

SAND REPORT

SAND2003-2880

Unlimited Release

Printed August 2003

Survey of Subsurface Treatment Technologies for Environmental Restoration Sites at Sandia National Laboratories, New Mexico

Clifford K. Ho, Lucas K. McGrath, and Jerome L. Wright

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.doe.gov/bridge>

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>



Survey of Subsurface Treatment Technologies for Environmental Restoration Sites at Sandia National Laboratories, New Mexico

Clifford K. Ho, Lucas K. McGrath, and Jerome Wright
Geohydrology Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0735
Contact: (505) 844-2384; ckho@sandia.gov

Abstract

This report provides a survey of remediation and treatment technologies for contaminants of concern at environmental restoration (ER) sites at Sandia National Laboratories, New Mexico. The sites that were evaluated include the Tijeras Arroyo Groundwater, Technical Area V, and Canyons sites. The primary contaminants of concern at these sites include trichloroethylene (TCE), tetrachloroethylene (PCE), and nitrate in groundwater. Due to the low contaminant concentrations (close to regulatory limits) and significant depths to groundwater (~500 feet) at these sites, few in-situ remediation technologies are applicable. The most applicable treatment technologies include monitored natural attenuation and enhanced bioremediation/denitrification to reduce the concentrations of TCE, PCE, and nitrate in the groundwater. Stripping technologies to remove chlorinated solvents and other volatile organic compounds from the vadose zone can also be implemented, if needed.

Acknowledgments

The authors thank Sue Collins for her overall assistance with this project. We also thank Cindy Ardito, Michael Skelly, Sue Collins, Ray Finley, and David Miller for their thorough and insightful reviews of this report. This work was funded by Project 7222 Task 01.10. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Contents

1. Introduction.....	7
1.1. Objectives and Scope	7
1.2. Overview of Report.....	7
2. Description of Sandia ER Sites.....	7
2.1. Tijeras Arroyo Groundwater (TAG)	9
2.2. Technical Area V (TA-V)	10
2.3. Canyons	10
3. Survey of Treatment Technologies.....	10
3.1. TCE and PCE Treatment Technologies	11
3.1.1. Soil Vapor Extraction	11
3.1.2. Air Sparging/Groundwater Circulation.....	14
3.1.3. Surfactant Enhanced Aquifer Remediation	17
3.1.4. Steam Injection	18
3.1.5. Pneumatic Fracturing Technology.....	19
3.1.6. Chemical Oxidation Technology	20
3.1.7. Permeable Reactive Barriers.....	22
3.1.8. Natural Attenuation.....	24
3.2. Nitrate Treatment Technologies	28
3.2.1. Reduction of Nitrate using Iron Powder	28
3.2.2. Remediation of Nitrate Contamination via Riparian Vegetation.....	30
3.2.3. Bioremediation of Nitrate Contamination	31
4. Summary and Recommendations.....	33
5. References.....	35

List of Figures

Figure 1. Map of Sandia Environmental Restoration (ER) sites	8
Figure 2. Soil vapor extraction system.	12
Figure 3. Air sparging of contaminated groundwater with removal of contaminated vapor with a vapor extraction system.....	14
Figure 4. Air sparging combined with groundwater circulation and vapor extraction.....	15
Figure 5. Pneumatic fracturing of contaminated soil.....	19
Figure 6. Chemical oxidation of PCE and TCE.....	21
Figure 7. Permeable reactive barrier (from Geo-Solutions web site http://www.geo-solutions.com/Default2.htm).	23
Figure 8. Natural degradation of common chlorinated contaminants to carbon dioxide and water.	25

List of Tables

Table 1. Summary of Sandia ER sites evaluated in this report as a basis for surveying remediation and treatment technologies.....	9
Table 2. Applicability of treatment technologies to Sandia ER sites.	34

1. Introduction

1.1. Objectives and Scope

The purpose of this report is to provide a summary of available remediation and treatment technologies that are applicable to several of the contaminated sites at Sandia National Laboratories, New Mexico. Unique features of the sites at Sandia include very low contaminant concentrations and very deep aquifers, which may prohibit the use of many of the in-situ remediation and treatment technologies for groundwater. The scope of this report focuses on remediation and treatment technologies for those groundwater contaminants that have been found above the maximum contaminant levels imposed by the United States Environmental Protection Agency (U.S. EPA). These contaminants include trichloroethylene (TCE), tetrachloroethylene (PCE), and nitrate. The maximum contaminant levels for these compounds are 5 µg/L for TCE and PCE, and 10 mg/L for nitrate.

1.2. Overview of Report

A brief overview and description of the Sandia Environmental Restoration (ER) sites is provided in Section 2, which also summarizes the contaminants of concern and other relevant details about the sites. Section 3 presents a survey of available technologies to remediate and/or treat the relevant contaminants at the Sandia ER sites. The survey consists of high-level summaries of various technologies that are applicable to the contaminants of concern. Each summary contains concise information regarding the nature and operation of the technology, names and contact information for commercial vendors along with costs (if available), advantages, disadvantages, and applicability to the Sandia ER sites. Finally, Section 4 provides a summary of recommended remediation and treatment technologies for the Sandia ER sites based on the results of the survey.

2. Description of Sandia ER Sites

Within the Sandia ER project, there are six areas of concern for current or potential groundwater contamination: (1) Tijeras Arroyo Groundwater (TAG); (2) Technical Area V (TA-V); (3) Canyons; (4) Chemical Waste Landfill; (5) Mixed Waste Landfill; and (6) Drains and Septic Systems. Figure 1 shows a map of these locations (except for the Drains and Septic Systems) relative to the city of Albuquerque and Kirtland Air Force Base. Of these areas, the first three are the focus for the technologies evaluated in this report. The last three areas have no groundwater contamination above the maximum contaminant levels imposed by the U.S. Environmental Protection Agency.

Additional details regarding the TAG, TA-V, and Canyons areas are provided in the sections below, along with a brief overview of the geologic setting. A summary of the contaminants of interest and other relevant details at these sites are summarized in Table 1.

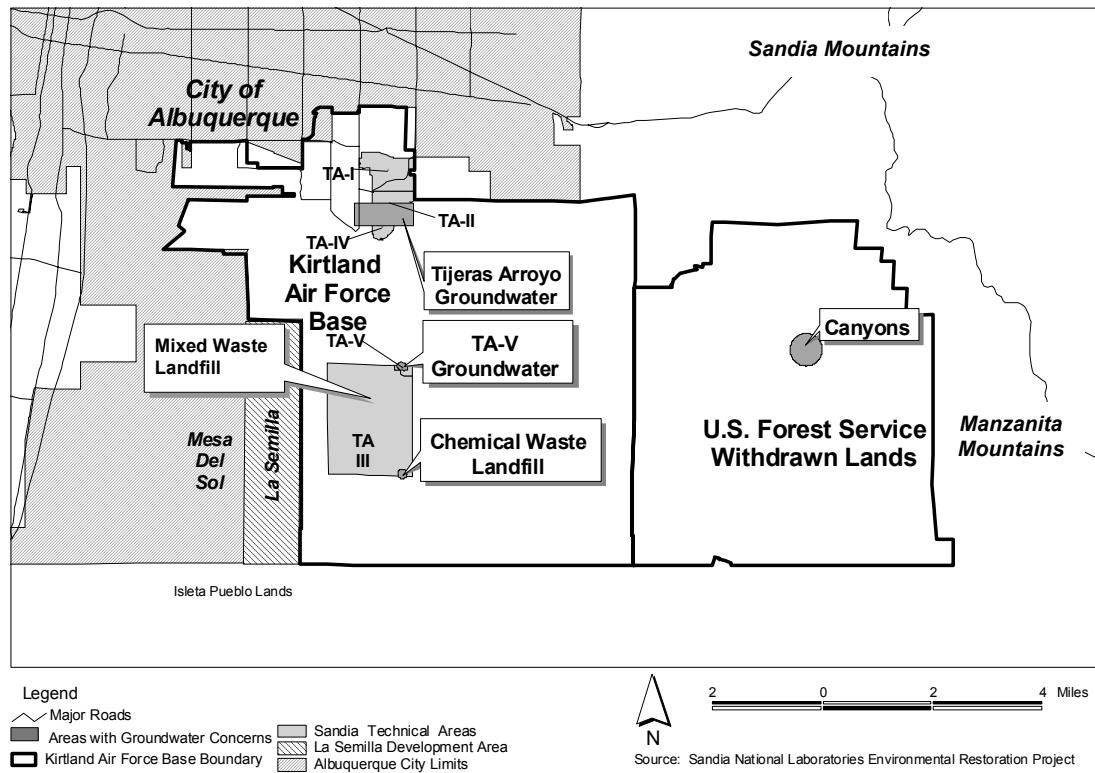


Figure 1. Map of Sandia Environmental Restoration (ER) sites.

The Sandia ER sites are located within the Kirtland Federal Complex, which is comprised of land owned, in part, by the United States Department of Energy (DOE) and Kirtland Air Force Base. This area is located on a high, arid mesa about five miles east of the Rio Grande in central New Mexico. The mesa is divided by the east-west trending Tijeras Arroyo that drains into the Rio Grande. The east side of the Kirtland Federal Complex is bounded by the southern end of the Sandia Mountains and the northern end of the Manzanita Mountains. The area slopes westward toward the Rio Grande, and the mean elevation of the Kirtland Federal Complex is approximately 5,300 ft above sea level.

The water table in the Middle Rio Grande Basin, which supplies the Albuquerque metropolitan area with its water supply, slopes gradually from the foothills of the Sandia and Manzanita Mountains towards the Rio Grande. The basin covers approximately 3,000 square miles and is approximately 70 miles long. The thickness of the basin exceeds 14,000 feet in some areas, but the primary water-bearing unit (the upper Santa Fe Group) is up to 2,000 feet thick (USGS, 2002). The eastern boundary of the basin in the vicinity of the Kirtland Federal Complex is defined by a series of faults that are parallel to and west of the Sandia and Manzano Mountains. The TAG, TA-V, Chemical Waste Landfill, and Mixed Waste Landfill sites lie to the west of these faults, and the Canyons sites lie to the east of these faults.

Table 1. Summary of Sandia ER sites evaluated in this report as a basis for surveying remediation and treatment technologies.

