PDHonline Course C671 (3 PDH)

Biological Treatment of Contaminated Soils

Instructor: John Huang, Ph.D., PE and John Poullain, PE

2020

PDH Online | PDH Center

In Situ Treatment Technologies for Contaminated Soil

ENGINEERING FORUM ISSUE PAPER

Contents

1.0 Introduction

This issue paper provides summary information on a wide variety of in situ technologies for the treatment of contaminated soil in both the vadose zone and saturated and unsaturated source zones. The in situ technologies presented involve applying chemical, biological, or physical processes to the subsurface to degrade, remove, or immobilize contaminants without removing the bulk soil.

Compared to excavation and ex situ treatment, the use of these technologies offers several benefits, such as addressing deep contamination and generally costing less.

The summary for each in situ technology includes a basic description of the technology, its implementation, applicability based on contaminants and site characteristics, general limitations, costs, and status of the technology's application. Information in this paper is intended to give project managers and engineers a basic understanding of the technology that will allow for further consideration of its applicability at a site. Project managers and engineers seeking guidance on the design and operation of these technologies should refer to the references listed in this paper and other material on the specific technology of interest.

The treatment technologies presented include common practices as well as innovative alternatives for treating contaminated soil and source zones in situ. The paper does not address technologies in the experimental phase, such as nanoscale iron injection, nor does it present containment technologies, such as capping, liners, and barrier walls.

Information provided in this paper comes from a number of sources. In general, every attempt has been made to use technical literature, including articles, textbooks, and U.S. Environmental Protection Agency (EPA) and other agency documents. Where appropriate and possible, Web links have been provided for additional information. This paper is not intended to serve as guidance or policy, nor does it indicate the appropriateness of using a technology at a specific site.

A system that uses in situ treatment combined with electrokinetic separation is the LasagnaT technique. In this system electrode arrays and treatment zones (e.g., crushed limestone, zero valent iron) are interlayered. The applied current causes the contaminants to move through the treatment zones where they are either destroyed or immobilized. LasagnaT was applied with some success to treat a TCE contaminated clay soil at the DOE gaseous diffusion plant in Paducah, Kentucky (U.S. DOE 2002).

Because of the limited application of electrokinetic separation, reliable cost data for full-scale applications are scarce. Costs will vary significantly depending upon the concentration of the target contaminant, presence of non-target ions, and soil characteristics and moisture content. Estimates from three vendors were collected by Van Cauwenberghe (1997) and ranged from $20 to $100 per cubic yard for one vendor to $60 to $225 per cubic yard for the high vendor estimate.

Cited and Other References

Alshawabkeh, A. 2001. Basics and Applications of Electrokinetic Remediation. Northeastern University, 95 pp. http://www1.coe.neu.edu/~aalsha/short course.pdf

Environmental Security Technology Certification Program (ESTCP). 2000. Final In-Situ Electrokinetic Remediation of Metal Contaminated Soils Technology Status Report, SFIM-AEC-ET-CR-99022. US Army Environmental Center, 30 pp, July 2000. http://www.estcp.org/documents/techdocs/ ISERMCS Report.pdf

NAVFAC. 2000. TechData Sheet: A Demonstration of Electrokinetic Remediation, TDS-2084-ENV, 2 pp.

Roulier; M., M. Kemper; P. Cluxton. 2002. Horizontal Configuration of the LasagnaT Treatment Technology. User Guide, EPA 600/R-02/033. U.S. Environmental Protection Agency, Office of Research and Development, 38 pp. http://nepis.epa. gov/pubtitleORD.htm

Saichek, R. and K. Reddy. 2005. Electrokinetically enhanced remediation of hydrophobic organic compounds in soils: A review. Critical Reviews in Environmental Science and Technology, 35: 115–192. http://www.uic.edu/classes/cemm/cemmlab/35-2-2005.pdf

U.S. DOE. 2002. Final Remedial Action Report for Lasagna[TM] Phase IIb In-Situ Remediation of Solid Waste Management Unit 91 at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky, OR/072037 &D1, 80 pp. http://www.rtdf.org/public/lasagna/ lasagna final a.pdf

U.S. EPA. 1997. Electrokinetic Laboratory and Field Processes Applicable to Radioactive and Hazardous Mixed Waste in Soil and Groundwater. EPA 402/R-97/006. Office of Radiation and Indoor Air. July 1997. http://nepis.epa.gov/pubtitleOAR.htm

U.S. EPA. 1999. Sandia National Laboratories In Situ Electrokinetic Extraction Technology Innovative Technology Evaluation Report, EPA 540/R-97/509. Office of Research and Development, 69 pp. http://www.epa.gov/ORD/SITE/reports/540r97509/ 540r97509.pdf

Van Cauwenberghe, L. 1997. Electrokinetics. Technology Overview Report. Ground Water Remediation Technologies Analysis Center.

3.2 Biological Treatment Technologies

Biological treatment involves the use of microorganisms or vegetation (phytoremediation). Many naturally occurring microorganisms (typically, bacteria and fungi) can transform hazardous chemicals to substances that may be less hazardous than the original compounds. Microrganisms also have been used to alter the valence of some hazardous metals (e.g., Cr(VI)), thereby making them less hazardous and less mobile. Several plant species have the ability to bioaccumulate heavy metals found in the soil, and some tree species can sequester, destroy, and/or evapotranspire various organic compounds.

Microbial bioremediation occurs under both aerobic and anaerobic conditions and at contaminated sites as either intrinsic and/or enhanced biodegradation. Intrinsic bioremediation depends on indigenous microorganisms to degrade contaminants without any amendments. Monitored natural attenuation (MNA) often relies on intrinsic bioremediation as an important removal mechanism. During enhanced bioremediation, biodegradation is facilitated by manipulating the microbial environment. Typically, the environment is manipulated by supplying amendments, such as air, organic substrates, nutrients, and other compounds, whose absence limit

treatment. In some cases, bioremediation has been enhanced by adding microbial cultures (bioaugmentation).

