquifer. An estimated 1.2x106 liters (7,800 barrels) of the spilled oil were recovered. The remaining oil infiltrated into the subsurface and provides a long-term, continuous source of hydrocarbons that dissolve in, and are transported with ground water.

The spill site became a USGS Toxic Substances Hydrology Program (TSHP) research site in 1983. USGS scientists studying the site found that toxic chemicals leaching from the crude oil were rapidly degraded by natural microbial populations. Significantly, it was shown that the plume of contaminated ground water stopped enlarging after a few years as rates of microbial degradation came into balance with rates of contaminant leaching. This was the first and best-documented example of intrinsic bioremediation in which naturally occurring microbial processes remediates contaminated ground water without human intervention. Evidence for microbial degradation of the petroleum hydrocarbons has been documented in several studies (Baedecker et al., 1993; Bennett et al., 1993; Eganhouse et al., 1993; Ryan et al., 1999). Five geochemical zones (fig. 19) have been identified in the ground water along a cross-section through the northern oil body.

The goal is to provide information and methods to help evaluate the potential for, and long-term performance of, natural and enhanced bioremediation of hydrocarbon contamination across the nation. The crude-oil spill site near Bemidji is one of the better characterized sites of its kind in the world. Results of research conducted on processes affecting the migration and fate of crude oil in the environment have provided fundamental knowledge that has been used to remediate similar sites worldwide. The Bemidji research project was the first to document that the extent of crude-oil contamination at a site can be largely limited by natural attenuation. Scientists studying and documenting natural attenuation at other contaminated sites have used many of the methods and approaches developed at the Bemidji site.

Description and History of Site - On August 20, 1979 approximately 16 kilometers northwest of Bemidji, Minnesota, the land surface and shallow subsurface were contaminated when a crude-oil pipeline burst, spilling about 1,700,000 L (liters) (about 10,700 barrels) of crude oil onto a glacial outwash deposit (fig. 16). Crude oil also sprayed to the southwest covering an approximately 7,500 m2 (square meter) area of land (spray zone). After cleanup efforts were completed about 400,000 L (about 2,500 barrels) of crude oil remained. Some crude oil percolated through the unsaturated zone to the water table near the rupture site (North oil pool, fig. 16). Some of this sprayed oil flowed over the surface toward a small wetland forming a second area of significant oil infiltration (South oil pool, fig. 16). The land surface is a glacial outwash plain underlain by stratified glacial outwash deposits. The water table ranges from near land surface to about 11 m below the land surface. About 370 wells and test holes had been installed as of 1998.

Research Results - The fate, transport, and multiphase flow of hydrocarbons depend on geochemical processes and on the processes of volatilization, dissolution, biodegradation, transport, and sorption (fig. 17). An interdisciplinary investigation of these processes is critical to successfully evaluate the migration of hydrocarbons in the subsurface. The investigation at the Bemidji site involved the collection and analysis of crude oil, water, soil, vapor, and sediment samples. The oil phase that occurs as floating product on the water table and as residuum on sediment grains provided a continued source of hydrocarbon to the ground-water and vapor plumes. Knowledge of the geochemistry of a contaminated aquifer is important to understanding the chemical and biological processes controlling the migration of hydrocarbon contaminants in the subsurface. Studies were also conducted to document the concentrations of gases in the unsaturated zone. Multiphase-flow modeling was used to study the oil movement after the spill. Transport and biodegradation modeling was used to simulate the evolution of the plume, evaluate factors limiting biodegradation, and to develop a mass balance for contaminants at the site and thus evaluate the amount and rate of removal of hydrocarbons by biodegradation.

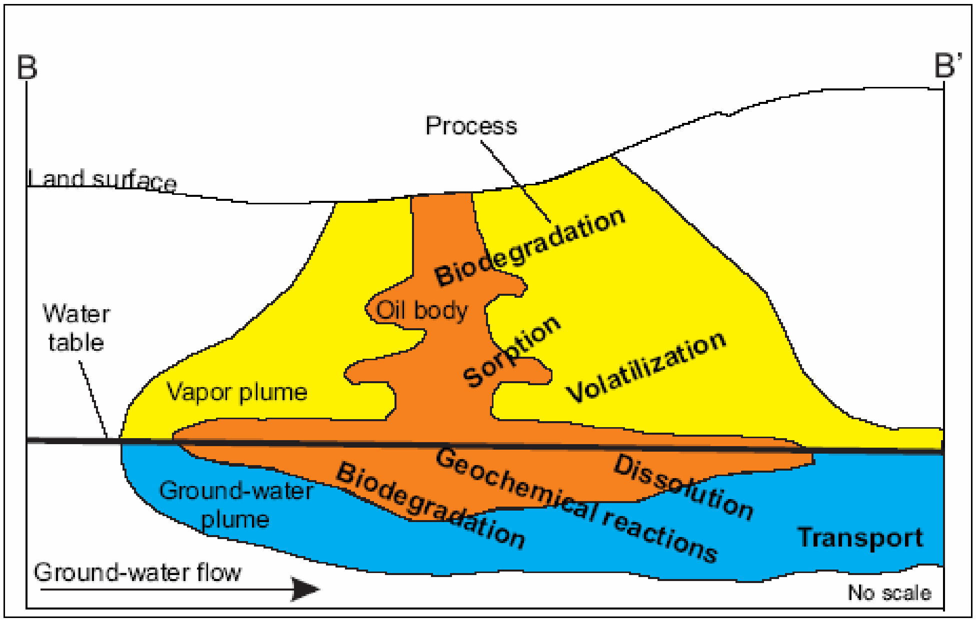


Figure 17: Processes critical to understanding the fate and transport of hydrocarbons in the subsurface at the Bemidji site. (USGS Fact Sheet 084-98)

Oil movement is affected by sediment properties, and their variability, which has resulted in a complex distribution of oil in the subsurface at the North oil pool (fig. 18). Geostatistical analysis and multiphase-flow simulations have been used to explain how spatial variability affects the oil distribution (Dillard and others, 1997). As of 1996, the leading edge of the oil floating on the water table at the North oil pool had moved about 40 m downgradient since the spill.

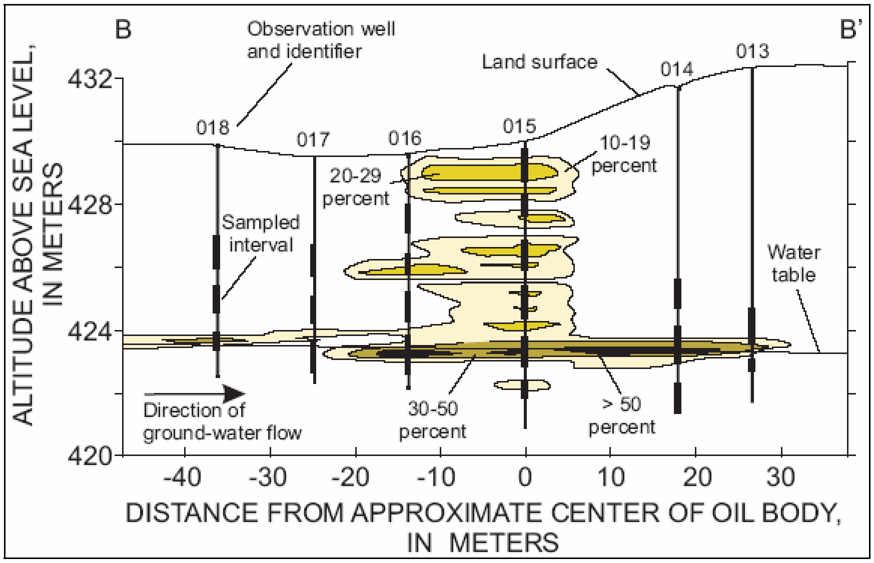


Figure 18: Oil saturation distribution at the north oil pool. (USGS Fact Sheet 084-98)

Degradation of the oil product has resulted in selective loss of soluble and volatile compounds through dissolution and volatilization. Mass loss rates of crude oil at different locations range from 0 to 1.25 percent per year. The total loss of oil mass was estimated at 11 percent from 1979-89 (Landon and Hult, 1991).

Eight transport zones have been identified; five geochemical zones have been identified at the North oil pool within the saturated zone (Baedecker and others, 1993; Bennett and others, 1993) (fig. 19) and three in the vadose zone (unsaturated zone above the water table). Zone 1 consists of oxygenated uncontaminated native ground water. Zone 2, which is below the spray zone, is characterized by low oxygen concentrations and high concentrations of total dissolved inorganic and organic carbon. Zone 3, beneath and immediately downgradient of the floating oil, consists of an anoxic plume of ground water containing high concentrations of hydrocarbons, dissolved manganese (Mn2+), iron (Fe2+), and methane (CH4). Zone 4, a transition zone from anoxic to oxygenated conditions, contains low concentrations of hydrocarbons as a result of aerobic degradation processes. Zone 5 consists of oxygenated water downgradient from the contamination plume that contains slightly higher concentrations of dissolved constituents, such as benzene, toluene, ethylbenzene, and xylene (BTEX).

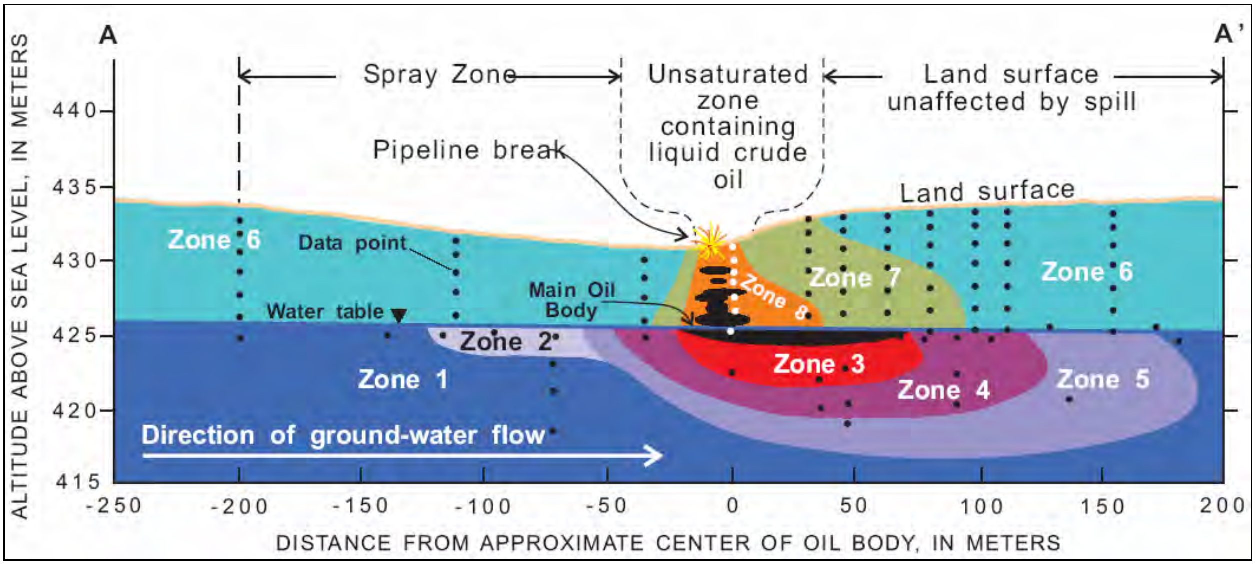


Figure 19: Geochemical zones in the unsaturated and saturated zones at the North oil pool, 1997. Locations of the monitoring wells sampled in this investigation shown with oil body and geochemical zones of contamination designated by Baedecker and others (1993). The ground water zones have the following characteristics: (I) native uncontaminated ground water, oxic; (II) high organic and inorganic carbon, sub-oxic; (III) high hydrocarbons, Mn2+, Fe2+, methane, anoxic; (IV) transition zone between III and V, sub-oxic; and (V) slightly elevated benzene, toluene, ethylbenzene, and xylenes (BTEX), oxic. The water table depth ranges from 8 to 9 m for the wells shown. (Modified from Baedecker and others, 1993 and Taken from Ryan et al., 1999; USGS Fact Sheet 084-98)

Long-term monitoring of the plume since 1984 has shown that, near the water table, the concentration of total dissolved organic carbon (TDOC) and dissolved oxygen (DO) downgradient from the oil body has remained relatively stable suggesting that degradation of the plume has reached equilibrium. In the anoxic zone (Zone 3), concentrations of reduced chemical species Mn2+, Fe2+, and CH4 have increased with time, indicating a sequence of Mn reduction, Fe reduction, and methanogenesis. With depletion of Mn(IV) near the oil body, Mn reduction has become a less important reaction. The data show that both Fe (III) reduction and methanogenesis are major reactions in the anoxic plume (Baedecker and others, 1993).

Although these geochemical processes have changed over time, the plume has not migrated as far as predicted considering the ground-water flow velocities and sorption constants for these compounds (Baedecker and others, 1993). As of 1996, the leading edge of the plume of ground water containing a total BTEX concentration greater than 10 micrograms per liter had moved only about 200 m downgradient, whereas advective flow of ground water since the spill has been about 500 m. The primary reason is that hydrocarbons have biodegraded under oxic and anoxic conditions. The rate of removal of organic contaminants by natural attenuation and the factors that affect rates of biodegradation are important considerations in making decisions concerning cleanup of contaminated ground water. Biodegradation of petroleum-derived hydrocarbons in oxic and sub-oxic environments is generally considered a more efficient attenuation mechanism than is biodegradation in anoxic environments. However, research at this site has demonstrated that biodegradation in anoxic environments can remove substantial amounts of hydrocarbons from ground water (Lovley and others, 1989; Baedecker and others, 1993; Eganhouse and others, 1993; Cozzarelli and others, 1994; Ryan et al., 1999).

Volatile oil components have left the subsurface through volatilization and biodegradation in, and diffusion through, the unsaturated zone. The distribution of gases (hydrocarbon, oxygen (O2), carbon dioxide (CO2), and CH4) in the unsaturated zone were quantified at the North oil pool during 1997 and used to identify three geochemical zones (fig. 15). Zone 6 exhibits near atmospheric concentrations of O2. Zone 7, a transition zone, is defined by lower concentrations of O2 (10-20 percent), hydrocarbon concentrations less than 1 part per million (ppm), and higher concentrations of CO2 (0-10 percent) and CH4 (0-10 percent). Zone 8, immediately above the oil body, is relatively anoxic and contains maximum concentrations of CO2 (>10 percent), CH4 (>10 percent), and hydrocarbon (>1 ppm).

The distribution of gases at the North oil pool has changed considerably since the spill. For example, as of 1985 the leading edge of the plume of hydrocarbon vapors (concentrations > 1 ppm, zone 7) in the unsaturated zone was about 150 m downgradient (Hult and Grabbe, 1988). As of 1997 the plume of vapors had receded to about 75 m downgradient (fig. 19) and the receding likely was due to aerobic biodegradation.

Leachate Plumes at a Municipal Solid-Waste Landfill

Municipal solid waste is a combination of non-hazardous wastes from households, commercial properties, and industries. The U.S.EPA reports that the United States produced about 230 million tons of solid waste in 1999, about 57 percent of which is disposed of in landfills (EPA, 1999). Disposal of municipal solid waste in landfills was largely unregulated prior to the 1970s. Most solid waste was deposited in unlined pits. Precipitation and ground water seeping through this waste produces leachate, which is water contaminated from the various organic and inorganic substances with which it comes in contact as it migrates through the waste. Leachate seeping from a landfill contaminates the ground water beneath the landfill, and this contaminated ground water is known as a plume. The normal movement of ground water causes the leachate plume to extend away from a landfill, in some cases for many hundreds of meters. Many studies have shown leachate plumes emanating from old unlined landfills. Estimates for the number of closed landfills in the United States are as high as 100,000 (Suflita and others, 1992).

Federal and state regulations were passed in the 1980s and 1990s to manage disposal of solid waste. Those regulations require that most landfills use liners and leachate collection systems to minimize the seepage of leachate to ground water. Although liners and leachate collection systems minimize leakage, liners can fail and leachate collection systems may not collect all the leachate that escapes from a landfill. Leachate collection systems require maintenance of pipes, and pipes can fail because they crack, collapse, or fill with sediment. The USEPA has concluded that all landfills eventually will leak into the environment (U.S.EPA, 1988). Thus, the fate and transport of leachate in the environment, from both old and modern landfills, is a potentially serious environmental problem.

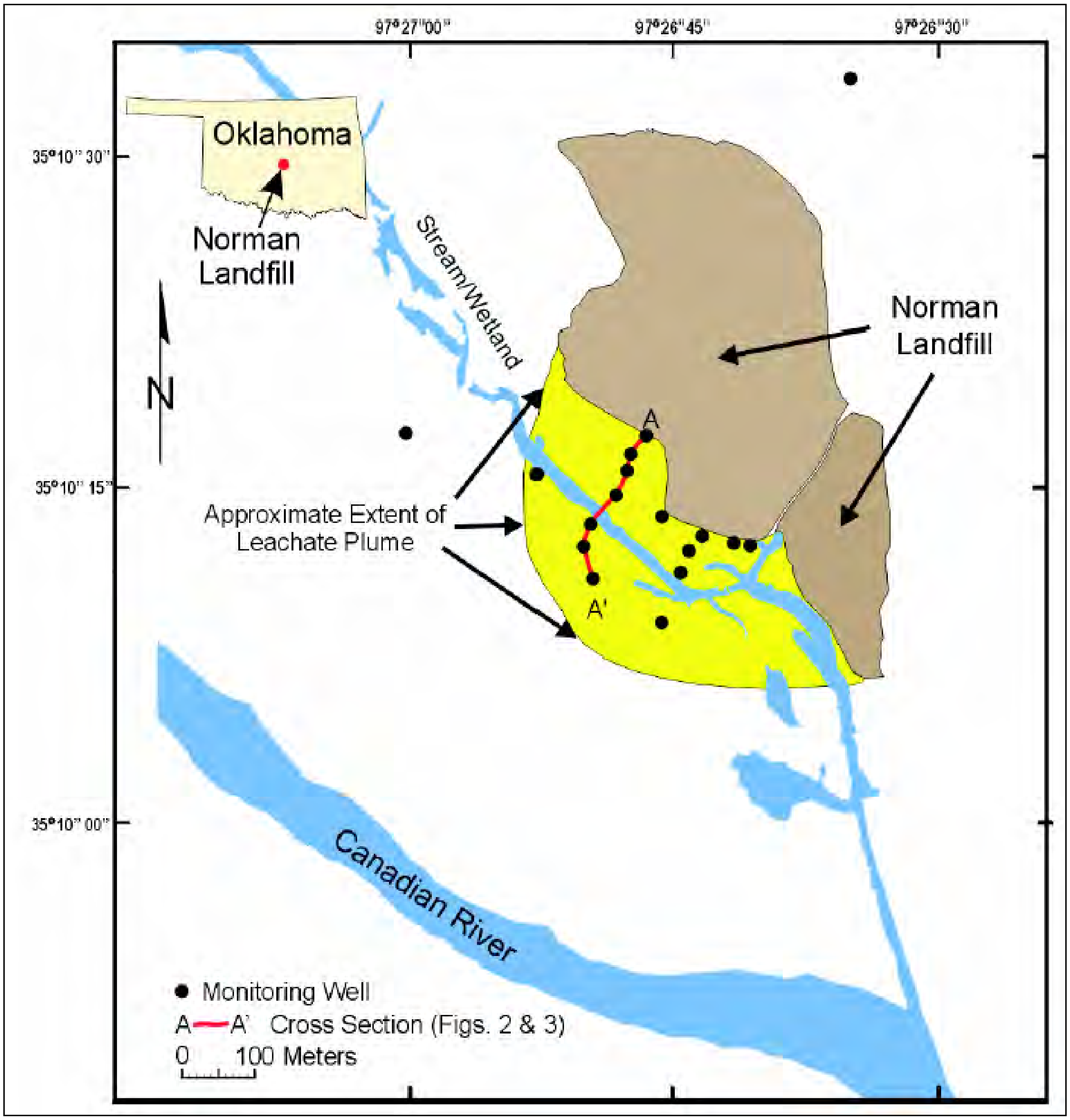


Figure 20: Map of the Norman Landfill Environmental Research Site (taken from Christenson and Cozzarelli, 2003, USGS Fact Sheet FS-040-03)

Site History/Source of Contamination - The Norman Landfill Environmental Research Site (fig. 20) is a closed municipal solid waste landfill, formerly operated by the city of Norman, Oklahoma. The landfill is sited directly on the Canadian River alluvial aquifer and has no liner or leachate collection system, so a leachate plume has developed in ground water in the aquifer.

The ground water and leachate plume flow away from the landfill toward the Canadian River, a large tributary of the Arkansas River that drains into the Mississippi River.

The Norman Landfill was designated a research site by the U.S. Geological Survey (USGS) through its Toxic Substances Hydrology Research Program. Monitoring wells and instruments have been installed in and adjacent to the leachate plume. A small stream and wetland overlie the leachate plume, and studies are in progress to determine the fate of leachate compounds that enter the wetland from the ground water. USGS hydrologists and technicians have accomplished comprehensive site characterization, which provides a wealth of information about the site hydrogeology and geochemistry.

This site characterization provides essential information to the scientists conducting research about the chemical, biological, and hydrologic processes in ground water and surface water affected by landfill leachate. Research is in progress at the site by scientists from the University of Oklahoma, Oklahoma State University, other universities, the USEPA, and the USGS. In addition to providing a laboratory for studies of ground and surface water contaminated by landfill leachate, the Norman Landfill Environmental Research Site is used to study other types of contaminant problems. The plume can be used to study microbiological and geochemical processes that are not specific to landfills. All research at the Norman Landfill Environmental Research Site is designed to investigate problems and processes that have a high transfer value to other subsurface contamination problems.

Comprehensive physical, chemical, and microbial characterizations at this and other USGS Toxic Substances Hydrology Program sites provide fundamental knowledge of the processes that control important types of contamination problems. This knowledge of fundamental processes can be generalized to a wide range of field conditions by comparing results to field and laboratory experiments at other sites with differing conditions and properties. The resulting knowledge and methods improve the effectiveness and reduce the cost of characterization and remediation at contaminated sites across the nation.

Scientists used a combination microbiological and geochemical approach to identify the important processes occurring in the aquifer contaminated by leachate from the Norman Landfill (Cozzarelli and others, 2000, Harris and others, 1999). The combined sciences of microbiology and geochemistry are called biogeochemistry. The Landfill researchers identified zones in the leachate plume where different biogeochemical processes are occurring.

Some evidence of natural attenuation at the Landfill is shown in figure 21 (Cozzarelli and others, 2000), illustrated as generalized hydrogeologic sections through the leachate plume in the aquifer. The three illustrations within figure 19 show chemical concentrations of important indicators of natural attenuation processes along the same vertical slice of the aquifer. These illustrations demonstrate that the leachate plume begins near the surface (on the left side of the figure), where the solid waste is stored in the landfill. Ground water flows to the south toward the Canadian River. The leachate plume migrates toward the bottom of the aquifer as it flows toward the river.

Sulfate occurs naturally in ground water in the Canadian River alluvial aquifer. Sulfate is depleted in the center of the leachate plume (fig. 21, ill. 2A) because the microorganisms use sulfate as an electron acceptor. When microorganisms transfer electrons to sulfate, it changes chemically to form dissolved sulfide or hydrogen sulfide gas. The highest rates of sulfate reduction have been measured at the plume boundaries, such as where fresh water from rainfall infiltrating the aquifer mixes with the contaminant plume (Cozzarelli and others, 2000), and causes the sharp concentration gradients observed in figure 21, ill. 2A.

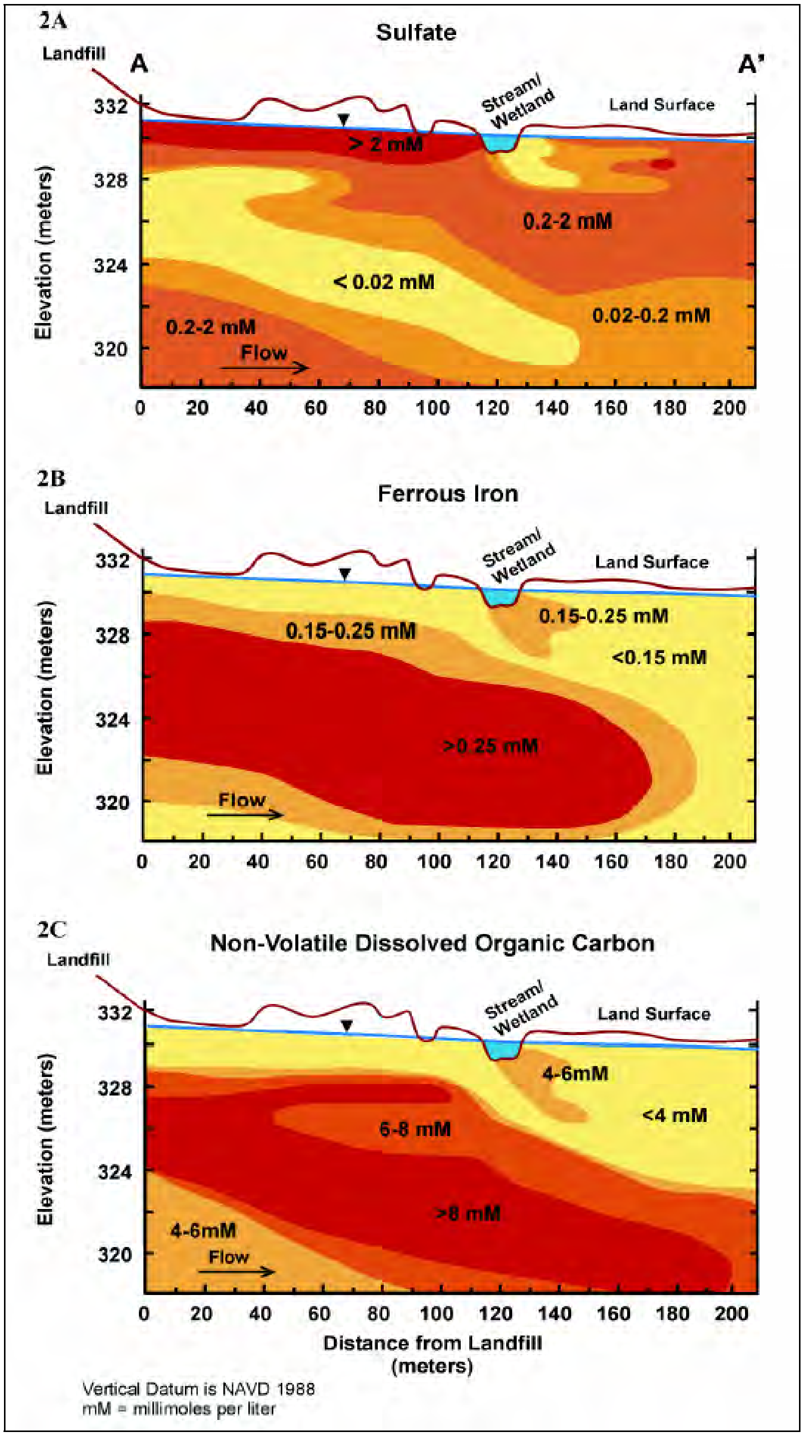


Figure 21: (illustrations 2A-C). Concentrations of electron acceptors and donors in the Norman Landfill leachate plume (USGS FS-040-03).

The degradation of organic contaminants occurs most rapidly at the plume boundaries. Iron occurs naturally as mineral coatings on sediments in the Canadian River alluvial aquifer. Dissolved iron concentrations increase in the leachate plume (fig. 21, ill. 2B) because microorganisms transfer electrons to the iron on the mineral coatings, which contain insoluble ferric iron, while degrading the organic contaminants. With the addition of an electron, the iron is reduced to ferrous iron, which dissolves in water. Although the solid-phase electron acceptor (ferric iron) cannot be measured in the ground water, the detection of the end product of the reaction (ferrous iron) in water provides evidence that iron reduction has occurred.

The concentration of non-volatile dissolved organic carbon (NVDOC) is shown in figure 21, ill. 2C and in fig 13 above. NVDOC is a measure of the organic contaminant compounds in the landfill. In the center of the plume, the concentration of NVDOC shows little change with distance, indicating that NVDOC is not efficiently degraded in this zone.

Researchers at Norman Landfill have learned that most of the natural attenuation occurs at the boundaries of the plume where electron acceptors are available. Sulfate concentrations are low in the center of the plume, as are measured rates of iron and sulfate reduction. The natural attenuation capacity of the aquifer, that is, its ability to attenuate contaminants, is depleted in the center of the leachate plume because microorganisms have used all the electron acceptors during migration of the leachate plume.

USGS and other scientists have been investigating volatile organic compounds (VOCs) in the leachate at Norman Landfill (Eganhouse and others, 2001). VOCs are organic compounds that tend to vaporize at room temperature and pressure. Examples include some of the compounds in gasoline, lubricants, paints, and solvents, some of which are highly toxic or carcinogenic. VOCs end up in landfills in many ways, including the disposal of ordinary household items such as cleaners or marking pens. Although VOCs make up less than 0.1 percent of the mass of organic carbon in the leachate plume, they are useful indicators of natural attenuation.

At Norman Landfill, USGS scientists compared concentrations of two different alkylbenzene isomers, n-propylbenzene and i-propylbenzene, in landfill leachate. Isomers of alkylbenzene have the same number and type of atoms, but the molecules have slightly different chemical structures. These different isomers have similar physical properties, so they should be affected by volatilization, dilution, and sorption in a similar manner.