	Tijeras Arroyo Groundwater (TAG) Area	Technical Area V (TA-V) Area	Canyons Area
Nitrate groundwater contamination (EPA MCL = 10 mg/L)*	up to 30 ppm	up to 25 ppm	up to 25 ppm
TCE groundwater contamination (EPA MCL = 5 µg/L)*	up to 10 ppb	up to 25 ppb	none detected
PCE groundwater contamination (EPA MCL = 5 µg/L)*	none detected	up to 8 ppb	none detected
Other groundwater contaminants	chlorinated volatile organic compounds (less than 5 ppb)	cis-1,2-DCE (4.5 µg/L; well below EPA MCL of 70 µg/L)	aromatic hydrocarbons, jet fuel additive (all below EPA MCLs)
Probable source of contamination	solid-waste management units	liquid-waste disposal system	burn-test discharge into unlined pit
Depth to groundwater (ft below ground surface)	450-575 (regional aquifer) 250-375 (perched water)	~500	120-380

*For aqueous concentrations, 1 mg/L \approx 1 ppm (parts per million), and 1 µg/L \approx 1 ppb (parts per billion). TCE: Trichloroethylene. PCE: Tetrachloroethylene. EPA: U.S. Environmental Protection Agency. MCL: maximum contaminant level.

2.1. *Tijeras Arroyo Groundwater (TAG)*

The Tijeras Arroyo Groundwater area consists of approximately 2.5 square miles covering Technical Areas I, II, and IV. The primary contaminants of concern for this area include trichloroethylene (TCE) and nitrate, but no confirmed sources or release areas have been identified. TCE was identified in five shallow groundwater monitoring wells and in one regional aquifer monitoring well. Concentrations were low, ranging from 1.0 to 9.6 parts per billion (ppb) (SNL/NM, 2001). Nitrate was found in a single shallow groundwater monitoring well at concentrations ranging from 3.3 to 26.5 parts per million (ppm) (SNL/NM, 2001). Potential sources of contamination in this area from solid-waste management units (SWMU) have been detailed in SNL/NM (2001). In addition, soil-vapor samples from a borehole near SWMU 46 revealed various volatile organic compounds (VOCs), including 10,000 parts per billion by volume (ppbv) of vapor-phase TCE at 137 feet below ground surface. These high concentrations have been very stable, and the vapor concentrations decline with increasing depths towards the water table at this location.

The depth to groundwater in the regional aquifer at this site ranges from 450 to 575 feet below ground surface, but declining water levels have been observed due to groundwater pumping. The groundwater flow direction is primarily north/northwest. A shallow system of perched groundwater has been observed up to 200 feet above the regional water table. Current assessments view the shallow groundwater system as becoming fully saturated due to moisture

additions from by man-made sources (leaking water mains and sewer lines, excess irrigation, etc.) (SNL/NM, 2001).

2.2. Technical Area V (TA-V)

The TA-V area consists of 35 acres in the northeast corner of TA-III where various research facilities are located (Figure 1). A liquid-waste disposal system in TA-V is believed to be the primary source of TCE contamination in the groundwater in this area (SNL/NM, 2001). Other primary contaminants of concern at TA-V include nitrate and cis-1,2-DCE, a degradation product of TCE. The measured aqueous concentrations of TCE and nitrate have exceeded the maximum contaminant levels (MCL) of 5 $\mu\text{g}/\text{L}$ and 10 mg/L, respectively, in several TA-V monitoring wells. The measured concentration of cis-1,2-DCE (4.5 $\mu\text{g}/\text{L}$) was well below the EPA MCL of 70 $\mu\text{g}/\text{L}$ (SNL/NM, 2001).

The groundwater depth at TA-V is approximately 500 feet below ground surface, and the regional groundwater flow direction is to the west. A 1- to 2-foot-high groundwater mound beneath TA-V was identified from potentiometric data from 1996 to 1998, with groundwater flowing north, south, and west from the potentiometric high of the mound (SNL/NM, 2001). The extent of the TCE groundwater contamination at TA-V has been estimated to be 1,100 feet long and 800 feet wide with uncertain vertical extent (SNL/NM, 2001).

2.3. Canyons

The Canyons area is located east of TA-V and TAG in the Manzanita Mountains (Figure 1). It consists of active and inactive solid-waste management units scattered over thousands of acres in three large canyons. Historical operations at the Canyons area included explosion, impact, and burn tests at various sites. The primary contaminant of concern in this area is nitrate, which has been measured at 25 mg/L (SNL/NM, 2001). Other contaminants that have been detected in the groundwater in this area include aromatic hydrocarbons and fuel additives, but the concentrations have been less than the EPA MCLs.

The groundwater in the Canyons area is located between 120 and 380 feet below ground surface, and the direction of flow is generally thought to be west. The contamination is thought to originate from burn-testing discharge into an unlined excavation pit. Contaminants have migrated at least 1,500 feet west of the site (SNL/NM, 2001).

3. Survey of Treatment Technologies

This section provides brief summaries of remediation and treatment technologies for both groundwater and unsaturated soils. Each summary contains a description of the technology (physics, operation, applicable contaminants, etc.), commercial vendors and pricing (if available), advantages and disadvantages, and applicability to Sandia ER sites.

Although the primary concern for the Sandia ER sites is groundwater contamination, technologies that address the unsaturated zone are included because of the potential for

contaminants to originate in the unsaturated zone. Also, based on the contaminants of concern identified in Table 1 for the Sandia ER sites of interest, the primary drivers for the survey were TCE, PCE, and nitrate. Technologies that address the remediation and treatment of TCE and PCE are often applicable to other chlorinated solvents (e.g., decay products from PCE and TCE) and other volatile organic compounds as well.

3.1. TCE and PCE Treatment Technologies

TCE and PCE are colorless liquids that have been used widely to degrease metal parts and textiles (as dry-cleaning agents). Releases of TCE and PCE into the environment are due to air emissions and wastewater emissions from industries that perform machining and metal finishing, paint and ink processing, electronic component fabrication, and rubber processing. According to the EPA's Toxics Release Inventory, TCE releases to water and land totaled over 291,000 pounds between 1987 to 1993, and releases of PCE to water and land totaled over 1 million pounds over the same time period.

TCE and PCE are volatile liquids, so they will tend to evaporate if released as a liquid into soils. However, TCE and PCE are more dense than water, so it will continue to migrate into the water table if released in sufficient quantities. TCE and PCE are not very soluble in water, so they can remain as a separate non-aqueous phase for long periods of time in the subsurface. Chronic exposure to TCE and/or PCE is suspected of causing liver damage, as well as cancer.

In-situ treatment methods for TCE and PCE in soils and groundwater are varied and can be categorized as follows: physical stripping (soil vapor extraction, air sparging, steam injection), surfactant flushing, chemical oxidation, reactive barriers, and natural attenuation (biodegradation, sorption, dilution). Ex-situ methods require the excavation of the contaminated soil followed by subsequent treatment of the contaminated soil (thermal desorption/destruction or chemical binding). Brief descriptions of the in-situ methods are provided in the following sections, along with their applicability to Sandia's ER sites.

3.1.1. Soil Vapor Extraction

3.1.1.1. General Description

Soil vapor extraction is used to treat soil that is contaminated with VOCs. This technology consists of venting air through the soil to evaporate and entrain contaminant vapors. The vapor and effluent gas are brought to the surface through vacuum extraction wells, where the contaminant vapors are treated or destroyed before the effluent gas is released back into the atmosphere (Figure 2). Characterization of the extent and location of the contaminant plume is necessary to determine the best locations to install extractions wells and air-injection wells.

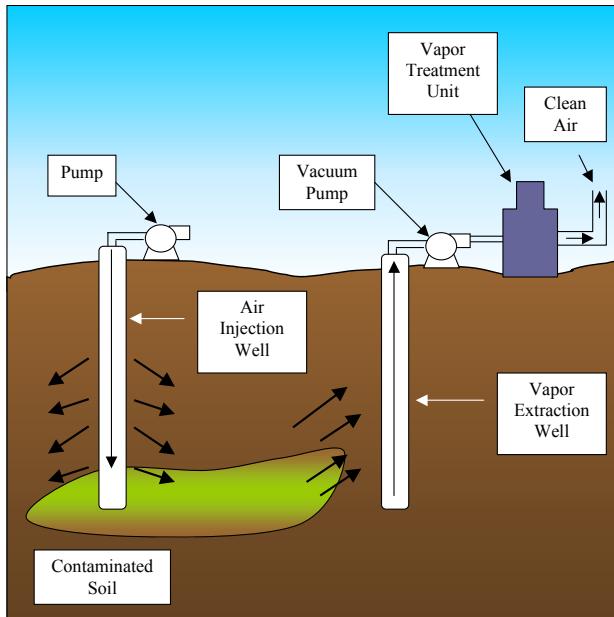


Figure 2. Soil vapor extraction system.

The performance of soil vapor extraction can be enhanced by heating the soil to increase the temperature and volatilization (vapor pressure) of the contaminants if a separate non-aqueous phase liquid (NAPL) is present. The soil can be heated by electrical resistance, electromagnetic heating, radio-frequency heating, or hot-air/steam injection. However, caution must be taken to prevent worker exposure to high voltages, steam, and other hazards.

Passive soil ventilation systems can also be designed by using barometric pumping to remove volatile organic compounds from the subsurface. Barometric pumping occurs as a result of natural fluctuations in the atmospheric pressure. When the atmospheric pressure is greater than the subsurface pressure, gas tends to move down into the wells and into the soil. Conversely, when the atmospheric pressure is less than the subsurface pressure, gas and contaminant vapors tend to move from the soil to the surface through the wells. The BaroBall™, developed at the Savannah River Site, acts as a diode and prevents the inflow of air through a well by a movable plastic sphere that seals the opening of the well, but it allows the outflow of gases. Therefore, passive ventilation of a site can occur without dispersion caused by the influx of air.

3.1.1.2. Cost

The cost of soil vapor extraction depends on a number of factors such as soil type, extent and nature of contamination, depth of contamination, number of wells required, vacuum capacity, duration of remediation, etc. (EPA, 1989). Treatment of contaminated vapors and recovered water also adds significantly to the cost. However, very low vapor concentrations (as found at Sandia) may not require treatment. Cost estimates range between \$10 and \$50 per cubic meter (\$10 and \$40 per cubic yard) of soil. Thermally enhanced vapor extraction has been estimated at \$130 per cubic yard. Passive (barometric pumping) ventilation systems require minimal operational costs following the installation of the wells.