3.2.1 Bioventing

Bioventing involves the injection of a gas into the subsurface to enhance the biodegradation of a contaminant. The gas can be used to keep the subsurface aerobic or anaerobic, or to provide a substrate that enables cometabolic degradation to occur.

Aerobic Bioventing

Aerobic bioventing has a robust track record in treating aerobically degradable contaminants, such as fuels. Bioventing involves supplying oxygen to contaminated unsaturated soils with low oxygen concentrations to facilitate aerobic microbial biodegradation. Using the supplied oxygen, the microbes oxidize the contaminants to gain energy and carbon for growth. Oxygen is typically introduced by air injection wells that push air into the subsurface.

Aerobically degradable contaminants may be treated by bioventing, but fuels have received the most attention. The U.S. Air Force Bioventing Initiative and the U.S. EPA Bioremediation Field Initiative evaluated bioventing at 125 sites contaminated by petroleum hydrocarbons. At sites where initial studies were positive, pilot-scale bioventing was installed and operated for one year. The experience from bioventing demonstrations at these sites was condensed into a manual (U.S. EPA 1995a & 1995b). The manual contains information on bioventing principles; site characterization; field treatability testing; system design, operation, and installation; site closure; and techniques to demonstrate the extent and mechanism for contaminant removal. Based on this research, bioventing proved to be an economical and effective method to treat unsaturated soil contaminated by petroleum products. Regulatory acceptance of this technology has occurred in 30 states and in all 10 EPA regions. The use of this technology in the private sector has increased following the U.S. Air Force Bioventing Initiative and the U.S. EPA Bioremediation Field Initiative. Estimated costs range from $10 to $60 per cubic yard (U.S. EPA 1995b).

In addition to fuels, aerobic bioventing has treated a variety of other contaminants, including nonhalo-genated solvents, such as benzene, acetone, toluene, and phenol; lightly halogenated solvents, such as 1,2-dichloroethane, dichloromethane, and chlorobenzene; and SVOCs, such as some PAHs (Figure 4). The principles outlined in the manual are also applicable for aerobically degradable non-fuel contaminants, but since the experience with these other types of contaminants is more limited, more information may be needed. For example, laboratory and pilot-scale studies may be needed to evaluate effectiveness, design the bioventing system, estimate treatment times, and demonstrate that biodegradation is the primary mechanism of removal. In evaluating the feasibility of treating other contaminants, the key is to understand the volatility relative to the biodegradability.

Bioventing is typically operated in air injection mode to alleviate low oxygen levels in the subsurface. The injection system should be designed considering soil gas permeability, contaminant diffusion and distribution, and environmental factors, such as moisture content, pH, temperature, and electron acceptor conditions. When building foundations or similar structures are close to the site, vacuum extraction wells, which draw air through the subsurface, may be used to avoid the buildup of contaminated, and possibly explosive, vapors in the building basements.

Extracted gases require treatment since volatile compounds may be removed from the ground. In cases of remote locations without electric power, passive air delivery systems may be used. These systems use one-way valves and changes in barometric pressure to deliver air to the subsurface; however, passive systems may have longer treatment times depending on the quantities of air supplied to the subsurface. Compared to soil vapor extraction, all bioventing delivery systems employ lower air flow rates that provide only the amount of oxygen required to enhance removal. When operated properly, the low flow rates of air injection do not result in the release of the contaminants into the atmosphere through volatilization.

To determine if bioventing is appropriate at a specific site, existing site data should be evaluated and, if needed, additional data collected. For example, information about the types, quantities, and three-dimensional distribution of contaminants is needed. This includes the presence and location of free product and whether there is a chance of

continuing contamination from leaking pipes or tanks. Bioventing alone is not sufficient to remediate sites with large quantities of free product or ongoing releases. Information about the historical water table levels and soil characteristics, such as gas permeability, is also needed. A soil gas survey can provide useful information, especially at sites with relatively shallow contamination (depths typically less than 20 ft). The soil gas survey is useful to determine whether oxygen-limited conditions exist. Low oxygen levels (less than five percent) are a good indicator that existing bacteria are capable of degrading the contaminants of concern, because soil gas in uncontaminated soil generally exhibits oxygen concentrations similar to ambient air. In addition, the soil gas survey can be useful in delineating the extent of contamination and identifying locations for vent wells and monitoring points. If this preliminary information looks promising, more specific information should be gathered, such as soil contaminant concentrations and distribution and soil characterization. Respiration rate, soil gas permeability, and oxygen radius of influence will be needed to properly design the system.