As shown in figure 22 below, the concentration of n-propylbenzene decreases much faster as leachate flows away from the landfill than does the concentration of i-propylbenzene. This decrease in concentration of n-propylbenzene is caused by biological degradation, indicating that biologically mediated natural attenuation is decreasing the concentrations of some contaminants at Norman Landfill. This technique of comparing alkylbenzene isomers as indicators of biological processes can be applied at sites with contaminants other than landfill leachate.

Field experiments are being carried out at Norman Landfill to investigate how the rate of natural attenuation may vary with aquifer permeability (permeability is a measure of the ability of a material to transmit fluid). These experiments use push-pull or single-well injection-withdrawal tests (Istok and others, 1997). During the injection phase of the test, a solution consisting of groundwater amended with tracers, electron donors, or electron acceptors is injected or “pushed” through a well into the aquifer. During the extraction phase, the test solution is pumped or “pulled” from the same well. Concentrations of tracers, reactants, and possible reaction products are measured as a function of time in order to construct breakthrough curves, measure reaction rates, and to compute mass balances for each solute.

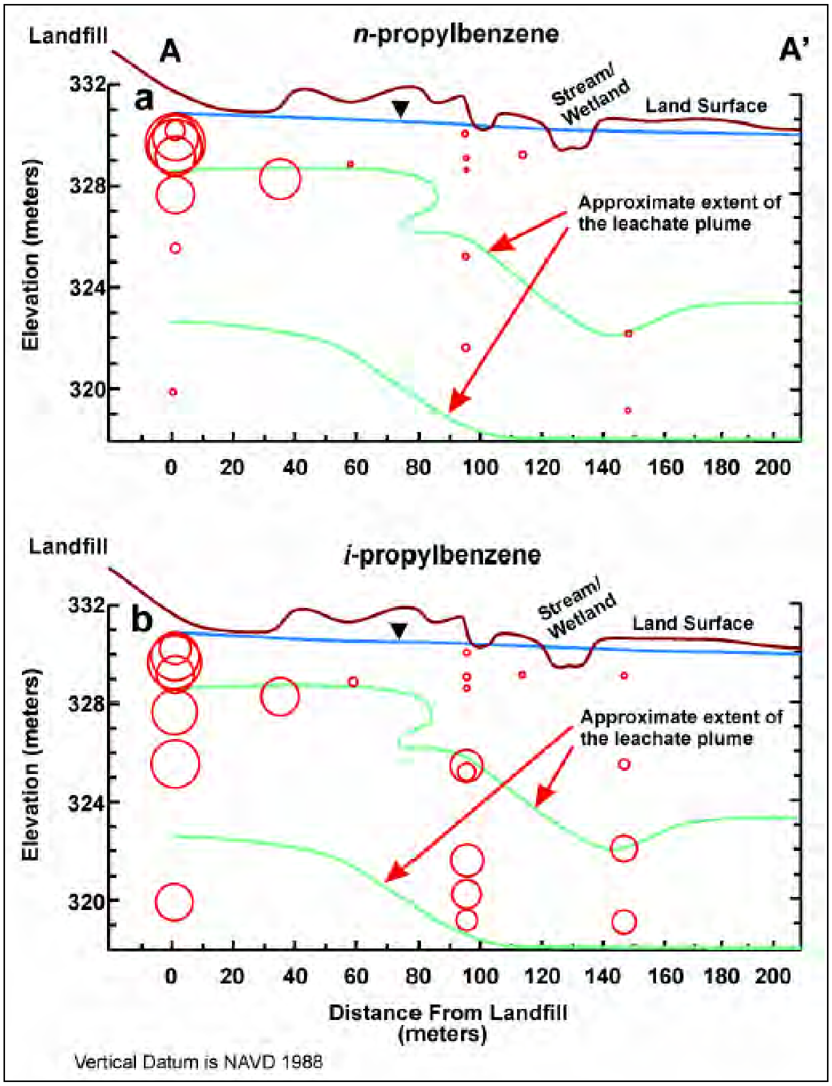


Figure 22: Distribution of the alkylbenzene isomers (a) n-propylbenzene and (b) i-propylbenzene in the leachateplume at Norman Landfill. Concentrations in micrograms per liter (Fg/L) are proportional to bubble diameter.Maximum concentration: n-propylbenzene = 0.80 Fg/L, i-propylbenzene = 1.24 Fg/L (from Eganhouse and others, 2001; USGS FS-040-03).

These tests can be conducted anywhere in the aquifer, making it possible to investigate processes and rates in different geologic textures and geochemical environments. Push-pull tests were conducted at Norman Landfill to measure biodegradation rates of simple organic acids in the leachate plume (Scholl and others, 2001). Wells were drilled into layers of three different types of sediments (medium sand, silt/clay lenses in sand, and poorly sorted gravel), each with a different permeability. Biodegradation rates of two simple organic acids, formate and lactate, were compared in the three different zones in the anoxic leachate plume at the site. These organic acids were used as microbial process indicators because they degrade at different rates depending on the dominant microbial processes. A conservative tracer (bromide) and the two organic acids were added to 50 or 100 liters of contaminated ground water pumped from each test well. The mixture was then re-injected and allowed to mix with the natural ground water. Daily samples were taken from the injection well until organic acids could no longer be detected. Although complete disappearance of the formate and lactate occurred within 7-9 days in all the wells, there were differences in degradation patterns. The results of the test show that the loss of lactate was due to natural attenuation and that there are differences in the rate of natural attenuation in areas of different permeability. These variable degradation rates may be related to microbial community structure, sediment chemistry, and water flow regime.

Research at the Norman Landfill Environmental Research Site has good implications for the further use of bioremediation as a clean-up strategy. Results show that chemicals leaching from old unlined landfills are contaminating groundwater, and that some of the contaminant concentrations are being reduced by natural attenuation. Modern landfills are designed to minimize contamination of groundwater, but modern landfills eventually may leak contaminants into the environment. Research results will be useful to scientists and regulators trying to determine the effects of landfill leachate on the environment.

Leachate Plumes at Federally Operated Facilities

The majority of federally controlled facilities have historically problems with extensive areas of subsurface contamination. Two previous completed projects are chosen below for further illustration of bioremediation technologies at federal facilities. The projects are Aerobic degradation field demonstration at Moffett Naval Air Station, Mountain View, California and bioremediation of TCE through Toluene injection at Edwards Air Force Base, California (EPA, 2000).

Site History/Source of Contamination - Moffett Naval Air Station (Moffett) was used for aircraft operations and maintenance, operated from 1933 to 1994. Moffett is located 35 miles south of San Francisco in Santa Clara County. In 1994, the Navy ceased operations and the airfield was transferred to the National Aeronautics and Space Administration (NASA). Soil and groundwater at the site are contaminated with petroleum products and chlorinated aromatic hydrocarbons (CAHs) such as tetrachloroethene (PCE) and trichloroethene (TCE). Moffett is adjacent to other Superfund sites in the Middlefield-Ellis-Whisman (MEW) study area, and a large groundwater plume crosses Moffett from off-site sources. This site was added to the National Priorities List (NPL) on July 22, 1987 and is being addressed through Federal actions. Several Records of Decision (RODs) have been signed for this facility, including RODs for OU 1 (Sites 1 and 2 Landfills), dated August 1997; OU 2 (East Side Soils), dated December 1994; and OU 5 (East Side Aquifers), dated June 1996. In addition, for the West Side Aquifers, the Navy adopted an adjacent site's ROD, dated 1989.

Moffett was selected by researchers from Stanford University for a field demonstration of in situ aerobic degradation to treat groundwater contaminated with CAHs. A series of experiments was conducted between September 1986 and November 1998 to evaluate native bacteria enhanced through addition of methane, toluene, and phenol in degrading CAHs, including PCE and TCE. At Moffett Field, groundwater was extracted from one well, amended chemically, and reinjected at another well located 6 meters (m) from the extraction well (see fig. 21 above for diagram). The wells, screened in a sand and gravel layer approximately 4 to 6 m bgs, created induced-gradient conditions in the aquifer.

Edwards Air Force Base (AFB), is located on the western portion of the Mojave Desert, about 60 miles north of Los Angeles, covers approximately 301,000 and is used for aircraft research and development. From 1958 through 1967, engines for the X-15 rocket airplane were maintained in facilities at the site, and trichloroethene (TCE) was used to clean the engines. The used TCE was disposed of at Site 19, an area of about 53 acres on the west side of Rogers Dry Lake, resulting in groundwater contamination. The contaminant plume extends approximately 3,200 ft down-gradient from the contamination source, and nearly the same distance cross-gradient. This site was added to the National Priorities List (NPL) on August 30, 1990, and is being addressed through Federal actions. A Record of Decision (ROD) had not been signed for this facility at the time of this report. A field demonstration of aerobic biodegradation was performed at Site 19. The area of the plume used for this field demonstration was about 400 meters (m) east of the contamination source.

At Edwards AFB, a two-well recirculation system was constructed; the system created separate bioactive zones in upper and lower aquifers. One well was used to extract groundwater from the lower aquifer, amend it chemically, and reinject the groundwater into the upper aquifer. The other well was used to extract groundwater from the upper aquifer, amend it chemically, and reinject the groundwater into the lower aquifer. The wells were spaced 10 m apart, and screened between approximately 6 and 24 m bgs.

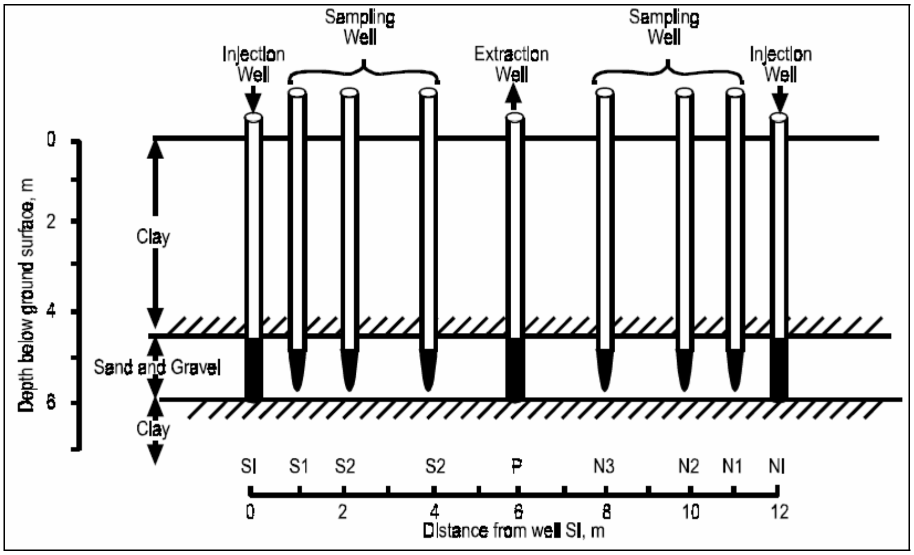


Figure 23: Cross-section of Well Field Used at Moffett (EPA-542-R-00-008)

Geology/Hydrogeology/Contaminant Characterization - As shown in Figure 23, the demonstration site (test zone) was approximately 4 to 6 meters (m) below ground surface (bgs), located in a shallow, confined aquifer (1.5 m thick) consisting of sands and gravels. The groundwater velocity ranged from 1.5 to 3 m/day and the hydraulic conductivity of the aquifer was 0.11 cm/sec. In addition, indigenous methanotrophic bacteria were reported to be present in the aquifer. The CAHs present in the test zone prior to the demonstration included 1,1,1-trichloroethane (TCA) and 1,1-dichloroethane (DCA). However, TCE, cis-dichloroethene (cis-DCE), trans-dichloroethene (trans-DCE), and vinyl chloride (VC) were not detected in the groundwater in the test zone. As described below, regulatory approval was obtained to inject TCE, cis- and trans-DCE, and VC into the groundwater for the demonstration.

Likewise, the Site 19 demonstration area at Edwards AFB contains two relatively homogeneous aquifers. The upper, unconfined aquifer is 8 m thick, and is separated by a 2 m aquitard from the lower confined aquifer. The lower, confined aquifer is approximately 5 m thick and lies above weathered bedrock. At the demonstration site, the concentration of TCE in the groundwater plume varied between 500 and 1,200 micrograms per liter (µg/L), with average

TCE concentrations in the upper and lower aquifer of 680 and 750 µg/L, respectively. No 1, 1-DCE was found at the site prior to the demonstration.

Technology Description - The demonstration of aerobic degradation was performed under induced-gradient conditions created by the extraction and injection of groundwater. As shown in Figure 23, groundwater was extracted at well P, amended chemically, and injected at wells SI and NI, located 6 m from extraction well P (information about the construction and operation of the wells was not provided). Regulatory approval was obtained for injecting TCE, cis- and trans-DCE, and VC into the groundwater.

A summary of the nine experiments that were conducted over three seasons of the demonstration, including the period of operation, groundwater extraction and injection rates, chemical amendments, and processes studied. The experiments included biostimulation (Biostim) to stimulate the activity of native methane-using bacteria, and biotransformation (Biotran) to transform TCE into lower chlorinated compounds. Tracer experiments, using bromide, were performed to evaluate organic transport and "Decmeth" experiments were performed to evaluate methane addition. Concentrations of CAHs, methane, DO, and bromide were monitored using the wells shown in Figure 23. An automated data acquisition and control system was used to provide as many as six sets of analyses per day at each of the sampling locations.

Additional experiments performed at the site included using phenol and toluene (alternative electron donors) as substrates in place of methane, and using hydrogen peroxide as an alternative to oxygen.

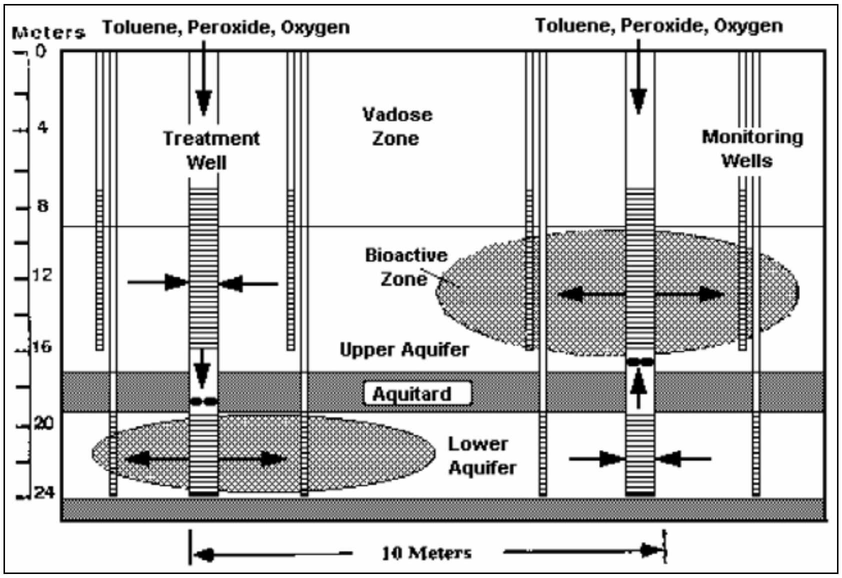


Figure 24: Cross-section of two-well cometabolic TCE biodegradation treatment system spanning two separate aquifers at Edwards AFB. Source: McCarty et al., Enviro Sci & Tech, 1998; Grindstaff, 1998)

The in situ bioremediation treatment system used at Site 19, shown in Figure 24, was designed based on the results from the demonstration at Moffett case study, and consisted of two 8-in diameter, PVC treatment wells installed approximately 24 m deep and spaced 10 m apart. Each treatment well was screened in both the upper and lower aquifers (15 m and 10 m, respectively), and a submersible pump, placed in each well, was used to draw contaminated water into the well through one of the screens. The initial flow rate for the wells was 38 liters per minute (L/min) to limit drawdown in the upper aquifer and pressure changes in the lower aquifer. The primary substrate (toluene) and oxygen were introduced into the wells via feed lines and mixed with the water using static mixers inside the wells. The groundwater, containing TCE, toluene, and oxygen, was discharged from the second screen into the aquifer, where a treatment zone developed around the well. As shown figure 24, treatment well 1 (T1) withdrew water from the upper aquifer and discharged it into the lower aquifer; while treatment well 2 (T2) withdrew water from the lower aquifer and discharged it into the upper aquifer. This process recirculated the water between the two aquifers creating a bioreactive treatment cell.

Treatment system operation included groundwater pumping, pulsed addition of toluene, and addition of dissolved oxygen (DO, as gaseous oxygen) and hydrogen peroxide (H2O2). The system was operated for 444 days. The demonstration included five phases, during which time the operating parameters were varied as follows:

phase 1; pre-operational studies (days 0 - 33)
phase 2; establishment of a toluene-degrading consortium (days 34 - 55)
phase 3; pre-steady-state operation (days 56 - 136)
phase 4; steady-state operation (days 142 - 271)
phase 5; balanced flow operation (days 317 - 444)

Technology Performance - Hydrogen peroxide was found to achieve TCE removals similar to those achieved using oxygen. While 1,1-DCE was partially transformed in the study with phenol, the transformation products were found to be toxic to the transforming bacteria.
Specific remedial goals were not established for this demonstration. The objective of the field demonstration was to collect data to be used in evaluating aerobic degradation of CAHs under several different experimental scenarios. Several methods were used to evaluate the amount of CAHs that were biodegraded in these experiments, including mass balances on the amounts of CAH injected and extracted, and comparison of breakthrough concentrations using controlled experiments and bromide tracers. Results showed that active use of methane in the treatment zone was required for biodegradation of CAHs, and that groundwater residence times in the treatment zone of 1-2 days resulted in biodegradation of TCE at 20 - 30%, cis-DCE at 45 -55%, trans-DCE at 80 - 90%, and VC at 90- 95%. The results indicated a similar degree of biodegradation of TCE over the three seasons of field testing, suggesting that there was no apparent increase in the ability of the bacteria to degrade TCE. In addition, results showed that an intermediate biotransformation product, trans-DCE oxide, was produced in a manner consistent with the expected transformation pathway for trans-DCE. Detailed analytical results for each of the nine experiments are provided for this case study. The results from the third season of the methane addition experiments and the experiments with phenol and toluene as primary substrates show that the use of phenol and toluene achieved higher percent removals of TCE (93 - 94%) compared with use of methane (19%).

Specific remedial goals (contaminant concentrations in groundwater) were not established for the demonstration. However, the objectives of the pilot study at Edwards AFB were to evaluate the advantages and limitations of in situ bioremediation for full-scale aquifer remediation. An area of 480 m2 (0.12 acres) was monitored using 20 monitoring wells. Fourteen of the monitoring wells surrounded treatment wells T1 and T2 in a diamond formation, and two wells were nested between the treatment wells. Other wells were located at the “compass points” (North, South, East, West) surrounding the site. The 14 diamond formation wells and three of the four compass point wells were screened in both the upper and lower aquifers, allowing sampling from each aquifer independently. A total of 10,500 samples were collected and analyzed automatically at the site throughout the course of the demonstration. Comparison of measured TCE concentrations at the treatment well discharge screens, and at monitoring wells located 7.5 m away from the screens, allowed estimation of TCE removal in the bioactive treatment zones surrounding the discharge screens.

The results shows that the average reduction of TCE during steady-state operation (days 145 - 271) was 87% in the upper aquifer bioactive zone and 69% in the lower aquifer adjacent to treatment well T1 discharge screen. During balanced flow operation (days 365 - 444), the average removal of TCE was 86% and 83% in the upper and lower aquifer bioactive zones, respectively. Over the duration of the demonstration, TCE concentrations were reduced by 97.7%, from 1,150 g/L (groundwater moving into the study area) to 27 g/L (groundwater moving out of the study area) and toluene removal generally exceeded 99.98%.

According to the study the overall TCE concentration reduction of 97.7% is higher than the removals reported as groundwater recirculated through the bioactive zone multiple times during the overall demonstration. The dual-well system was found to be technically feasible for remediation of TCE in a two aquifer system.

No information was provided about potential degradation products from this demonstration. The researchers presumed that toluene degraded aerobically to carbon dioxide and water, and TCE was co-metabolized, ultimately producing carbon dioxide, water, and chloride ions. No exceptions to established quality assurance/quality control (QA/QC) protocols were noted in the available information.

CAPITAL COSTS ($)	
Total treatment costs (treatment wells, mixers Pumps, deionized water system, etc.)	62.707
Total monitoring costs (19 monitoring wells, pumps, Tubes and connectors, valves and fittings)	260,746
Total Capital Costs	323,453
Annual Operating Costs ($)	
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

Table 1: Capital and Operation Costs for Aerobic In Situ Bioremediation at Edwards AFB. Source: Adapted from: Rowans, 1998; (Grindstaff, 1998)

Technology Cost - No information was provided about the cost for the in situ bioremediation treatment system used at Moffett. However, Table 1 provides an example costs incurred in similar projects of this type. The information contained in the table shows the actual cost for the in situ bioremediation treatment system used for the demonstration at Edwards AFB, including capital and operation and maintenance costs. Software is available [EPA, 2001] for estimating costs of applying this technology at a site with specified characteristics. These actual costs are provided as an example in the software user's guide.

Summary Observations and Lessons Learned - The results of the field demonstration at Moffett showed that native bacteria enhanced with methane, phenol, or toluene, plus oxygen or hydrogen peroxide was effective in degrading CAHs in groundwater. Concentrations of CAHs were reduced by as much as 94% for TCE, 92% for cis-DCE, and 98% for VC. Native bacteria enhanced with phenol and toluene achieved higher removal rates for TCE than bacteria enhanced with methane. The results from the field experiments were consistent with the results from batch soil column laboratory testing using aquifer solids from the test zones. The presence of 1,1-DCE in the groundwater was found to be toxic to the bacteria, and should be considered when evaluating this technology for use in other applications. However, the relatively low concentration of phosphate in the groundwater did not limit the biodegradation of CAHs at this site.

According to the researchers, other phosphate minerals may have dissolved in the groundwater to replenish this mineral as it was being removed by the bacteria. During the field demonstration, the use of alternating pulsed addition of methane and oxygen minimized biofouling in the area near the injection well.

The dual-well system met the objectives of the pilot study, and was found to be technically feasible for remediation of TCE in a two aquifer system. In addition, this technology might be feasible for use in a single aquifer system where low permeability layers separate lower and upper zones, and where vertical hydraulic conductivity is significantly lower than horizontal conductivity. Alternatively, with a relatively homogeneous single aquifer system, groundwater might be pumped to the surface from one location and then reinjected at another location with chemical amendments added at the surface or down-well at the injection location.

Prevention of well clogging was identified as an important operational consideration for application of this technology. To control well clogging during this demonstration, site operators used well redevelopment (three times in the upper and twice in the lower aquifer) and addition of hydrogen peroxide, which increased the operational costs.

The extensive network of monitoring wells was a major capital cost component for this application. The monitoring system was installed to allow a detailed evaluation of the treatment system’s performance. Monitoring of this magnitude would likely not be required for a full-scale application.

OTHER PAST PROJECTS

Chlorinated solvents, New Jersey

Chlorinated solvents are a particularly common contaminant in the heavily industrialized Northeast. Because their metabolic processes are so adaptable, microorganisms can use chlorinated compounds as oxidants when other oxidants are not available. Such transformations, which can naturally remediate solvent contamination of ground water, this study has been extensively documented by USGS scientists at Picatinny Arsenal, New Jersey.

Gasoline contamination, Galloway, New Jersey

Gasoline is probably the most common contaminant of ground water in the United States. Studies at this site have demonstrated rapid microbial degradation of gasoline contaminants and have shown the importance of processes in the unsaturated zone (the zone above the water table) in degrading contaminants.

Sewage effluent, Cape Cod, Massachusetts

Disposal of sewage effluent in septic drain fields is a common practice throughout the United States. Systematic studies of a sewage effluent plume at Massachusetts Military Reservation (formerly known as Otis Air Force Base) led to the first accurate field and laboratory measurements of how rapidly natural microbial populations degrade nitrate contamination (denitrification) in a shallow aquifer.

Agricultural chemicals in the midcontinent

Agricultural chemicals affect the chemical quality of ground water in many Midwestern States. Studies in the midcontinent have traced the fate of nitrogen fertilizers and pesticides in ground and surface waters. These studies have shown that many common contaminants, such as the herbicide atrazine, are degraded by biological (microbial degradation) and non-biological (photolytic degradation) processes.

Pesticides, San Francisco Bay Estuary

Pesticide contamination of rivers and streams is a matter of concern throughout the United States. Field and laboratory studies in the Sacramento River and San Francisco Bay have shown the effects of biological and non-biological processes in degrading commonly used pesticides, such as molinate, thiobencarb, carbofuran, and methyl parathion.

Lessons Learned

Scientists studying the crude oil spill at the Bemidji site, found that toxic chemicals leaching from the crude oil were rapidly degraded by natural microbial populations. Significantly, it was shown that the plume of contaminated ground water stopped enlarging after a few years as rates of microbial degradation came into balance with rates of contaminant leaching. This was the first and best-documented example of intrinsic bioremediation in which naturally occurring microbial processes remediates contaminated ground water without human intervention. Some of the findings from that project are listed below as lessons learned.

Research at this site has provided a comprehensive documentation of natural attenuation of hydrocarbons in a contaminated aquifer under both aerobic and anaerobic conditions. Project results are an often-cited example of natural attenuation, promoting its widespread adoption for use to remediate oil and gasoline contaminated sites.

Research results from this project are directly applicable to decisions to use natural attenuation to remediate similar sites, to design performance monitoring, and to prioritize sites for remedial action, which may result in less expensive remedial actions.

The freezing drive shoe sampler, developed at the Bemidji site by Murphy and Herkelrath (1996), enables efficient recovery of saturated, unconsolidated sandy sediments; recovery of such samples was not possible using standard coring methods. The method enabled estimation of oil saturation (the fraction of pore space occupied by oil) in the subsurface.

The comprehensive study of the oil distribution in the unsaturated and saturated zones at the Bemidji site is unique. New methods were developed to determine the fraction of the pore space occupied by oil, water, and air in unconsolidated sediments. The oil distribution data have been used to test numerical models of multiphase flow.

A two-dimensional, multispecies solute-transport model code with biodegradation (BIOMOC) was developed to quantify natural rates of biodegradation, to evaluate natural attenuation as a long-term remedial strategy, and to design performance monitoring. This code can be readily applied to other systems and has been used at several other sites within the United States.

Technology Transfer

The Hanahan Site, the Bemidji site and the Norman Landfill Bioremediation Projects are just three of many successful bioremediation experiments that can be traced to basic research carried out by USGS scientists developed as part of the Toxic Substances Hydrology Program. Together, these studies laid the technical foundation that enabled bioremediation to be applied at other locations. The Methods and technologies are now being used by private contractors, State environmental managers, and other Federal agencies to address contaminant problems throughout the United States.

Future Challenges

Although bioremediation holds great promise for dealing with intractable environmental problems, it is important to recognize that much of this promise has yet to be realized. Specifically, there is still much to be learned about how microorganisms interact with different hydrologic environments. As these understanding increases, the efficiency and applicability of bioremediation will grow rapidly ultimately delivering: (1) greater scientific confidence in utilizing natural processes as a risk-based management option; (2) technical guidance, including simple models, guidelines based on type scenarios, and training; and (3) promotion of natural attenuation, when appropriate, as a cost-efficient in-situ remediation practice.

MONITORED NATURAL ATTENUATION AND ENHANCED PASSIVE REMEDIATION (MNA/EPR) ALTERNATIVE PROJECT AND TECHNOLOGY ACCELERATION IMPLEMENTATION PLAN (DOE)

The Savannah River Site (SRS) occupies approximately 310 square miles of land adjacent to the Savannah River, principally in Aiken and Barnwell counties of western South Carolina. SRS is owned by the United States Department of Energy (DOE). Management and operating services are currently provided by Westinghouse Savannah River Company LLC (WSRC). SRS has historically produced special nuclear materials for our nation's defense programs. This effort was discontinued in 1988. SRS has also provided nuclear materials for the space program, as well as for medical, industrial, and research efforts up to the present. Chemical and radioactive wastes are by-products of nuclear material production processes. These wastes have been treated, stored, and in some cases, disposed of at SRS. Waste materials handled at SRS are regulated and managed under Resource Conservation Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA).

In accordance with Section 120 of CERCLA, DOE has negotiated a Federal Facility Agreement (FFA) with the United States Environmental Protection Agency (EPA) and South Carolina Department of Health and Environmental Control (SCDHEC) to coordinate remedial activities at SRS as one comprehensive strategy to fulfill these dual regulatory requirements: RCRA/CERCLA units at SRS are subject to a multi-stage remedial investigation process that includes investigation and characterization of potentially impacted environmental media (such as soil, sludge, sediment, groundwater, and surface water) comprising the waste site and surrounding areas;

- the evaluation of risk to human health and the environment;
- the evaluation and screening of several remediation alternatives;
- final selection of the remedy which will protect human health and the environment, based on the National Oil and Hazardous Substance Contingency Plan (NCP) selection criteria;
- implementation of the selected alternative;
- verification of adequacy and completion of remedial action; and
- evaluation of the effectiveness of the selected remediation technique.

These steps are iterative in nature and are documented in several reports. The remedy selection process, including the final selected remedy, is summarized in the Record of Decision (ROD) for the waste unit. The completion of the ROD process requires agreement between DOE, EPA, SCDHEC, and the public (Ganguly et al., 1999).