3.1.1.3. Advantages

- Commercial technology that has been applied widely for in-situ remediation of VOCs.
- Minimal disturbance to site operations
- Can be combined with other remediation technologies (e.g., bioremediation, air sparging).
- Can remove large quantities of contaminant if the air-flow path is through the contaminant source.
- Cost competitive with other in-situ remediation technologies.
- Technology is already approved by EPA for VOCs in the vadose zone (EPA, 1996a)
- Technology has been applied at the Chemical Waste Landfill at Sandia (SNL/NM 2003)

3.1.1.4. Disadvantages

- Treatment for extracted vapors and water may be costly if concentrations are high.
- Used primarily to treat the unsaturated zone. Air sparging must be implemented to treat the saturated zone.
- Heterogeneities and low-permeability zones can reduce the efficiency of this technology by causing mass-transfer limitations (Ho and Udell, 1992).
- Difficult to achieve concentration reductions greater than about 90%.
- Thermally enhanced vapor extraction requires high voltages to heat the soil.

3.1.1.5. Applicability to Sandia ER Sites

This technology may be applicable to ER sites that contain high concentrations of VOCs in the unsaturated zone (e.g., TAG site). However, it may not be cost effective at remediating very low concentrations due to mass-transfer limitations. It is not applicable to remediating groundwater, except when combined with air sparging.

3.1.1.6. Vendors/Contacts/References:

- BaroBall™ web site: <http://www.srs.gov/general/enviro/erd/technology/Pages/d03.html>
- EPA, 1989. *Terra Vac, In Situ Vacuum Extraction System*, EPA RREL, Applications Analysis Report, Cincinnati, OH, EPA Report EPA/540/A5-89/003.
- EPA, 1996a, User's Guide to the VOCs in Soils Presumptive Remedy, EPA 540/F-96/008, <http://www.epa.gov/superfund/resources/presump/finalpdf/vc.pdf>

- EPA Soil Vapor Extraction web site: <http://www.epa.gov/swerust1/cat/sve1.htm>
- Ho, C.K. and K.S. Udell, 1992, An Experimental Investigation of Air Venting of Volatile Liquid Hydrocarbon Mixtures from Homogeneous and Heterogeneous Porous Media, *J. Contam. Hydrol.*, 11, 291-316.
- Sandia National Laboratories, May 2003, “Chemical Waste Landfill: Corrective Measures Study, Remedial Action Proposal, Post-Closure Care Plan,” Environmental Restoration Project, Sandia National Laboratories, Albuquerque, NM.
- Terra Vac Soil Vapor Extraction: <http://terravac.com/web/toolsve.htm>
- Thermal Enhanced Vapor Extraction: <http://www.sandia.gov/Subsurface/factshts/ert/teves.pdf>

3.1.2. Air Sparging/Groundwater Circulation

3.1.2.1. General Description

Air sparging is a remediation technology that reduces the concentrations of VOCs in groundwater by injecting clean gas, usually oxygen or clean air, into the groundwater. The injected air causes the volatile contaminants to partition from the aqueous phase into the gas phase (bubbles). The gas-phase contaminants in the vadose zone can then be treated by a separate technology, usually soil vapor extraction, to remove the contaminants from the vadose zone. Air sparging can be used to remove several volatile groundwater contaminants such as chlorinated solvents, aromatic hydrocarbons, oils, and fuels (Miller, 1996). Figure 3 shows an air sparging system in the saturated zone with vapor extraction wells removing the volatilized compounds from the vadose zone.

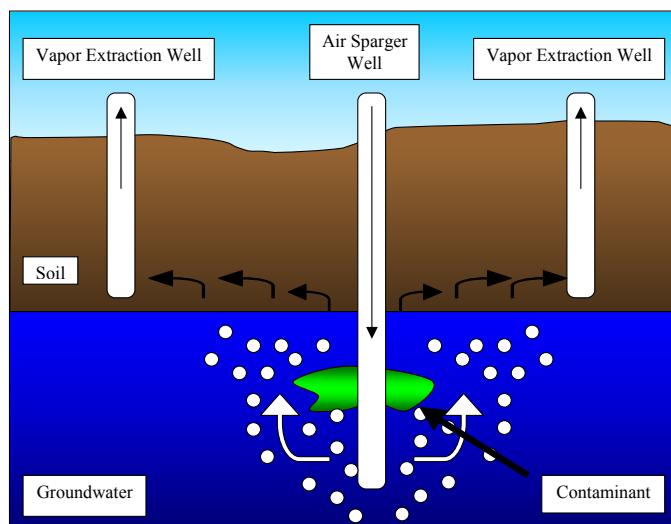


Figure 3. Air sparging of contaminated groundwater with removal of contaminated vapor with a vapor extraction system.

Groundwater circulation is a similar remediation technology in which wells are designed and placed to continuously circulate the groundwater while air is injected into the groundwater (EPA, 1998a). A common design is to use a double-cased well as shown in Figure 4. Water enters the lower screen when air is injected through the air injection line located in the inner casing. This injection decreases the density of the surrounding water and allows it to rise. The injected air also accelerates the transition of the contaminant to vapor, similar to air sparging. The water is drawn up the inner casing and continues to be stripped of contaminants until it reaches the outer casing and the upper screen, which is located above the water table. The clean water then passively moves through the vadose zone back into the water table to be re-circulated. The vapors that are stripped from the contaminated groundwater are then extracted to the surface using vacuum extraction.

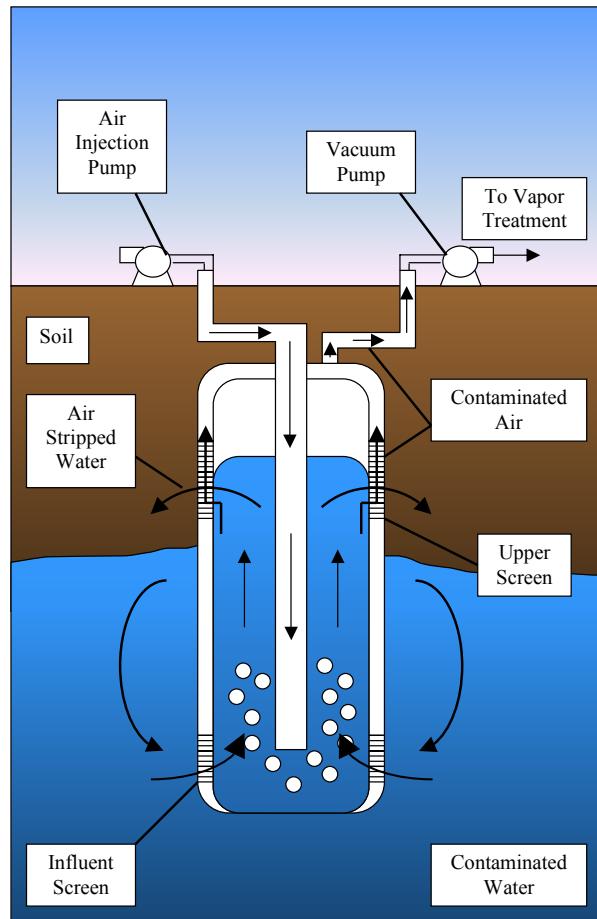


Figure 4. Air sparging combined with groundwater circulation and vapor extraction.

3.1.2.2. Cost

The cost of air sparging varies considerably from site to site. One reported cost was \$10.36 per cubic yard of soil remediation, but no treatment of extracted vapors was included (Miller, 1996). Another cost estimate reported ~\$100K per well for groundwater circulation (EPA, 1998a).

3.1.2.3. Advantages

- Proven technology that can be implemented using existing monitoring wells.
- Air sparging with oxygen has the ability to enhance the natural biodegradation of the VOCs from aerobic microbes.

3.1.2.4. Disadvantages

- This process only shifts the compound from water to air. VOCs need to be removed from the vadose zone with a separate technology.
- Effectiveness will rely on the permeability and heterogeneous nature of both the vadose and saturated zones. Zone of remediation is dependent on extent of “bubbling” in the saturated zone, which can be quite limited.
- May cause groundwater mounding.

3.1.2.5. Applicability to Sandia ER Sites

Because the concentrations in the groundwater are very low at SNL ER sites (see Table 1), air sparging is not a practical option. In addition, the use of air sparging and vapor extraction 500 ft below the surface is likely not cost effective. The heterogeneous soils in the vadose and saturated zones could also limit mass transfer.

3.1.2.6. Vendors/Contact/References

- EPA, 1998a, Field Applications of In Situ Remediation Technologies: Ground-Water Circulation Wells, EPA 542-R-98-009, <http://clu-in.org/download/remed/gwcirc.pdf>
- Miller, R.R., 1996, Air Sparging, Ground-Water Remediation Technologies Analysis Center, Report TO-96-04: http://www.gwrtac.org/pdf/Sparge_o.pdf
- Subsurface Volatilization and Ventilation System, Billings & Associates, Inc.: <http://www.clu-in.org/products/site/complete/democomp/billings.htm>
- Terra Vac Air Sparging: <http://www.terravac.com/web/tools.htm>

3.1.3. Surfactant Enhanced Aquifer Remediation

3.1.3.1. General Description

Surfactant enhanced aquifer remediation is an enhanced pump-and-treat remediation technology that is used to remediate dense non-aqueous phase liquids (DNAPLs) from groundwater. A surfactant is pumped into the contaminated region to increase the dissolution or mobilization of the contaminant. A surfactant molecule has both a hydrophobic and a hydrophilic region. Because of this dual nature, the surfactant molecules accumulate at the DNAPL-water interface, which reduces the interfacial tension and increases the mobilization of the DNAPL. The groundwater is then pumped through wells to bring the contaminated water to the surface, where the contaminants can be treated.

3.1.3.2. Cost

As with all remediation technologies, the cost of surfactant enhanced aquifer remediation depends greatly on the specific size and nature of contamination at the site. One study (ESTCP, 2001) provides estimates of costs ranging from \$280 per cubic yard for a 1-acre (43,560 ft²) site (assuming a 10-ft thick aquifer) to ~\$1,700 per cubic yard for a 2,500 ft² site (assuming a 10-ft thick aquifer). The relatively large costs may be due to the inclusion of estimates for laboratory testing, surfactant selection, characterization, and performance assessment. Other estimates given previously may not include these total-life-cycle costs of remediation.

3.1.3.3. Advantages

- Introduction of surfactants increases mobilization of DNAPLs in groundwater and provides increased efficiency of pump-and-treat technology.

3.1.3.4. Disadvantages

- Additional chemicals are introduced into the subsurface.
- Efficiency of pump-and-treat can still be greatly impeded by heterogeneities and low-permeability zones of contamination.
- Effective only with non-aqueous phase liquids. Not applicable to low concentration aqueous contaminants.