and amount of contaminant removed, oxygen supply, and carbon dioxide generation, as well as mass balances relating the three amounts, may be useful in establishing bioremediation as the primary mechanism of removal. For sites where non-fuel contaminants are to be treated by bioventing, other factors may be considered in establishing biological
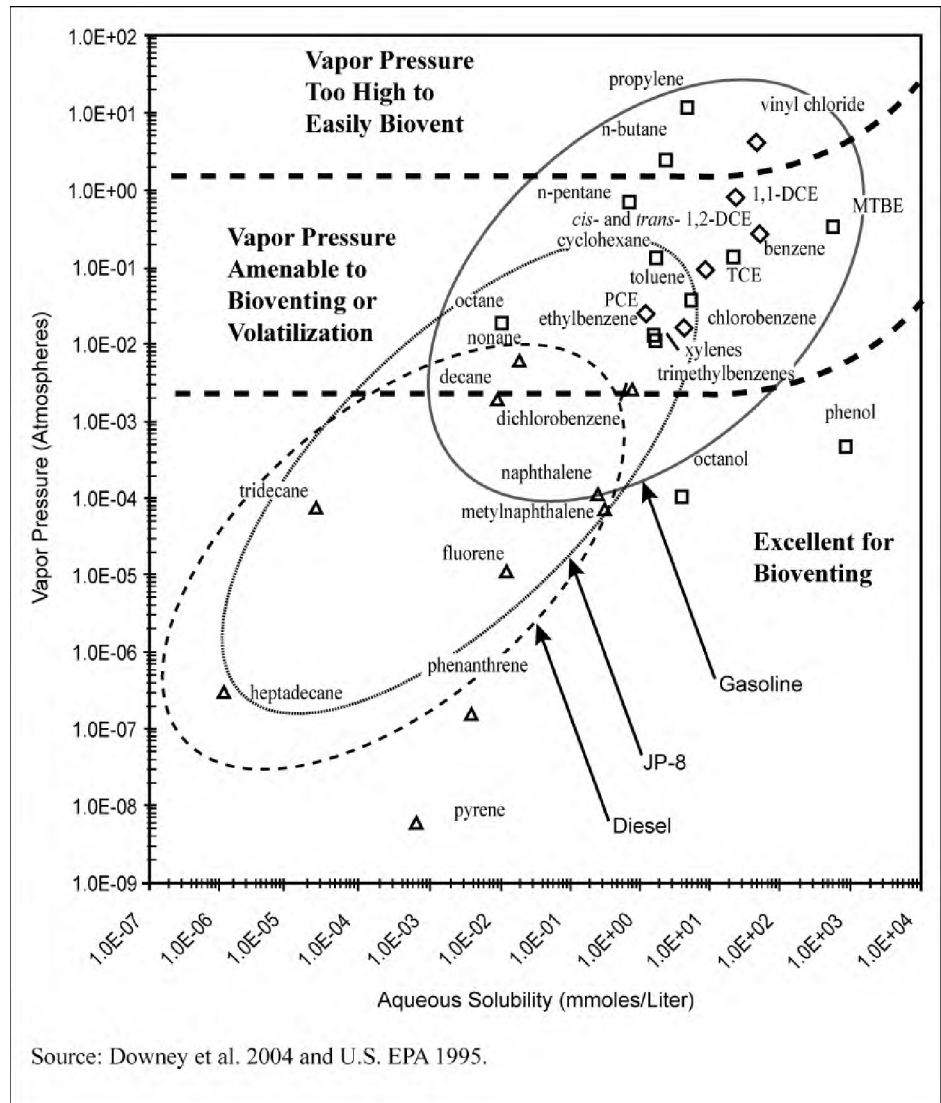
Source: Downey et al. 2004 and U.S. EPA 1995.

Figure 4. Amenability of Common Contaminants to Bioventing Technologies (aerobic, anaerobic, and cometabolic)

Performance monitoring, after a bioventing system has been installed, typically includes soil gas monitoring to ensure that the site is well oxygenated, in situ respiration testing to monitor the progress of remediation, and operation and maintenance of the bioventing system. At some sites, surface emissions sampling may be needed. At sites using extractive bioventing, the degree of volatilization versus biodegradation may be determined by measuring offgas concentrations. Injection-based systems may be briefly reconfigured to gain similar information. Measurements of the rate

activity as the primary mechanism of removal. Finally, measurement of stable isotope ratios may be useful in qualitatively validating biodegradation as the mechanism of contaminant removal. This measurement is not required, but it is available to resolve regulatory concerns.

Aerobic bioventing has proven to be a useful cleanup technology at many sites under a variety of

conditions, but like all technologies, bioventing has some limitations. One limitation revolves around the ability to deliver oxygen to the contaminated soil. For example, soil with an extremely high moisture content may be difficult to biovent due to reduced soil gas permeability. Similarly, low permeability soils limit the ability to distribute air through the subsurface; however, in both cases, the design of the bioventing system may compensate for low permeability. Sites with shallow contamination also pose a problem to bioventing because designing the system to minimize environmental release and achieve sufficient aeration, may be difficult. In this situation, operating in extraction mode may be needed.

Another limitation is that aerobic bioventing will not stimulate contaminant removal if the contaminated zone is aerobic. If a soil gas survey measures soil oxygen levels consistently above five percent, then the soil is sufficiently aerated for biodegradation to occur, and oxygen is not limiting degradation. Bioventing will not enhance removal in this situation. This situation is unusual, and if encountered, may indicate that some other species, such as metals, is inhibiting degradation.

While relatively inexpensive, aerobic bioventing can take a few years to clean up a site, depending on the contaminant concentrations and site-specific removal rates. For petroleum hydrocarbon sites, the heavier the product being treated, the longer the remediation time. If a quicker cleanup is needed, other technologies may be more appropriate.

Anaerobic Bioventing

While aerobic bioventing is useful for degrading many hydrocarbons, some chlorinated compounds are not effectively treated aerobically. Microbes may degrade these contaminants directly via anaerobic reductive dechlorination or through anaerobic cometabolic pathways. Anaerobic reductive dechlorination is a biological mechanism, typically marked by sequential removal of chlorine ions from a molecule. Microbes possessing this pathway gain energy from this process. In some situations, microorganisms fortuitously degrade contaminants, while gaining energy and carbon from other compounds (cometabolites). These organisms usually do not obtain any benefit from contaminant degradation, and the removal process is called cometabolism. Anaerobic bioventing may involve both anaerobic

reductive dechlorination and anaerobic cometabolism to destroy the contaminants of concern.

Anaerobic bioventing uses the same type of gas delivery system as aerobic bioventing, but instead of injecting air, nitrogen and electron donors (e.g., hydrogen and carbon dioxide) are used. The nitrogen displaces the soil oxygen, and the electron donor gas facilitates microbial dechlorination. Volatile and semivolatile organic compounds may be produced during anaerobic bioventing that are not anaerobically degradable. Volatile compounds may be aerobically degraded in the soil surrounding the treatment zone. Semivolatile compounds may be treated by following anaerobic bioventing with aerobic bioventing. Since aerobic and anaerobic bioventing share similar gas delivery systems, the switch can be made by simply changing the injected gas.