Overview of DOE's MNA/EPR and Bioremediation Technologies

U.S. Department of Energy's (DOE) has implemented a plan that will be developed in collaboration with regulatory agencies as input for regulation updates and guidance documents, as appropriate. The project is called the Monitored Natural Attenuation and Enhanced Passive Remediation (MNA/EPR) Technology Alternative Project. Its objective is supposed to be narrowly focused on providing the scientific and policy support to facilitate implementing appropriate passive cleanup and cost effective monitoring strategies leading to responsible completion of active remediation activities at high risk DOE waste sites. MNA/EPR describes natural processes that mitigate exposure and risk and that are self-sustaining once implemented or requires minimal adjustments to maintain functionality. The overall MNA/EPR project effort is to be performed as a collaboration between DOE science and operations organizations at the target sites along with regulatory agencies, stakeholders, industry, and universities, as identified in the approved Alternative Project Plan.

The plan describes the project initiation activities, individual roles and responsibilities, milestones, and budget for the project. A primary product of this project will be a collaboratively developed MNA/EPR protocol that will facilitate widespread use and acceptance. Central to the passive remediation technologies involved in MNA/EPR is the focus on the use of bioremediation technologies in several projects.

Bioremediation technologies use microorganisms to treat contaminants by degrading organic compounds to less toxic materials, such as Carbon Dioxide (CO_2), methane (CH_4), water (H_2O), and a variety of inorganic salts. These technologies include intrinsic or enhanced bioremediation and can be performed in situ (in place) or ex situ (removal) under aerobic (in the presence of oxygen) or anaerobic (absent of oxygen) conditions. It should be pointed out here that there is a small difference between the two processes. During enhanced bioremediation, amendments are typically added to the media to supplement biodegradation processes. Amendments include nutrients (such as nitrogen and phosphorus), electron donors (such as methanol or lactic acid for anaerobic processes), electron acceptors (such as oxygen for aerobic processes, ferric iron or nitrate for anaerobic processes), or additional microbes (bioaugmentation) [EPA, 1994; EPA, 2000]. With intrinsic bioremediation, no such enhancements are involved. Likely benefits of enhancement maybe shorter clean-up times, better levels of clean-up, and higher occurrences of successful clean-ups.

As previously mentioned, in situ bioremediation is the preferred approach since it is less invasive and ultimately less costly. Technologies include source treatment technologies such as bioventing and slurry-phase lagoon aeration, and groundwater technologies such as biosparging and in situ aerobic or anaerobic treatment. Amendments are generally added using direct injection and/or groundwater recirculation systems. For direct injection (illustrated in Figure 4), amendments are added to the contaminated media through injection points. With groundwater recirculation systems, contaminated groundwater is extracted, amendments are mixed with the groundwater ex situ, and the amended groundwater is re-injected into the subsurface, usually upgradient of the contaminated zone (a process known as pump and treat - P&T). One configuration for a groundwater recirculation system is to extract and re-inject groundwater in a single stratum or at a common groundwater elevation. An alternative configuration is extraction and re-injection at different elevations in a single treatment cell, creating vertical circulation.

Major Objectives

The major objective DOE’s waste management and cleanup plan is to develop the “next generation” MNA/EPR protocol for chlorinated solvents that will be broadly accepted by regulators, end users, technologists and the public in the states of South Carolina, Tennessee and Washington and EPA Regions four and ten. The implementation activities and overall structure of this project (fig. 25), along with the specific science selected for systematic deployment and documentation is supported by the following key objectives:

- Expand the definition of MNA to include enhanced Natural Attenuation and all forms of sustainable passive natural remediation.
- Gain regulatory concurrence in the states and regions overseeing the Savannah River Site, Hanford, and Oak Ridge sites – while working with interstate and national regulatory partners to contribute to national MNA efforts.
- Advance the science and broaden the understanding of natural attenuation and remediation systems.
- Establish and document new monitoring paradigms that provide high levels of performance for reduced costs.

Key considerations in achieving the project objectives include:

- Maintain focus on acceptable end state(s) and the transitional steps that lead to the end state(s).
- Set clear boundaries for expanding MNA concepts and develop consensus with regulators and stakeholders.
- Emphasize a systems approach for both MNA processes and MNA monitoring.

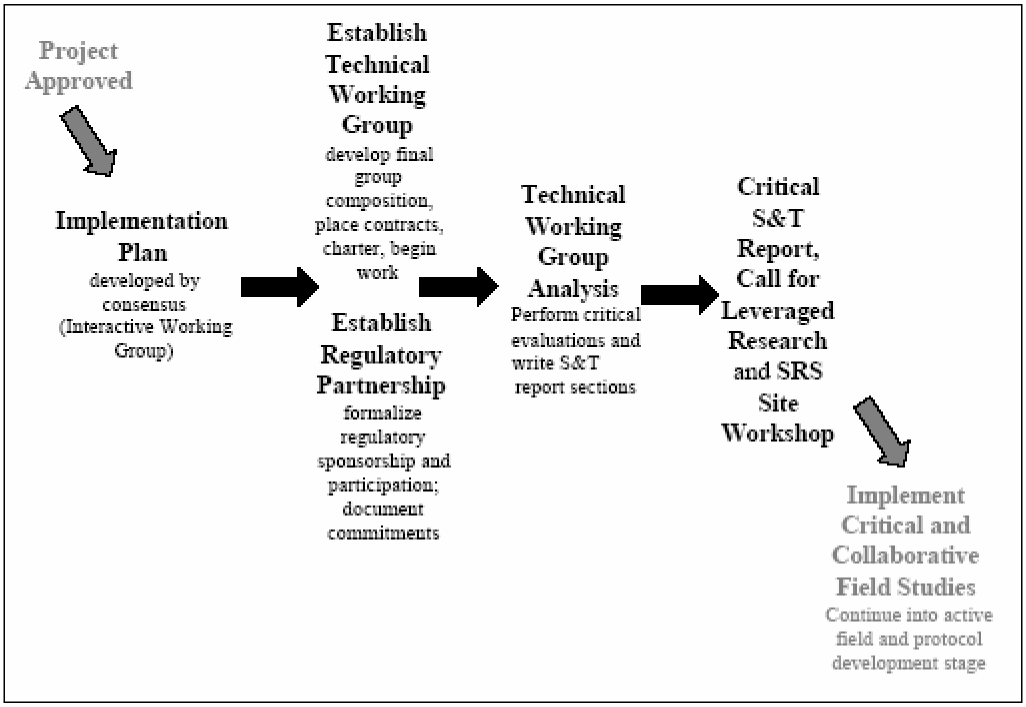


Figure 25: MNA/EPR Alternative Project Start-Up Sequence

Project Start-Up Activities

To efficiently meet the project objectives, an intense period of project initiation activities were planned. The purpose of these activities was to critically evaluate the specific science, technology, implementation, and regulatory concepts that had been proposed for this project and to identify the most promising in terms of potential to accelerate and facilitate the use of MNA/EPR. This evaluation was to be performed by the Technical Working Group (TWG) and the results to be documented in a milestone document, “Critical Science and Technology Targets to Support Monitored Natural Remediation of Chlorinated Organic Solvents”. This report served as the foundation of the project as it moves into the field research and protocol development phases. As shown in Figure 25, the report (hereinafter designated the science and technology (“S&T Report”) report will be used as the basis for a detailed research specification, for collaborative and leveraged research. The science and technology specification articulates the specific types of work deemed by the TWG as having the most impact on future viability and usability of MNA/EPR. The emphasis of this specification will be for field studies.

It is anticipated that approximately 90 % of the studies will be field based. The specification will be used as the basis of identifying critical field efforts and opportunities to leverage participation and cooperation with science programs such as EMSP and NABIR in DOE, SERDP in DOD, and STAR in EPA.

Scientific Basis

The TWG will critically evaluate past MNA/EPR protocols, along with related research. This critical review process will be organized into several lines of inquiry as specified below. The team will document the potential benefits of progress in each line of inquiry and the resulting improvement in the applicability and usability of MNA. For each line of inquiry, the evaluation factors shall include but not be limited to the specific benefits resulting from progress (with the most credit going to items that result in a positive “step change” in MNA/EPR progress); regulatory/stakeholder acceptability; collateral and lifecycle issues; potential cost of the required S&T; and the potential for leveraging existing science efforts.

The historical protocol review, the review of national and international performance history of MNA/EPR for chlorinated solvents, and the critical assessment of the potential value of advancement in the identified lines of inquiry will be included in the milestone S&T Report. The specific titles and the contents of the lines of inquiry will be finalized by the TWG. The lines of inquiry will, however, align with the conceptual model, approach, and core values described in the approved Alternative Project Plan:

- Processes must be based on natural mechanisms.
- Processes must be sustainable and allow closure of the site from the perspective of active treatment.
- Processes can expand traditional definition of MNA to allow enhancements and reconfiguration (as long as the resulting mechanisms are naturally sustainable).
- New Approaches should build on and link to past MNA protocols.
- New Approaches should focus on the basis for transition from active to passive to MNA/EPR and defining a valid and environmentally protective exit strategy for active remediation.
- New approaches should emphasize the concept of working toward an “agreed” risk based end state.

The following is a preliminary outline of the potential lines of inquiry and specific examples of science and technology to be evaluated. Importantly, the list includes a relatively comprehensive list of ideas that are being examined in current research programs, but all of these will not be determined to be promising or appropriate to incorporate into the “next generation” protocol. Determination of potential value of any concept will be a primary function of the TWG and will be the basis for subsequent inclusion in the S&T Report and the leveraged research specification. This critical evaluation process is the primary mechanism for the project to manage costs, maintain schedule, and to assure that the product will provide the best value to DOE.

Lines of inquiry:

- Incorporation of latest research on mechanisms and rates of processes that occur without any enhancement. This includes abiotic degradation, anaerobic biodegradation, aerobic biodegradation, and phytoremediation (either in the rhizosphere or through uptake and subsequent processes). This would also include the latest research on abiotic degradation and consider sorption, dispersion and possibly in-stream processes such as volatilization or other processes that affect contaminant bioavailability.
- Incorporation of latest research on processes that create permanent or semipermanent (sustainable) treatment capacity in the system. This includes the possibility of halorespiring zones, substrates and conditions needed to generate and maintain such

zones, etc. This would link to the potential applicability of inexpensive characterization and monitoring of the bulk conditions (a surrogate) or microbial nucleic acids (low-cost bioassessment) as improved documentation techniques. Evaluate how far down this path is appropriate for a MNA/EPR protocol – is fertilization or other periodic maintenance OK with criteria to transition to monitoring only?

- Incorporation of research on the active biological, chemical and physical processes occurring at major system interfaces such as the vadose groundwater interface and the groundwater surface water interface. Examine MNA/EPR potential for NAPL or "near NAPL" environments (as is being studied extensively in DOD).
- Incorporation of research on deployment and enhancements based on large-scale modification of hydrology, reconfiguration of the system, and similar actions. One example is -- expanding existing interfacial zones where treatment is occurring but total treatment is needed to fully address plume delivery (flux). Other examples include deployment of sustainable treatment zones, modification or alteration of plants (community structure and biomass, fertilization), isolation schemes (for deep fractured system for example), and schemes for sustainable large-scale alteration of bulk properties and master geochemical variables (pH, redox, etc.). This work would emphasize study of collateral damage, life-cycle analysis of benefits and costs, systems engineering evaluation, etc.
- Examination of need and uncertainties associated with different conditions – notable "outcropping systems" such as those in the east, "vadose systems" as in the west, and fractured/karst systems.
- Incorporation of national and international data on experiences (successes and failures) of MNA/EPR for chlorinated solvents to date.

There have been a number of technology assessment and needs assessments over the past several years that are relevant to MNA/EPR of chlorinated solvents. Notable examples include the NAS review, "Natural Attenuation for Groundwater Remediation", and the recent DOE Technical Targets effort, "Technical Targets: A Tool to Support Strategies Planning in the Subsurface Contaminants Focus Area". These will be key resources to the team to simplify and streamline their task.

Characterization and Long-Term Monitoring

The structure and concept for efforts to advance Characterization and Long-Term Monitoring are the same as those for the scientific basis – i.e., (1) review of the state-of-practice and the state-of-science, and (2) critical evaluation of the potential benefits of different types of activity organized into lines of inquiry. Specific titles and contents of the lines of inquiry will be finalized by the TWG. They are aligned with the conceptual model, approach, and core values described in the MNA/EPR Project Plan:

- Develop clear strategies for the distinct needs associated with MNA/EPR characterization and then long-term monitoring.
- Develop responsive characterization and monitoring approaches that beneficially use data to refine and improve decisions and interpretations.
- Emphasize integrating measures, such as flux, remote sensing and other averaging and volumetric methods.
- Refine the idea of "multiple lines of evidence" in current protocols and develop a defensible approach to define a "quorum of evidence" that will be acceptable (given

natural variability and uncertainty). The goal is to refine and streamline characterization and monitoring, not to add more parameters to a long list of requirements for MNA/EPR.
- Emphasize large-scale design and monitoring concepts. Document performance and robustness using overall mass balances and MNA process/condition mapping to supplement or replace the traditional requirement of "plume stability."
- Emphasize system and ecosystem monitoring concepts.

The overarching goal of the characterization and monitoring developments will be to facilitate MNA/EPR by reducing costs while maintaining or enhancing the information available to document that the system is protecting the public and the environment. The following is a preliminary outline of the potential lines of inquiry and specific examples of science and technology to be evaluated. Importantly, the list includes a relatively comprehensive list of ideas that are being examined in current research programs, but all of these will not be determined to be promising or appropriate to incorporate into the "next generation" protocol. Determination of potential value of any concept will be a primary function of the TWG and will be the basis for subsequent inclusion in the specification.

Lines of inquiry:

- Incorporate latest research and scientific logic to enhance the existing multiple lines of evidence concept. This includes a responsive characterization process based on conditional rules (i.e., no need to measure reduced gases at sites with measurable dissolved oxygen).
- Develop a paradigm that includes some of the spatial process mapping (GIS) and other items highlighted in the NAS review of the previous protocol.
- Lay out a clear "quorum of evidence" concept.
- Incorporate the latest bioassessment tools. These include nucleic acid probes, fatty acid profiles, taxonomy, structure and function screening profile systems, fluorescence methods, and other tools. Many of these technologies have been examined for innovative field deployment in DOE – at SRTC, ORNL, and other labs. Other bioassessment tools include hyperaccumulators (possibly coupled with remote sensing) and macrobioaccumulators (clams, etc.), and biomarkers (ecosystem structure and species composition). These latter tools integrate exposure and may provide a more realistic measure of impact. This is a key topic because there have recently been significant advancements in basic scientific knowledge relative to the microbial biodegradation of chlorinated solvents. For example, it is now widely known that halo-respiring bacteria are primarily responsible for the complete in situ anaerobic biodegradation of chlorinated solvents observed at most anaerobic sites. This knowledge has impacted remedial strategies resulting in new efforts to intentionally alter in situ conditions to develop and optimize this microbial activity (e.g. biostimulation). In other cases, the absence of in situ halo-respiring bacteria has pointed to the need for inoculation of deficient sites with seed cultures of these important chlorinated solvent–degrading bacteria (bioaugmentation). In both cases, bioassessment is a key step in determining the presence, or potential, of a given site for MNA of chlorinated solvents as well as tracking the presence and numbers of key microorganisms during the remediation process.
- Incorporate latest research on remote sensing, geophysics, and flux monitoring. This includes both instrumentation and interpretation and deployment options (horizontal

wells, lidar, remote sensing, and others). Examine lessons from agriculture and soil science ("smart farming") and potential for cross over applicability.

- Incorporate the latest research on surrogate measures to reduce costs. These include bulk and master variable properties such as redox potential, as well as indicator species (e.g., Cl-) and specialized tools such as total halocarbons, degree of chlorination sensors, etc.
- Incorporate latest research on bioinformatics and modeling. This includes data mining, neural networks, incorporating new types of data, integrating diverse types of data, working at sites with large amounts of data and determining the value of data to justify reducing the number and frequency of analyses. Consider the latest progress in both forward and inverse predictive modeling and the potential value of large-scale mass balance models (i.e. simple balancing delivery and treatment capacity) as an alternative that might be used at many sites.
- Incorporate the latest research on state-of-the-art sensors. Determine the value of sensors in characterization and in monitoring MNA/EPR systems. Examine the need for sensors that provide high frequency data. Examine alternative configurations that use on-off sensor signals rather than concentration signals as a way to reduce costs. Evaluate passive and cumulative sensors that would act similarly to bioconcentration.
- Incorporate the latest research on monitoring system configuration. This includes focusing monitoring on designed or identified monitoring points (weak points that would serve as indicators of performance throughout the system) and focus on interface monitoring.

THE SAVANNAH RIVER SITE (SRS)

The Savannah River Site (SRS) is one of several government-owed sites in the U.S. Department of Energy (DOE) nuclear defense complex. The SRS is located on 325 square miles along the Savannah River primarily in Aiken and Barnwell counties, South Carolina (fig 26). This site was constructed during the early 1950's to produce basic materials used in the fabrication of nuclear weapons. In addition, it has also produced materials for use in medical research, and space exploration. Over the last 50 years, five production nuclear reactors have been built and operated resulting in the generation of vast amounts waste by-products. Large amounts of solid and liquid wastes were generated in the course of construction and operation of the reactors and associated fuel fabrication, processing, and waste handling operations. These include high-level liquid waste, solid transuranic waste, low-level waste (solid and liquid), hazardous waste, mixed waste and sanitary waste. The SRS has operated since 1950 and up until the 1970's; most of this waste was burned, buried, or dumped in "rubble pits" near the reactor areas (Canyons) or other major facilities. This practice has resulted in large areas of land and huge amounts of both surface and groundwater contaminated with dangerous long-lived radioactive, non-radioactive and heavy metal pollutants, persistent organic pollutants (POPs), persistent bioaccumulative toxins (PBTs) among others.

Environmentally recalcitrant compounds, such as polychlorinated biphenyls (PCBs) and persistent organic pesticides (POPs) such as dichlorodiphenyl trichloroethane (DDT), are to be found in several onsite groundwater contamination plumes. Simply stated, SRS is home to almost every known type of chemical contaminant existing. Of critical importance is the Savannah River, which flows along the southwestern border of Savannah River Site and is used as a drinking water supply for approximately 65,000 primarily low-income and minority people 100 miles down river in the communities of Port Wentworth, Georgia and in Beaufort and Jasper Counties of South Carolina. SRS uses water drawn from the Savannah River (and Par Pond) as secondary reactor coolant which is them discharged back into the river.

NEPA Relevance

The U.S. Department of Energy (DOE) has developed an integrated approach to address the treatment, storage and disposal of site-generated waste. Near-term program emphasis has been placed on the construction and start-up of new facilities for the stabilization/solidification of high-level waste, the treatment of stored transuranic waste in preparation for future shipment to the Waste Isolation Pilot Plant in New Mexico, and the incineration of low-level hazardous and mixed waste. About 30 million gallons of high-level waste containing nearly 600 million curies of radioactivity, is currently stored in underground tanks at the Savannah River Site. This waste is slated to be pretreated in order to concentrate most of the radioactivity into a smaller fraction (10 percent) of the original volume. In addition, the SRS is the home of Defense Waste Processing Facility (DWFP) which is receiving Spent Nuclear Fuel (SNF) rods from foreign research reactors, is a temporary site for plutonium disposition (including pit disassembly) and for the development of an accelerator for tritium production.

With the marriage of new and old cleanup missions continuing at the site, people of color communities continually find themselves disenfranchised from significant involvement in Environmental Management's clean up activities at SRS. There continues to exist a critical need for resources to be channeled to community based organizations, with the aim of increasing their research capacity and collaboration with technical experts. Armed with scientific reviews conducted by scientists, researchers and community gives more credibility and power to the voice of communities as they interact with DOE and administrators (e.g. WSRC) of their sites.

This report focuses the discussion of MNA/EPR as it is implemented at the Savannah River Site (SRS) because it is necessary that the process is understood by marginalized communities. In addition, these communities must be able to review and comment on the use of specific technologies that are being used in the SRS clean-up process and environmental management's new accelerated strategy. It is understood that bioremediation technologies (discussed above) will be used as part of the new accelerated strategy at SRS. Unfortunately, the neighboring minority and low income communities are completely unaware of its use, impact and role in cleaning up contamination at SRS. This report is therefore a needed and necessary to focus the spotlight on bioremediation as a clean up technology and analyzes what role it will play in the new accelerated clean up strategy at SRS as outlined in the Performance Management Plan (PMP).

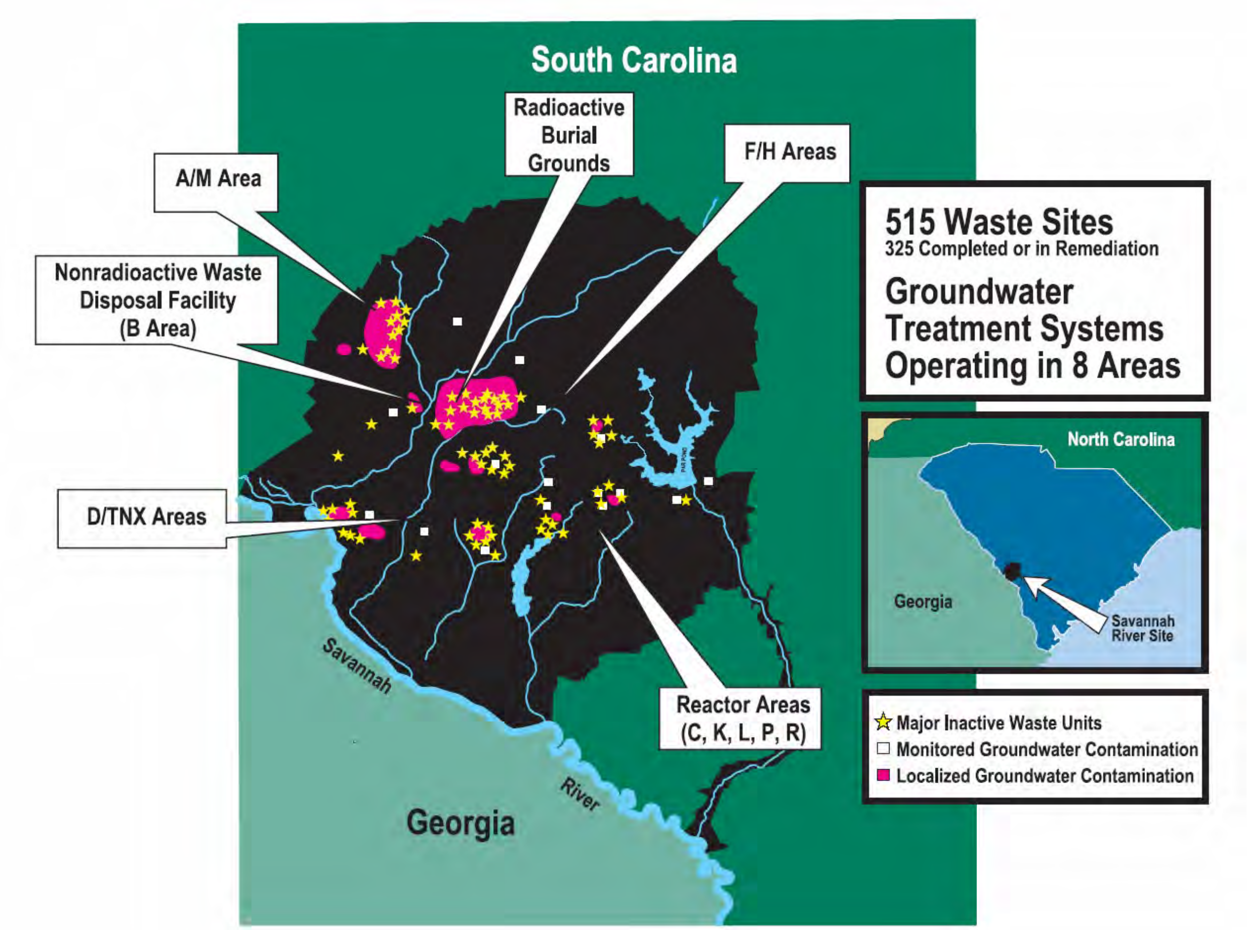


Fig. 26: Schematic of the SRS General Separations Areas, associated waste disposal facilities and contamination areas (adapted from)

Waste Management at SRS

At the Savannah River Site (SRS), waste was generated as a result of the manufacturing of plutonium, tritium and other nuclear materials required to support national defense. SRS manages high-level waste, low-level waste, hazardous waste, mixed waste, transuranic waste and sanitary (non-radioactive, non-hazardous) waste. Not all wastes are compatible with MNA technologies and therefore the discussion and scope of their remediation is differed. Only those waste and associated contaminated sites that have been determined as compatible with bioremediation technologies as outline in the MNA/ERP or S&T report are mentioned. This report does not serve as a comprehensive review, only as a discussion of the potential use of bioremediation as part of the cleanup process as included in the new accelerated clean up strategy at SRS outlined in the Performance Management Plan (PMP).

Waste minimization program

SRS has an active waste minimization program to reduce volume and/or avoid production of all waste types generated onsite. Efforts to reduce or eliminate waste before it is generated include process modification, use of alternative process material, recycling and reuse. Efforts to reduce waste after it has been generated include segregation of non-radioactive and non-toxic materials and waste compaction. This report summarizes several demonstration and test projects to show whether the incorporation of bioremediation technologies as part of an accelerated cleanup program is scientifically sound and feasible. It does not address activities involving the remediation of high level radioactive wastes owing to their characteristics rendering them, for the most part, incompatible with bioremediation processes and therefore outside the scope of this discussion.

Selection of Wastes Type and Locations for Field Testing

The goal of MNA/EPR program is to develop the “next generation” protocol for monitored natural attenuation and natural remediation. The first step in this process must be to identify both the areas where the science and technology tools need development, refinement and testing under real conditions and the type interfaces where studies must occur. Several waste units have been evaluated to determine the levels of contamination present, the interfaces available and the impact of testing at the waste unit to the regulatory path.

There are some 545 waste units at SRS currently under consideration for some type of cleanup. The general locations of 515 around the SRS are shown in figure 26. Some of these are described in the following paragraphs. Since each site offers specific opportunities for testing, those projects that are selected herein are selected because they collectively can present a reasonable picture of current clean-up efforts, particularly those that pertain to the use of bioremediation technologies. The first group of sites are at various stages of the MNA/EPR process and presents good opportunities for further cleanup studies

Composite Analysis - There are two currently active radioactive waste disposal facilities at SRS, located in E-Area and Z-Area. Both of these are in the central part of the site, known as the General Separations Area (Figs. 27, 28). This name arises because two large chemical separations plants are located there. Each of these sites has completed at least one Composite Analysis (DOE, 1998). The work at Savannah River was used to demonstrate both the process and the results. These and similar activities are not evaluated in this report.

Sanitary Waste - Sanitary Waste or municipal solid waste is solid waste that is neither radioactive nor hazardous as defined by the AEA or RCRA. Sanitary Waste consists of materials that would be received by a municipal sanitary landfill (office waste, food, garbage, refuse and other solid wastes that are similar to those generated by most households) and industrial waste (construction debris, scrap metals, wood waste, etc). there are several locations used for disposal (landfills) these wastes types (see fig 28 and 31 below) on site.

Low-level Waste (Solid) - The site's solid low-level wastes include such items as contaminated protective clothing, tools and equipment that have become contaminated with small amounts of radioactive material. In October 1994, SRS opened engineered concrete vaults for the permanent disposal of solid low-level waste. Low-level waste which is very low in radioactivity may also be disposed in trenches if the waste meets acceptance criteria based on a long-term (10,000-year) radiological performance assessment. Limits are derived to ensure performance criteria such as drinking water standards are adhered to.

Two types of vaults are used, one for low-activity waste (LAW - waste radiating less than 200 mrem/hour) and one for intermediate-activity waste (waste radiating greater than 200 mrem/hour). The concrete used in both vaults was specially formulated. Its composition is designed to mitigate cracking, extending the vault life.

The trenches (ET) opened in 1994 are called slit trenches because they are long and narrow, measuring 20 feet wide and 600 feet long. These are used primarily for disposal of soil from potentially contaminated areas containing no measurable radioactivity. In February 2001, SRS began disposal of low-level waste with extremely low radioactive content in Engineered Trench #1. This "drive-in" trench, located inside E-Area, is designed to extend the useful life of the existing Low Activity Waste Vaults (LAWV) and allow shallow land burial of selected low-level waste. A large percentage of waste (approximately 65 percent); currently stored in the existing LAWV is a candidate for future trench disposal. This approach will enable the more robust LAWVs to be reserved for higher activity low-level waste.

The E-Area Engineered Trench (fig. 27) measures 200 feet in length by 20 feet in width and is located on the north side of the old radioactive waste burial ground. The primary water way is the Upper Three Runs-Crounch Branch Streams. It is equipped with a concrete sump and pump system (including sample station) to manage anticipated rainfall. The trench is also equipped with a vadose zone monitoring system (VZMS) installed around the perimeter. With the ET #1 now fully operational, SRS expects to extend the valuable and expensive LAWV space until 2024.