3.1.3.5. Applicability to Sandia ER Sites

Because the groundwater concentrations are so low, this technology is not applicable to the sites at Sandia. If a DNAPL source term were located, this technology may be applicable, but other remediation technologies (air sparging) may be more cost effective.

3.1.3.6. Vendors/Contact/References

- EPA, In Situ Remediation Technology Status Report: Surfactant Enhancements, Report EPA542-K-94-003, April 1995. <http://www.clu-in.org/download/remed/srfctnt.pdf>

- ESTCP (Environmental Security Technology Certification Program), 2001, Surfactant Enhanced DNAPL Removal: <http://www.estcp.org/documents/techdocs/199714.pdf>

3.1.4. Steam Injection

Steam injection was originally used by the petroleum industry to recover oils from subsurface reservoirs. The steam lowered the viscosity of heavy oils and increased the volatility of light oils. In the past decade, this process has been adapted to recover organic contaminants both in the vadose zone and in the saturated zone (EPA, 1998b). The high-pressure, high-temperature steam displaces and volatilizes the contaminants. Typically, the steam-injection wells are placed around the perimeter of the contaminated zone, and a recovery well is placed in the middle. Cycling of steam injection and soil vapor extraction has been found to be effective at enhancing the recovery of contaminants.

3.1.4.1. Cost

The cost associated with steam injection depends on site-specific attributes. Reported costs for a field demonstration were between \$78/m³ and \$92/m³ (EPA, 1998b).

3.1.4.2. Advantages

- Capable of reducing contaminant levels to very low concentrations due to combination of high-pressure (displacement) and high-temperature (volatilization) steam.
- Can be combined with soil vapor extraction to produce effective remediation even in low permeability zones.
- Effective at removing separate-phase contaminants.

3.1.4.3. Disadvantages

- Production of steam requires high-voltage equipment, and working with steam is inherently dangerous.
- Steam fronts can move contaminants deeper into the water table or into undesirable locations.

3.1.4.4. Applicability to Sandia ER Sites

Steam injection is not applicable to the saturated-zone sites where contaminant concentrations are low and no separate-phase contaminant (free product) exists. Application of this technology to the vadose zone is also not practical when a separate-phase contaminant liquid is not present. The use of soil vapor extraction to remediate contaminant vapors from the vadose zone would be a more cost-effective option.

3.1.4.5. Vendors/Contact/References

- EPA, 1998b, Ground Water Issue, Steam Injection for Soil and Aquifer Remediation, EPA/540/S-97/505. <http://www.epa.gov/tio/tsp/download/steaminj.pdf>
- Steam Tech Environmental Services, Inc.: <http://www.steamtech.com/>

3.1.5. Pneumatic Fracturing Technology

3.1.5.1. General Description

The process of pneumatic fracturing involves injecting pressurized gas into soil. The gas causes the soil to part causing fractures in the structure of the soil and increasing current fractures. This process enhances the overall permeability of the soil and allows liquids and vapors to pass more easily through the soil. This enhances the ability of a separate technology (e.g., soil vapor extraction, surfactant flushing, chemical oxidation) to remove the contaminant from the fractured soil. Common technologies used with pneumatic fracturing include chemical oxidation and soil vapor extraction. Figure 5 shows a schematic of pneumatic fracturing with a vapor extraction system that removes the contaminant from the subsurface.

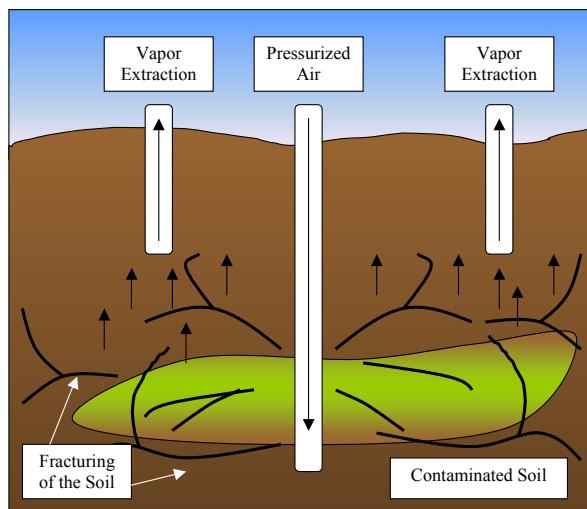


Figure 5. Pneumatic fracturing of contaminated soil.

3.1.5.2. Cost

The cost of pneumatic fracturing is slightly higher than the cost of soil vapor extraction without enhanced fracturing (EPA, 1995; Terra Vac, Pneumatic Soil Fracturing)

3.1.5.3. Advantages

- Can make other remediation technologies more effective by increasing the permeability of the soil.

- Can inject zero-valent iron or other chemicals into the fractured region to treat the contamination.

3.1.5.4. Disadvantages

- Does not remediate the contaminants directly.

3.1.5.5. Applicability to Sandia ER Sites

This technology is not particularly applicable to Sandia ER sites where unconsolidated sediments predominantly exist. If it is used in low permeability regions, it must be used in conjunction with a technology that can treat or remove the contaminant from the subsurface. It is only a “primer” technology that will make other remediation technologies more effective.

3.1.5.6. Vendors/Contacts/References

- ARS Technologies, Inc., Pneumatic Fracturing: <http://arstechnologies.com/> <http://arstechnologies.com/gases.html> (nice animation describing pneumatic fracturing)
- EPA, 1995, In Situ Remediation Technology Status Report: Hydraulic and Pneumatic Fracturing, EPA 542-K-94-005, http://www.gwrtac.org/pdf/Epa_frac.pdf
- Terra Vac, Inc. Pneumatic Soil Fracturing: <http://www.terravac.com/web/toolspsf.htm>

3.1.6. Chemical Oxidation Technology

3.1.6.1. General Description

This is a groundwater treatment technology that utilizes chemical oxidation/reduction in an in-situ environment. Oxidation/reduction of VOCs is a proven method in the degradation of VOCs to other byproducts that are safer. The chemical oxidation cleanup process consists of physically pumping various chemicals (e.g., peroxide, ozone, permanganate) into the contaminated groundwater. Once the pumped chemicals come into contact with a contaminant, a chemical reaction will take place. Figure 6 demonstrates this chemical reaction with PCE and TCE. The by-products of this oxidation/reduction reaction include carbon dioxide and water, and chloride ions in the case of chlorinated VOCs. The injection of chemicals can be enhanced by pneumatic fracturing when the soil has low permeability.

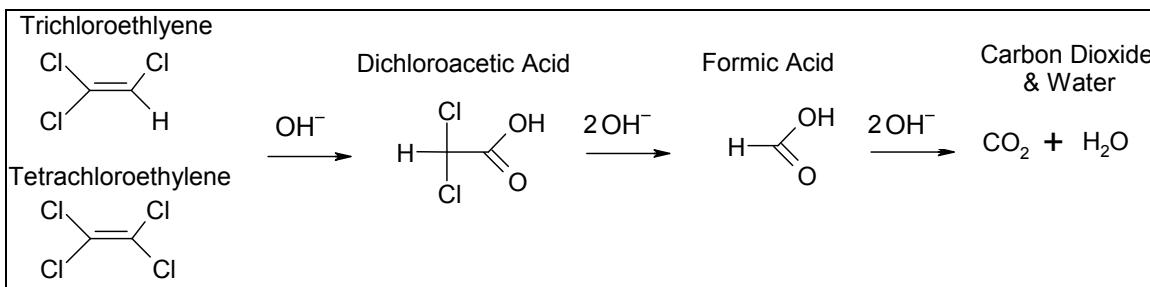


Figure 6. Chemical oxidation of PCE and TCE.

3.1.6.2. Cost

The vendor ISOTEC has estimated that the cost of chemical oxidation would be between \$5-\$50 per cubic yards of contaminated area. The \$5 dollar per cubic yard cost is for the lower concentrations of containments. The treatment would last for 3 to 6 months. The lowest concentration of TCE that this treatment has been tested in was an environment that had a TCE water concentration of 96.9 ppb. The treatment resulted in non-detectable concentrations of TCE.

3.1.6.3. Advantages

- In-Situ Treatment
- Can treat a variety of contaminants. Examples of potential contaminants that are amenable to treatment by the ISOTEC Process include BTEX, MTBE, chlorinated ethenes (PCE, TCE, DCE, VC), chlorinated ethanes (TCA, DCA), PAHs, pentachlorophenol (PCP), and chlorinated pesticides.

3.1.6.4. Disadvantages relative to other technologies

- This treatment is not suitable for treatment of VOCs in the vadose zone.
- Stops natural anaerobic dechlorination.
- Treatment is localized to regions where chemical can be injected.

3.1.6.5. Applicability to Sandia ER sites, limitations, costs

Chemical oxidation can be used at the Sandia ER groundwater sites, but because the location of the source term is uncertain and the concentrations are so low in groundwater, the injection of chemicals into contaminated wells is not warranted or practical.

3.1.6.6. Vendors/Contact/References

- ARS Technologies, Inc., Chemical Oxidation: <http://arstechnologies.com/chemox.html>

- EPA, 1998c, Field Applications of In Situ Remediation Technologies: Chemical Oxidation, EPA 542-R-98-008.
- ISOTEC, Inc., In Situ Oxidative Technologies: <http://www.insituoxidation.com/>

3.1.7. Permeable Reactive Barriers

3.1.7.1. General Description

A permeable reactive barrier is a physical barrier that is installed down gradient from the path of the contaminant. A deep hole or trench is dug in the ground and then backfilled with a permeable barrier material. As the contaminated groundwater moves through the barrier, the barrier either transforms the compound into less harmful byproducts through a chemical reaction or irreversibly absorbs the contaminant (Figure 7). In order to treat chlorinated contaminants the most common barrier used is a granular iron barrier. The iron barrier is composed of iron-bearing minerals that dehalogenate (remove the chlorine atoms of) the chlorinated solvents, ultimately producing ethene and ethane, which are easily biodegraded (EPA, 1997). This technology can treat high and low levels of VOCs. In a case study at Seattle, WA the levels of TCE were reduced from 11,000 µg/L to 3.4 µg/L using an iron barrier.

An alternative method to using “walls” to introduce zero-valent iron has been implemented by ARS Technologies, Inc. Their FEROXSM process uses an open well to inject iron powder as a slurry into the contaminated regions. An advantage of this approach is that it can be used to treat the source region without waiting for the contaminants to migrate downstream.