Anaerobic bioventing is an emerging technology that may be useful in treating highly chlorinated compounds, such as PCE, TCE, pentachlorophenol (PCP), some polychlorinated biphenyls (PCBs), and pesticides, such as lindane and dichlorodiphenyl-trichloroethane (DDT). Due to the limited experience with this technique, laboratory, pilot, and field demonstrations are recommended to apply this technology with confidence to remediate a site.

Particular attention should be paid to the formation of degradation products and whether contaminants are converted to non-toxic compounds. For example, sites contaminated by PCE and TCE may not show complete dechlorination, rather dechlorination stalls at cis-1,2-dichloroethene (cis-DCE) or vinyl chloride (VC). Since VC is more toxic than the original contaminants, incomplete dechlorination would not be acceptable. The cis-DCE or VC stall may be due to the availability of an electron donor or the indigenous microbial community. If the electron donor is limited, additional donor should be added. If the indigenous culture is not able to completely dechlorinate the solvents, the site could be switched to another type of bioventing (e.g., cis-DCE is aerobically degradable through cometabolism, and VC is aerobically degradable). Laboratory testing can demonstrate whether complete dechlorination occurs at a site, provide information about suitable electron donors and the quantities required, estimate removal rates, and demonstrate whether hazardous byproducts are formed.

As with the other bioventing technologies, the ability to deliver gases to the subsurface is important. Soil with a high moisture content or low gas permeability may require careful design to deliver appropriate levels of nitrogen and electron donor. Sites with shallow contamination or nearby buildings are also a problem, since this technology is operated by injecting gases. In addition, anaerobic bioventing can take a few years to clean up a site depending on the contaminant concentrations and site-specific removal rates. If a quicker cleanup is needed, other technologies may be more appropriate. Finally, no rigorous cost models have been developed for anaerobic bioventing; however, the costs should be similar to aerobic bioventing with the following additional costs: laboratory treatability test and field testing; nitrogen and electron donor additions; and additional soil and gas analyses.

Cometabolic Bioventing

Cometabolic bioventing involves injecting air into the subsurface along with a suitable gaseous substrate to promote cometabolic reactions with the target compound. As with anaerobic cometabolism, some microorganisms fortuitously degrade contaminants while oxidizing other compounds (cometabolites) for energy and carbon. The organisms usually do not obtain any benefit from contaminant degradation. A suitable substrate should be determined in the laboratory but may include methane, ethane, propane, butane, and pentane. The delivery system is similar to other bioventing technologies and subject to many of the same limitations. Cometabolic bioventing is applicable to contaminants, such as TCE, trichloroethane (TCA), ethylene dibromide, and dichloroethene (DCE), that resist direct aerobic degradation. This technology is not applicable to PCE.

The Bioremediation Consortium under the Remediation Technology Development Forum (RTDF) conducted cometabolic bioventing demonstrations at Dover and Hill Air Force Bases (AFB). At Dover AFB, a field demonstration of cometabolic bioventing was done at Building 719. The site was contaminated with fuel and solvents during engine inspection and maintenance operations. The targeted contaminants of the demonstration were TCE, as high as 250 mg/kg; TCA, 10 to 1,000 mg/kg; and DCE, 1 to 20 mg/kg. Laboratory tests were used to select propane as the cometabolic substrate and predict that a substrate acclimation period would be needed. The test plot was acclimated to propane addition through pulsed propane/air injections for three months, and then the test plot was operated for 14 months with continuous propane injection. Concentrations of TCE, TCA, and DCE were reduced to less than 0.25, 0.5 and 0.25 mg/kg, respectively. Soil chloride accumulation confirmed biodegradation as the mechanism of removal (U.S. EPA 2000).

Because experience with cometabolic bioventing is limited, laboratory and pilot-scale studies are recommended to evaluate effectiveness, select a cometabolite, identify needs for acclimation periods, design the system, and estimate treatment times. Operational costs should be similar to those of aerobic bioventing except for the addition of the substrate gas and additional monitoring of soil and soil gas.

Cited and Other References

Abriola, L., J. Lang, and K. Rathfelder. 1997. Michigan Soil Vapor Extraction Remediation (MISER) Model: A Computer Program to Model Soil Vapor Extraction and Bioventing of Organic Chemicals in Unsaturated Geological Material, EPA 600/R-97/099. U.S. EPA, Office of Research and Development, 260 pp. http://nepis.epa.gov/pubtitle ORD.htm

Downey, D., R. Miller, and T. Dragoo. 2004. Procedures for Conducting Bioventing Pilot Tests and Long-Term Monitoring of Bioventing Systems. Air Force Center for Environmental Excellence. NTIS: ADA423587. 80 pp. http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=ADA423587&Location= U2&doc=GetTRDoc.pdf

NAVFAC. 2003. FINAL REPORT: Addendum –Natural Pressure-Driven Passive Bioventing, TR-2221-ENV, 74 pp. http://enviro.nfesc.navy.mil/ erb/erb a/restoration/technologies/remed/bio/tr-22 21-biovent.pdf

NAVFAC. 2000. Passive Bioventing in Stratified Soils and Shallow Groundwater Conditions, NFESC TDS-2083-ENV, 6 pp. http://enviro.nfesc.navy.mil/ erb/erb a/restoration/technologies/remed/bio/tds-2083biovent.pdf

NAVFAC. 2003. Final Report: Addendum –Natural Pressure-Driven Passive Bioventing, TR-2221-ENV, 74 pp. http://enviro.nfesc.navy.mil/erb/erb_a/restor ation/technologies/remed/bio/tr-2221-biovent.pdf

NAVFAC. 2006 (Nov). Bioventing Cost Estimator. Naval Facilities Engineering Command. Webpage. http://enviro.nfesc.navy.mil/erb/erb_a/restoration/technologies/remed/bio/BVCE.XLS