Low-level Waste (Liquid) - Liquid low-level waste is a by-product of the separations process and tank farm operations. This waste is treated in the Effluent Treatment Facility (ETF) (fig. 27). This facility treats the liquid waste for discharge to a National Pollutant Discharge Elimination System (NPDES) permitted outfall, effectively capturing all chemical and radioactive contaminants except tritium. The effluent from this outfall enters Four Mile Branch Stream and subsequently finds its way to the Savannah River. The state-of-the-art process includes: pH adjustment, submicron filtration, organic removal, reverse osmosis and ion exchange. ETF replaced the seepage basins that were used until November 1988.

C-Area Reactor Groundwater Operable Unit

Contaminant plumes are associated with historical releases from the C-Area reactor and its support facilities (fig 26). The unit is well characterized and the flow model is complete for this unit. The plume contains trichloroethylene (TCE) (9,600,000 µg/L (max)) and Tritium (57,000 pCi/mL (max)). TCE is present in source, aqueous and fringe concentrations. Contaminants are present in the vadose zone and throughout plume to the discharge zone. Depth to groundwater is approximately 80 ft at the source. TCE is present at the vadose zone/groundwater interface. Even though sampling of Castor Creek surface water has not detected TCE above the maximum contaminant limit (MCL) of 5 µg/L, the flow model indicates TCE should be present at the surface water/groundwater interface. The Remedial Investigation/Baseline Risk Assessment, revision 0, was to be submitted December 2003. The project team is considering several likely response actions including Monitored Natural Attenuation, recirculation wells, permeable treatment walls (barriers), air sparge/Soil Vapor Extraction (SVE), phytoremediation (spray irrigation), and dam construction / wetlands management for this area. A potential disadvantage for this site is the difficulty of access to the distal plume and Castor Creek. A portion of Castor Creek is a steep incised channel in the plume discharge area, limiting the size of the hyporheic zone. In summary, some opportunities exist for site work/studies at the distal end of the plume and discharge area.

CMP (Chemical, Metals and Pesticides) Pits

The Chemicals, Metals, and Pesticides (CMP) Pits are located in the central portion of the Savannah River Site (SRS) in the area of the radioactive waste burial ground (fig 26, 27 and 28). The waste unit consists of seven unlined pits that occupy the top of a knoll at an elevation of 310 ft above mean sea level. The pits were constructed in 1971 to dispose of solvents, pesticides, and lighting ballast components; it received waste until 1979. Subsequent monitoring detected solvents in the groundwater. In 1984, the contents of the pits were excavated, the pits were then back-filled, and an infiltration cover was installed. During excavation of the drums, an area to the west of the pits was used for material staging. This area, which later became known as the ballast area, contains surface soils that are contaminated with low levels of pesticides and polychlorinated biphenyls (PCBs). A maintenance action was conducted in 1996 to minimize erosion by placing six inches of soil over the ballast area, thus improving the perimeter drainage and erosion control.

Remediation of the residual subsurface solvent contamination in the vadose zone beneath the pits began in 2000 with the deployment of a soil vapor extraction (SVE) system. Surface soils in the ballast area are contaminated with pesticides and PCBs that exceed risk-based remediation goals (RG) or cleanup levels. The majority of the contamination is confined to the top two feet of soil with a limited amount detected down to 5 ft below land surface. The soil consists of hardpan sandy clay with cobbles, and is lacking organic materials and most normal soil nutrients. Initial characterization of the site indicates that the soils are only sparsely populated with natural microbial concentrations and are not suitable for bioremediation without substantial amendment additions.

Vadose and groundwater contamination is associated with the CMP disposal pits. Characterization of this unit is complete. The Corrective Measures Study/Feasibility Study (CMS/FS) is in preparation with the Proposed Plan being submitted in April 2004. This is a major disadvantage for this unit because the decision making process for the remedial action is very far along. At present, an interim action of SVE and air sparging is in operation. The preferred final remedial option is a small-scale phytoremediation (pump and treat and treatment of surface soils) and a mixing zone.

Perchloroethylene (PCE), Trichloroethylene (TCE) and Lindane are present in the upper aquifer system. PCE concentrations range from 18,800 µg/L to <1 µg/L and TCE concentrations range from 4,200 µg/L to <1 µg/L. PCE and TCE are present at both the vadose zone/groundwater interface and the surface water/groundwater interface. PCE and TCE are present in the aqueous phase at the vadose zone/groundwater interface. Depth to groundwater ranges from approximately 100 ft to 20 ft below ground surface. The vadose zone - groundwater interface is important at the CMP Pits and is a good resource for scientific studies. However, the infrastructure for the air sparging and SVE units is located on the surface of the vadose zone/groundwater interface area and makes access very difficult. At present, characterization data does not indicate PCE and TCE are discharging to Pen Branch from the main plume. A small plume to the north of the main plume contains low levels of PCE that is discharging to Pen Branch. There are no access issues at the surface water/groundwater interface. Because of topography, hyporheic zone is limited in extent in the groundwater discharge downgradient of CMP Pits.

The plume at the CMP Pits is well characterized and standard flow modeling is complete. In summary, this is a promising site for study but the OU is far along in the RCRA/CERCLA process. There is little opportunity for immediate use of the technical protocol at this OU. The technical protocol will need to be applied as a long-term strategy.

Observations and lessons learned

With the discrete samples for individual windrows, concentrations of contaminants of concern (COC) were reduced to less than the new RG levels in nearly all cases. In a few discrete sample cases, the levels of COC did not quite achieve the RG levels, but would almost certainly get below RG levels with additional time.

Enhanced bioremediation based on horse manure, molasses, appropriate soil amendments and moisture is a process that can be duplicated to give reproducible results within an acceptable time frame.

Technology Cost

Contract costs for Phase 1 were $690,000 to remediate 600 yd^3 of soil or $1,150/$yd^3$. Because of the increased efficiencies achieved in Phase 2, the same quantity of soil was remediated in three months instead of six for $350,000 or $585/ yd^3. These unit costs are relatively high for enhanced bioremediation and are principally due to two factors. The quantities of soil involved in Phase 1 and Phase 2 are relatively low. Full-scale bioremediation is normally conducted on soil quantities much higher than deployed in this TS, which would reduce the unit cost. In addition, the largest individual component of the cost of this process is the rental or capitalization of the Microenfractionator® machine itself.

L-Area Southern Groundwater Operable Unit

Contaminant plumes are associated with historical releases from the L Reactor and its support facilities (fig 26). Characterization of the unit began in 1999. The post-characterization scoping meeting was held on January 28, 2003. Tritium, perchloroethylene (PCE) and trichloroethylene (TCE) are present in the upper aquifer system. Concentrations of PCE and TCE are low, ranging from a high of 155 $\mu g\ L^{-1}$ to a low of < $1 \mu g\ L^{-1}$. PCE and TCE are present at both the vadose zone/groundwater interface and the surface water/groundwater interface. Depth to groundwater ranges from approximately 50 ft to 8 ft below ground surface (bgs). Both interfaces are easily accessible. The contamination is from multiple point sources ranging in size from direct discharge of drums/buckets of spent cleaning solutions to seepage basins. The locations where the PCE and TCE are present at the vadose zone/groundwater interface are not identified. The concentrations would be in the aqueous phase. The surface water/groundwater interface occurs at the boundary of L Lake. This is a classic MNA setting with PCE and TCE concentrations being in the fringe range. In addition, L Lake sediments are contaminated to varying degrees with cesium-137 (Cs). Thus, there may be contact issues for working in the sediments. The Remedial Investigation Report for this unit is scheduled for submittal in February 2004. Overall this unit is a promising site for studies at the surface water/groundwater interface.

P-Reactor Groundwater Operable Unit

Contaminant plumes are associated with historical releases from the P-Area Reactor and its support facilities. Pre-characterization activities at this unit began in 2002. To date, Trichloroethylene (TCE), perchloroethylene (PCE) and tritium have been identified in the upper aquifer system. Concentrations of TCE range from 21,100 ug L^{-1} to <1 ug L^{-1} with much lower concentrations of PCE (range 365 ug L^{-1} to <1 ug L^{-1}). TCE and PCE are present at both the vadose zone/groundwater interface and the surface water/groundwater interface. Depth to groundwater is approximately 50 ft below ground surface. Both interfaces are accessible.

The surface water/groundwater interface that occurs on the eastern bank of Steel Creek will present some access issues, but they can be managed. There may be contact issues related to cesium -137 (Cs) present in the sediments of Steel Creek. The source(s) of the contamination have not been identified at this time. The early characterization work indicates the potential for a dense non-aqueous phase liquid (DNAPL) source near the reactor facilities.

In summary, this unit presents a good opportunity for field studies due to accessibility, contaminant concentrations at the surface water/groundwater interface and the unit being in the very early phase of the regulatory process. Because of its regulatory status, accessibility, and lack of conflicting activities, the IWG considers this site as potentially serving as the principal “Field Test Bed for MNA/EPR of chlorinated solvents.”

Savannah River Site Soil & Groundwater Closure Projects

The Soil and Groundwater Closure Projects (SGCP) completed several key initiatives to accelerate the cleanup schedule. Integrated with Site D&D (Decontamination and Decommissioning), SGCP embraced an area closure concept that deploys innovative technologies to achieve program completion 14 years sooner than previously planned.

While using innovative technologies has always been a cornerstone of SGCP’s success, area closures became an integral part of the closure plan when the U.S. Environmental Protection Agency and South Carolina Department of Health and Environmental Control signed a Memorandum of Agreement supporting the concept. In accelerating the cleanup schedule, SGCP revised the baseline to close a minimum of 46 waste units through 2006, adding another 29 for a total of 75 waste unit closures as a goal. These closures will be completed without compromising worker safety. In 2003, 23 waste sites were safely closed, exceeding the goal of 13 (fig. 26).

The Savannah River Site plans to complete up to more than 70 additional waste sites in the next three years. Closure of these waste sites by the end of 2006 represents one-third of the entire to-go scope in the SGCP program and includes final closure of the largest and highest risk site, the central Old Radioactive Waste Burial Ground shown in figure 27 below. This site is located between F-Area (on left) and H-Area (on right). In the foreground (bottom right) is one of the seepage basins found on site.

Figure 27: SRS plans to complete up to more than 70 additional waste sites in the next three years.

Closure of these waste sites by the end of 2006 represents one-third of the entire to-go scope in the SGCP program and includes final closure of the largest and highest risk site, the central Old Radioactive Waste Burial Ground shown above in the center (see fig. 28 for schematic of the area). It is located between F-Area Canyon (on left) and H-Area Canyon (on right). In the foreground (bottom right) is one of the seepage basins found on site. The boomerang-shaped E-Area Engineered Trench can be seen in the back area of the clearing.

General Separations Area Consolidation Unit

Grout activities were completed at the 10 remaining underground solvent tanks in the Old Radioactive Waste Burial Ground (ORWBG) shown in green in figure 28, (also pictured in fig. 27 above). This is the program's highest risk site. Site preparation and remedial design was completed at the General Separations Area Consolidation Unit (GSACU) in preparation for remedial action. The GSACU was formed last year when three nearby waste unit closures were consolidated with the ORWBG closure. The GSACU accelerates closure of the four individual waste units by two years and achieves 99 percent risk reduction to future site workers when completed.

Ford Building Seepage Basin

The final remedial action for the Ford Building Seepage Basin was completed when the remaining contaminated soil from an earlier underground tank removal action was excavated. The contaminated soil was placed on the basin floor with similar insignificant contamination. The basin was then filled and covered with native soil. The action marked the closure of 300 waste units, over half of the program's original 515 waste units (see fig 26). The remainder of sites below includes more detailed descriptions of demonstration and testing projects completed recently.

TNX Operable Unit

A pilot-scale, nuclear-research facility at the TNX site located close to the bank of the Savannah River (fig 37) introduced several radionuclides and metals into an unlined seepage basin. These materials have since migrated by overland flow (runoff), subsurface flow (groundwater), and direct discharge (outfall pipe) into a gully into an adjoining wetland site (WSRC, 1999). Among the contaminants that have entered the wetland area is the bioaccumulative heavy metal Mercury (Hg), which was introduced to the seepage basin as aqueous mercury nitrate (Figure 36). Mercury is classified as a neurotoxin; it was detected in 97 of 98 sediment surface samples, ranging from 0.007 mg/kg to 30.8 mg/kg. Hg concentrations in an adjoining uncontaminated portion of the site ranged from 0.007 to 0.12 mg/kg. A surface sediment concentration of 1-mg/kg Hg was measured as far as 300-m southwest from the point source (Figure 36).

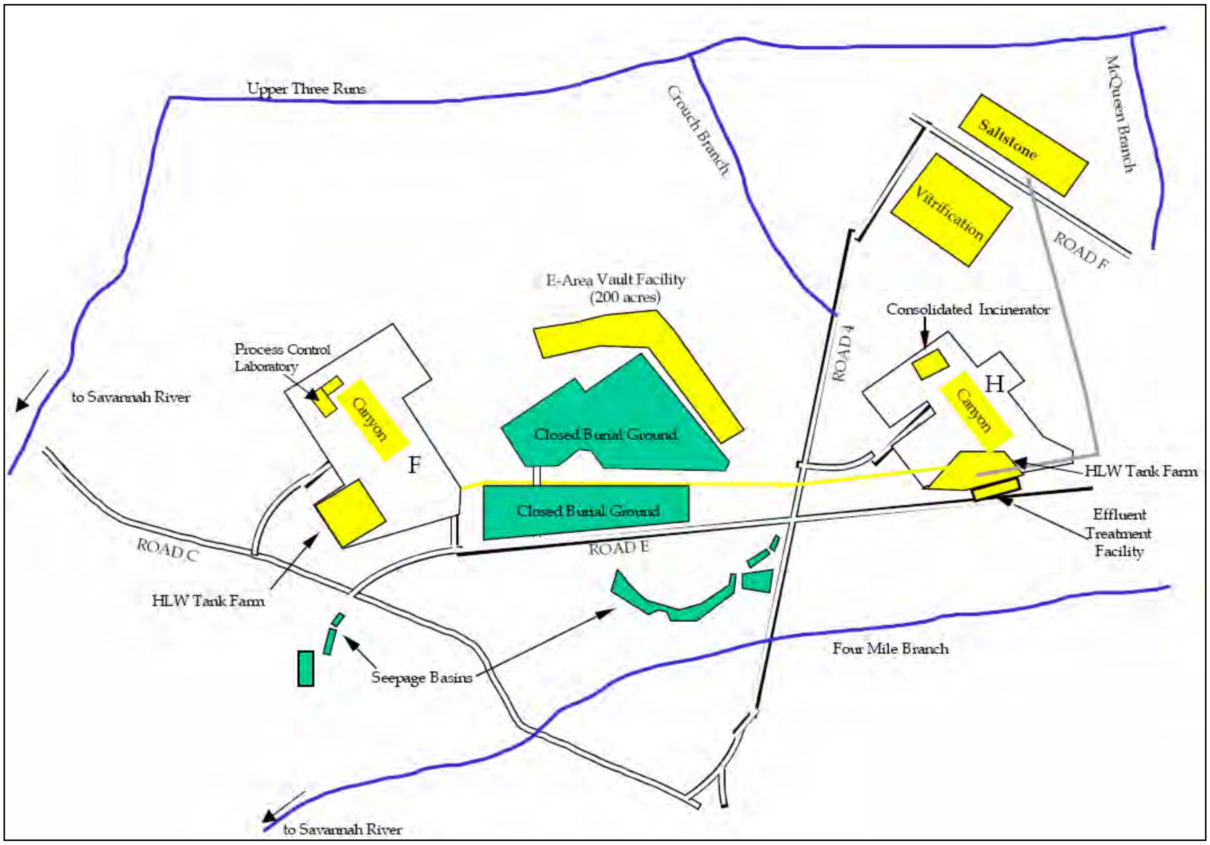


Figure 28: Schematic of the central location at the Savannah River Site (SRS) of the General Separations Area. F-Area and H-Area Canyons and support structures are shown in yellow. Soil and Groundwater remediation projects in closure includes the old radioactive wastes burial ground (ORWBG) and seepage basins (shown in green) (adapted from Cook, 2002)

The objective of this study was to characterize Hg sorption to sediments in the area of the TNX OU with the intention of providing a conceptual geochemical model for use in risk assessment calculations and to provide guidance for the selection of an appropriate in-situ remediation strategy. The approach discussed here was to characterize the sediment Hg through a series of adsorption and desorption tests. Data generated from these tests, as well as field measurements of the oxidation-reduction potential, were then used to predict Hg speciation at the contaminated site.

Total Hg concentrations in the sediments were as high as 10-mg/kg, whereas, associated pore water Hg concentrations were below detection, <0.010-mg/L. Sediment Hg was not in an exchangeable form, and <8% of it was associated with organic matter. The remainder of the Hg was strongly associated with Fe-oxides and/or with a precipitated phase, presumably a sulfide. Sediment Hg concentrations were significantly correlated (r = 0.94) to Fe-oxide concentrations. Thermodynamic calculations based on field Eh/pH measurements and laboratory results suggest that under present field conditions, meta-cinnabar (HgS) would not be stable due to the relatively low pH (~4.2) and sulfate concentrations (0.14-mM) and high Eh levels at the study site. However, these calculations indicate that meta-cinnabar may have formed when the Hg first entered the wetland at elevated concentrations (~5-mg/L). Given the ecologically sensitive nature of the wetland and the fact that the Hg is strongly bound to the sediment, it was concluded that a monitored natural attenuation approach for site remediation may be appropriate.

The Record of Decision (ROD) for the TNX Operable Unit (OU) was submitted to the U.S. Environmental Protection Agency (EPA) and the South Carolina Department of Health and Environmental Control (SCDHEC) for review and approval. The unit's cleanup remedy was integrated with building demolition activities as part of the T-Area closure concept. Construction activities for the TNX OU cleanup remedy were scheduled to begin in September 2004.

Upper Three Runs Projects

A-Area Miscellaneous Rubble Pile

Remediation activities, including soil removal, are under way at the A-Area Miscellaneous Rubble Pile. The field investigation and characterization identified construction rubble and ash material as primary waste concerns. Final remediation will include a one-foot soil cover (about 6,000 cubic yards) and an active soil vapor extraction technology to remove solvents from the subsurface soils.

M-Area Settling Basin and A-014 outfall

It has been estimated that over 13 million pounds of chlorinated degreasing solvents, including trichloroethylene (TCE) and perchloroethylene (PCE) were used at SRS during reactor operations. Although much of the waste volume was reduced by evaporation, over 3 million pounds, including 317,000 pounds of TCE, were discharged to the M-Area Settling Basin and the A-014 outfall. The M-Area Settling Basin and A-014 outfall were unlined and much of these solvents seeped into the subsurface contaminating the groundwater. The associated groundwater zones in A/M Area (i.e. M-Area and Lost Lake Aquifers) discharge to seeplines adjacent to Tims Branch and Upper Three Runs Creek (WSRC-TR-99-00113; Brigmon, 2000).

This site at the SRS facility was added to the National Priorities List on November 21, 1989. A Record of Decision (ROD) had not been signed for this facility at the time of this report. M-Area was used for aluminum forming and metal finishing operations. 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 Trichloroethylene (TCE) and Tetrachloroethene (PCE) groundwater contamination in M-Area of the 300 square mile SRS site. The solvents later migrated into the groundwater producing a TCE and PCE plume. From the 1950's to the 1980's, wastewaters from Area M operations were discharged to an unlined settling basin and a nearby stream, resulting in soil and groundwater in the area becoming contaminated with high levels of chlorinated solvents, primarily trichloroethlyene (TCE) and tetrachloroethene (PCE). Dense non-aqueous phase liquids (DNAPLs) have also been observed.

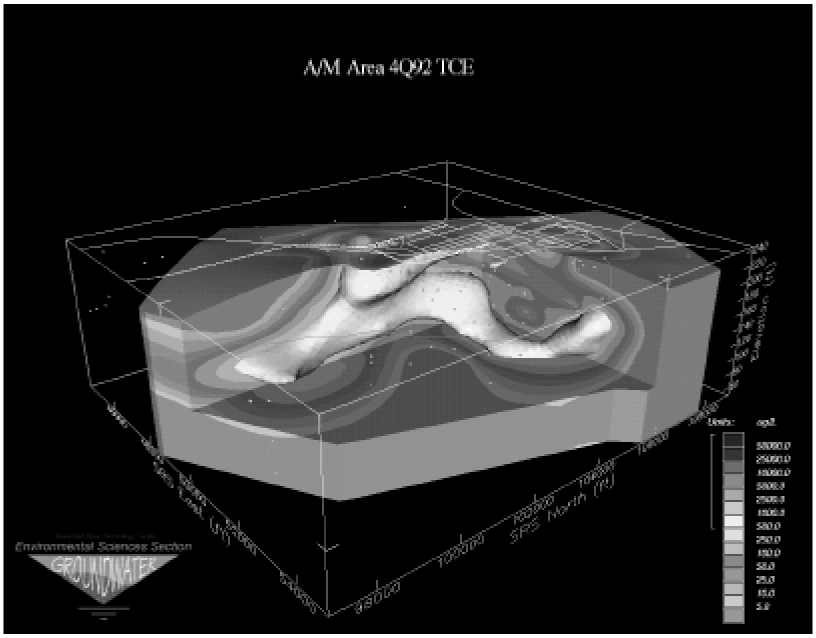


Figure 29: Cut-away diagram showing the 3D structure of a real groundwater plume at A-/ M-Area TCE cleanup site (taken from Looney, 2000)

In September 1985, a full-scale pump and treat system began operating at the site. Methane enhanced bioremediation (MEBR) or biosparging using horizontal wells was the innovative technology tested at this site (DOE, 1996; EPA, 1998; Gerdes, 1999). The aerobic MEBR project 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 (methane), nutrients (nitrogen and phosphorus), and air into the contaminated zone of the aquifer.

In the past several other remediation programs were tested or demonstrated using the contaminant plume at M-Area. DOE, as part of the volatile organic compound (VOCs) in Non-Arid Soils Integrated Demonstration program, tested several innovative technologies to augment the pump and treat (P&T) system in M-Area. The demonstration site was located within the VOC groundwater plume, estimated to cover about 1200 acres and to be about 150-ft thick. Prior to the demonstration, concentrations of TCE and PCE in groundwater ranged from 10 to 1,031 $\mu g\ L^{-1}$ and 3 to 124 $\mu g\ L^{-1}$, respectively. Sediment TCE and PCE concentrations ranged from 0.67 to 6.29 $mg\ kg^{-1}$ and 0.44 to 1.05 $mg\ kg^{-1}$, respectively (DOE, 1996; EPA, 1998; Gerdes, 1999). A more detailed discussion on the field demonstration of Methane Enhanced Bioremediation (MEBR) using horizontal wells as a cleanup technology is included below.

Geology/Hydrogeology/Contaminant Characterization – a 3D model of the M-Area plume and general surrounding area is shown in figure 29. The demonstration area is underlain by relatively permeable sands with thin lenses of clayey sediments. The contaminated aquifer lies in a tan clay zone, 30 to 47 meters (m) below ground surface (bgs). The clay layers generally were relatively thin and discontinuous, with thicker clay layers found at depths of 90 and 160 feet below ground surface (bgs). The water table is located 36.5 m bgs. The water table occurred at depths ranging from 120 and 135 feet bgs. The groundwater flow was radial, extending outward from a groundwater plateau under the demonstration area. In addition, there was a moderate downward gradient beneath the site, with vertical flow rate estimated to be 2 to 8 feet/year (DOE, 1996; Gerdes, 1999).

Matrix Characterization	Value
Soil Type	sand, clay, and gravel
Depth to Groundwater	ranges from 120 to 135 feet bgs
Thickness of Aquifer(s)	150 feet
DNAPL Present	None identified
Groundwater Velocity	15 to 100 feet/year (horizontal)

Table 2: Characterization of M-Area aquifer

Technology Description - Figure 30 presents a process schematic of the methane enhanced bioremediation (MEBR) system used for the demonstration at the M-Area. The system included two horizontal wells. The “lower” horizontal well was placed below the water table (saturated zone) at a depth of 175 feet bgs, with a screen length of 310 feet. The “upper” horizontal well was placed in the vadose zone at a depth of 80 feet bgs, with a screen length of 205 feet. Air and gas were injected into the saturated zone through the lower horizontal well at a rate of 200 scfm (Standard Cubic Foot per Minute). Air and contaminants were then extracted from the vadose zone through the upper horizontal well at a rate of 240 scfm. A thermal catalytic oxidizer, operated at 825° C, was used to treat the extracted vapors, prior to discharge to the atmosphere (DOE, 1996, 1998; WSRC, 1998).

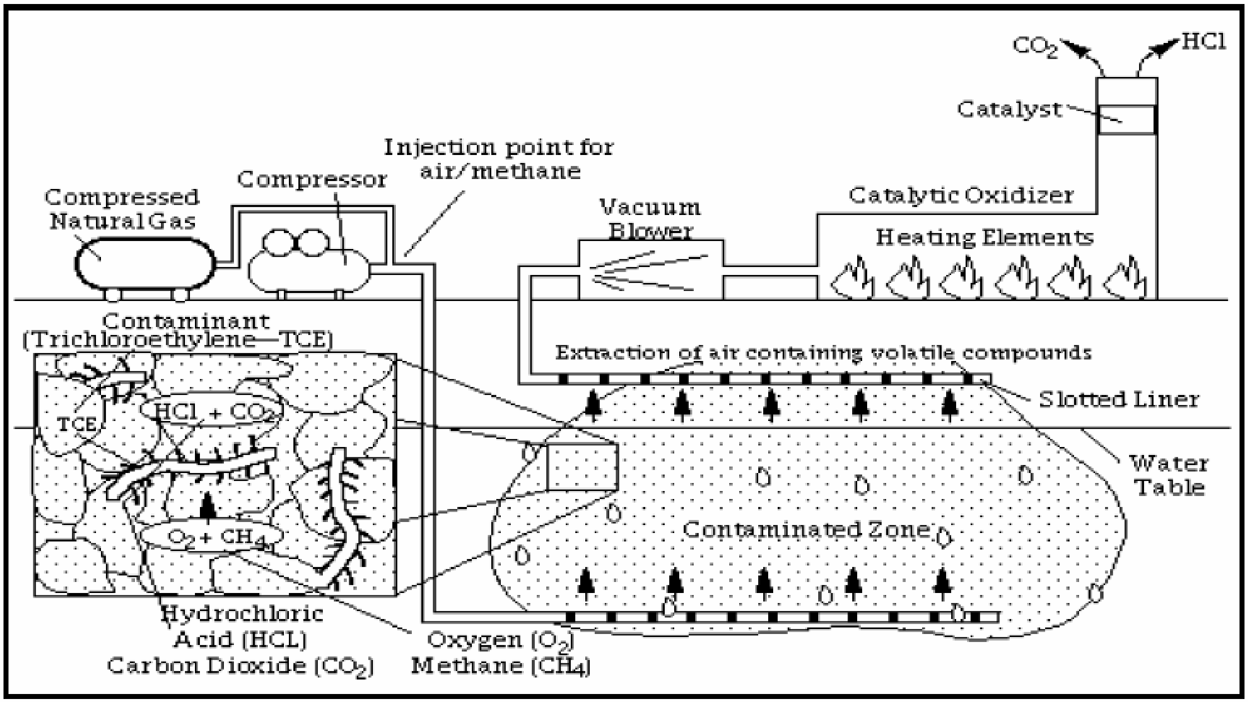


Figure 30: Conceptualized schematic of the Methane Enhanced Bioremediation (MEBR) and Soil Vapor Extraction Field Demonstration Using Horizontal Wells at Savannah River Site M-Area, Aiken, South Carolina [DOE, 1996]

The methane-air mixture as well as nutrients was introduced to stimulate the growth of methanotrophs which produce the enzyme monooxygenase (MMO). The 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 (DOE, 1996, 1998; WSRC, 1998).

An upper horizontal extraction well, located in the unsaturated zone of the aquifer, 23 m bgs, was used to extract air containing Volatile Organic Compounds (VOCs) that had not been oxidized. The extracted air plus VOCs were treated further in a catalytic oxidizing furnace (CatOx system). Carbon dioxide (CO_2) and hydrochloric acid (HCl) were released into the atmosphere.

Figure 30 above shows a schematic of the process. The system was operated for 429 days. A monitoring system consisting 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 2g L^{-1}. The final concentrations were below the drinking water standard of 5g L^{-1} 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.

Operational Mode	Description of System Operation
Baseline Test	Initial vacuum extraction of vadose zone gases at a range of 240 scfm
Baseline Test	Addition of air sparging – simultaneous injection of air into the saturated zone coupled with vacuum extraction of the vadose zone at a rate of 202 scfm (84% of the first baseline test)
Nutrient Addition – 1	Addition of 1% methane
Nutrient Addition – 2	Addition of 4% methane
Nutrient Addition – 3	Pulsed 4% methane addition at a range of 8 hr. every two days
Nutrient Addition – 4	Continuous addition of a combination of nitrous oxide at 0.007% and triethyl phosphate at 0.007% in air in combination with pulses of 4% methane
Tracer tests	Helium tracer tests to measure the amount of injected methane consumed by the indigenous microbes
Microbiological Assays	Comparison of microbial assays for monitoring and control of in situ bioremediation

Table 3: Modes of operation for the MEBR system Demonstration [DOE, 1996, 1998]

Technology Performance - The demonstration was performed in six different operational modes, as described in Table 3. These included baseline tests of the vapor extraction and injection systems, a series of nutrient additions, a tracer test, and an assessment of microbiological assays for monitoring performance.