3.1.7.2. Cost

One ESTCP (1999) field demonstration presented a detailed cost for the construction, monitoring, and management of a reactive permeable barrier used at Moffett Field. The total cost was ~\$800K. The site contained chlorinated volatile organic compounds, and a funnel-and-gate permeable reactive barrier composed of granular zero-valent iron was used. The flow-through thickness of the barrier was 6 feet and was lined on either side by 2 ft of pea gravel. The width of the barrier was 10 ft, and the height of the barrier was approximately 20 feet. The reactive portion of the barrier was located approximately between 15 and 35 feet below the ground surface. The estimated groundwater velocity through the barrier ranged between 0.2 to 2 feet/day. It was estimated that if the barrier retained its performance over approximately 6 years, the barrier would be more cost-effective than a groundwater pump-and-treat system. It should be emphasized that these costs are associated with a shallow groundwater system. Deep aquifers (such as at Sandia) would make this treatment method impractical.

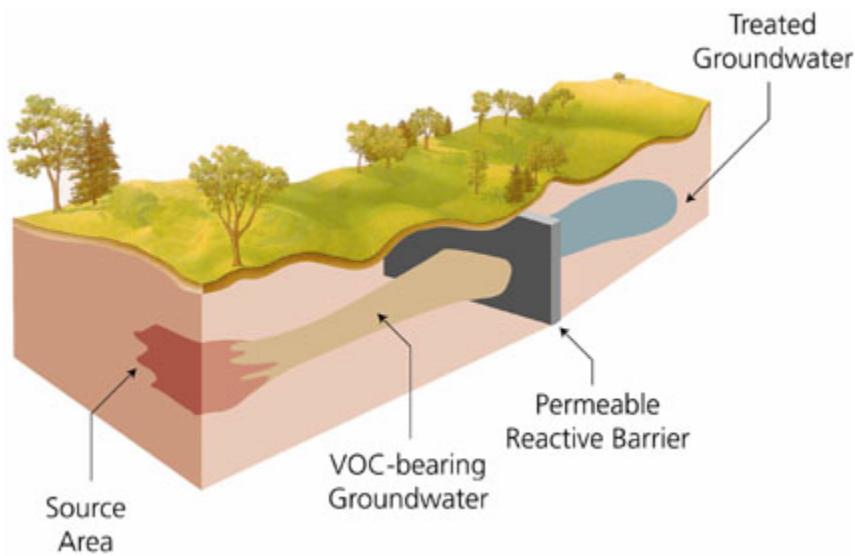


Figure 7. Permeable reactive barrier (from Geo-Solutions web site <http://www.geo-solutions.com/Default2.htm>).

3.1.7.3. Advantages

- Permeable reactive barriers can incorporate multiple materials that treat different contaminants (e.g., VOCs, metals, radionuclides).
- The system is passive; it does not require pumps.
- Once the barrier is installed, no additional costs (other than monitoring) are required.

3.1.7.4. Disadvantages

- Emplacement of the barrier can be disruptive to the site, and the barrier is placed downstream of the contaminant plume.
- It is a permanent barrier; it cannot be easily moved.
- Because it is a passive system, it may take years for the contaminated groundwater to pass through.

3.1.7.5. Applicability to Sandia ER sites, limitations, costs

This technology is not applicable to the sites at Sandia because of the groundwater depths (> 120 feet).

3.1.7.6. Vendors/Contacts/References

- ARS Technologies, Inc., Chemical Oxidation: <http://arstechnologies.com/> <http://arstechnologies.com/solids.html>
- EPA, 1997, Permeable Reactive Subsurface Barriers for the Interception and Remediation of Chlorinated Hydrocarbon and Chromium(VI) Plumes in Groundwater, EPA/600-F-97/008: <http://www.epa.gov/ada/download/fact/remediat.pdf>
- ESTCP (Environmental Security Technology Certification Program), 1999, Cost and Performance Report: Permeable Reactive Wall Remediation of Chlorinated Hydrocarbons in Groundwater: <http://www.estcp.org/documents/techdocs/199604.pdf>
- Permeable Reactive Barrier Network, list of vendors: <http://www.prb-net.org/>
- Geo-Solutions, Inc., Reactive Barriers: <http://www.geo-solutions.com>

3.1.8. Natural Attenuation

3.1.8.1. General Description

Natural attenuation is a process in which the environment reduces the concentration of or contains a contaminant naturally without human intervention. Natural attenuation can occur through the processes of dilution, dispersion, biodegradation, and irreversible sorption of contaminants in groundwater (EPA, 1996b, 1999). In some cases natural attenuation can effectively reduce or remove the contaminant faster than engineered processes. Monitored Natural Attenuation refers to a process in which the concentrations and location of the contaminants are closely monitored to determine where and when natural attenuation is occurring.

Biodegradation removes the contaminant from the groundwater by changing the chemical composition of the contaminant. Many naturally occurring microbes will metabolize common contaminants into carbon dioxide and water over period of time. Figure 8 shows the natural degradation of several common contaminants.

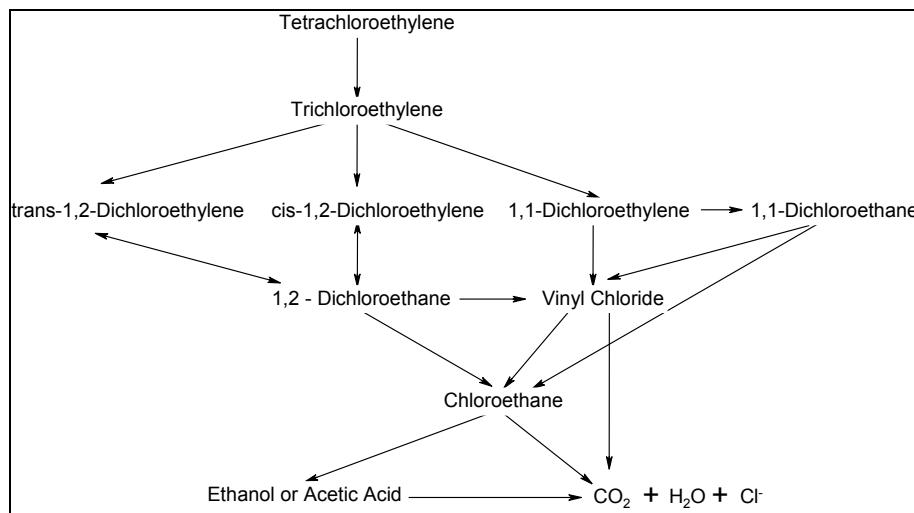


Figure 8. Natural degradation of common chlorinated contaminants to carbon dioxide and water.

Natural attenuation can take place over a wide variety of concentrations. In the case of biodegradation, microbe numbers increase under high concentrations of contaminants but will decrease rapidly after the food source has been used up. In order to investigate if a site can sustain biodegradation, a comprehensive study of the site must be conducted. The study should evaluate the extent and magnitude of the contamination, the chemical characteristics of the groundwater, the degradation rates of the contaminants, and the rate of contaminant plume migrations.

Bioremediation can also be enhanced by the addition of electron donors (substrates) and/or nutrients to increase bacterial growth in the subsurface. The compound that is injected to stimulate microbial growth depends on the type of bacteria being stimulated to degrade the contaminant of interest. The most predominant types of bacteria in the subsurface are heterotrophic, which require organic carbon substrates that serve as a source of energy. In addition, bacteria are classified as either aerobic (requiring oxygen) or anaerobic (requiring an environment devoid of oxygen). Aerobic microbes can be stimulated by injecting additional oxygen via air sparging in the saturated zone or soil vapor extraction in the unsaturated zone.

One example of enhanced bioremediation has been implemented by a company called Regenesis, which has developed a process of injecting a Hydrogen Release Compound (HRC®) directly into the contaminated groundwater in several areas surrounding the contaminated zone. Naturally occurring anaerobic microbes slowly break down the HRC® and release lactic acid via hydrolysis. The microbes metabolize the lactic acid producing acetic acid and nicotinamide adenine dinucleotide (NADH). NADH is reduced using an enzyme in the microbe to produce hydrogen, which is then used by naturally reductive dehalogenator microbes to remove the halogens from the chlorinated solvents. Once the molecule has been fully dehalogenated further aerobic degradation can take place. The entire process takes place over a period of 18 months. In the case of PCE and TCE the HRC treatment will reduce the molecules to ethene, which will eventually degrade to carbon dioxide and water.

Phytoremediation is another process by which organic compounds can degrade naturally. Phreatophytic species such as hybrid poplars and eastern cottonwoods have demonstrated the ability to take up TCE from both soil and water. Their roots are deep, and they have a fast growth rate. Postulated mechanisms for the degradation of TCE by these species include the effect of the enzyme dahlogenase, which is exuded from the roots and transforms or mineralizes TCE. In addition, phreatophytes may remove TCE through metabolism.

Irreversible sorption is another attenuation process in which contaminants attach to underground particles and are removed from the groundwater. This process is common with hydrophobic chemicals such as fuels and oils, which tend to bind to other hydrophobic materials such as clays minerals and organic materials. This reduces the concentration in the groundwater by effectively containing the contaminant. The contaminant is removed from the groundwater but not destroyed.

The process of dilution and dispersion is achieved by the mixing of contaminants with relatively clean groundwater. Precipitation that infiltrates into the subsurface can seep underground to dilute contaminated groundwater. In addition, contaminants will disperse as the groundwater flows down gradient. The overall effect is to reduce the concentration of the contaminants over time; however, this process does not remove the contaminant from the groundwater.

3.1.8.2. Cost

If enhanced bioremediation methods are not used, the only costs associated with natural attenuation are for monitoring the contaminant attenuation of the site. AFCEE (1999, p. 5-1) estimated that the average present-day cost to implement monitored natural attenuation at 11 Air Force sites for periods ranging from 10 to 49 years (average of 26 years) with an average network of 17 wells and 3 surface-water stations was \$480,000. Enhanced bioremediation costs depend on the type of substrate or nutrient being injected.

3.1.8.3. Advantages

- Completely passive. No operational costs other than monitoring.
- Could be cheaper, faster, and more effective than engineered solutions.
- Natural attenuation occurs in both the vadose zone and the saturated zone.
- Can be used in conjunction with other active remediation technologies.

3.1.8.4. Disadvantages

- The contaminants may not naturally degrade or dilute significantly over time.
- This method requires monitoring to determine if natural attenuation is occurring.
- The duration of monitoring may be indefinite.