Shah, J.K., G.D. Sayles, M.T. Suidan, P. Mihopoulos, and S. Kaskassian. 2001. Anaerobic bioventing of unsaturated zone contaminated with DDT and DNT. Water Sci Technol. 2001;43(2):35-42. Abstract at http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&list_uids=11380202&dopt=Abstract

Shewfelt, K., H. Lee, and R. Zytner. 2005. Optimization of nitrogen for bioventing of gasoline contaminated soil. J. Environ. Eng. Sci. 4(1): 29-42. http://pubs.nrc-cnrc.gc.ca/rp/rppdf/s04-040.pdf

U.S. EPA. 1995a. Manual: Bioventing Principles and Practices, Volume I: Bioventing Principles, EPA 540/R-95/534a. Office of Solid Waste and Emergency Response and Office of Research and Development, 94 pp. http://nepis.epa.gov/pubtitleOSWER.htm

U.S. EPA. 1995b. Manual: Bioventing Principles and Practices, Volume II: Bioventing Design, EPA 540/R-95/534b. Office of Solid Waste and Emergency Response and Office of Research and Development, 94 pp. http://nepis.epa.gov/pubtitleOSWER.htm

U.S. EPA. 2000. Cost and Performance Report: Cometabolic Bioventing at Building 719, Dover Air Force Base Dover, Delaware. Office of Soild Waste and Emergency Response, 6 pp. http://costperformance.org/pdf/Dover719Bio.PDF

U.S. EPA. 2002. Innovative Technology Evaluation Report: Envirogen Propane Biostimulation Technology for In-Situ Treatment of MTBE Contaminated Ground Water, EPA 600/R02/092. Office of Research and Development, 152 pp. http://www.epa.gov/ada/download/reports/600R02092/600R02092-full.pdf

U.S. EPA. 2006. In Situ and Ex Situ Biodegradation Technologies for Remediation of Contaminated Sites, EPA 600/R-06/015. http://www.epa.gov/nrmrl/publications.html

3.2.2 Phytoremediation

Phytoremediation uses plants to extract, degrade, contain, or immobilize contaminants in soil, groundwater, and other contaminated media. The phytoremediation mechanisms used to treat contaminated soil in situ are phytoextraction, rhizodegradation, phytodegradation, phytovolatilization, and phytostabilization.

Phytoremediation is best used to treat large areas of shallow contamination. Because high levels of contaminants may be toxic to plants and inhibit their growth, phytoremediation is best applied to low and moderate levels of contamination, used in conjunction with other treatment methods, or used as a final polishing step in site remediation.

The various mechanisms of phytoremediation can treat a wide range of contaminants, including metals, VOCs, PAHs, petroleum hydrocarbons, radionuclides, and munitions, although not all mechanisms are applicable to all contaminants. Phytoremediation may take longer than other technologies to treat a site, but it has the potential to be less expensive than excavating and treating large volumes of soil ex situ.

There are a number of limitations to the technology that must be considered before it can be implemented at a site. The depth of the contamination requiring treatment must be within the range of depth of plant root growth; thus, treatment of contaminated soil typically focuses on the upper 8 to 10 inches of the soil horizon, although the roots of hybrid poplar trees, a species commonly used in phytoremediation, can grow to depths of about 15 feet. Contaminants must be in contact with the root zone to be treated; therefore, a denser root mass is preferred to help contact more of the contamination. Because treatment depends on this contact with the root zone, phytoremediation is limited by the rate of root growth. Slower growth rates increase the time required to treat a site, and winter months may shut down the treatment system completely while plants are dormant.

Another limitation of phytoremediation is possible bioconcentration of contaminants up the food chain. Several phytoremediation mechanisms work by incorporating the contaminant into the plant or holding it within the root zone. The contaminated vegetation and root zone may impact plant-eating

animals and soil organisms. This is particularly a concern with metals and radionuclide contamination that accumulate in plants and the root zone. Most plants do not accumulate significant levels of organic contaminants (U.S. EPA 2000); thus, bioconcentration is of less concern. The potential for plant-eating animals to be exposed is greatest when these contaminants accumulate in fruits, seeds, and leaves, so monitoring the fate of contaminants within the plants is important. To avoid bioconcentration in the food chain, contaminated plants can be harvested for disposal, destruction, or the extraction of metals for reuse ("phytomining"). In these cases, perimeter fencing and overhead netting can be installed to prevent animals from consuming contaminated plant matter.

Finally, it is important to ensure that unwanted transfer of contaminants from soil to other media, such as the volatilization of organic compounds to the atmosphere through plant uptake and transpiration, does not occur or that the transfer results in the destruction of the contaminants. Evaluating the limitations of phytoremediation in its various applications, as well as assessing its potential effectiveness at contaminated sites, can be done in laboratory and field studies prior to implementation. Samples of site soil containing the target contaminants in a range of concentrations should be tested using the specific plants under consideration. Ultimately, sites undergoing phytoremediation must be monitored to assess the fate of contaminants.

In general, phytoremediation has been implemented at a number of sites at full-scale (U.S. EPA 2006). Also, a wide range of site conditions, plants, and contaminants have been studied under laboratory or field testing. As of this publication, phytoemediation technologies have been selected 18 times by the Superfund program.

Phytoextraction

Phytoextraction involves the uptake of contaminants by plant roots, with subsequent accumulation in plant tissue, which may require that the plant be harvested and properly disposed of. This mechanism is typically used to treat inorganic contaminants, such as metals, metalloids, and radionuclides. Organic contaminants are more likely to be transformed, rather than accumulated, within the plant tissue. Successful field applications of phytoextraction to up take metals have

been limited; however, there is some promising research for using phytoextraction on mercury and persistent organic pollutants.