After just over one year (384 days) of operation, measured concentrations of PCE and TCE in sediments were reduced to below detectable limits, and concentrations of PCE and TCE in groundwater were reduced to below 5 ppb each for PCE and TCE. In addition, soil gas concentrations decreased by more than 99%. The system removed about 17,000 lbs of VOCs through a combination of vacuum extraction and biodegradation. The concentration of TCE and PCE in the sediments before and after the demonstration was used to calculate the mass of VOCs degraded. The vacuum component of the system removed 12,096 lbs of VOCs and the biological component degraded 4,838 lbs of VOCs.

The addition of methane stimulated the growth of methanotrophs. During the 1% methane addition phase, the population of methanotrophs increased by several orders of magnitude, to levels close to 100,000 MPN/ml. During the 4% methane addition phase, the population of methanotrophs increased initially, and then decreased as a result of nutrient depletion. The addition of nitrogen and phosphorous nutrients with pulsed methane stimulated microbial activity, and was reported to have optimized bioremediation and mineralization of TCE and PCE in groundwater and sediments. The results of the helium tracer tests indicated that more than 50% of the injected methane was consumed by indigenous microbes before it reached the extraction well. No results were provided from the microbiological assays.

The zone of influence of the extraction well in the vadose zone was reported to be greater than 200 feet based on pressure measurements. The sparge zone of influence in the saturated zone, measured using electrical resistance tomography, was reported to be a “complex three-dimensional network of channels” extending as far as 100 feet from the injection well. The system was operational 90% of the time and no problems were reported during the demonstration (DOE, 1996, 1998; WSRC, 1998).

Element	**Cost ($)**
Site cost	5,400
Equipment cost	9,200
Design and Engineering	10,000
Mobile equipment	18,000
Well Installation	183,000
Other fixed equipment	183,732
Mobilization	43,075
Total Capital Equipment and Mobilization Cost	**452,407**
Monitoring maintenance	71,175
Consumables	122,215
Demobilization	43,075
Total O and M Costs	**236,465**

Table 4: Project Costs for Full-scale MEBR Application [DOE, 1996, Gerdes, 1999]

Technology Cost - Table 4 presents the projected costs for full-scale application of MEBR. The projected capital costs were $452,407 (including equipment costs amortized over 10 years, and costs for well installation and mobilization), and the projected operation and maintenance (O&M) costs were $236,465 (including monitoring, consumables, and demobilization) (DOE, 1995, 1996; Gerdes, 1999).

Actual cost appears to be somewhat different. 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 (DOE, 1996, 1998; WSRC, 1998).

Observations and Lessons Learned - The *in situ* bioremediation (MEBR) system demonstrated at M-Area removed about 17,000 lbs (16,934 lbs) of VOCs. Of that total, about 12,000 lbs (12,096 lbs) were removed through vacuum extraction and an estimated 5,000 lbs (4,838 lbs) through normal biodegradation processes. According to DOE (1996) the addition of nitrogen and phosphate nutrients in conjunction with 4% pulsed methane provided the best results of the four nutrient addition campaigns tested (see table 4 above). 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.

A further conclusion of some technical importance observed during the operation of the project is that while no toxic intermediates were produced during the demonstration, the use of technical grade methane was found to be growth inhibiting because it contained small amounts of acetylene which is poisonous to the microbes (DOE, 1996; WSRC, 1998). This observation is consistent with the findings of other studies and laboratory experimental models.

The primary objective of the 1994 pilot-scale aerobic bioremediation demonstration at SRS M-Area 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. By comparison a cost-benefit analysis completed at Los Alamos National Laboratory showed that in situ bioremediation could reduce costs by more than 30% compared to a baseline technology of SVE/pump and treat. Accordingly, DOE was able to conclude that this method of in situ bioremediation could reduce the time required to remediate a site by 5 to 7 years compared to SVE/pump and treat. The project was considered so successful that DOE received a patent for MEBR technology in December 1987 (DOE, 1996; WSRC, 1998).

More recently, M-Area has more recently been selected for the construction of the Dynamic Underground Stripping (DUS) project at the M-Area Settling Basin. Construction was scheduled for mechanical completion in September 2004. It is estimated that one million pounds of solvents will be removed from the subsurface over three years of operation. DUS is a key part of the M-Area closure and accelerates cleanup of the A/M groundwater contamination plume (fig. 29) by decades.

The B-Area Sanitary Landfill (SLF) or Non-Radioactive Waste Disposal Facility (NRWDF)

Geology/Hydrogeology/Source Contaminant Characterization - The Non-Radioactive Waste Disposal Facility (NRWDF) at the Savannah River Site (SRS) received sanitary waste, construction material, as well as rags soaked with PCE and TCE for over 20 years (WSRC, 1996). Solid waste was disposed of in an unlined, 70-acre trench-and-fill sanitary landfill (Non-Radioactive Waste Disposal Facility) at the Department of Energy's Savannah River Site (SRS) (Fig. 27). The original 32-acre unlined site received sanitary waste from cafeterias, shops, construction areas, and offices. It reached capacity in 1987, at which time the 16-acre northern and 22-acre southern expansions were opened (Fig. 28). The southern expansion reached capacity and was closed in 1993.

From 1974 to 1994, some of the waste sent to the original landfill consisted of rags and wipes soaked with chlorinated solvents, including tetrachloroethene (PCE) and trichloroethene (TCE). Contamination of the underlying groundwater (GW) with landfill leachate containing these solvents resulted in a settlement agreement with SCDHEC (91-51-SW). A plume containing low levels of PCE, TCE, and dechlorination products has migrated beyond the landfill boundaries towards a wetland. Upper Three Runs Creek is approximately 2,310 feet from the landfill and flows to the Savannah River. The flood plain and the creek are believed to be the point of discharge for groundwater downgradient of the landfill.

Most of the landfill has been capped with an impermeable barrier to minimize infiltration of surface water. Monitored natural attenuation (MNA) is being considered for groundwater remediation. Considerable amounts of geochemical data have been collected at various locations in and around the landfill site. However, field measurements of in situ ethene formation have not been made. Since the landfill has aged considerably and the presence of available organic carbon has declined, enhancing dechlorination by addition of an electron donor is another remediation approach worthy of consideration.

The SLF began operating in 1974 and reached capacity in 1987 at which time expansions were added to increase its capacity to 70 acres resulting in the current configuration known as the NRWDF.

Quarterly groundwater monitoring (starting in 1984) of NRWDF leachate indicated the presence of PCE, TCE, and microbial transformation products including cis-dichloroethylene (cDCE) and vinyl chloride (VC); however, no other chlorinated ethenes were known to have been disposed of at the NRWDF. The groundwater monitoring data provides convincing evidence that monitored natural attenuation (MNA) of chlorinated ethenes has occurred via reductive dechlorination, including detection of VC down gradient from the PCE/TCE plume. Sections of the NRWDF subsurface are aerobic and others anaerobic. It is now understood that complete biodegradation of Chloroethane (CE) may occur under aerobic (Coleman et al., 2002), co-metabolic (Bowman et al., 1993), or anaerobic (Hendrickson et al., 2002) conditions given the optimal microbial populations and environmental parameters. Recent microcosm studies with NRWDF groundwater demonstrated that low redox conditions were established but methanogenesis or anaerobic dechlorination was not observed (Freedman et al., 2001). This work suggested a nutrient deficiency, inadequate inoculum, or an inhibitory contaminant such as heavy metals may have contributed to the microcosm inactivity.

Brigmon et al., 2001 in their study incorporated several direct microbiological analyses to better understand what role microorganisms play in the transformation of PCE and TCE in the NRWDF subsurface. These analyses are part of a larger bioremediation campaign that is currently under consideration as a potential NRWDF clean-up strategy. A hope (Brigmon et al., 2001) is to better understand the dynamics of environmental microbiology in the NRWDF subsurface and how it relates to the potential degradation and/or metabolism of chlorinated ethenes. The current MNA campaign also includes analysis of physical factors related to remediation of the NRWDF, such as sorption, dilution, and volatilization (Wiedemeir et al., 1995). In situ subsurface biodegradation is more difficult to study because the subsurface environment is inherently complex and is composed of a diverse microbial community.

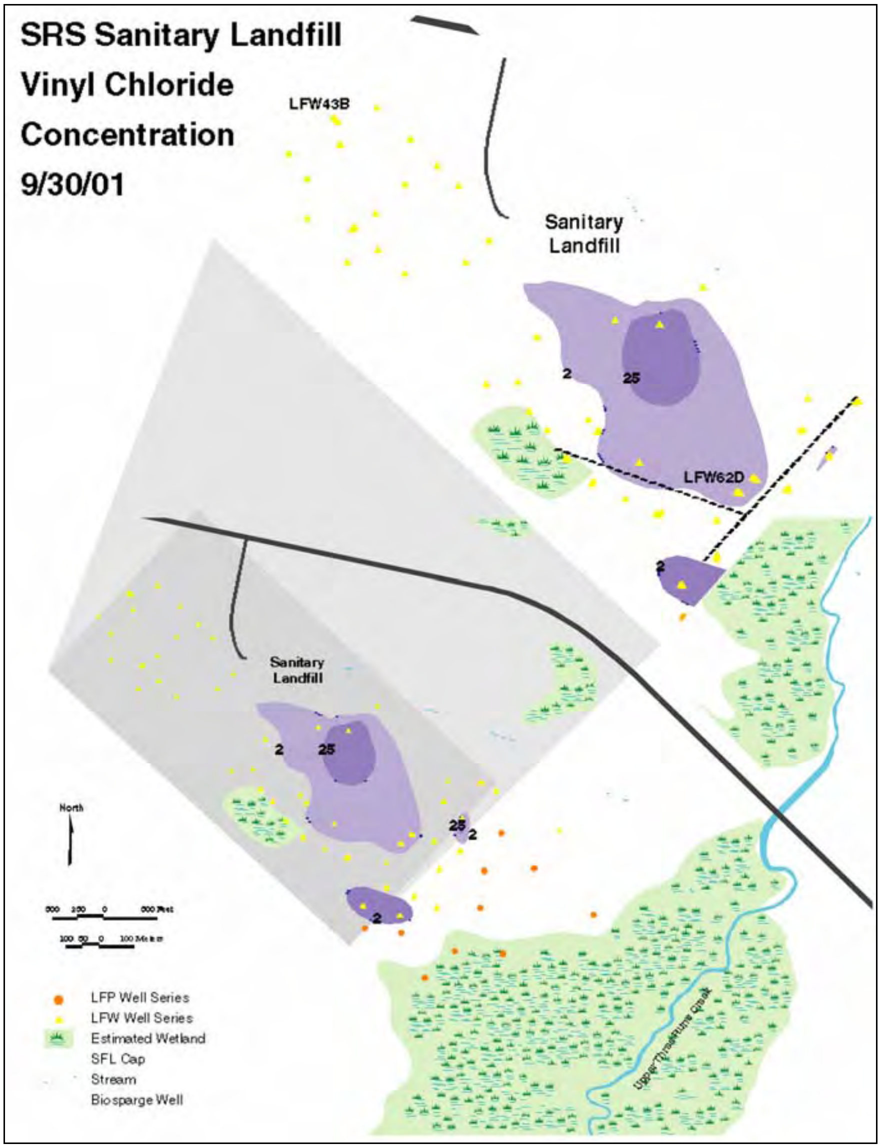


Figure 31: Location of groundwater monitoring wells LFW 43B and LFW 62D relative to the Vinyl Chloride plume at the SRS NRWDF Sanitary Landfill (taken form Brigmon et al., 2002)

Technology Description - A pilot-scale gaseous injection remediation test system was designed and installed within the TCE plume to validate the use of in situ biodegradation of chlorinated solvents (WSRC, 1996). The test system consists of three sparge wells, a gas extraction well, and 14 nested monitoring points. Each nested monitoring location within the TCE plume has two mini-wells in the unsaturated soils (one shallow = 10 feet below ground surface [bgs]; one deep = 16 ft bgs) and two mini-wells in the saturated soils (one shallow = 30-40 ft bgs; one deep = 45-55 ft bgs).

During this test, air, methane, nitrogen, phosphorous, and helium were injected for approximately 8 hours a day, followed by 16 hours of no injection (for six consecutive days). This injection contained a mixture of 15 scfm (Standard Cubic Foot per Minute) air blended with

4% methane (CH_4), 0.07 % Nitrous Oxide (N_2O), 0.007 % to 0.01 % Phosphate (Triethyl Phosphate (TEP), $(C_2H_5)_3PO$) and 1.0% Helium (He) injected as a tracer.

Once gas injection had begun water samples were collected every 24 hours from wells 2s, 9s, and 14s for microbial and groundwater contaminant data. Total bacterial counts were accomplished by the Acridine Orange Direct Count Method (AODC) methodology. Methanotrophic bacteria were quantified using the Direct Fluorescent Antibody (DFA) procedure and the Most-Probable-Number (MPN) technique (Brigmon et al., 1998b). Groundwater samples were analyzed for volatile organic compounds (VOCs) as previously described (Brigmon et al., 1998a). Vadose zone gas samples were taken to monitor possible volatilization.

Technology Performance - An in situ optimization test in the NRWDF has proven that gaseous nutrient injection stimulates subsurface CE bioremediation by selective biostimulation of methanotrophic bacteria (Brigmon et al., 1999). There is presently a biosparge system in operation at the landfill consisting of 400 ft and 600 ft horizontal injection wells (Brigmon, 2002). Through application of the fatty methyl ester (FAME) technique it was found that the groundwater microbial communities in NRWDF individual wells did not vary over a 6-week interval (Glucksman et al., 2000). In contrast, marked differences in both abundance and composition of FAMEs were observed in profiles from spatially distinct wells located 300 m apart.

Because the understanding of the microbial component of the NRWDF subsurface is limited, the study (Brigmon et al., 2001) sought to provide detailed information about this microbial community using a combination of rapid direct analytical techniques that could discriminate differences between groundwater microbial communities. Brigmon et al., 2001 also sought to use these data to identify bacteria that have been shown to be capable of the biodegradation of PCE and TCE. Furthermore, Brigmon et al., 2001 planned to use findings from this research as the foundation for an ongoing bioremediation campaign at the NRWDF. Brigmon et al., 2001 reported the molecular, phospholipid fatty acid analysis (PLFA), and metabolic evidence to support the fact that microbial diversity was higher in the CE-contaminated well as compared to the pristine well. Integrated investigations of specific site parameters and microbial community dynamics are needed as a basis for environmental restoration efforts. The microbial characterization is essential for the eventual remedial technology selection. Brigmon et al., (2001) hypothesize that the NRWDF leachate provides multiple substrates to enhance the microbial diversity of the groundwater, as we observed at the contaminated well LFW 62D.

This study (Brigmon et al., 2001) provides significant insight regarding characteristics associated with microbial communities in the CE contaminated NRWDF aquifer. In situ biodegradation is the preferred technology for environmental restoration at this and related sites because contaminants are destroyed in place, not simply moved to another location or immobilized (Bouwer et al., 1994). Microbial biodegradation of subsurface contaminants, while site specific, is highly dependent on the in situ environment (Haack and Bekins, 2000). The aquifers at the Savannah River Site offer many unique environments, including contaminated and pristine, that have been proven to host different microbial communities (Bowman et al., 1993). These microbial populations have been significantly altered in some area of SRS to achieve environmental restoration goals (Kastner et al., 2000).

Data (Molecular (16S rDNA), substrate utilization (BIOLOG), and PLFA profiles) obtained from at the NRWDF landfill and provides evidence that the microbial populations in aquifers can vary based on geochemical parameters. The direct isolation of rRNA and PLFA from groundwater microbial communities eliminates the bias introduced by enrichment and cultivation. Furthermore, the use of BIOLOG to evaluate groundwater physiological potential without processing allows a metabolic “fingerprint” to be taken of a given sample. Moreover, the 16S rRNA, BIOLOG and PLFA data taken from different locations on the same site can demonstrate microbial activity, structure, and dynamics in the presence of chlorinated ethenes. Based on this information, future studies could identify molecular components in the bacteria that provide an enhanced ability to degrade the chlorinated ethenes PCE, TCE, and daughter products cDCE and VC. The data will also provide a significant contribution since the CE natural attenuation rates are being evaluated at this site (Freedman et al., 2001). This information will provide an ability to compare biodegradation rates between groundwater monitoring wells based on different microbial populations. Moreover, using the 16S rRNA, BIOLOG, and PLFA data can potentially validate differences observed in CE biodegradation rates between two distinct groundwater sources. For example, differences in the molecular results (16S rRNA data) and population dynamics (PLFA and BIOLOG) between groundwater sources could be more easily understood if differences are observed simultaneously in the geochemical data. Collectively, data obtained in this study will provide a fundamental understanding of microbial diversity with respect to groundwater contamination. The 16S rRNA and PLFA data provides information on the exact species composition combined with the BIOLOG data as an indication of the metabolic activity allows characterization of the groundwater consortia as it relates to bioremediation potential.

The contaminants found within well LFW 62D included PCE, TCE, cDCE, and VC. The methane monooxygenase of methane-oxidizing bacteria (methanotrophs), such as Methylomonas, Methylobacter, Methylosinus, Methylococcus, and Methylomicrobium, can co-metabolize these CE under the right conditions (Rosenzweig et al., 1993). Therefore, an environment with methane and CE may enrich for these methane oxidizers. The 16S rDNA data showed that 28% of the bacterial clones sequenced clustered with the type I methanotrophs. Since this microbial characterization work was complete, a campaign using biosparging was initiated at the landfill (Figure 32). The results form Brigmon et al., (2002) imply that in situ bioremediation utilizing methanotrophs may be effective in the vicinity of LFW 62D. The pumping of methane, air, and other nutrients into this community will potentially enrich the methane-oxidizing members in this community further to cometabolize the CE. The enrichment of these organisms expediting the degradation of the contaminating plume will be monitored. Of interest here are the molecular and PLFA (Figures 32 and 33) results for the groundwater from LFW 43B. This well was selected as a noncontaminated source to compare with the contaminated groundwater LFW 62D as it was upgradient from the CE plume and historically had never demonstrated any groundwater contamination. The phylogenetic analysis revealed a low diversity with all clones closely related to P. gessardii and P. libaniensis that were previously described in spring water. The PLFA demonstrated similar results with most of the phospholipids common to pseudomonads. Results from BIOLOG demonstrated a wider range of substrate utilization for LFW 43B (Figure 9) potentially due to the greater proportion of pseudomonads.

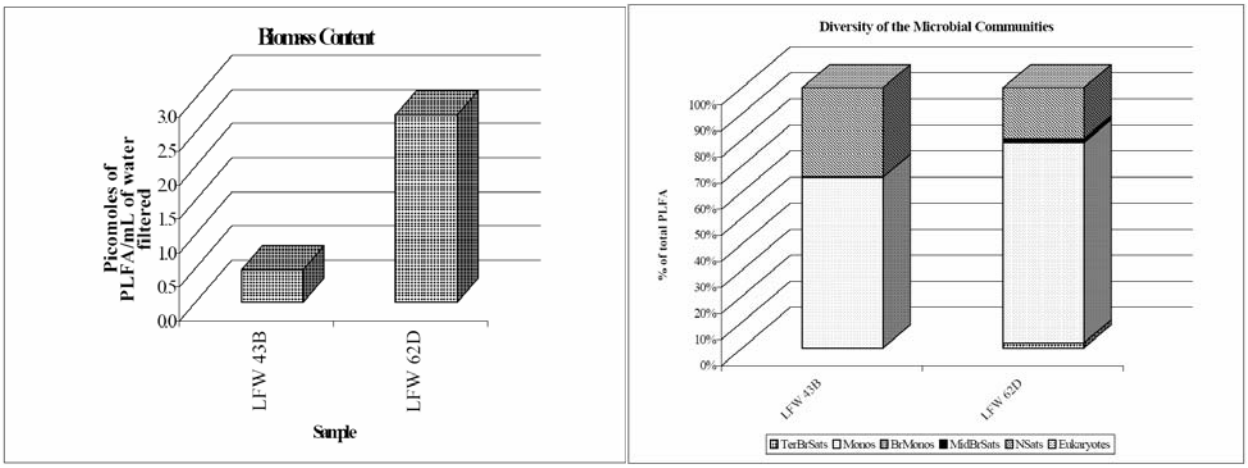


Figure 32: Groundwater biomass content and diversity as measured by percentage of total groundwater PLFA for LFW 43B and LFW62D (taken from Brigmon et al., 2001)

Results from biological analyses are useful to compare differences in microbial communities from spatially different non contaminated and contaminated groundwater, and develop a baseline for future analyses. Bioremediation is known to be more successful where there is indigenous diverse population of microorganisms capable of mineralizing a wide range of substrates (Green and Scow, 2000). At the SRS, microbial characterization has proven to be of critical importance in determining the successful outcome of field-scale bioremediation deployments (Bowman et al., 1993; Enzien et al., 1994; Hazen, 1996; Brigmon et al., 1999 and Kastner et al., 2000). Future microbial analyses at this and other SRS sites will help determine whether and how subsurface microbial communities change as contaminate plumes advance through them.

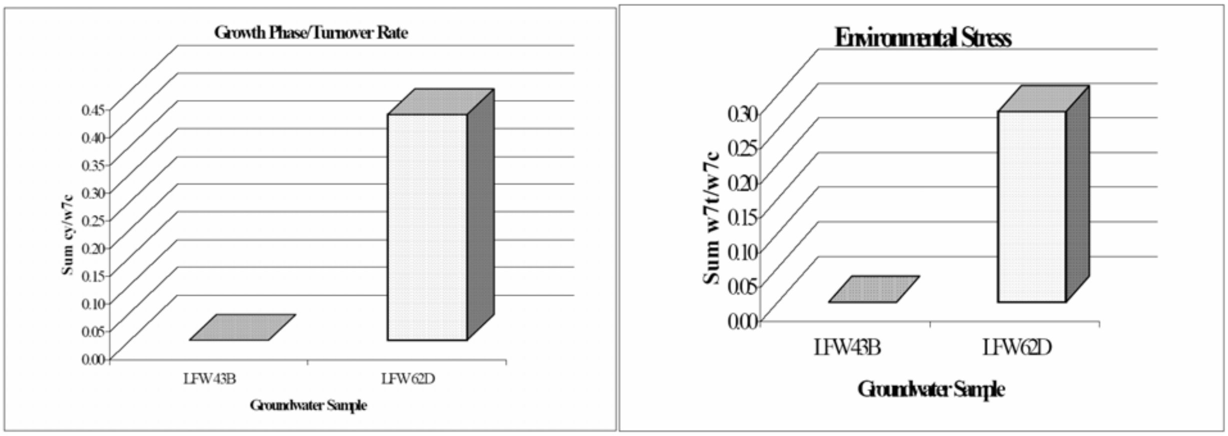


Figure 33: Growth phase and comparative membrane permeability in the LFW Gram negative communities (taken from Brigmon et al., 2001)

In addition, this information can lead to management practices of these indigenous microbial communities to maintain the diversity and activity needed to achieve long term environmental restoration goals. The combination of non-selective characterization techniques was useful to further the understanding of CE-contamination on groundwater microbial communities.

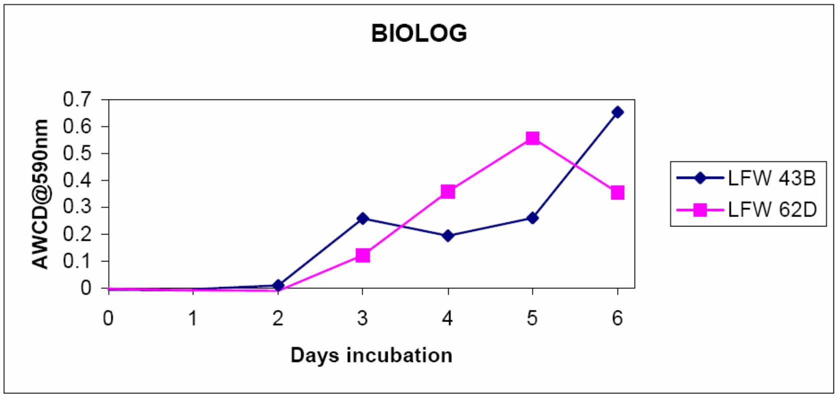


Figure 34: Average BIOLOG well color development in LFW 43B; OCRD = 0.131 and in LFW 62D; OCRD = 0.220 and number of individual BIOLOG substrates utilized (>0.1 OD590nm) over time in LFW 62Dand LFW 43B (taken from Brigmon et al., 2001)

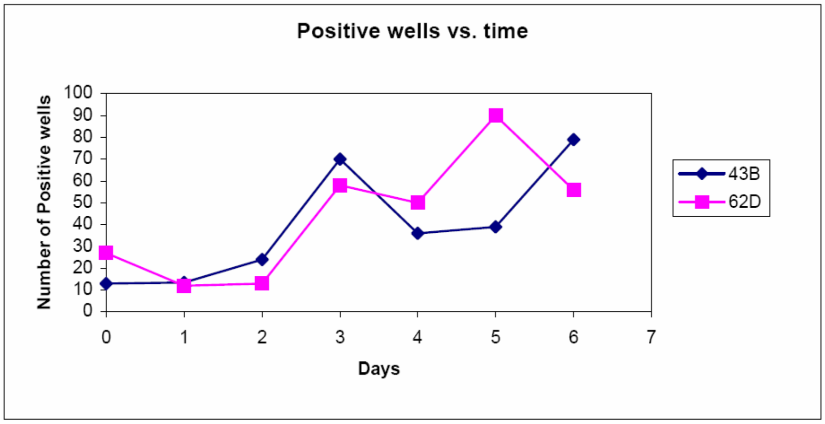


Figure 35: Average BIOLOG well color development in LFW 43B; OCRD = 0.131 and in LFW 62D; OCRD = 0.220 and number of individual BIOLOG substrates utilized (>0.1 OD590nm) over time in LFW 62Dand LFW 43B (taken from Brigmon et al., 2001)

Phytoremediation

Phytoremediation is an emerging technology that utilizes plants and associated microbes to remediate contaminated soils, sediments, and water. Bioremediation of chlorinated solvents, both natural and accelerated, is more and more exemplified by phytoremediation and biodegradation by rhizosphere microorganisms. This process is really another form of biodegradation in which certain plants can remove, transfer, stabilize and destroy contaminants in soil, sediment, sludge, groundwater, surface water, and leachate through several processes (Schnoor, 2002; Pivetz, 2001; Newman et al., 1997; Miller, 1996; Schnoor et al., 1995; Anderson et al., 1993; Walton and Anderson, 1990). An important prerequisite for plant uptake is that the contaminants are nontoxic to the plant. Past studies (e.g. Burken and Schnoor, 1998; Briggs et al., 1982) have shown that plants have the capacity to withstand relatively high organic and inorganic contaminant concentrations without toxic effects.

The phytoremediation pathways (fig. 36) involve three mechanisms:

1. Rhizodegradation (root system), or the breakdown of organic contaminants by microbial activity enhanced by the presence of plant roots,
2. phytodegradation, the breakdown of contaminants by plant metabolic processes, and

3. transrespiration (leaf system), physical processes including volatilization and transpiration.

A Phytoremediation project is usually conducted in two phases. Phase 1 of the project involves evaluating and optimizing the effectiveness of the delivery system (i.e. getting the maximum possible amount of contaminant from the aquifer to the rhizosphere). Phase 2 involved process development and proof of principal experimentation.

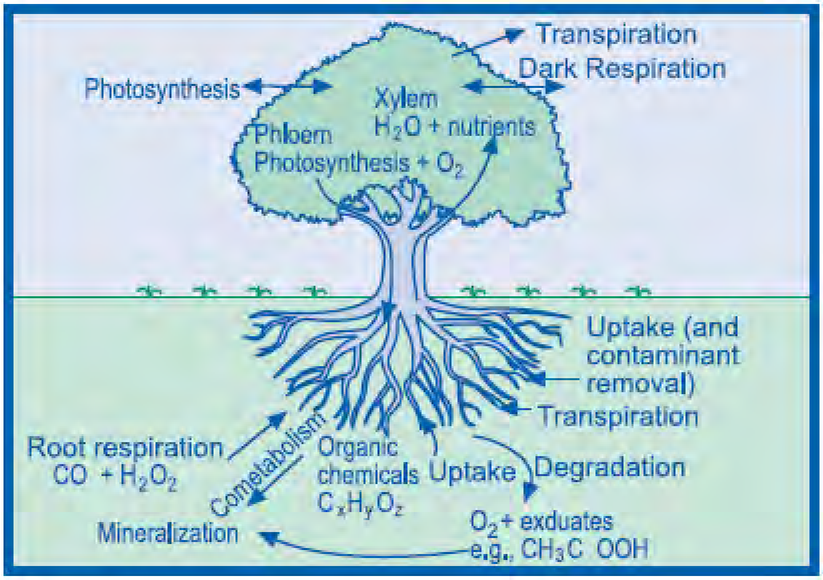


Figure 36: generalized concept model of Phytoremediation technology (taken from EPA,)

Southern Sector Projects

Phytoremediation appears to be an excellent technology to intercept and control plume migration. Recent characterization work has delineated widespread plumes (1-2 miles) of low concentration (40 ppb –10-ppm range) trichloroethylene (TCE) and perchloroethylene (PCE) contaminated groundwater. Previous studies at the Savannah River Site (SRS) demonstrated degradation of low concentrations of chlorinated solvents by plants and associated rhizosphere microorganisms (Anderson et. al., 1993). The potential for phytoremediation of chlorinated solvents has been demonstrated by projects at the Miscellaneous Chemical Basin, Southern Sector of A- and M-Area and TNX/D-Area. Phytoremediation deployments are underway for TCE and PCE phytoremediation in select areas (Tims Branch and D-Area).