3.1.8.5. Applicability to Sandia ER Sites

Natural attenuation of TCE and other chlorinated solvents is likely to occur at the Sandia ER sites. Although phytoremediation is not applicable to the sites at Sandia because of the groundwater depths, sorption and dispersion of contaminants are likely. In addition, evidence of the potential for biodegradation of volatile organic compounds at the Chemical Waste Landfill was observed through laboratory studies of soil samples in the upper 80 ft of the CWL vadose zone (SNL/NM, 1999). However, evidence of biodegradation from site characterization data was weak. Other processes including evaporation and diffusion made the identification of biodegradation processes difficult.

Monitoring at SNL ER sites is ongoing, so the implementation of monitored natural attenuation is, in fact, already occurring. The use of more rigorous monitoring methods to obtain more spatially and temporally continuous measurements of contaminant concentrations may be needed. Real-time in-situ sensors that monitor TCE concentration, temperature, atmospheric pressure, relative humidity, and groundwater depth are currently being tested at the Chemical Waste Landfill at Sandia (www.sandia.gov/sensor/cwl). The effectiveness of natural attenuation for various site conditions can be evaluated at the following web site: <http://www.sandia.gov/eesector/gs/gc/na/mnahome.html>.

3.1.8.6. Vendors/Contacts/References

- AFCEE (Air Force Center for Environmental Excellence), 1999, Natural Attenuation of Chlorinated Solvents Performance and Cost Results from Multiple Air Force Demonstration Sites, <http://www.afcee.brooks.af.mil/er/ert/download/chlorsolventsreport.pdf>
- Cunningham, S. D., T. A. Anderson, A. P. Schwab, and F. C. Hsu, 1996, Phytoremediation of soils contaminated with organic pollutants, Advances in Agronomy, 56, 55-107.
- Lay, J.D., Phytoremediation of Trichloroethylene (TCE), <http://www.hort.agri.umn.edu/h5015/99fpapers/lay.htm>.
- EPA, 1996b, A Citizen's Guide to Natural Attenuation, EPA 542-F-96-015, <http://www.clu-in.org/products/citguide/natural.htm>
- EPA, 1999, Monitored Natural Attenuation of Chlorinated Solvents, EPA/600/F-98/022, <http://www.clu-in.org/download/techdrct/tdchl-solv.pdf>
- Regenesis, Accelerating Natural Attenuation: www.regenesis.com
- Sandia Natural Attenuation Program: <http://www.sandia.gov/eesector/gs/gc/snap.html>
- Sandia National Laboratories (SNL), 1999, Chemical Waste Landfill Vapor Extraction Voluntary Corrective Measures Final Report, Environmental Restoration Project, Sandia National Laboratories, Albuquerque, NM, draft report.

3.2. Nitrate Treatment Technologies

Nitrates are nitrogen-oxygen compounds that combine with other organic and inorganic compounds. Primary sources of organic nitrates that may contaminant drinking water include human sewage and livestock manure, especially from feedlots. The primary inorganic nitrates are potassium nitrate and ammonium nitrate, which are used widely as fertilizers, and are found in explosives as well. Excess nitrates can leach into rivers and soils, where they can then be transported to groundwater that is used for human consumption. Nitrates are very soluble and do not adsorb onto soil particles; therefore, nitrates have a high potential to migrate to groundwater. In addition, nitrates are not volatile, so they are likely to remain in water until consumed by plants or other organisms.

Excessive levels of nitrate in drinking water can cause serious illness and sometimes death. Infants are more susceptible to nitrate contamination because the conversion of nitrate to nitrite within the body interferes with the oxygen-carrying capacity of the child's blood, which causes shortness of breath and blueness of the skin.

Methods for in-situ remediation of nitrate contamination include the following: (1) introduction of materials into the subsurface to transform nitrates to nitrogen and other byproducts; (2) transformation of nitrates using riparian vegetation; and (3) transformation of nitrates through enhanced microbial denitrification. These methods are described in the following sections.

3.2.1. Reduction of Nitrate using Iron Powder

3.2.1.1. General Description

This treatment process utilizes zero-valent iron (Fe^0) to remediate nitrate-contaminated water and soil. The iron acts as a reducing agent for the nitrate (NO_3^-) to form nitrogen gas, water, and other byproducts. Chew et al. (1998) conducted a series of batch and column experiments by mixing sand and iron powder with solutions of nitrate and atrazine. Three different types of iron powder were used: laboratory grade iron powder from Fisher, Inc. (40 mesh, about 0.02 mm in diameter); industrial grade iron powder from U.S. Metals (about 0.5 mm in diameter); and rusted industrial grade powder (about 0.5 mm in diameter). Results showed that the rusted iron powder worked best at removing nitrate in the batch experiments, but nitrate removal was dependent on pH in the column experiments. Atrazine was removed in both cases. Nitrate reduction using iron powder has also been observed by Alowitz and Scherer (2002), Gandhi et al. (2002), and Westerhoff (2003).

The application of this method would require the contaminated groundwater to be filtered through the iron mixtures. This can be done ex situ, or, preferably, in situ through the use of a permeable reactive barrier. The permeable reactive barriers are installed by digging trenches and backfilling the trenches with the desired material. The materials can be combined to provide a combination of remediation technologies such as air sparging, bioremediation, and chemical reduction. It should be noted that Ritter et al. (2002) reported that the iron used in permeable walls is an impure commercial material that is covered with a passive layer of Fe_2O_3 , which can inhibit contaminant reduction. However, their study showed that this layer was readily removed from the commercial iron (Connelly iron) when contacted with Millipore water, and the

subsequent corrosion products of magnetite and green rust that formed on the iron did not interfere with TCE degradation. Previous studies by Ritter (2000) showed, however, that the formation of magnetite and green rust resulted in the reduction of only a small amount of nitrate. This observation, coupled with the fact that the reduction product is ammonium (an undesirable contaminant), led to their conclusion that the use of granular iron permeable walls was questionable for nitrate remediation.

ARS Technologies has alternative patented technology (FEROXSM) to inject zero-valent iron powder into the subsurface. An open borehole or direct-push casing is used to insert the injectors into the subsurface. Once in place, zero-valent iron powder is injected into the formation as a slurry or as a dry material. Both procedures use nitrogen gas as the carrier fluid. Their web site (<http://arstechnologies.com/solids.html>) contains additional details and results of this technology.

3.2.1.2. Advantages

- Use of iron powder may be effective in remediating multiple contaminants (nitrate, atrazine, TCE, chromium VI, arsenate, others).
- Treatment is passive and in situ.
- Monitoring can be focused to determine performance of reactive barrier
- Cost of the iron material is low, but the primary cost is for emplacement and monitoring. Initial costs can be greater than pump-and-treat, but long-term costs are lower.

3.2.1.3. Disadvantages

- Permeable reactive barriers require trenching to emplace materials downstream of contaminant plume. Not feasible for large groundwater depths and requires knowledge of contaminant extent and migration.
- Permeable reactive barriers may clog from byproducts of chemical reactions.

3.2.1.4. Applicability to Sandia ER sites

The introduction of zero-valence iron as a reducing agent for nitrates may be applicable to the Sandia ER sites, but because the depths to the groundwater are so large, a cost-effective means of distributing the iron powder must be used. ARS Technologies has an injection technology based on open wells that may be applicable. Emplacement of permeable barriers consisting of iron would not be practical.

3.2.1.5. Vendors/Contacts/References

- Alowitz, M.J. and M.M. Scherer, 2002, Kinetics of Nitrate, Nitrite, and Cr(VI) Reduction by Iron Metal, *Environmental Science & Technology*, v.36, no.3, p.299-306.
- ARS Technologies, Inc.: Injection of Iron Powder: <http://arstechnologies.com/solids.html>

- Chew, C.F., T.C. Zhang, and J. Shan, 1998, Removal of Nitrate/Atrazine Contamination with Zero-Valent Iron-Promoted Processes, in proceedings of the 1998 Conference on Hazardous Waste Research.
URL: <http://www.engg.ksu.edu/HSRC/98Proceed/29Chew/29chew.pdf>
- GeoSierra LLC, Installs permeable reactive barriers. www.geosierra.com
- Ghandhi, S., B.T. Oh, J.L. Schnoor, and P.J.J. Alvarez, 2002, Degradation of TCE, Cr(VI), Sulfate, and Nitrate Mixtures by Granular Iron in Flow-Through Columns under Different Microbial Conditions, Water Research, v. 36, no. 8, 1973-1982.
- Ritter, K., M.S. Odziemkowski, and R.W. Gillham, 2002, An In-Situ Study of the Role of Surface Films on Granular Iron in the Permeable Iron Wall Technology, J. Contaminant Hydrology, v. 55, no. 1-2, 87-111.
- Ritter, K., 2000, A Study of the Reduction of Nitrate and the Effect of Nitrate on the Reduction of Trichloroethylene (TCE) by Connelly Granular Iron, Thesis Abstract, U. Waterloo. http://www.science.uwaterloo.ca/earth/theses/abstracts/ritter_kaylene.html.
- Westerhoff, P., 2003, Reduction of Nitrate, Bromate, and Chlorate by Zero Valent Iron (Fe-0), J. Environmental Engineering-ASCE, v. 129, no. 1, 10-16.

3.2.2. Remediation of Nitrate Contamination via Riparian Vegetation

3.2.2.1. General Description

Riparian zones are regions around rivers and streams that link water and dry land. Riparian vegetation can also be found around irrigation ponds, gravel pits, and ditches. These zones can be extremely effective in removing nitrate from shallow groundwater, and they are most effective when the shallow groundwater can be accessed by plant roots and when a low permeability zone exists beneath the root zone (rhizosphere) to hold the water. However, if permeable soils exists, surface and subsurface water can pass quickly to deep groundwater levels without allowing sufficient contact time between the riparian zone's root system and the contaminated groundwater, thus rendering the riparian zone less effective.

Nitrate, nitrite, and ammonium are taken up by the roots of the vegetation, and the nitrogen in the plant material is consumed or decomposed and returned to the environment as N₂. Vegetation in the riparian zone is especially effective for nitrate remediation because of the following (Lowrance et al., 1985): (1) riparian soils generally possess strong water-storage capacities because of high clay and organic-matter content; (2) water tables are shallow and seasonal variations cause the groundwater to come into contact with plant roots and soil microbes; and (3) close contact with the surface provides carbon for microbial denitrification (see Section 3.2.3 for more information).

3.2.2.2. Advantages

- Advantages include low operational cost, low maintenance, and long-term remediation capabilities. Costs are determined by the size of the riparian zone and the necessary labor involved in initiating and maintaining the appropriate vegetation. Another advantage is that the process works in concert with microbial denitrification and is environmentally friendly.