Plants used in phytoextraction include Indian mustard, pennycress, and alyssum sunflowers. They are typically effective only in the top one foot of soil because of their shallow root systems and generally slow growth. Ba iiuelos et al. (2005) has shown that Indian mustard can be genetically modified to grow in contaminated soil with greater biomass to hyper-accumulate selenium in a shorter time than un-modified Indian mustard. In other genetic research, Meagher (undated) is modifying various plant species to survive in mercury-contaminated soil and to transform organic mercury into ionic and/or metallic mercury. The mercury is either sequestered in the plant or transpired.

Persistent organic pollutants, many of which are pesticides, resist biodegradation and may remain in the environment for decades. White (2001) and Mattina (2000) have shown that a number of plants are capable of extracting chemicals, such as chlordane and 2,2-bis(p-chlorophenyl) 1, 1 -dichloro-ethene (p.p'-DDE), and storing them in their roots, leaves, and fruits.

Rhizo deg radatio n

Rhizodegradation is essentially "plant-assisted bio-remediation" in that the root zone enhances micro-bial activity, thus increasing the breakdown of organic contaminants (such as petroleum hydro-carbons, PAHs, pesticides, BTEX, chlorinated sol-vents, PCP, PCBs, and surfactants) in the soil. The term comes from "rhizosphere," which is the zone of soil influenced by plant roots. This zone extends only about 1 mm from each root.

The presence of plant roots increases soil aeration and moderates soil moisture, making conditions more favorable to bioremediation. Bioremediation is enhanced by the production of root exudates, such as sugars, amino acids, and other compounds, that can stimulate the population growth and activity of native microbes. Root exudates may also serve as food for the microbes, which can result in cometa-bolism of contaminants as degradation of exudates occurs. Because the microbes consume nutrients, the plants in a rhizodegradation plot often require additional fertilization.

The advantage of rhizodegradation is the actual breakdown of contaminants, rather than their translocation; thus, harvesting is not necessary. In some instances, complete mineralization of the contaminant can occur. Success, however, is site-specific, and laboratory microcosms may not reflect the microbial conditions encountered in the field. Petroleum hydrocarbons have been shown to be successfully degraded in the rhizosphere; however, degradation of aged hydrocarbons has been demonstrated to be more problematic.

Phyto deg radatio n

Like phytoextraction, phytodegradation involves the uptake of contaminants; however, the contaminants are subsequently broken down through metabolic processes within the plant. Phytodegradation also comprises the breakdown of contaminants in the soil through the effects of enzymes and other compounds produced by the plant tissues (other than the roots).

Phytodegradation is applicable to organic contaminants. Their uptake is affected by their hydrophobicity, solubility, and polarity. Moderately hydrophobic and polar compounds are more likely to be taken up after sorbing to plant roots (Schnoor et al. 1995 and Bell 1992). Contaminants with the potential for phytodegradation include chlorinated solvents, herbicides, insecticides, PCP, PCBs, and munitions.

Phyto volatili.Zatio n

Phytovolatilization is the uptake of a contaminant into a plant and its subsequent transpiration to the atmosphere, or the transformation or phytodegradation of the contaminant with subsequent transpiration of the transformation or degradation product(s) to the atmosphere. Phytovolatilization is more commonly applied to groundwater, but can also be applied to soluble soil contaminants.

Phytovolatilization involving transformation or degradation of the contaminant has the advantage of potentially creating a less toxic product that is transpired; however, this also poses a potential drawback in that degradation of some contaminants, like TCE, may produce even more toxic products (e.g., vinyl chloride). This possibility has to be assessed on a site-specific basis, and measurement of transpired compounds can be difficult. Once in the atmosphere, these products may be more effectively degraded by sunlight (photodegradation) than they would be by the plant (phytodegradation).

Both organic and inorganic contaminants have been treated by phytovolatilization. Inorganic contaminants include selenium, mercury, and arsenic; however, simply volatilizing a contaminant may not be an acceptable alternative.

Phy to s ta b ili.Za tio n

Phytostabilization is a mechanism that immobilizes contaminants—mainly metals—within the root zone, limiting their migration. The contaminants are immobilized by adsorption of metals to plant roots, precipitation of metal ions (e.g., due to a change in pH), formation of metal complexes, or a change to a less toxic redox state. Phytostabilization can occur when plants alter the chemical and microbial makeup of the soil (e.g., through the production of exudates or carbon dioxide), which affects the fate and transport of the soil metals. Phytostabilization also encompasses the use of plants to prevent migration of soil contaminants with wind and water erosion, leaching, and soil dispersion.

Since contaminants are retained in the soil, phytostabilization does not require the harvesting and disposal of plants. A phytostabilization system must be evaluated, however, to ensure that translocation of contaminants into the plant tissue is not occurring. Since contaminants remain in the root zone, the health of the plants must be maintained to prevent future release of contaminants when the plants die or are inadvertently destroyed. Maintenance may include the addition of fertilizers or soil amendments.

Cited and Other References

Bell, R.M. 1992. Higher Plant Accumulation of Organic Pollutants from Soils. EPA Office of Research and Development. Risk Reduction Engineering Laboratory, Cincinnati, Ohio. EPA 600/R-92/138.

Baiiuelos, G. et al. 2005. Field trial of transgenic Indian mustard plants shows enhanced phytoremediation of selenium-contaminated sediment. Environ. Sci. Technol. 39: 1771-1777.

Brigmon, R. et al. 2003. FY02 Final Report on Phytoremediation of Chlorinated Ethenes in Southern Sector Seepline Sediments of the Savannah River Site. U.S. DOE, 171 pp. http://sti.srs.gov/full text/tr2002557/tr2002557.pdf

Ibeanusi, V. and D. Grab. 2004. Radionuclide Biological Remediation Resource Guide, EPA 905/B-04/001. U.S. EPA, Region 5, 68 pp. http://cluin.org/download/remed/905b04001.pdf

ITRC. 2001. Phytotechnology Technical and Regulatory Guidance Document. Interstate Technology and Regulatory Council, 123 pp. http://www.itrcweb.org/Documents/PHYTO-2.pdf

Mattina, M., W. Iannucci-Berger, and L Dykas. 2000. Chlordane uptake and its translocation in food crops. Agric. Food Chem. 48(5): 1909-1915.