The ongoing Southern Sector (Tims Branch) treatability study is part of a multi-year field study of SRS seepline-soil systems maintained under saturated conditions. The field research has the objective of determining the efficiency of plants and soil for in situ bioremediation of the VOCs, TCE and PCE, under seepline conditions. The primary focus is on determining how trees, seepline groundcover, soil microbial communities, and geochemical and surface-volatilization processes affect these waste components in contaminated groundwater that flows through surface seepline areas. FY2000 represented an initial acclimation phase for soil and plant systems and will facilitate examination of seepline phyto- and bioactivity in subsequent growth season in FY2001. The Southern Sector project has concentrated on groundwater upgradient of the seepline at Tims Branch.

D-Area/TNX OU

D-Area at SRS has a large dilute groundwater plume of TCE (mostly <100 µg L^{-1}) that is close to the Savannah River (fig 26). Most of the TCE-contaminated groundwater occurs near the bottom of an approximately 9-15 m thick aquifer, well below the depth of typical tree root penetration. Wilde et al., (2003) studied a drip irrigation component of the proposed phytoremediation process which provided a means to allow plant and associated microbial communities an opportunity to remediate contaminated groundwater from depths otherwise unavailable to plant systems. The overall objective of this D-Area project was to evaluate a novel drip irrigation-phytoremediation process (Figure 38) for remediating volatile organic contaminants (VOCs), primarily trichloroethylene (TCE), from this contaminated groundwater. The process has the potential to be less expensive and more beneficial to the environment than traditional TCE remediation technologies. It could safely reduce plumes of TCE in D-Area groundwater to below drinking water standards (<5 µg/L), while facilitating the growth of plants that can be used in timber production. The removal of TCE is effectuated by both abiotic (adsorption, absorption, volatilization) and biotic (phytoremediation) pathways.

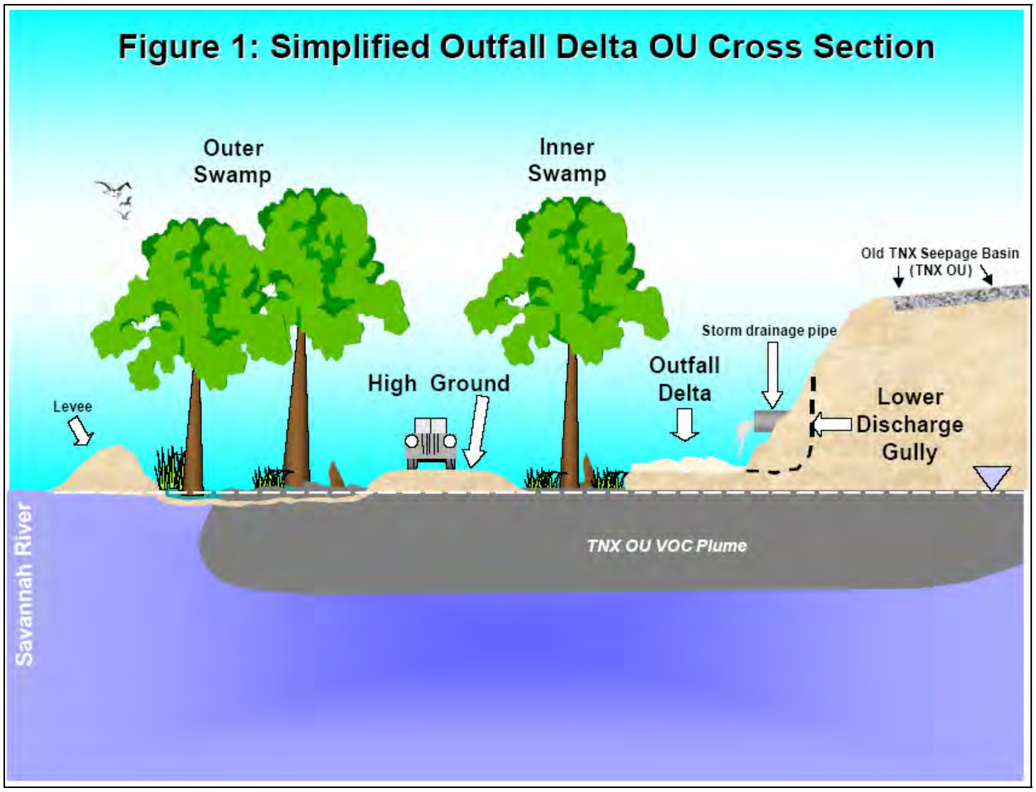


Figure 37: Simplified cross sectional view of the TNX Outfall Delta operable unit.

Technology Description - For the Southern Sector project, Well MSB 88C was selected as the groundwater supply because of its VOC concentrations (TCE 188 ppb, PCE 55 ppb) and proximity to the seepline. Three phytoreactors were deployed with soil from the seepline. Phytoreactors 1 and 2 were planted with loblolly pines (Pinus taeda) and hybrid poplars (Trichocarpa X deltoides) respectively. Loblolly pine is a native SRS species. Phytoreactor 3 was left non-vegetated as a soil control to evaluate monitored natural attenuation (MNA). The phytoreactors were supplied with a continuous flow of contaminated groundwater.

Drip irrigation has been initiated at four 0.2 acre test plots in D-Area as part of a recently initiated field study to evaluate the use of plants for treating TCE-contaminated groundwater from an aquifer 30-50 feet below the surface. The project was conducted in two phases. Phase 1 involved setup and evaluation of the system while Phase 2 involved process development and proof of principal experimentation. The novel process to be tested involves pumping TCE-contaminated groundwater from the deep subsurface and distributing it via a network of shallow drip emitters to the rhizosphere regions of vegetative test plots where degradation processes can be effectuated by plants and their associated microflora. Phase 1 of the project involves evaluating and optimizing the effectiveness of the delivery system in getting the maximum possible amount of TCE from the aquifer to the rhizosphere. Subsequent work will focus on comparatively evaluating and optimizing the ability of various plants to detoxify the contaminant and to determine feasible treatment flow rates and operational costs.

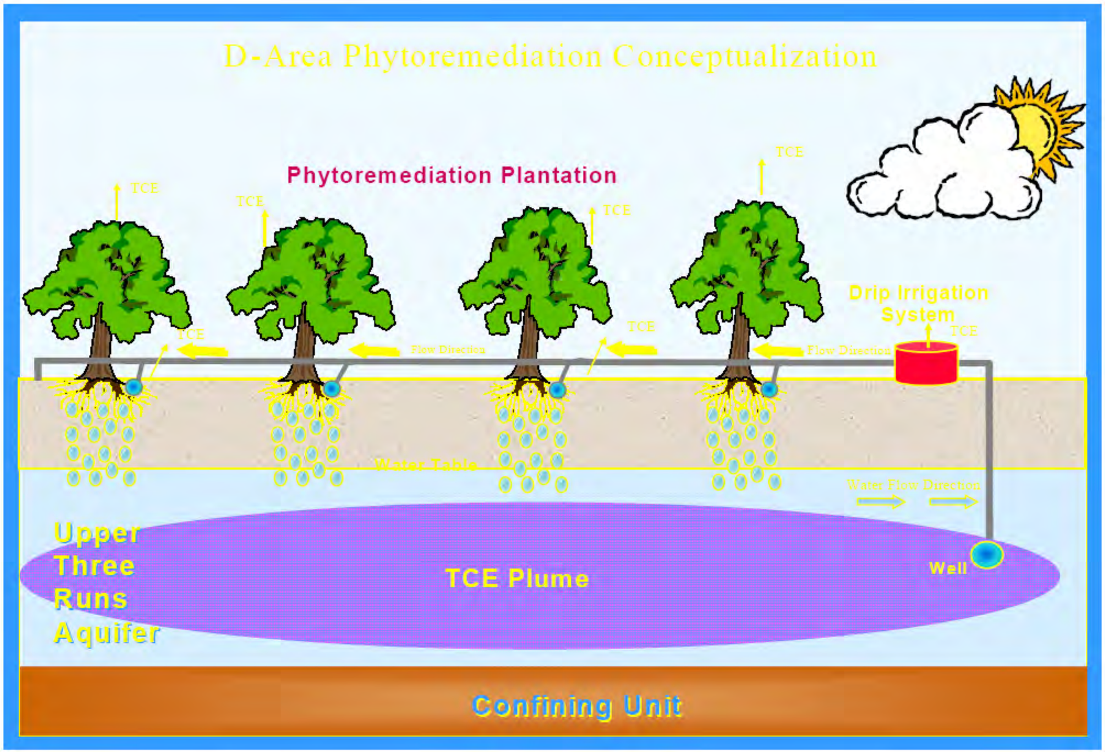


Figure 38: Conceptual design of SRS D-Area drip irrigation/phytoremediation project system (taken from Wilde et al., 2003)

Technology Performance - Results to date from the Southern Sector project demonstrate that the loblolly pine phytoreactors can remove up to 90 % of the TCE and 80 % of the PCE. The hybrid poplar phytoreactors demonstrated up to 100% removal of the groundwater contaminants. No detectable amounts of these VOCs were found in transrespiration, soil volatilization, or soil core testing. Microbial activity in the phytoreactors and seepline soils is under investigation using anaerobic microcosms for assessing biotransformation of TCE and PCE.

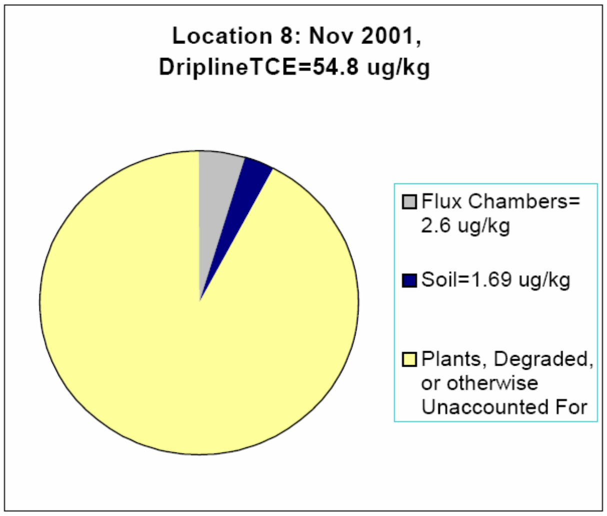


Figure 39: Preliminary mass balance for TCE dissipation (taken from Wilde et al., 2003)

The results suggest that the drip irrigation/phytoremediation process that was tested in D-Area provides a viable alternative to remove TCE-contaminated groundwater and simultaneously grow trees (i.e. Cottonwoods) that would not otherwise be able to survive. The data clearly show that TCE was reduced to non-detectable levels within the upper 0.6 m of soil in all test plots utilized. It appears that the presence of trees retards volatilization. However, a definitive understanding of the pathways being utilized for TCE dissipation and the relative importance of each has not been achieved at this point nor has the maximum loading of TCE to the system without breakthrough (TCE penetrating >2.4 m in the soil column) been determined.

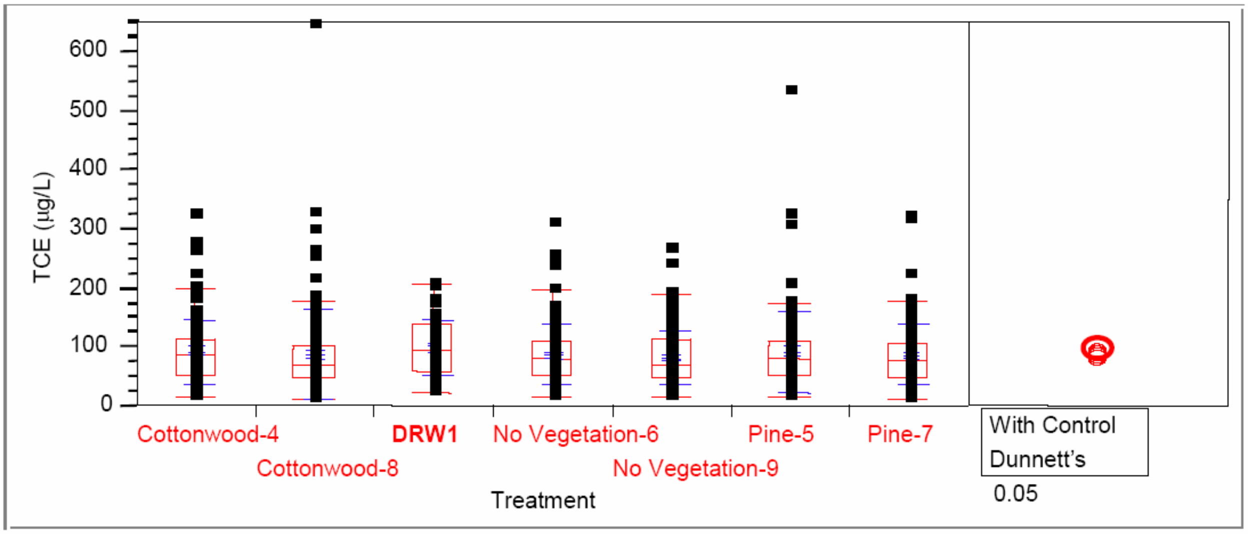


Figure 40: Mean concentrations (µg L^{-1}) of TCE at Well DRW-1 and Plots 4-9 (taken from Wilde et al., 2003)

Figure 39 shows the percent of water TCE (from dripline measurements) that can be accounted for by TCE in soil samples and volatilization (converted flux chamber measurement). The mass balance illustration shows that at least 92% of TCE was unaccounted for, degraded or possibly metabolized in plants. Overall, the results of the study suggested that the process provides a viable method to remove TCE-contaminated groundwater. The data clearly show that TCE was reduced to non-detectable levels within the upper two feet of soil (rhizosphere) in all test plots with the flow rates that were tested. However, Wilde and others (2003) also concluded that initial attempts at describing degradation rates and mass balance calculations were inconclusive and indicative of a need for more testing.

Observations and Lessons Learned - The results of this project, with concurrent SRS studies, will enable better predictions of the VOC removal at the seepline. The first year, FY2000, represented an initial acclimation phase for soil and plant systems and facilitated the examination of seepline phyto- and bioactivity in subsequent growth season in FY2001. Initial results indicate that phytoremediation and MNA have considerable potential for the removal of TCE and PCE in the Tims Branch flood plain and seepline.

There are very few remediation options for ecologically sensitive wetland areas. Application of phytoimmobilization at the TNX OD site has a number of attributes, but also an important limitation, namely that it will likely not clean up the site of all radionuclides. Among its attributes, phytoimmobilization uses existing natural biogeocycling processes and simply interrupts these processes by accumulating the contaminants in the geomat. Additionally, it should greatly reduce the cost of waste disposal by creating a concentrated waste in the sequestering agent. However, the fact that not all the contaminants will be cleaned in a timely manner compromises its utility, thereby requiring that we further evaluate other remediation approaches and/or the clean up goals of the site (Kaplan et al., 2001).

At the D-Area site, further system operation, plant and microbial analyses, soil column testing, and evapotranspiration measurements would be needed to complete the evaluation of the drip irrigation-phytoremediation process and to determine the optimal use of this technology. However, the D-Area project is highly significant in that most work in the phytoremediation area has been associated with significantly higher concentrations of volatile organic contaminants (VOC's) (Burken and Schnoor, 1998, Newman et al, 1997, Doty et al., 2000). In FY2001 the influent supply and effluent system will have major changes including raising the height of the supply tank and increasing the diameter of influent and effluent system piping to improve the groundwater flow rate continuity. The addition of a slow-release fertilizer to the surface soils will be implemented next year. In FY2001 the groundwater influent and output was monitored more stringently to better evaluate the contaminant removal. A surface drain system is under construction to allow for surface runoff and a surface–litter layer will be placed in each phytoreactor to minimize the development of a surface-clogging biomass. At SRS and other sites much of the VOC groundwater contamination with the exception of source areas are in lower (ppb) concentrations (WSRC-TR-00113, 1999).

MONITORING NATURAL ATTENUATION

After closure and the selection of MNA as the remedy of choice, long term monitoring is necessary. DOE conceptual monitoring network shown in figure 41 forms the technical basis for the MNA management zone. It is an areal view of the flow dynamic model discussed above. All monitoring should occur within or at the boundary of the MNA management zone. The MNA management zone is defined by the core team and encompasses the maximum projected plume boundary based on understanding of flow, transport, and attenuation processes and quantitatively accounts for all remaining uncertainties. This region can be thought of as providing a natural reaction bed of sufficient size to accommodate the anticipated performance of the natural attenuation processes.

Three types of monitoring (Figure 41) are typically required for the implementation of an MNA remedy, 1) Performance monitoring (within and immediately adjacent to the plume); 2) Detection monitoring (at the boundary of the MNA management zone); and 3) Ambient monitoring (upgradient of the plume).

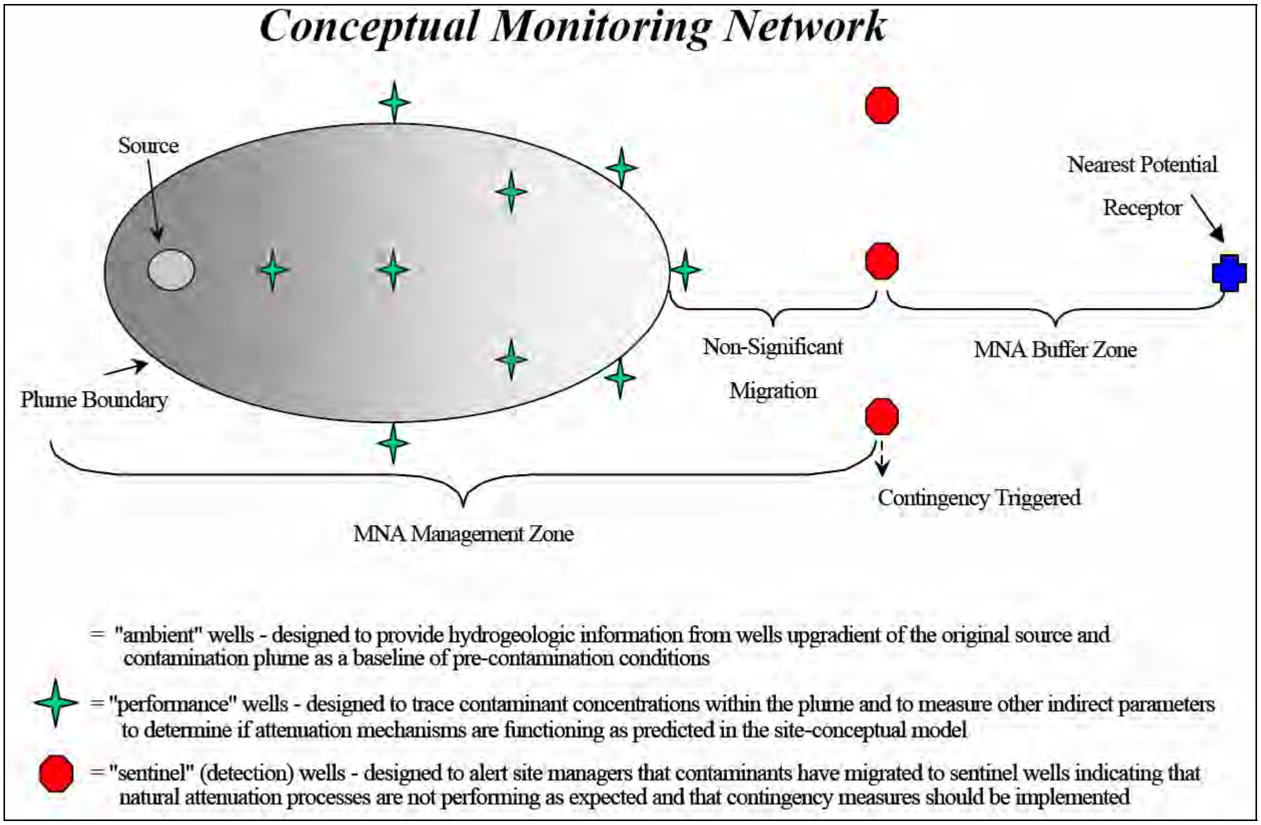


Figure 41: diagram of DOE Conceptual Monitoring Network (DOE, 1999)

Performance monitoring takes place within and immediately surrounding the existing contaminant plume (Figure 41) utilizing, to the greatest extent possible, existing monitoring locations (e.g., wells, boreholes). Monitoring locations within the plume are needed to track the evolution of plume behavior as well as to assess the efficacy of attenuation processes. Since some site characterization will have been conducted prior to selection of MNA as the remedy of choice, monitoring system design often begins with the adequacy of the existing monitoring network. Some monitoring locations will provide more valuable data than others. For example, monitoring locations that are located where evidence suggests natural attenuation processes are presently occurring may provide more useful information for developing and calibrating the conceptual site model shown in fig. 41.

DISCUSSION

This report reviews bioremediation as an environmental cleanup technology. It discusses the primary concepts and processes involved in the application of these technologies to actual site cleanup projects. The report further discusses the application of these technologies at DOE facilities, particularly the Savannah River Site (SRS) in South Carolina, as part of the Monitored Natural Attenuation and Enhanced Passive Remediation (MNA/EPR) Technology Alternative Project. The applicable remediation processes are recapped below using the descriptions of the Remediation Technologies Screening Matrix and Reference Guide, Version 4.0, from the Federal Remediation Technologies Roundtable (FRTR). Figures 42-44 show a statistical breakdown of the number of superfund projects monitored between FY1982 and FY2002 nationwide.

As mentioned above, bioremediation uses microorganisms to degrade organic contaminants in soil, sludge, solids, and groundwater either in situ or ex situ. It can also be used to make metals or metalloids less toxic or mobile. When treating organic contaminants, the microorganisms break down contaminants by using them as a food source or cometabolizing them with a food source. Aerobic processes require an oxygen source, and the end-products typically are carbon dioxide and water. Anaerobic processes are conducted in the absence of oxygen, and the end-products can include methane, hydrogen gas, sulfide, elemental sulfur, and dinitrogen gas. *Ex situ* bioremediation technologies for groundwater typically involve treating extracted groundwater in a bioreactor or constructed wetland. In situ techniques stimulate and create a favorable environment for microorganisms to grow and use contaminants as a food and energy source, or to cometabolize them. Generally, this process involves providing some combination of oxygen, nutrients, and moisture, and controlling the temperature and pH. Microorganisms that have been adapted for degradation of specific contaminants are sometimes applied to enhance the process. For the treatment of metals and metalloids, it involves biological activity that promotes the formation of less toxic or mobile species, by either creating ambient conditions that will cause such species to form, or acting directly on the contaminant. The treatment may result in oxidation, reduction, precipitation, coprecipitation, or another transformation of the contaminant.

Phytoremediation is a process that uses plants to remove, transfer, stabilize, or destroy contaminants in soil, sediments, or groundwater. The mechanisms of phytoremediation include enhanced rhizosphere biodegradation (takes place in soil and groundwater immediately surrounding plant roots), phytoextraction (also known as phytoaccumulation, the uptake of contaminants by plant roots and the translocation/accumulation of contaminants into plant shoots and leaves), phytodegradation (metabolism of contaminants within plant tissues), and phytostabilization (production of chemical compounds by plants to immobilize contaminants at the interface of roots and soil). Phytoremediation applies to all biological, chemical and physical processes that are influenced by plants (including the rhizosphere) and that aid in the cleanup of contaminated substances. Phytoremediation may be applied in situ or ex situ to soils, sludges, sediments, other solids, or groundwater (FRTR, 2001; EPA, 2004).

Chemical Treatment, also known as chemical reduction/oxidation, typically involves reduction/oxidation (redox) reactions that chemically convert hazardous contaminants to compounds that are nonhazardous, less toxic, more stable, less mobile, or inert. Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). The oxidizing agents used for treatment of hazardous contaminants in soil include ozone, hydrogen peroxide, hypochlorites, potassium permanganate, Fenton's reagent (hydrogen peroxide and iron), chlorine, and chlorine dioxide. This method may be applied *in situ* or *ex situ* to soils, sludges, sediments, and other solids, and may also be applied to groundwater *in situ* or ex situ (P&T). P&T chemical treatment may also include the use of ultraviolet (UV) light in a process known as UV oxidation.

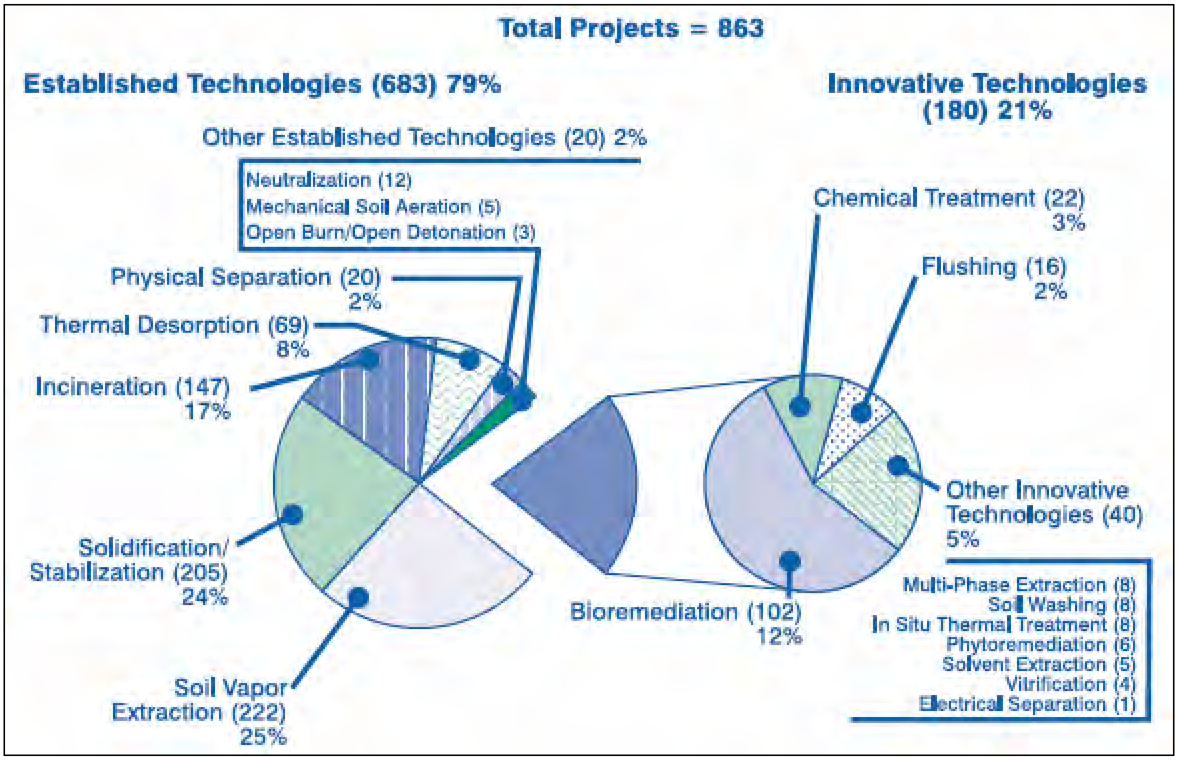


Figure 42: Superfund Remedial Actions: Innovative Applications of Source Control Treatment Technologies (FY 1982 - 2002). Information is based on an estimated 70% of FY 2002 RODs. (adapted from EPA 2004)

The EPA Annual Status Report (ASR- 11th edition) documents the status and achievements, as of March 2003, of treatment technology applications for soil, other solid wastes, and groundwater at Superfund sites. It includes analysis of 17 types of source control (primarily soil) treatment technologies, 10 types of in situ groundwater treatment technologies, 8 types of groundwater P&T technologies, and 1 groundwater containment technology. The data in the report were gathered from Superfund Records of Decision (ROD) from fiscal year (FY) 1982 - 2002, Close-out Reports (COR) from FY 1983 - 2002, and project managers at Superfund remedial action sites. The ASR examines those technologies mentioned previously including in situ and ex situ treatment technologies for source (soil, sludge, sediment, other solid-matrix wastes, and non-aqueous phase liquids [NAPL]) contaminants, in situ and ex situ groundwater treatment technologies (pump and treat [P&T]) and vertical engineered barriers (VEB). This edition of the Annual Status Report (ASR) provides a summary of the 1,811 technology applications identified for Superfund remedial actions. The report compiles information from FY 2000, 2001, and approximately 70% of 2002 RODs. It also reports detailed information regarding 743 groundwater P&T projects. More detailed information is provided on the application of chemical treatment, one of several innovative technologies whose use has been increasing in recent years, particularly for the in situ treatment of dense non-aqueous-phase liquids (DNAPL), which historically have been difficult to treat. Figure 18 depicts the number and types of innovative and established technologies used. As shown, innovative treatment technologies represent 21% of all technologies used for source control. Bioremediation makes up more than half of the innovative applications (102). In situ chemical treatment and flushing are the second and third most frequently selected innovative technologies. Innovative technologies being used for fewer than 9 projects at Superfund sites are listed under the other innovative technology category, which includes a total of 7 technologies and 40 applications. In figure 18 innovative technologies are defined as alternative treatment technologies that have a limited number of applications and limited data on cost and performance. Innovative technologies have the potential for providing more cost-effective and reliable alternatives for cleanup of contaminated soils and groundwater. Hence, the selection of monitored natural attenuation (MNA) remedies for groundwater is also emerging as an approach of choice. The selection of groundwater treatment technologies may also depend on site-specific factors, such as soil type and hydrogeology. For example, air sparging may be an effective treatment for VOCs at a site with sandy soil, but may not be effective at a site with tightly packed clay soil.