3.2.2.3. Disadvantages

- The disadvantage of this method is that it relies on the uptake of nitrates by plant roots; therefore, the groundwater must be near the soil surface and in prolonged contact with the rhizosphere, and the soil must have a strong potential for water storage.

3.2.2.4. Applicability to Sandia ER Sites

Because the depth to groundwater at the Sandia sites is greater than 100 feet below the ground surface at all relevant sites, the use of vegetation (and Riparian zones) is not directly applicable. The arid climate also limits the amount of water that percolates naturally through the rhizosphere. As identified in Table 1, the suspected source of contamination is from discharges from solid-waste management units, liquid-waste disposal systems, or unlined pits.

Appropriate vegetation could be planted in soils and surface locations where nitrate sources are thought to originate, but the arid climate of Albuquerque may not be conducive to abundant plant growth.

3.2.2.5. Vendors/Contacts/References

- Hornbeck, J.H., 1999, "Biological Remediation of Nitrate (NO₃⁻) Pollution at the Land/Water Interface," <http://www.hort.agri.umn.edu/h5015/99fpapers/hornbeck.htm>
- Lowrance, R., R. Leonard, and J. Sheridan, 1985, Managing Riparian Ecosystems to Control Nonpoint Pollution. Journal of Soil and Water Conservation, Jan/Feb, 87-91.

3.2.3. Bioremediation of Nitrate Contamination

3.2.3.1. General Description

Naturally occurring bacteria in the subsurface can covert nitrate to nitrogen gas via a process called denitrification. This anaerobic reduction-oxidation process relies on bacteria that can be either heterotrophic or autotrophic. Heterotrophic bacteria require organic matter for energy and growth, and several studies have investigated the use of various materials ranging from pecan shells to coconut shells to provide the organic material and substrate for the bacteria to grow on. The organic carbon is oxidized by the bacteria during the transfer of electrons to the nitrate, producing nitrogen gas and water. Chemical energy released during this process is used by the

bacteria to grow more biomass. Autotrophic bacteria obtain energy from inorganic materials using carbon dioxide as their sole carbon source.

Methods employing heterotrophic bacteria have been investigated by Strietelmeier et al. (2001). They used a highly porous, slowly degradable, biobarrier that was composed of pecan shells, which provided the organic carbon used by the heterotrophic bacteria. Strietelmeier et al. (2001) found that significant reductions in nitrate were obtained using the pecan shells and mixtures of pecan shells with dog food. Both systems reduced nitrate levels from ~0.5 to 9.7 millimolar to levels below the detection level, but an unwanted byproduct from the dog-food mixture was increased levels of ammonia. In addition to nitrate reduction, perchlorate was also greatly reduced using this biobarrier. Other organic carbon sources, such as coconuts, have also been investigated by researchers at the University of Canterbury in New Zealand.

This biobarrier concept, similar to the permeable reactive barrier concept, involves construction of a permeable wall of a porous carbon-based material, which is placed in a trench at a 90 degree angle to the groundwater flow. This trench must extend to at least the width and depth of the contaminant plume in question. Barrier technology is largely applicable to shallow plumes (less than 20 feet deep), but permeable reactive barriers have been placed up to 70-ft deep.

In-situ remediation methods employing autotrophic bacteria have been investigated by Haugen et al. (2002). An advantage of using autotrophic bacteria is that carbon dioxide is used as the carbon source, so introduction of external organic carbon is not needed. Hydrogen or sulfur compounds are used as electron donors, and the nitrate acts as the electron acceptor. When hydrogen gas is used as the electron donor, nitrate is reduced to nitrogen gas and hydrogen gas is oxidized to water. The growth rate of autotrophic bacteria is typically slower than heterotrophic bacteria, so the risk of biological growth in distribution systems is lessened.

Haugen et al. (2002) performed laboratory experiments to test the feasibility of remediating nitrates from groundwater using autotrophic denitrification with hydrogen gas as the electron donor. Silicone hollow-fiber membranes were used to supply hydrogen gas into a simulated groundwater environment with nitrate. Results demonstrated that nitrate levels could be effectively removed by supplying adequate amounts of H₂ to the groundwater through the use of hollow-fiber membranes. Nitrate removal was accomplished with small increases in total organic carbon or effluent turbidity. Haugen et al. (2002) recommend this method as a potential in-situ treatment for nitrate contamination. An advantage of in situ treatment is that the aquifer acts as both a biochemical reactor and a filter for the removal of biological byproducts.

3.2.3.2. Advantages

- Bioremediation methods, in particular the use of autotrophic bacteria, are inexpensive relative to traditional methods.
- Bacteria are typically indigenous to the aquifer environments.

3.2.3.3. Disadvantages

- Heterotrophic denitrification requires the use of external organic carbon sources (e.g., pecan shells or coconut shells).

- The successful performance of nitrate-reducing bacteria requires the appropriate bacteria, nutrients, and environmental conditions (e.g., pH, temperature, etc.)

3.2.3.4. Applicability to Sandia ER Sites

The use of heterotrophic and autotrophic bacteria in monitored natural attenuation may be feasible for the sites at Sandia. The effectiveness of biodegradation, however, at very low contaminant concentrations is uncertain. In addition, the proper nutrients and electron donors (in the case of autotrophic bacteria) will probably need to be supplied to provide an adequate remedial response. Hollow-fiber membranes may be applicable, but this technology is still emerging.

3.2.3.5. Vendors/Contacts/References

- Strietelmeier, B.A., M.L. Espinosa, J.D. Adams, P.A. Leonard, and E.M. Hodge, 2001, Use of a Unique Biobarrier to Remediate Nitrate and Perchlorate in Groundwater, in Proceedings of the 2001 International Containment & Remediation Technology Conference and Exhibition, June 10-13, 2001, Orlando, FL. <http://www.clu-in.org/perchlorate/download/Strietelmeier1.pdf> <http://www.clu-in.org/perchlorate/download/Strietelmeier2.ppt>
- Haugen, K.S., M.J. Semmens, and P.J. Novak, 2002, A Novel In Situ Technology for the Treatment of Nitrate Contaminated Groundwater, Water Research, v. 36, no. 14, 3497-3506.

4. Summary and Recommendations

The primary contaminants of concern for the Tijeras Arroyo Groundwater, Technical Area V, and Canyons sites are trichloroethylene (TCE) tetrachloroethylene (PCE), and nitrate. The low concentrations of these contaminants coupled with the large depths to the water table at these sites prohibits the use of many of the remediation technologies surveyed (see Table 1).

Based on the technologies surveyed in this report, we recommend that the application of monitored natural attenuation be employed to document the reduction of concentrations of TCE, PCE and nitrate in the groundwater that is already occurring naturally. If deemed feasible and necessary, enhanced bioremediation may be implemented as well. However, strong evidence of the potential effectiveness of enhanced bioremediation at the Sandia ER sites is lacking. Active stripping technologies such as soil vapor extraction may be employed to reduce concentrations of volatile organic compounds in the unsaturated zone, if needed. Table 2 provides a summary of the treatment technologies and their applicability to the Sandia ER sites.

Finally, it is useful to discuss past corrective measures studies at Sandia. Previous corrective measures studies have been conducted for the Mixed Waste Landfill (Goering et al., 2002) and Chemical Waste Landfill (SNL/NM, 2003) at Sandia. Goering et al. determined that the groundwater at the Mixed Waste Landfill was free of contamination; therefore, their conclusions focused on monitoring as opposed to remediation or treatment technologies. The Chemical

Waste Landfill report (SNL/NM, 2003) detailed past corrective measures that included soil vapor extraction and excavation, which effectively removed the source of groundwater contamination at this site. The final remedy proposed in that report focused on the design of a vegetative cover system over the Chemical Waste Landfill. In contrast, the proposed recommendations in this report have focused on treatment technologies for low levels of contaminant concentrations (near MCLs) in the groundwater.

Table 2. Applicability of treatment technologies to Sandia ER sites.

	Tijeras Arroyo Groundwater (TAG) Area	Technical Area V (TA-V) Area	Canyons Area
TCE and PCE Remediation Technologies			
<u>Soil Vapor Extraction</u>	Possibly applicable for VOC removal in the vadose zone	Possibly applicable for VOC removal in the vadose zone	N/A
<u>Air Sparging/Groundwater Circulation</u>	May be applicable for perched water zone	N/A (depth to groundwater prohibitive)	N/A
<u>Surfactant Enhanced Aquifer Remediation</u>	May be applicable for perched water zone	N/A (depth to groundwater prohibitive)	N/A
<u>Steam Injection</u>	Possibly applicable for VOC removal in the vadose zone. Soil vapor extraction may be more cost effective.	Possibly applicable for VOC removal in the vadose zone. Soil vapor extraction may be more cost effective.	N/A
<u>Pneumatic Fracturing</u>	May be applicable to enhance other remediation methods	May be applicable to enhance other remediation methods	N/A
<u>Chemical Oxidation</u>	Applicable (depth to groundwater may be prohibitive)	Applicable (depth to groundwater may be prohibitive)	N/A
<u>Permeable Reactive Barrier</u>	N/A (depth to groundwater prohibitive)	N/A (depth to groundwater prohibitive)	N/A
<u>Natural Attenuation</u>	Applicable	Applicable	N/A
Nitrate Remediation Technologies			
<u>Reduction of Nitrate using Iron Powder</u>	Possibly applicable if cost-effective means of distributing the iron powder is used.	Possibly applicable if cost-effective means of distributing the iron powder is used.	Possibly applicable if cost-effective means of distributing the iron powder is used.
<u>Nitrate Remediation via Riparian Vegetation</u>	N/A (depth to groundwater prohibitive)	N/A (depth to groundwater prohibitive)	N/A (depth to groundwater prohibitive)
<u>Bioremediation/Denitrification of Nitrate</u>	Denitrification of nitrates is applicable, but nutrients and substrates may need to be added to promote bacterial growth.	Denitrification of nitrates is applicable, but nutrients and substrates may need to be added to promote bacterial growth.	Denitrification of nitrates is applicable, but nutrients and substrates may need to be added to promote bacterial growth.