Meagher, R. 2006 (October). Mercury Research. http://www.genetics.uga.edu/rbmlab/phyto/mercurypol.html

Pivetz, B. 2001. Ground Water Issue: Phytoremediation of Contaminated Soil and Ground Water at Hazardous Waste Sites, EPA 540/S-01/500. U.S. EPA, Office of Research and Development, 36 pp. http://www.epa.gov/ada/download/issue/epa_540 s01_500.pdf

Remediation Technologies Development Forum. 2006 (October). Evaluation of Phytoremediation for Management of Chlorinated Solvents in Soil and Groundwater. Phytoremediation of Organics Action Team, Chlorinated Solvents Workgroup, 42 pp. http://www.rtdf.org/public/phyto/chlor_solv management.pdf

Reynolds, C. 2004. Cost and Performance Report: Field Demonstration of Rhizosphere-Enhanced Treatment of Organics-Contaminated Soils on Native American Lands with Application to Northern FUD Sites, ERDC/CRREL LR-04-19. U.S. DoD, Environmental Security Technology Certification Program, 53 pp. http://stinet.dtic.mil/oai/oai?&verb=getRecord&metadataPrefix=html&identifier=ADA43103 5

Schnoor, J., L. Licht, S. McCutcheon, N. Wolfe, and L. Carreira, 1995. Phytoremediation of Organic and nutrient contaminants. Environ. Sci. Technol. 29:318A-323A.

Schnoor, J. 1997. Technology Evaluation Report: Phytoremediation, TE-98-01. Ground-Water Remediation Technologies Analysis Center, 43 pp.

U.S. EPA. 2000. Introduction to Phytoremediation, EPA 600/R-99/107. Office of Research and Development, 104 pp. http://www.cluin.org/download/remed/introphyto.pdf

U.S. EPA. 2003. Innovative Technology Evaluation Report: Phytoremediation of Groundwater at Air Force Plant 4 Carswell, Texas, EPA 540/R-03/506. Office of Research and Development, 12 pp. http://www.epa.gov/ORD/NRMRL/pubs/540r03506/540R03506.pdf

U.S. EPA. 2004. Treatment Technologies for Site Cleanup: Annual Status Report (Eleventh Edition). EPA 542/R-03/009. http://clu-in.org/asr

U.S. EPA. 2006 (October). Phytoremediation Profile Database. http://www.cluin.org/products/phyto

White, J. 2001. Plant-facilitated mobilization and translocation of weathered 2,2-bis(p-chlorophenyl) 1,1-dichloroethene (p.p'-DDE) from agricultural soil. Environ. Toxicol. Chem. 20(9): 2047-2052.

3.2.3 Monitored Natural Attenuation

Monitored natural attenuation (MNA) encompasses the dilution, dispersion, chemical and biological degradation, sorption/precipitation, and/or radioactive decay of contaminants in soil and groundwater (U.S. EPA 1999). It has been applied mainly to groundwater contamination, but the same principles apply to soil. Because MNA is a passive process in which the reduction in contaminant concentration is due solely to natural mechanisms, continuous sources of significant contamination should be addressed before implementing MNA. If MNA is implemented, reaching remediation goals may take longer than other remedies.

Site contaminants most amenable to MNA include petroleum hydrocarbons, low-molecular weight alcohols, ketones, esters, ethers, and iron and manganese. Under a narrow range of conditions, MNA may be applicable to halogenated solvents, lightly halogenated aromatics, polychlorinated biphenyls, nitroaromatics, some pesticides, and chromium, copper, cadmium, lead, zinc, and nickel (NRC 2000).

A full characterization of subsurface conditions at the site, including a delineation of the extent of contamination and the development of a site conceptual model, are necessary before MNA can be

considered. As part of the characterization, the microbial species present (more important for chlorinated compounds), redox potential, pH conditions, mineralogy, and geochemistry should be evaluated. If the evaluation concludes that the conditions may exist to support natural attenuation, the next step is to determine if it is occurring. This is accomplished by looking at such parameters as microbial respiration products, chemical reaction products, prevalent metal species, degradation products, and declining concentrations of target compounds/species over time. For a more complete list and discussion, see Kram and Goetz 1999. If a large amount of historical data is not available to confirm that the contaminant mass is stabilized or contracting, it probably will be necessary to model the fate and transport of the contaminants to show that migration is unlikely to occur.

Performance monitoring is an integral part of any MNA effort (Pope et al. 2004 and Wiedemeier, Lucas, and Haas 2000). The monitoring system should be tailored to site conditions to enable detection of any changes in the assumptions used to select MNA. Key parameters, such as degradation products or an increase in target metal concentration that would indicate mobilization, should be chosen along with an appropriate frequency. The frequency of sample collection is related to the uncertainties inherent in the site conceptual model and the consequences of failure. As a precaution, a preapproved site remedial contingency plan should be created that can be implemented if monitoring indicates MNA is not meeting the project's performance goals.

The Naval Facilities Engineering Command provides an estimate for implementing MNA of between $50,000 and $200,000 per acre. This cost does not include site characterization, which may be higher than that for a site not being considered for MNA. These cost estimates were developed for a groundwater scenario.