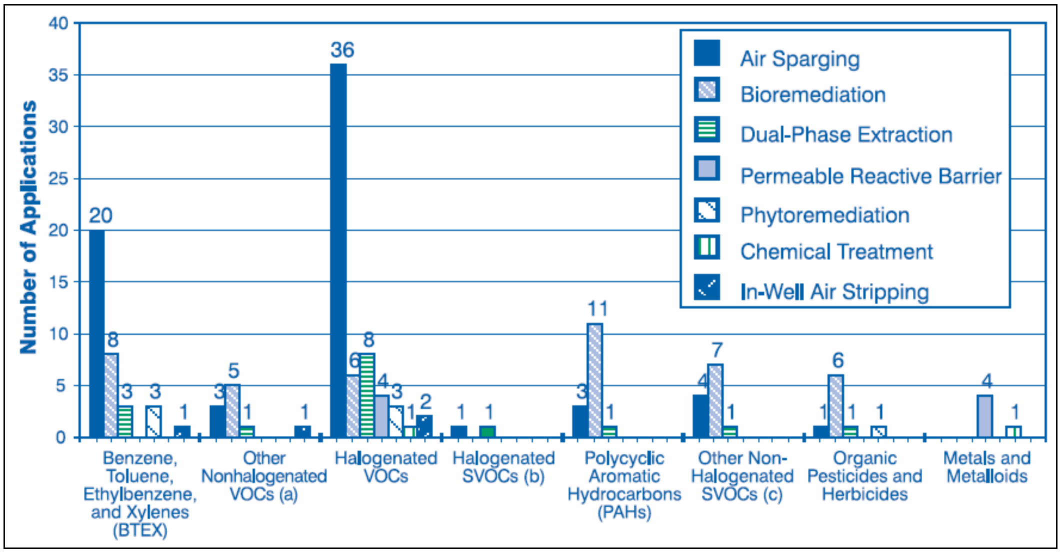


Figure 43: Contaminants Treated by In Situ Groundwater Treatment Technologies for Superfund Remedial Actions (FY 1982 - FY 1999)*
* SVOCs = Semivolatile organic compounds; VOCs = Volatile organic compounds;
a. Does not include benzene, toluene, ethylbenzene, and xylene (BTEX);
b. Does not include halogenated semivolatile pesticides and herbicides;
c. Does not include polycyclic aromatic hydrocarbons (PAH). (adapted from EPA 2001)

Figures 43 and 44 shows histogram plots of contaminants treated by in situ groundwater treatment technologies for Superfund remedial actions during periods FY 1982 - FY 1999 and FY1982-2002 respectively. The plots show the number of projects, type of contamination and number of selection of each treatment type. As Figure 43 shows, BTEX and halogenated VOCs are treated most frequently using air sparging. PAHs and other non-halogenated SVOCs, which are not as volatile as BTEX and halogenated VOCs, but can be destroyed through microbial processes, are treated most frequently by bioremediation.

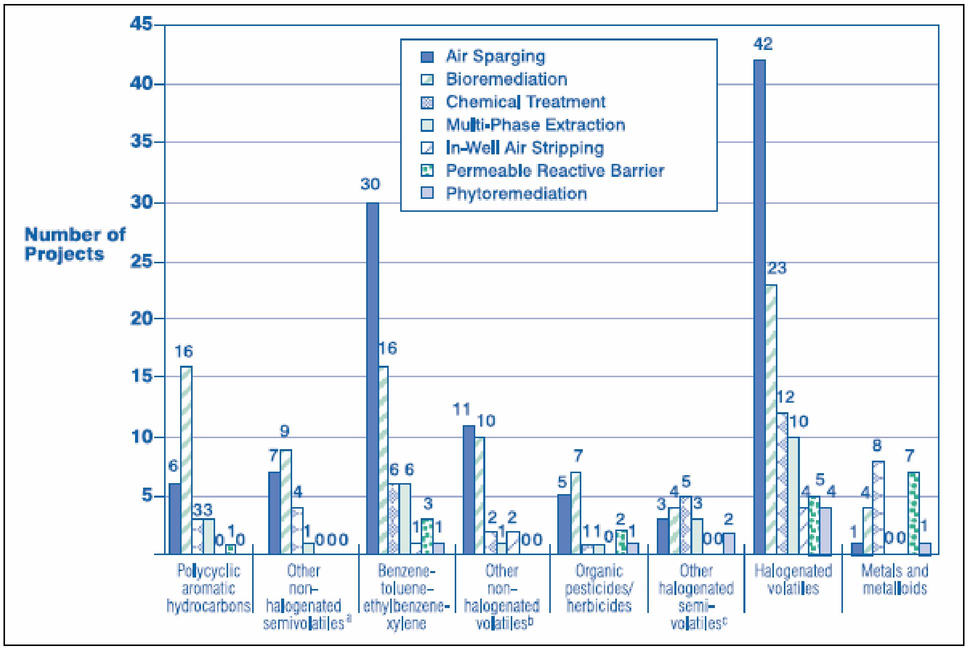


Figure 44: Superfund Remedial Actions: Contaminants Treated by In Situ Groundwater Technologies (FY 1982 - 2002)*
* Includes information from an estimated 70% of FY 2002 RODs.
a Does not include polycyclic aromatic hydrocarbons.
b Does not include benzene, toluene, ethylbenzene, and xylene.
c Does not include organic pesticides and herbicides. (adapted from EPA 2004)

Dissolved-phase halogenated VOCs may be difficult to remove from groundwater in low-permeability matrices using air sparging. Metals and metalloids are typically not amenable to air sparging, bioremediation, and multiphase extraction. One exception is the use of *in situ* bioremediation to reduce hexavalent chromium to its less toxic trivalent form. This technology, which uses biological activity to create conditions that result in chemical reduction of chromium, is being applied at three sites. At one additional site, bioremdiation to treat arsenic is currently planned. Metals and metalloids may undergo chemical reactions with certain substances to form compounds that are less toxic or mobile. The PRBs were used most often to treat halogenated VOCs, metals, and metalloids. Figure 44 shows more recent data (FY1982 – FY2002) and can be used to identify changes in the selection of technologies. For example, between FY1999 and FY2002, the number of projects selecting bioremediation technologies has double (43 to 89). For the most frequently selected technologies in the Superfund remedial program, the report analyzes similar selection trends over time, contaminant groups treated, quantity of soil and groundwater treated, status of project implementation and overall costs (fig. 43, 44).

Included below is a listing of several summarized facts taken from the EPA 2004 ASR.

Overall use of treatment at Superfund remedial action sites:

- At almost two-thirds (62%) of sites on the National Priorities List (NPL), the remedy already implemented or currently planned includes treatment of a source or groundwater (including groundwater P&T remedies).

- The complexity of RODs has been increasing. The proportion of RODs addressing both soil and groundwater contamination has increased from 20% in FY 1997 to 56% in FY 2002.
- Of the 2,610 RODs and ROD amendments signed from FY 1982 - 2002, 1,505 (58%) included treatment remedies.

Use of treatment for source control:

- The percentage of RODs selecting source control treatment as a remedy increased from 40% in FY 2000 to 52% in FY 2002 (about 70% of FY 2002 RODs were available for this report).
- *In situ* technologies make up 42% of all source control treatments at Superfund remedial action sites. Since the inception of the Superfund program in FY 1982, the use of in situ source control treatments at these sites has been increasing to the current level of 45% in FY 2002.
- *In situ* soil vapor extraction (SVE) is the most frequently used source control treatment technology (25% of source control projects), followed by ex situ solidification/stabilization (18%) and off-site incineration (12%).
- The percentage of completed source control treatment projects increased from 47% in FY 2000 to 54% in FY 2002.
- Innovative applications account for 21% of all source control treatments. Bioremediation is the most commonly applied innovative technology, representing about half of innovative applications for source control treatment.
- Approximately 75% of the source control treatment projects address organic contaminants. Just over 25% address metal or metalloid contaminants. Some of these projects address both organics and metals.
- Since FY 1982, nearly three times as much contaminated soil has undergone remediation by in situ treatment (40 million cubic yards [cy]) than by ex situ treatment (13 million cy). Approximately 42% (24 million cy) of the total volume of soil undergoing treatment is being treated by in situ SVE.

Use of treatment and MNA for groundwater:

- Groundwater treatment was part of the remedy at 71% of Superfund sites that selected a groundwater remedy.
- The percentage of groundwater RODs selecting *in situ* treatment as a remedy increased from none in FY 1986 to 24% in FY 2002.
- At 51% of NPL sites, a groundwater treatment remedy (including in situ groundwater treatment and P&T) is currently planned or already being implemented.
- For all remedies selected from FY 1982 - 2001, P&T was the most frequently selected groundwater remedy, followed by MNA and *in situ* treatment.
- The percentage of RODs selecting only MNA as a remedy for groundwater rose from 6% in FY 1986, when MNA was first selected without another groundwater treatment remedy, to a peak of 32% in FY 1998. However, this percentage has since decreased to 4% in FY 2002.
- The contaminants most commonly treated by groundwater P&T systems were chlorinated volatile organic compounds (VOC), nonchlorinated VOCs, metals, and metalloids.

- More than half of P&T systems use air stripping (biosparging) as a treatment technology. Other commonly used technologies include activated carbon adsorption, filtration, and metals precipitation.
- Most P&T projects (52%) are operational.

Long-Term Stewardship Program

Many of the completed waste sites at SRS are now in DOE's Long-Term Stewardship Program. Of the 300 completed waste sites, 27 are in the inspection and maintenance program. Inspections vary from monthly to annually. The program also includes scheduled inspections and maintenance activities on more than 2,000 groundwater monitoring wells sitewide. Long term monitoring conducted operations and maintenance at 13 remedial groundwater treatment systems and completed soil vapor extraction operations at the Miscellaneous Chemical Basin. Similar to any large industrial facility, construction and operation of SRS resulted in many significant adverse environmental impacts. However, the SRS Environmental Restoration Program has been the most active and successful program in the DOE complex in incorporating new technologies into its work to accelerate cleanup and reduce costs (Looney, 2000). Approximately 15,000 cubic feet of low-level radioactive waste, 17,000 cubic feet of hazardous and mixed waste, and 78,000 cubic feet of CERCLA sanitary waste were characterized, packaged, and shipped to proper disposal facilities. The SGCP closure program closes inactive waste sites and improves the quality of groundwater, site streams, and the Savannah River. SRS has treated more than 3 billion gallons of groundwater, removed more that 800 thousand pounds of contamination from soil and groundwater and has completed or is actively cleaning up more than 300 of its 500 contaminated acres. MNA in general and bioremediation technologies have played a significant role in these accomplishments.

The U.S. Department of Energy (DOE) is also taking steps to create a better understanding of their activities at SRS within the surrounding communities. Last November, Ms. Karen Adams of the Soils and Groundwater Project met with community leaders for a presentation on Monitored Natural Attenuation (MNA): Working with Nature to Clean Contaminated Groundwater. The goal of MNA Project at SRS is to support cleanup completion of groundwater contaminated with solvents at the site. One of the objectives is to improve the existing Environmental Protection Agency's (EPA) instructions by November 2006, to make MNA more user-friendly through better science, policy, cost-effective characterization and monitoring.

REFERENCES

American Academy of Environmental Engineers (1995). Innovative site remediation technology, Vol. 1: Bioremediation, ed. W.C. Anderson. Annapolis, Maryland.

American Society for Testing and Materials (1998). Standard guide for accelerated site characterization for confirmed or suspected petroleum releases, ASTM E 1912-98. Conshohocken, Pennsylvania.

American Society for Testing and Materials (1998). Standard guide for remediation of ground water by natural attenuation at petroleum release sites, ASTM E 1943-98. Conshohocken, Pennsylvania.

Anderson, T.A., E.A. Gutherie., and B.T. Walton (1993). “Bioremediation in the Rhizosphere”. Environmental Science and Technology 27: 2630-2636.

Balkwill, D.L., (1989) “Numbers, Diversity, and Morphological Characteristics of Aerobic Chemoheterotrophic Bacteria in Deep Subsurface Sediments from a Site in South Carolina.” Geomicrobiol. J. 7:33-52.

Black, H., (1995) Wisconsin gathers evidence to support intrinsic bioremediation. The bioremediation report, August: 6-7.

Borden, R.C., C.A. Gomez, and M.T. Becker (1995) Geochemical indicators of intrinsic bioremediation. Ground Water 33, no.2:180-89.

Brigmon, R.L., M. Saunders, D.L. Altman, E.W. Wilde, C.J. Berry, M. Franck, P. Mckinsey, S. Burdick, K. Sessions, A. Stanhope, and C. Tuckfield (2001) FY01 Phytoremediation of Chlorinated Ethenes in the Southern Sector of Seepline Sediments of the Savannah River Site. WSRC-TR-2001-00437.

Cook, J (2002) Comprehensive Environmental Management System Approach:The Right Tool for Stewardship, Savannah River Technology Center Aiken, South Carolina, WSRC-MS-2002-00651

Forster, J. (1995) “Determination of Soil pH”. In K. Alef and P. Nammipieri (Eds.). Methods in Applied Soil Microbiology and Biochemisty. Academic Press.

Gilbert, R.O. (1987) Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold Co., New York, NY, 320p.

Hinchee, R.E., J.T. Wilson, and D.C. Downey. (1995) Intrinsic bioremediation. Columbus, Ohio: Battelle Press.

Hobbie J. E., Daley, R. J., Jasper, S. (1977) “Use of Nuclepore Filters for Counting Bacteria by Fluorescence Microscopy. Appl. Env. Microbiol.13:1225-1229

Karscig, T. Newman, R. S. Crampton, R. A. Hashmonay, M.G. Yost, P. E. Heilman, J. Duffy, M. P. Gordon and S.E. Strand, (1999) "Remediation of Trichloroethylene in an Artificial Aquifer with Trees: A Controlled Field Study," Environmental Science and Technology 33:2257-2265.

Klecka, G.M., J.T. Wilson, E. Lutz, N. Klier, R. West, J. Davis, J. Weaver, D. Kampbell, and B. McAllister, P.M., and C.Y. Chiang. 1993. A practical approach to evaluating natural attenuation of contaminants in groundwater. Groundwater Monitoring & Remediation 14, no.2:161-73.

McNab, W.W., Jr. and B.P. Dooher. (1998) A critique of a steady-state analytical method for estimating contaminant degradation rates. Ground Water 36, no.6:983-87.

Newman, L.A., X. Wang, I.A. Muiznieks, G. Ekuan, M. Ruszaj, R. Cortellucci, D. Domroes, G. New Jersey Department of Environmental Protection (1996) Site remediation program, technical requirements for site remediation, proposed readoption with amendments: N.J.A.C. 7:26E, authorized by Robert J. Shinn, Jr., Commissioner.

Norris, R.D., R.E. Hinchee, R.A. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward. (1994) Handbook of bioremediation. Boca Raton, Florida: Lewis Publishers.

Salanitro, J.P. (1993) The role of bioattenuation in the management of aromatic hydrocarbon plumes in aquifers. Groundwater Monitoring & Remediation 13, no. 4:150-61.

U.S. Department of the Army. (1995) Interim Army policy on natural attenuation for environmental restoration, (12 September) Memorandum from the Assistant Chief of Staff for Installation Management. Washington, D.C.: the Pentagon.

U.S. Department of Energy (1995) In Situ Bioremediation Using Horizontal Wells; Innovative Technology Summary Report. Office of Environmental Management/Office of Technology Development. Aiken, SC.

U.S. Department of Energy, (1996) In Situ Bioremediation of Using Horizontal Wells, Demonstrated at M-Area, Savannah River Site. Office of Environmental Management, Office of Technology Development. Aiken, SC.

U.S. Department of Energy, (1999) Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites. Office of Environmental Restoration.

U.S. Department of Energy, (1999) Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites. Office of Environmental Restoration.

U.S. Environmental Protection Agency (1978). Radionuclide interactions with soil and rock media, Vol. 1: Element chemistry and geochemistry, EPA 520/6-78-007, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1988a) Section 5.3.3.1. Natural attenuation with monitoring. Guidance on remedial actions for contaminated groundwater at Superfund sites, OSWER Directive 9283.1-2, EPA/540/G-88/003, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1988b). Groundwater modeling: an overview and status report, EPA/600/2-89/028, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1989) Methods for evaluation attainment of cleanup standards, Vol. 1: Soils and solid media, EPA/230/02-89-042, Office of Solid Waste. Washington, D.C.

U.S. Environmental Protection Agency (1990a) National oil and hazardous substances pollution contingency plan (NCP); final rule, Federal Register 55, no. 46:8706 and 8733-34. Washington, D.C.

U.S. Environmental Protection Agency (1990b). Corrective action for releases from solid waste management units at hazardous waste management facilities; proposed rule, Federal Register 55, no. 145:30825 and 30829. Washington, D.C.

U.S. Environmental Protection Agency (1990c) Suggested ROD language for various ground water remediation options, OSWER Directive 9283.1-03, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1991a). Guide to developing Superfund no action, interim action, and contingency remedy RODs, Superfund Publication 9355.3-02FS (Fact Sheet), Office of Emergency Remedial Response. Washington, D.C.

U.S. Environmental Protection Agency (1991b). A guide to principal threat and low level threat wastes, Superfund Publication 9380.3-06FS (Fact Sheet, November version), Office of Emergency Remedial Response. Washington, D.C.

U.S. Environmental Protection Agency (1992a). Final comprehensive state ground water protection program guidance, EPA 100-R-93-001, Office of the Administrator. Washington, D.C.

U.S. Environmental Protection Agency (1992c). Quality assurance and control in the development and application of ground-water models, EPA/600/R-93/011, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1993a). Guidance for evaluating the technical impracticability of ground-water restoration, OSWER Directive 9234.2-25, EPA/540-R-93-080, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1993b). Guidance document on the statistical analysis of ground-water monitoring data at RCRA facilities, Office of Solid Waste. Washington, D.C.

U.S. Environmental Protection Agency (1993c). Data quality objectives process for Superfund: Interim final guidance, EPA/540-R-93-071, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1993d). Methods for evaluation attainment of cleanup standards, Vol. 2: Ground Water, EPA/230/R-92/014, Office of Policy, Planning, and Evaluation. Washington, D.C.

U.S. Environmental Protection Agency (1993e). Compilation of ground-water models, EPA/600/R-93/118, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1994a). Proceedings of symposium on natural attenuation of groundwater, EPA/600/R-94/162, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1994b). Methods for monitoring pump-and-treat performance, EPA/600/R-94/123, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1994c). EPA requirements for quality assurance project plans (QAPP) for environmental data operations, EPA/QA/R-5, Office of Water. Washington, D.C.

U.S. Environmental Protection Agency (1994d). The hydrocarbon spill screening model (HSSM), Vol. 1: User's guide, EPA/600/R-94-039a, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1994e). Assessment framework for groundwater model applications, OSWER Directive 9029.00, EPA 500-B-94-003, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1994f). Ground-water modeling compendium, EPA 500-B-94-004, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1994g). A technical guide to ground-water model selection at sites contaminated with radioactive substances, EPA 402-R-94-012, Office of Air and Radiation. Washington, D.C.

U.S. Environmental Protection Agency (1994h). Guidance for conducting external peer review of environmental models, EPA 100-B-94-001, Office of Air and Radiation. Washington, D.C.

U.S. Environmental Protection Agency (1994i). Report of the agency task force on environmental regulatory modeling, EPA 500-R-94-001, Office of Air and Radiation. Washington, D.C.

U.S. Environmental Protection Agency (1995). The hydrocarbon spill screening model (HSSM), Vol. 2: Theoretical background and source codes, EPA/600/R-94-039b, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1995a). Chapter IX: Natural attenuation. How to evaluate alternative cleanup technologies for underground storage tank sites: A guide for corrective action plan reviewers, EPA 510-B-95-007, Office of Underground Storage Tanks. Washington, D.C.

U.S. Environmental Protection Agency (1995b). Guidance for data quality assessment, EPA/QA/G-9, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1995c). Guidance for the preparation of standard operating procedures (SOPs) for quality-related documents, EPA/QA/G-6, Quality Assurance Division. Washington, D.C.

U.S. Environmental Protection Agency (1996a). Presumptive response strategy and ex-situ treatment technologies for contaminated ground water at CERCLA sites, Final Guidance, OSWER Directive 9283.1-12, EPA 540-R-96-023, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1996b). Corrective action for releases from solid waste management units at hazardous waste management facilities; advance notice of proposed rulemaking, Federal Register 61, no. 85:19451-52.

U.S. Environmental Protection Agency (1996c). Documenting ground-water modeling at sites contaminated with radioactive substances, EPA 540-R-96-003, Office of Air and Radiation. Washington, D.C.

U.S. Environmental Protection Agency (1996d). Three multimedia models used at hazardous and radioactive waste sites, EPA 540-R-96-004, Office of Air and Radiation. Washington, D.C.

U.S. Environmental Protection Agency (1996e). Notes of Seminar--Bioremediation of hazardous waste sites: Practical approaches to implementation, EPA 510-B-95-007, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1997a). Proceedings of the symposium on natural attenuation of chlorinated organics in groundwater; Dallas, Texas, September 11-13, EPA/540/R-97/504, Office of Research and Development. Washington, D.C.

U.S. Environmental Protection Agency (1997b). The role of CSGWPPs in EPA remediation programs, OSWER Directive 9283.1-09, EPA F-95-084, Office of Solid Waste and Emergency Response. Washington, D.C.

U.S. Environmental Protection Agency (1997c). (Draft) Geochemical processes affecting sorption of selected contaminants, Office of Radiation and Indoor Air. Washington, D.C.

U.S. Environmental Protection Agency (1997d) (Draft) The K model and its use in D contaminant transport modeling, Office of Radiation and Indoor Air. Washington, D.C.

U.S. Environmental Protection Agency (1998a). Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water, EPA/600/R-98/128, National Risk Management Research Laboratory, Ada, Oklahoma.

U.S. Environmental Protection Agency (1998b). Policy and program requirements for the mandatory agency-wide quality system, EPA Order 5360.1 CHG 1, Office of Research and Development, Washington, D.C.

U.S. Environmental Protection Agency (2004) Treatment Technologies for Site Cleanup: Annual Status Report (eleventh edition), EPA-542-R-03-009

U.S. Environmental Protection Agency, Air Force, Army, Navy, and Coast Guard (1996a) Commonly asked questions regarding the use of natural attenuation for chlorinated solvent spills at federal facilities, Fact Sheet, Federal Facilities Restoration and Re-Use Office. Washington, D.C.

U.S. Environmental Protection Agency, Air Force, Army, Navy, and Coast Guard (1996b) Commonly asked questions regarding the use of natural attenuation for petroleum contaminated sites at federal facilities, Fact Sheet, Federal Facilities Restoration and Re-Use Office. Washington, D.C.

Westinghouse Savannah River Company (1998) Methane Enhanced Bioremediation for the Destruction of Trichloroethylene Using Horizontal Wells. Technology Catalog Site Remediation Profiles.

Westinghouse Savannah River Company (2003) Summary Document of Workshops for Hanford, Oak Ridge and Savannah River Site as part of the Monitored Natural Attenuation and Enhanced Passive Remediation for Chlorinated Solvents – DOE Alternative Project for Technology Acceleration. Savannah River Site Aiken, SC WSRC-RP-2003-1044

Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen (1995) Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. United States Air Force Center for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, San Antonio, Texas.

Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, J.E. Hansen, and P. Haas (1996) Technical protocol for evaluating the natural attenuation of chlorinated ethenes in groundwater. Proceedings of the petroleum hydrocarbons and organic chemicals in groundwater: Prevention, detection, and remediation conference, Houston, Texas, November 13-15.

Wilson, J.T., D.H. Kampbell, and J. Armstrong (1993) Natural bioreclamation of alkylbenzenes (BTEX) from a gasoline spill in methanogenic groundwater. Proceedings of the second international symposium on in situ and on site bioremediation, San Diego, California, April 5-8.

Wilson. (1996) Intrinsic remediation of chlorinated solvents in groundwater. Proceedings of intrinsic bioremediation conference, London W1, United Kingdom, March 18-19.

Wisconsin Department of Natural Resources (1993) ERRP issues guidance on natural biodegradation. Release News, Emergency and Remedial Response Section, February, vol. 3, no.

OTHER SOURCES OF INFORMATION

http://www.epa.gov/ORD/WebPubs/biorem/
EPA Office of Research and Development, information on passive and active bioremediation
http://www.epa.gov/ada/kerrlab.html
EPA Office of Research and Development, R.S. Kerr Environmental Research Laboratory
http://www.epa.gov/OUST/cat/natatt.htm
EPA Office of Underground Storage Tanks, information on natural attenuation
http://www.epa.gov/swerffrr/chlorine.htm
EPA Federal Facilities Restoration and Reuse Office, fact sheet on natural attenuation of chlorinated solvents
http://www.epa.gov/swerffrr/petrol.htm
EPA Federal Facilities Restoration and Reuse Office, Fact sheet on natural attenuation of petroleum contaminated sites
http://www.epa.gov/hazwaste/ca/subparts.htm
EPA Office of Solid Waste, information on RCRA Subpart S
http://www.epa.gov/swerosps/bf/
EPA Office of Outreach Programs, Special Projects, and Initiatives, information on Brownfields
http://www.epa.gov/oerrpage/superfnd/web/programs/clp/quality.htm
EPA Office of Emergency and Remedial Response, information on data quality
http://es.epa.gov/ncerqa/qa/qatools.html
EPA Office of Research and Development, National Center for Environmental Research and Quality Assurance, information on data quality, quality assurance and quality control
http://clu-in.com
EPA Technology Innovation Office, information on hazardous site cleanups

GLOSSARY AND ACRONYMS

Abiotic – Nonbiological process; also used to refer to nonbiological degradation process.
Accuracy – the ability of an analytical method to measure the true concentration of a contaminant (see bias, precision).
Actinides – radioactive elements with atomic numbers equal to or greater than that of actinium (i.e., 88). The term refers to the heaviest elements, starting with actinium and continuing to the end of the periodic table. Transuranic elements are a subset of the actinide elements and include those with atomic numbes larger than uranium. Actinide elements are all radioactive.
Activity – the mean number of decays per unit time of a radioactive nuclide expressed as disintegrations per second. Units: becquerel (Bq), formerly curie (Ci).
Adsorption – Removal of a substance from air or water by collecting the substance on the surface of a solid material; process used in pollution control systems such as activated carbon adsorption systems.
Advection – The process of transfer of fluids (vapors or liquid) through a geologic formation in response to a pressure gradient that may be caused by changes in barometric pressure, water table levels, wind fluctuations, or infiltration.
Aerobic – Condition in which oxygen is present; also used to refer to a type of microbe that requires oxygen to live and reproduce.
Aerobic oxidation (cometabolic) – Microbial breakdown of a contaminant during which a contaminant is oxidized by an enzyme or cofactor produced during microbial metabolism of another compound with oxygen. In such a case, the oxidation of the contaminant does not yield any energy or growth benefit for the microbe mediating the reaction.
Aerobic oxidation (direct) – Microbial breakdown of a compound during which the compound serves as an electron donor and as a primary growth substrate by the microbe mediating the reaction. Electrons that are generated by the oxidation of the compound are transferred to oxygen.
Aerodynamic diameter (AD) – the physical diameter of a particle of unit density (1 gram per cubic centimeter) that has the same gravitational settling velocity as the particle of interest.
Aerosol – a suspension of solid and/or liquid particles in a gas (like air).
Air- or bio-sparging – 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.
Air filter – a solid matrix used in an air sampler to collect particulates from the air, which is drawn by an air pump through the filter. Air filters are least efficient for particle sizes of about 0.3 microns and collect smaller and larger particles more efficiently.
A-line – the facility in the F-Area where uranyl nitrate was converted to uranium oxide.
Aliquot – a fraction of a substance taken for sampling purposes.
Ambient air monitoring – monitoring of the air outside of buildings (see effluent monitoring).
Analytical method – a laboratory test used to detect the amount of a contaminant.
Anaerobic – Condition in which no oxygen is present; also used to refer to a type of microbe that is able to live and reproduce in the absence of oxygen.
Anaerobic reductive dechlorination (cometabolic) – A biodegradation reaction in which a chlorinated hydrocarbon is reduced by an enzyme or cofactor produced during microbial metabolism of another compound in an environment devoid of oxygen. In such a case, biodegradation of the chlorinated compound does not yield any energy or growth benefit for the microbe mediating the reaction.

Anaerobic reductive dechlorination (direct) – A biodegradation reaction in which bacteria gain energy and grow as one or more chlorine atoms on a chlorinated hydrocarbon are replaced with hydrogen in an environment devoid of oxygen. In the reaction, the chlorinated compound serves as the electron acceptor and hydrogen serves as the direct electron donor. Hydrogen used in this reaction typically is supplied indirectly by the fermentation of organic substrates. The reaction is also referred to as halorespiration or dehalorespiration.

Anisokinetic sampling – a sampling condition that involves a mismatch between the air or \fluid velocity in the sampling probe and that in the stack releasing airborne effluents. It is a source of bias in effluent sampling. In contrast, isokinetic sampling, in which the two velocities are equal, results in an unbiased sample of the stack effluent.