TCE: Trichloroethylene; PCE: Tetrachloroethylene; N/A: Not applicable

5. References

- AFCEE (Air Force Center for Environmental Excellence), 1999, Natural Attenuation of Chlorinated Solvents Performance and Cost Results from Multiple Air Force Demonstration Sites, <http://www.afcee.brooks.af.mil/er/ert/download/chlorsolventsreport.pdf>
- Alowitz, M.J. and M.M. Scherer, 2002, Kinetics of Nitrate, Nitrite, and Cr(VI) Reduction by Iron Metal, Environmental Science & Technology, v.36, no.3, p.299-306.
- ARS Technologies, Inc., Chemical Oxidation: <http://arstechnologies.com/> <http://arstechnologies.com/chemox.html>
- ARS Technologies, Inc., Pneumatic Fracturing: <http://arstechnologies.com/> <http://arstechnologies.com/gases.html> (nice animation describing pneumatic fracturing)
- ARS Technologies, Inc., Chemical Oxidation: <http://arstechnologies.com/> <http://arstechnologies.com/solids.html>
- ARS Technologies, Inc.: Injection of Iron Powder: <http://arstechnologies.com/solids.html>
- BaroBall™ web site: <http://www.srs.gov/general/enviro/erd/technology/Pages/d03.html>
- Chew, C.F., T.C. Zhang, and J. Shan, 1998, Removal of Nitrate/Atrazine Contamination with Zero-Valent Iron-Promoted Processes, in proceedings of the 1998 Conference on Hazardous Waste Research.
URL: <http://www.engg.ksu.edu/HSRC/98Proceed/29Chew/29chew.pdf>
- Cunningham, S. D., T. A. Anderson, A. P. Schwab, and F. C. Hsu, 1996, Phytoremediation of soils contaminated with organic pollutants, Advances in Agronomy, 56, 55-107.
- Environmental Protection Agency (EPA) Soil Vapor Extraction web site: <http://www.epa.gov/swerust1/cat/sve1.htm>
- EPA, In Situ Remediation Technology Status Report: Surfactant Enhancements, Report EPA542-K-94-003, April 1995. <http://www.clu-in.org/download/remed/srfctnt.pdf>
- EPA, 1995, In Situ Remediation Technology Status Report: Hydraulic and Pneumatic Fracturing, EPA 542-K-94-005, http://www.gwrtac.org/pdf/Epa_frac.pdf
- EPA, 1989. *Terra Vac, In Situ Vacuum Extraction System*, EPA RREL, Applications Analysis Report, Cincinnati, OH, EPA Report EPA/540/A5-89/003.
- EPA, 1996a, User's Guide to the VOCs in Soils Presumptive Remedy, EPA 540/F-96/008, <http://www.epa.gov/superfund/resources/presump/finalpdf/vc.pdf>

- EPA, 1996b, A Citizen's Guide to Natural Attenuation, EPA 542-F-96-015, <http://www.clu-in.org/products/citguide/natural.htm>
- EPA, 1997, Permeable Reactive Subsurface Barriers for the Interception and Remediation of Chlorinated Hydrocarbon and Chromium(VI) Plumes in Groundwater, EPA/600-F-97/008: <http://www.epa.gov/ada/download/fact/remediat.pdf>
- EPA, 1998a, Field Applications of In Situ Remediation Technologies: Ground-Water Circulation Wells, EPA 542-R-98-009, <http://clu-in.org/download/remed/gwcirc.pdf>
- EPA, 1998b, Ground Water Issue, Steam Injection for Soil and Aquifer Remediation, EPA/540/S-97/505. <http://www.epa.gov/tio/tsp/download/steaminj.pdf>
- EPA, 1998c, Field Applications of In Situ Remediation Technologies: Chemical Oxidation, EPA 542-R-98-008.
- EPA, 1999, Monitored Natural Attenuation of Chlorinated Solvents, EPA/600/F-98/022, <http://www.clu-in.org/download/techdrct/tdchl-solv.pdf>
- ESTCP (Environmental Security Technology Certification Program), 1999, Cost and Performance Report: Permeable Reactive Wall Remediation of Chlorinated Hydrocarbons in Groundwater: <http://www.estcp.org/documents/techdocs/199604.pdf>
- ESTCP (Environmental Security Technology Certification Program), 2001, Surfactant Enhanced DNAPL Removal: <http://www.estcp.org/documents/techdocs/199714.pdf>
- Ghandhi, S., B.T. Oh, J.L. Schnoor, and P.J.J. Alvarez, 2002, Degradation of TCE, Cr(VI), Sulfate, and Nitrate Mixtures by Granular Iron in Flow-Through Columns under Different Microbial Conditions, *Water Research*, v. 36, no. 8, 1973-1982.
- GeoSierra LLC, Installs permeable reactive barriers. www.geosierra.com
- Geo-Solutions, Inc., Reactive Barriers: <http://www.geo-solutions.com/Default2.htm>
- Goering, T.J., G.M. Haggerty, D. Van Hart, and J.L. Peace, 2002, Mixed Waste Landfill Groundwater Report, 1990 through 2001, Sandia National Laboratories, Albuquerque, New Mexico, SAND2002-4098, Sandia National Laboratories, Albuquerque, NM.
- Haugen, K.S., M.J. Semmens, and P.J. Novak, 2002, A Novel In Situ Technology for the Treatment of Nitrate Contaminated Groundwater, *Water Research*, v. 36, no. 14, 3497-3506.
- Ho, C.K. and K.S. Udell, 1992, An Experimental Investigation of Air Venting of Volatile Liquid Hydrocarbon Mixtures from Homogeneous and Heterogeneous Porous Media, *J. Contam. Hydrol.*, 11, 291-316.
- Hornbeck, J.H., 1999, "Biological Remediation of Nitrate (NO₃⁻) Pollution at the Land/Water Interface," <http://www.hort.agri.umn.edu/h5015/99fpapers/hornbeck.htm>

- ISOTEC, Inc., In Situ Oxidative Technologies: <http://www.insituoxidation.com/>
- Lay, J.D., Phytoremediation of Trichloroethylene (TCE),
<http://www.hort.agri.umn.edu/h5015/99fpapers/lay.htm>.
- Lowrance, R., R. Leonard, and J. Sheridan, 1985, Managing Riparian Ecosystems to Control Nonpoint Pollution. Journal of Soil and Water Conservation, Jan/Feb, 87-91.
- Miller, R.R., 1996, Air Sparging, Ground-Water Remediation Technologies Analysis Center, Report TO-96-04: http://www.gwrtac.org/pdf/Sparge_o.pdf
- Permeable Reactive Barrier Network, list of vendors: <http://www.prb-net.org/>
- Regenesis, Accelerating Natural Attenuation: www.regenesis.com
- Ritter, K., 2000, A Study of the Reduction of Nitrate and the Effect of Nitrate on the Reduction of Trichloroethylene (TCE) by Connelly Granular Iron, Thesis Abstract, U. Waterloo. http://www.science.uwaterloo.ca/earth/theses/abstracts/ritter_kaylene.html.
- Ritter, K., M.S. Odziemkowski, and R.W. Gillham, 2002, An In-Situ Study of the Role of Surface Films on Granular Iron in the Permeable Iron Wall Technology, J. Contaminant Hydrology, v. 55, no. 1-2, 87-111.
- Sandia National Laboratories (SNL), 1999, Chemical Waste Landfill Vapor Extraction Voluntary Corrective Measures Final Report, Environmental Restoration Project, Sandia National Laboratories, Albuquerque, NM, draft report.
- Sandia National Laboratories (SNL), 2001, Long-Term Monitoring Strategy for Groundwater, Environmental Restoration Project, Sandia National Laboratories, Albuquerque, NM, draft report.
- Sandia National Laboratories (SNL), May 2003, “Chemical Waste Landfill: Corrective Measures Study, Remedial Action Proposal, Post-Closure Care Plan,” Environmental Restoration Project, Sandia National Laboratories, Albuquerque, NM.
- Sandia Natural Attenuation Program: <http://www.sandia.gov/eesector/gs/gc/snap.html>
- Subsurface Volatilization and Ventilation System, Billings & Associates, Inc.: <http://www.clu-in.org/products/site/complete/democomp/billings.htm>
- Steam Tech Environmental Services, Inc.: <http://www.steamtech.com/>
- Strietelmeier, B.A., M.L. Espinosa, J.D. Adams, P.A. Leonard, and E.M. Hodge, 2001, Use of a Unique Biobarrier to Remediate Nitrate and Perchlorate in Groundwater, in Proceedings of the 2001 International Containment & Remediation Technology Conference and Exhibition, June 10-13, 2001, Orlando, FL.
<http://www.clu-in.org/perchlorate/download/Strietelmeier1.pdf>
<http://www.clu-in.org/perchlorate/download/Strietelmeier2.ppt>

- Terra Vac, Inc. Air Sparging: <http://www.terravac.com/web/toolsas.htm>
- Terra Vac, Inc. Pneumatic Soil Fracturing: <http://www.terravac.com/web/toolspsf.htm>
- Terra Vac, Inc. Soil Vapor Extraction: <http://terravac.com/web/toolsve.htm>
- Thermal Enhanced Vapor Extraction:
<http://www.sandia.gov/Subsurface/factshts/ert/teves.pdf>
- United States Geological Survey (USGS), 2002, Ground-water Resources of the Middle Rio Grande Basin, USGS Fact Sheet 088-02, September, 2002.
- Westerhoff, P., 2003, Reduction of Nitrate, Bromate, and Chlorate by Zero Valent Iron (Fe-0), J. Environmental Engineering-ASCE, v. 129, no. 1, 10-16.

Distribution

External

Cindy Ardito (1)
Intera
6501 Americas Pkwy N E
Albuquerque, NM 87110-5375
cardito@intera.com

Internal

1	MS-0701	P. Davies, 6100
1	MS-0701	W. Cox, 6100
1	MS-0735	C. Ho, 6115
1	MS-0735	L. McGrath, 6115
1	MS-0735	J. Wright, 6115
1	MS-0735	R. Finley, 6115
1	MS-0750	M. Walck, 6116
1	MS-0751	L. Costin, 6117
1	MS-0750	T. Hinkebein, 6118
1	MS-1087	F. Nimick, 6132
1	MS-1087	S. Collins, 6133
1	MS-1088	D. Miller, 6134
1	MS-1087	Michael Skelly, 6134
1	MS-1087	John Copland, 6133
1	MS-1087	Tim Jackson, 6134
1	MS-1126	Gary Bailey, 6134
1	MS-1089	Tim Goering, 6134
1	MS-1087	Stacy Griffith, 6133
1	MS-1089	Mike Sanders, 6133
1	MS-1042	Franz Lauffer, 3121
1	MS-9018	Central Technical Files, 8945-1
2	MS-0899	Technical Library, 9616