Cited and Other References

Brauner, J. et al. 2004. Implementing Monitored Natural Attenuation and Expediting Closure at Fuel-Release Sites. Air Force Center for Environmental Excellence, 247 pp. http://stinet.dtic.mil/cgibin/Get TRDoc?AD=ADA426387&Location=U2&doc=Get TRDoc.pdf

Chapelle, F. et al. 2003. Methodology for Estimating Times of Remediation Associated With Monitored Natural Attenuation, Water-Resources Investigations Report 03–4057. U.S. Geological Survey, 58 pp. http://pubs.usgs.gov/wri/wri034057/

Kennedy, L., J. Everett, and J. Gonzales. Undated. Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) Protocol. Air Force Center for Environmental Excellence, 284 pp. http://www. afcee.brooks.af.mil/products/techtrans/monitored naturalattenuation/amiba/AMIBA%20Protocol.PDF

Kram, M. and F. Goetz. 1999. User's Guide: Natural Attenuation General Data Guide, UG-2035-ENV. NAVFAC, 38 pp. http://stinet.dtic.mil/cgi-bin/Get TRDoc?AD=A361097&Location=U2&doc=Get TRDoc.pdf

Looney, B. and K. Vangelas. 2004. Compatibility of Alternative Chlorinated Solvent Source Treatment Strategies with Monitored Natural Attenuation, WSRC-MS-2004-00236. U.S. DOE, Savannah River, 22 pp. http://sti.srs.gov/fulltext/ms2004236 /ms2004236.pdf

NAVFAC. 1998. Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities. 92 pp. http://enviro.nfesc.navy.mil/erb/erb a/support/wrk grp/artt/mna1198.pdf

NRC. 2000. Natural Attenuation for Groundwater Remediation. National Academy of Sciences, National Research Council, 292 pp. http://books. nap.edu/catalog/9792.html

Pope, D. et al. 2004. Performance Monitoring of MNA Remedies for VOCs in Ground Water, EPA/600/R-04/027, U.S. EPA, Office of Research and Development. http://www.epa.gov/ada/down load/reports/600R04027/600R04027 fm.pdf

U.S. EPA. 1999. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive 9200.4-17P. Office of Solid Waste and Emergency Response, 41 pp. http://nepis.epa.gov/pubtitleOSW ER.htm

Wiedemeier, T., M. Lucas, and P. Haas. 2000. Designing Monitoring Programs to Effectively

Evaluate the Performance of Natural Attenuation. U.S. DoD, Air Force Center for Environmental Excellence, 55 pp. http://www.afcee.brooks.af.mil/pro duct s/techtrans/MonitoredNaturalAttenuation/ltm.pdf

Wilson, J., J. Cho, B. Wilson, and J. Vardy. 2000. Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions, EPA 600/R-00/006. U.S. EPA, Office of Research and Development, 59 pp. http://www.epa.gov/ada/download/reports/mtbe report.pdf

Wilson, J. et al. 2001. Evaluation of the Protocol for Natural Attenuation of Chlorinated Solvents: Case Study at the Twin Cities Army Ammunition Plant, EPA 600/R-01/025. U.S. EPA, Office of Research and Development, 49 pp. http://www.epa.gov/ada/download/reports/epa 600 r01 025.pdf

Wilson, J., P. Kaiser, and C. Adair. 2005. Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites, EPA 600/R-04/1790. U.S. EPA, Office of Research and Development, 89 pp. http://www.epa.gov/ada/download/reports/600R04179/600R04 179.pdf

3.3 Thermal Treatment Technologies

Five technologies are grouped under the in situ thermal treatment classification: electrical resistance heating, steam injection and extraction, conductive heating, radio-frequency heating, and vitrification. With the exception of vitrification, all of these treatment technologies rely on the addition of heat to the soil to increase the removal efficiency of volatile and semivolatile contaminants. Vapor extraction is an integral part of these remediation systems to ensure the removal and treatment of mobilized contaminants. Liquid extraction is also used during steam injection, and sometimes with other thermal technologies when groundwater flow rates are high and/or when the contaminant being recovered is semivolatile.

In situ vitrification is unique among the thermal technologies in that the temperatures used will vitrify soil. The stable glass that is formed by vitrification will immobilize any nonvolatile contaminants that are present, including metals and radioactive materials.

Davis (1997) provides a general discussion of the effects of heat on chemical and physical properties of organic contaminants. Vaporization is the main mechanism used in these technologies to enhance the recovery of VOCs. Vapor pressures of organic compounds increase exponentially with temperature, causing significant redistribution to the vapor phase as the subsurface is heated. When a NAPL is present, the combined vapor pressure of the NAPL and water determine the boiling temperature, and co-boiling of the two liquids occurs at temperatures less than the boiling point of water. Thus, by raising the temperature of the subsurface above the co-boiling temperature, NAPL can be removed. Continued heating of the subsurface recovers contaminants from the dissolved and adsorbed phases as well.

Increasing the temperature also decreases viscosity, increases solubility, and decreases adsorption, all of which aid in the recovery of VOCs and SVOCs. For some SVOC NAPLs, such as creosote, viscosity reduction may be an important mechanism for increased contaminant recovery (Davis 1997). Hydrolysis may play a role in the destruction of some contaminants (e.g., chlorinated methanes and ethanes) as the soil temperature approaches $100\,^{\circ}C$; however, the breakdown products may be more recalcitrant than the original contaminants (Washington 1995).

Care should be taken in designing the systems to ensure that all plumbing, including monitoring wells, are capable of withstanding high heat. In the presence of clay, vadose zone heating by resistivity, conductance, or radio frequency may result in some settlement of the treatment area due to the drying of the clay.

Cited and Other References

Davis, E. 1997. Ground Water Issue: How Heat Can Enhance In-situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique, EPA 540/S-97/502. U.S. EPA., Office of Research and Development, 18 pp. http://www.cluin.org/down load/remed/heatenh.pdf

USACE. 2006. Interim Unified Facilities Criteria: In Situ Thermal Remediation, Hazardous, Toxic, and Radioactive Waste, UFC 3-280-05. U.S. DoD, 258 pp. http://www.environmental.usace.army.mil/sve .htm