Atomic number – the number of protons in the nucleus of an atom.

Background radioactivity – radioactive elements in the natural environment including those in the crust of the earth (like radioactive potassium, uranium, and thorium isotopes) and those produced by cosmic rays. The term background is also sometimes used in this report to indicate radioactive elements present in the environment that are not a direct result of SRS activities (e.g. atmospheric weapons testing fallout, see definition for fallout). The term background can also refer to chemicals, such as heavy metals.

Beta particle (ionizing radiation) – a charged particle emitted from the nucleus of certain unstable atomic nuclei (radioactive isotopes), having the charge and mass of an electron. Energetic beta particles penetrate the dead skin layer. The beta particle is not stopped in matter as quickly as an alpha particle.

bgs – below ground surface

Bias – a systematic distortion of measurements that makes the results inaccurate. Accuracy is a measure of how close a value is to the true number, or a measure of the correctness of a measurement. Precision refers to the ability of an analytical method to reproduce the same result upon repeated trials.

Bioaugmentation – The addition of 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 aboveground reactors or from specially cultivated strains of bacteria having known capabilities to degrade specific contaminants.

Bioavailability –

Bioenergetics – The energy and mass transfer kinetics that are defined by microbial cell metabolism.

Biomass – All the living material in a given area.

Bioremediation – A process by which microorganisms, fungi, and plants degrade pollutant chemicals through use or transformation of the substances.

Biota – living organisms.

Bioventing – see Air- Bio-sparging.

B-line – the facility in which plutonium nitrate solution was purified and converted into plutonium metal.

Blanks – samples containing extremely low concentrations of a contaminant, which are used to assess contamination from laboratory equipment and other steps in an analytical procedure.

Burial grounds – radioactive waste disposal areas located between the two separations areas, 200-F and 200-H. One disposal area was 76 acres used from 1953 until 1972; the other, 119-acre site, was used from 1972 until the 1990s.

Capillary forces – Forces that govern fluid flow through small diameter pathways, such as in subsurface soil particles.

Canyon – the long, narrow, and deep, thick-walled concrete structure in which fissionable materials that had been irradiated in the reactors were chemically separated from fission products and from each other. The hot canyon was the more heavily shielded canyon in which the majority of the fission products were removed and the desired products were separated. The less heavily shielded canyon was referred to as the warm canyon.

cfm – cubic feet per minute, a measure of the rate of flow of a liquid or gas.

Chemical symbols – abbreviations for different elements and compounds. Examples of symbols for elements include U for uranium, Pu for plutonium, O for oxygen, C for carbon and Cl for chlorine. Examples of symbols for compounds include CCl_4 for carbon tetrachloride and PuO_2 for plutonium dioxide.

CIIS (Chemical Information and Inventory System) Database – a database originally developed at SRS to comply with Community/Worker-Right-to-Know legislation and to help organize annual inventory data for EPA reporting requirements. The database inventory contains over 51,000 entries.

CMX – the code letters designating a facility that developed and tested various reactor components.

Collection efficiency – the percentage of the total amount of a contaminant present in ambient air, which is collected by an air sampler. Collection efficiency is strongly dependent upon the size of the particles that carry the contamination, as well as other factors, such as wind speed.

Compositing – a combining of samples before analysis, usually done to improve sensitivity and/or reduce analytical cost. A quarterly composite of air filters is comprised of all filters collected within a calendar quarter (3 months).

Concentration – the amount of a material of interest in a given volume or mass.

Contamination – unwanted radioactive or other material or the deposition of radioactive material in the environment or other place.

Chlorinated aliphatic hydrocarbons (CAHs) – Manmade, chlorine-containing organic compounds widely used as solvents and degreasers in various industries. Typical CAHs include tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC).
Confining layer Impermeable layer (such as clay) that impedes the vertical migration of groundwater or NAPL.

Dana Plant – a facility in Dana, Indiana which produced heavy water by the GS process.

Degraded water – heavy water that became diluted with light or natural water.

Degreasers – large vats located in the M Area that contained heated and cooled solvents that were used to remove grease from reactor components.

Detection level – the lowest amount of a contaminant which can be detected with a certain degree of confidence by an analytical method. For radioactivity measurements, detection level is the same as minimum detectable activity (See also minimum detectable concentration, MDC, and lower limit of detection, LLD).

Deuterium – synonym for 2H, an isotope of hydrogen of double mass (atomic mass = 2).

Disintegration – one decay of a radioactive atom. (See dpm).

Deuterium oxide (D_2O) – heavy water.

DOE – U.S. Department of Energy. The DOE is responsible for the sites in the U.S. at which weapons materials have been produced or handled, including the Savannah River Plant.

Generally, private contractors, such as Du Pont have operated the weapons facilities for the DOE. (See ERDA, AEC.)

Domain – the area considered within the study. For this dose reconstruction the domain extends 50 miles in all directions from the SRS boundary; the domain also includes Columbia, SC and an area on either side of the Savannah River to the coast.

Dose – a general term denoting the quantity of radiation or energy that is absorbed by the body. There are technical terms with specific definitions, such as absorbed dose, equivalent dose, and effective dose.

Dose reconstruction – a study process in which historical information is used to estimate the amounts of toxic materials released from a facility, how the materials could have moved offsite, and the exposure of the public to those materials. Dose reconstruction involves past releases, not present, or future releases. The study period for this Savannah River Site dose reconstruction is 1951–1992.

dpm – abbreviation for disintegrations per minute, a rate of radioactive decay. There are 2.22 dpm per picocurie. (See curie.)

DW Process – a separation process which involved the separation of light and heavy water by fractional distillation. The DW (distillation) process uses the difference in volatility between hydrogen oxide (H_2O) and deuterium oxide (D_2O) in the water to separate them using five stages of distillation in bubble cap tray towers.

Du Pont – the Atomic Energy Commission appointed Du Pont to operate the site in 1950. They ran the site until March 30, 1989 when Westinghouse Savannah River Company took over the responsibility.

Degradation – Chemical or biological breakdown of a complex compound into simpler compounds. The breakdown may occur as a result of a single reaction or multiple reactions.

Dense non-aqueous phase liquid (DNAPL) – Chlorinated solvents that are minimally soluble in water, more dense than water, and present in concentrations large enough to form pools of free liquid. DNAPLs tend to sink and accumulate on a non-permeable layer (aquitard) at the bottom of a confined aquifer.

Diffusion – The movement of suspended or dissolved particles (or molecules) from an area of higher concentration to one in which concentrations are lower. This process tends to distribute the particles or molecules more uniformly.

Dispersion – The process by which a substance or chemical spreads and dilutes in flowing groundwater or soil gas.

Electron acceptor – A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors, such as organic compounds (or sometimes reduced inorganic compounds, such as sulfide), to an electron acceptor. Electron acceptors are compounds that are reduced during the process and include oxygen; nitrate; iron (III); manganese (IV); sulfate; carbon dioxide; or, in some cases, chlorinated aliphatic hydrocarbons, such as carbon tetrachloride, PCE, TCE, DCE, and VC.

Electron donor – A compound capable of supplying (giving up) electrons during oxidation/reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors, such as organic compounds (or sometimes reduced inorganic compounds, such as sulfide), to an electron acceptor. Electron donors are compounds that are oxidized during the process and include fuel hydrocarbons and native organic carbon.

Enhanced bioremediation – Bioremediation of organic contaminants by microbes supplemented by increasing the concentration of electron acceptors, electron donors, or nutrients in groundwater, surface water, and soil.

Effluent – a gas or liquid that flows from a process, building, or site into the surrounding environment.

Effluent monitoring – the measurement of a contaminant or other property (e.g. flow rate) in the effluent (air or liquid discharged) from a building or holding pond.

EML – Environmental Measurements Laboratory (see HASL).

Environmental monitoring – the measurement of a material in the environment at regular time intervals. Monitoring for contaminants often involves the collection of an environmental sample, (like stream water), preparation of the sample in the laboratory, and analysis of the prepared sample using an analytical instrument.

Environmental transport – the mechanisms by which substances can be carried from their source to other points in the environment. Surface water runoff and air dispersion by wind are examples of environmental transport mechanisms.

Exposure (to hazardous substances) – conditions or circumstances causing humans or other living things to come into contact with toxic materials.

Exposure pathways – the means by which humans are exposed to toxic substances. The key exposure pathways are air and water, with most exposures via inhalation, drinking water, crops, other foods, and direct radiation.

Exogenous bacteria (also called nonindigenous) – Bacteria that have been obtained from a source other than the native site.

Groundwater recirculation treatment system – A closed-loop, hydraulically-contained system based on a design of downgradient extraction and upgradient injections wells; sometimes referred to as a recirculating treatment cell.

Hydrophobicity – Tendency to repel water.

Geometric Mean (GM) – a measure of the central point of a skewed distribution. The geometric mean of a set of positive numbers is the exponential of the arithmetic mean of their logarithms. It is typically used to describe skewed distributions (e.g. lognormal distributions).

Geometric Standard Deviation (GSD) – a measure of the spread of a skewed distribution. A large GSD indicates a wide range of measured or calculated values. The geometric standard deviation of a lognormal distribution is the exponential of the standard deviation of the associated normal distribution.

Grab samples – samples, usually of relatively small volume, which are taken at random or at pre-selected frequencies. These samples define the concentration of a contaminant at the specific time when they are collected and differ from continuous or proportional samples that reflect a time-averaged concentration.

Gross alpha – measurements that refer to the total (or gross) amount of alpha particles in an environmental sample. Besides materials released from the Savannah River Plant, like plutonium and americium, naturally occurring substances in the environment, like uranium and thorium, emit alpha particles and would contribute to the gross alpha measurement.

Gross beta – measurements that refer to the total (or gross) amount of beta particles in an environmental sample.

GS process – the method of extracting heavy water containing deuterium from naturally occurring water by the exchange of deuterium between water and hydrogen sulfide (H_2S) at different temperatures. The deuterium will migrate toward a water stream at lower temperatures and to H_2S at higher temperatures.

Half-life, radioactive – the time required for half the atoms of a radioactive substance to disintegrate. During one half-life, the number of radioactive atoms in a material is reduced by one-half. Each radionuclide has a unique half-life. Tritium decays with a half-life of 12.3 years, and plutonium-239 decays with a half-life of about 24,000 years. The term half-life can also be used to describe the time required for the amount of a radionuclide or chemical in a biological compartment (e.g., vegetation, sediment, water, human or other animal tissue) to be reduced by one-half.

HASL – the Health and Safety Laboratory, in New York City, operated by the Department of Energy and its predecessors, is known for long-term global monitoring of radionuclides in the environment and for development of analytical techniques for measuring radioactivity in environmental media. Later became known as the Environmental Measurements Laboratory (EML).

Health physics – an interdisciplinary science focused on the radiation protection of humans and the environment. Health physics combines the elements of physics, biology, chemistry, statistics, and electronic instrumentation to protect individuals from the effects of radiation.

Heavy water – water in which nearly all of the hydrogen is the heavy isotope, deuterium; deuterium oxide (D_2O).

Heavy Water Plant – a facility in the D-Area at SRS that began producing heavy water (deuterium oxide) in 1953 to moderate and cool the site's reactors. The facility stopped production in 1981 because there was a sufficient supply of heavy water.

HEPA filter – a high-efficiency particulate air filter used to remove contaminants from exhaust gases prior to discharge.

HM process – an acronym for "H-Modified," the HM process was a modified Purex process, used in the H Canyon to separate uranium from plutonium, neptunium, and other fission products. The Purex process was used in H Canyon prior to the May 1959 startup of the HM process.

Ingestion – radionuclides or chemicals taken into the body by eating or drinking are taken in by ingestion.

Inhalation – radionuclides or chemicals taken into the body by breathing are inhaled.

Inventory – the total amount of a contaminant in a defined space, e.g. the amount of plutonium in the sediment of a reservoir.

Ion exchange – a process for selective removal of a chemical constituent from a particular solution.

Isotopes – different forms of elements having the same atomic number (number of protons) but different numbers of neutrons. Different isotopes of a particular element generally have essentially identical chemical properties. Plutonium-239 and plutonium-240 are isotopes of plutonium that can not be distinguished from one another by typical analytical methods.

Leachate - the liquid that is the product of the liquid content of the waste, infiltrating precipitation, and ground water if the waste is below the water table.

Media – a type of environmental sample, such as air, soil, vegetation or water.

Median – the central point of a distribution. Half of the values are larger than the median value and half are smaller. (See percentiles.)

Metabolic – Having to do with the energy producing processes conducted in cells.

Methanogenic – Referring to the formation of methane by certain anaerobic bacteria during the process of anaerobic fermentation.

Micron (μm) – a micrometer or micron is a unit of length equal to one-millionth (10-6) of a meter. A human hair, for reference, is about 100 microns thick.

Minimum detectable concentration (or activity) – the lowest concentration of a contaminant (or amount of radioactivity) that can be detected with a certain degree of confidence by an analytical method (see detection level).

Moderator – a material used in a reactor to slow down neutrons; when neutrons collide with nuclei, they lose speed, making them more likely to be captured by fuel or target materials.

Monitored natural attenuation (also known as Passive bioremediation) – Use of natural subsurface processes, such as dilution, volatilization, biodegradation, adsorption, and chemical reactions with subsurface materials to reduce contaminant concentrations.

Monitoring – obtaining measurements at regular time intervals.

Monte Carlo procedure – a method that uses computer-generated pseudo-random numbers to make calculations with statistical distributions. In this study, Monte Carlo methods have been used to estimate statistical distributions that represent uncertainties in estimated quantities, such as source term release estimates. This approach contrasts with a deterministic approach in which a calculation is based upon point estimates of the various parameters and yields a single result. The Monte Carlo calculation carries the underlying uncertainty in the parameters forward and displays it in the magnitude of the distribution of results. A statistical risk management computer program, called Crystal Ball™ (Decisioneering, 1993) was used in this study for some of the uncertainty analyses.

Nutrients – Elements required for microbial growth. In bioremediation, the term generally refers to elements other than carbon, hydrogen, and oxygen that are required to promote the growth of bacteria. Typical nutrients include nitrogen and phosphorus.

Nuclear materials – materials used to produce a nuclear reaction such as uranium and plutonium.

Nuclide – a species of atom having a specific mass, atomic number, and nuclear energy state.

Outcrop – a place where groundwater is discharged to the surface. At SRS, groundwater outcrops in several places to enter site streams. (Also referred to as seepline)

Percentiles – a method for making descriptive statements about a large data set. Percentiles are defined in such a way that a large set of data, arranged from its smallest to its largest value, is divided by its percentiles into 100 classes containing nearly equal numbers of data. The exact rules for defining the percentile numbers are complicated, but the effect is that approximately 5% of the data are less than or equal to the 5th percentile, and approximately 95% of the data are greater than or equal to the 5th percentile (similar statements hold for the other percentiles). The median is defined as the 50th percentile, which divides the data (approximately) into halves (if there are an odd number of data, the middle value is the median; if there are an even number, the average of the two middle values is the median). In this document, uncertainty distributions are indicated by their 5th, 50th, and 95th percentiles. Observations above the 95th percentile have only a 5% probability of occurrence, as do observations below the 5th percentile. The 50th percentile is presented as the best estimate.

pico – a prefix that multiplies a basic unit by 1/1,000,000,000,000 or 1 x 10–12. For example, 1 picocurie equals 1 x 10^{-12} curie, or one-trillionth of a curie.

Plume – the concentration profile of an airborne or waterborne release of material as it spreads from its source. A plume from a coal-fired power plant, for example, may be visible for some distance from its stack, with the concentration of its components decreasing with distance from the stack and from the centerline of the plume. After the plume becomes invisible because of dilution, it continues to be diluted with increasing time and distance. Atmospheric dispersion models of this process predict concentrations within a plume far downwind and far beyond the point at which a plume becomes invisible. Similar modeling for releases from nuclear facilities can estimate the impacts of releases long past by reconstructing exposure and dose estimates.

Plutonium (Pu) – silvery, white radioactive metal (atomic number 94) used in casting, rolling and forming, and machining and final assembly of nuclear weapons components. Its most important isotope is plutonium-239, produced by neutron irradiation of uranium-238. Plutonium-239 decays by emitting alpha particles and has a 24,065-year half-life.

Precision – the ability of an analytical method to reproduce the same result upon repeated trials. (See bias.)

Purex process – a process to separate uranium and plutonium from each other and from fission products by means of solvent extraction. The solvent used at the SRS was a solution of tributyl phosphate in “Ultrasene,” a high-grade kerosene. The process was used in the F Canyon. The HM process replaced the Purex process in 1959.

Purging – releasing the water from the reactor basins to the seepage basins, allowing the tritium to evaporate.

QA/QC – quality assurance/quality control programs are established to assure accurate and reproducible results from environmental monitoring.

Radiation – energy moving in the form of particles or waves. Familiar radiations are heat, light, radio waves, and microwaves. Ionizing radiation is a very high frequency form of electromagnetic radiation. It is invisible and cannot be sensed without the use of detecting equipment.

Reactor – the nuclear reactors in the 100 areas at the SRS.

Red-oil explosion – an explosion that can result from the presence of organic materials with nitric acid (NOx) and high temperature; the rapid exothermic nitration of the organic material can lead to a “red-oil explosion.”

Sand filters – at SRS, these underground filters were rectangular concrete structures with beds made of layers of coarse stone and succeeding layers of finer and finer gravel and sand for a total filter depth of about 8.5 feet. They were designed to filter the air exhausted from the canyon buildings.

Seepage basins – unlined excavated bowl-shaped areas for receiving liquid wastes from numerous facilities onsite. They were designed to allow infiltration of the liquid into the ground, thus decreasing the total volume of liquid released to onsite streams. The first seepage basins were put into operation in 1954.

Seepline – see outcrop.

Sensitivity – ability of an analytical method to detect small concentrations of a contaminant.

Separation areas – the F-Area and H-Area where fissionable materials that had been irradiated in the reactors were chemically separated from fission products and from each other.

Sorption – The action of soaking up or attracting substances; a general term used to encompass the processes of absorption, adsorption, ion exchange, and chemisorption.

Substrate – A source of energy or molecular building block used by a microorganism to carry out biological processes and reproduce.

Source term – the quantity, chemical and physical form, and the time history of contaminants released to the environment from a facility.

Spatial trend (or spatial distribution) – a description of how a contaminant is distributed in the environment, for example with distance away from the facility. Two-dimensional trends in measurements are sometimes illustrated with isopleths.

Spiked samples – samples to which a known amount of the contaminant has been purposefully added to assess the accuracy of an analytical method.

Strike – a type of precipitation (head end) process in the separations area in which manganese nitrate and potassium permanganate were added to a treatment tank to form a manganese oxide precipitate.

Tank farm – series of interconnected underground tanks used at SRS for storage of high-level radioactive liquid wastes.

Time trend (or temporal trend) – a description of how the concentration of a contaminant changes over time at the same place.

Toxicity assessment – an evaluation of the types of health effects usually caused by specific substances, and the quantity (or dose) required to cause the effects.

Toxicologic review – an evaluation of the presence, use, and possible releases of toxic substances and the resulting potential for exposure or hazard to occur.

Transuranics – nuclides having an atomic number greater than uranium (i.e., greater than 92); all known transuranium elements are radioactive.

Tritium (T) – synonym for 3H, a radioactive isotope of hydrogen of triple mass (atomic mass = 3).

Tritium reservoirs – small pressure vessels of various shapes that were filled with tritium gas under high pressure for use as components of a thermonuclear weapons. These are the only weapons components that were produced at the SRS.

Uncertainty – a general term used to describe the level of confidence in a given measurement or estimated quantity. Uncertainty depends on the amount and quality of the evidence (data) available. Uncertainties in the results of this study arise primarily from bias and imprecision in available measurements, absence of measurements at some times and places, lack of knowledge about some physical processes and operational procedures, and the approximate nature of mathematical models used to predict the transport of released materials.

Uranium (U) – a naturally occurring radioactive metal with atomic number 92, the heaviest natural element. Small amounts are present in soil, coal and rock materials, water, plants, and animals.

Validation – the process of comparing predicted concentrations of a material in the environment, based on source term reconstruction and environmental transport models, with historical measured concentrations to demonstrate that the models, within their domain of applicability, adequately represent the system they are intended to describe.

Volatilization – The process of transfer of a chemical from the aqueous or liquid phase to the gas phase.

Water table – ground water that is held by a natural basin of clay overlain with sand or sandy clay and isolated from principal aquifers.

LIST OF ACRONYMS

ADP – Adenosine diphosphate
ACGIH – American Conference of Governmental Industrial Hygienists
AEC – Atomic Energy Commission
AFB – Air Force Base
AFCEE – Air Force Center for Environmental Excellence
ASR – Annual Status Report
AIRS – Air Information Reporting System (database)
AODC - Acridine Orange Direct Count Method
ATP – Adenosine triphosphate
ATSDR – Agency for Toxic Substances and Disease Registry
BFSS – Bioremediation in the Field Search System
BHC – Benzene Hexachloride
BTEX – Benzene, Toluene, Ethylbenzene, and Xylenes
BTU – British Thermal Unit
CA – Corrective Action
CE – Chloroethane
CAHs – Chlorinated aliphatic hydrocarbons
CAS – Chemical Abstract Service (number)
CCI – Company Chemical Inventory (Du Pont's)
CCl_4 (CT) – Carbon Tetrachloride
cDCE - cis-dichloroethylene
CERCLA – Comprehensive Environmental Response, Compensation, and Liability Act
CF – Chloroform
CFR – Code of Federal Regulations
CIIS – Chemical Information and Inventory System (Database)
CM – Chloromethane
CMP – Chemical, Metal and Pesticide (Pits)
CMX – code letters designating a facility at SRS for the development and testing of various reactor components and auxiliaries.
CO_2 – Carbon dioxide
cpm – counts per minute
Cr^{+3} – Trivalent Chromium
Cr^{+6} – Hexavalent Chromium
CVOC – Chlorinated Volatile Organic Compound
DCA – Dichloroethane
DCE – Dichloroethene
DCE – Dichloroethene
DDD – Dichlorodiphenyldichloroethane
DDE – Dichlorodiphenyldichloroethene
DDT – Dichlorodiphenyltrichloroethane
DNAPL – Dense non-aqueous phase liquid
DOD – U.S. Department of Defense
DOE – U.S. Department of Energy
DOI – U.S. Department of the Interior

DP – Savannah River Laboratory research and development reports, originated by the Atomic Energy Division, Engineering Department, and or contractors
DPS – Savannah River Laboratory internal documents issued jointly by Technical Information Service (SRL) and Plant Records Division (SRP)
DPSOL – Du Pont Savannah River Plant Operating Log
DPSOP – Du Pont Savannah River Plant Operating Procedure
DPST – Savannah River Laboratory internal correspondence, memos, reports
DPSTL – Savannah River Laboratory Operating Log
DS – Demonstration Scale
DUS - Dynamic Underground Stripping
DWPF – Defense Waste Processing Facility
EIS – Environmental Impact Statement
EML – Environmental Measurements Laboratory (see HASL).
EPA – U.S. Environmental Protection Agency
EPA REACH IT – EPA REmediation And CHaracterization Innovative Technologies
EPRTK – Emergency Planning and Community Right-to-know Act
ERDA – Energy Research and Development Administration
ESD – Explanation of Significant Differences
ETF - Effluent Treatment Facility
FAME - fatty methyl ester
FDA – Food and Drug Administration
Fe^0 – Zero-valent iron
Fe^{2+} – Iron (II) ion
FMF – (Naval) Fuel Manufacturing Facility
FRTR – Federal Remediation Technologies Roundtable
FS – Full Scale
FY – Fiscal Year
GAEPD – Georgia Environmental Protection Division
GIS – Geographic Information System
GM – Geometric Mean
GSD – Geometric Standard Deviation
GSACU - General Separations Area Consolidation Unit
GW – Groundwater
GWQCB – Georgia Water Quality Control Board
HAW – high activity waste
H_2O_2 – Hydrogen peroxide
HCl – Hydrogen chloride
HEPA – high-efficiency particulate air (filters)
HEAST – Health Effects Assessment Summary Tables
HLW – high-level radioactive waste
HRC – Hydrogen release compound
HS – Hydrogen sulfide ion
IARC – International Agency for Research on Cancer
ISCST – Industrial Source Complex Short Term (model)
JOAAP – Joliet Army Ammunition Plant

Kow	– octanol-water partition coefficient
LAW	– Low Activity Waste
LDR	– Land Disposal Restrictions
LETF	– Liquid Effluent Treatment Facility
LLD	– lower limit of detection. (See detection level).
LNAPL	– Light non-aqueous phase liquid
MC	– Methylene chloride
MCL	– Maximum Contaminant Levels (Drinking Water Standards)
MDA	– minimum detectable activity. (See MDC).
MDC	– minimum detectable concentration. (See definition below).
MDL	– minimum detection limit. (See detection level).
MEBR	– Methane enhanced bioremediation
mg/kg	– Milligrams per Kilogram
MNA	– Monitored natural attenuation
MOA	– Memorandum of Agreement
MSDS	– Material (or Manufacturer) Safety Data Sheets
MtEB	– Methyl Tertiary Butyl ether
NAAQS	– National Ambient Air Quality Standards
NAD	– Nicotinamide adenine dinucleotide
NAPL	– Non-aqueous phase liquid
NC	– Not Calculated
NCRP	–National Council on Radiation Protection and Measurements
NESHAPs	– National Emission Standards for Hazardous Air Pollutants
NNEMS	– National Network of Environmental Management Studies
NPDES	– National Pollution Discharge Elimination System
NIOSH	– National Institute of Occupational Safety and Health
NR	– Not Reported
NRWDF	– Non-Radioactive Waste Disposal Facility
NSCEP	– National Service Center for Environmental Publications
NTP	– National Toxicology Program
ORC	– Oxygen release compound
ORNL	– Oak Ridge National Laboratory
ORWBG	– Old Radioactive Waste Burial Ground
OSHA	– Occupational Safety and Health Administration
OU	– Operable Unit
PAHs	– Polycyclic Aromatic Hydrocarbons
PBTs	– Persistant Bioaccumulative Toxins
PCBs	– Polychlorinated Biphenyls
PCE	– Tetrachloroethene
PCP	– Pentachlorophenol
PDWS	– Primary Drinking Water Standards
PEL	– permissible exposure limit
PHC	– Petroleum Hydrocarbons
PMP	– Performance Management Plan
POL	– Petroleum, Oil, and Lubricant
POPs	– Persistant organic pollutants

PRB	– Permeable reactive barrier
Pu	– plutonium
PVC	– Polyvinyl chloride (pipe)
RBOF	– Receiving Basin for Offsite Fuels
RCRA	– Resource Conservation and Recovery Act
RfC	– reference concentration
RfD	– reference dose
RM	– river mile
ROD	– Record of Decision
SARA	– Superfund Amendments and Reauthorization Act of 1986
SCDHEC	– South Carolina Department of Health and Environmental Control
SCRAM	– an acronym for Safety Control Rod Ax Man. A SCRAM entails dropping the safety rods in a reactor to shut down the reaction.
SGCP	– Soil and Groundwater Closure Projects
SLF	- Sanitary Landfill
SREL	– Savannah River Ecology Laboratory
SRL	– Savannah River Laboratory (named Savannah River Technology Center, SRTC in 1992)
SRP	– Savannah River Plant (former designation for SRS and the production facilities)
SRS	– Savannah River Site
SRTC	– Savannah River Technology Center formerly called Savannah River Laboratory
SVE	– Soil Vapor Extraction
SVOC	– Semivolatile Organic Compound
SWDF	– Solid Waste Disposal Facility
TBP	– Tributyl phosphate or tri-n-butyl phosphate
TCA	– Trichloroethane
TCDD	– Trichlorodibenzodioxin
TCE	– Trichloroethene
Tetryl	N-methyl-n,2,4,6-tetranitroaniline
TLLa	– total long-lived alpha activity
TLV	– Threshold Limit Value
TNT	– Trinitrotoluene
TNX	– code name for the first pilot or semi-scale works facility at the SRS for the development and testing of equipment for the chemical separations processes
TPH	– Total Petroleum Hydrocarbon
TRI	– Toxic Release Inventory
TRU	– transuranic (refers to nuclides with atomic number greater than that of uranium
TSCA	– Toxic Substances Control Act
TSHP	– Toxic Substances Hydrology Program
TWA	– time weighted average
U	– uranium
UIC	– Underground Injection Control
UNSCEAR	– United Nations Scientific Committee on the Effects of Atomic Radiation
USGS	– U.S. Geological Survey
UST	– Underground storage tank

VC – Vinyl chloride
VOCs – Volatile Organic Compounds
VZMS – vadose zone monitoring system
WSRC – Westinghouse Savannah River Company; took over the site operations from Du Pont in March 1989.

UNIT of MEASUREMENT

g – gram
kg – kilogram
mg – milligram (10-3 g)
ppb – parts per billion
ppm – parts per million
ppt – parts per thousand
µg – micrograms (10-6 g)
y – year
d – day
M – meter
cy – Cubic Yard
L – liter (A metric unit of volume, equivalent to about 1.1 quarts.)
Gal – gallon
Kilo – a prefix that multiplies a basic unit by 1000. For example, 1 kilogram = 1000 grams.
pCi – picocurie (see curie, pico)
scfm – Standard Cubic Foot per Minute