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Application, Performance, and Costs of Biotreatment Technologies for Contaminated Soils

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ACRONYMS AND ABBREVIATIONS

A	acetone
AFB	Air Force Base
AFCEE	U.S. Air Force Center for Environmental Excellence
ARAR	Applicable or Relevant and Appropriate Requirement
ASTM	American Society for Testing and Materials
BAP	benzo(a)pyrene
BB	brominated biphenyl
BDAT	Best Demonstrated Available Treatment Technology
BFSS	Bioremediation in the Field Search System
BGS	Below Ground Surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
CA	Corrective Action
CAH	chlorinated aliphatic hydrocarbon
CB	chlorobenzene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFA	Civilian Federal Agencies
CFR	Code of Federal Regulations
CFU	colony forming units
CO_2	carbon dioxide
COC	contaminant of concern
CSF	cancer slope factor
CSTR	continuously stirred tank reactor
CWA	Clean Water Act
DAF	dilution attenuation factor
DCA	dichloroethane
DCE	dichloroethylene
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DGGE	denaturing gradient gel electrophoresis
DNAPL	dense, nonaqueous-phase liquid
DNT	dinitrotoluene
DO	dissolved oxygen
DoD	United States Department of Defense
DOE	United States Department of Energy
DRO	diesel range organics
DTSC	Department of Toxic Substances Control
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FAME	fatty acid methyl ester
Fe^{3+}	Ferric Iron
FRTR	Federal Remediation Technologies Roundtable

GAC	granular activated carbon
GE	General Electric
GW	groundwater
H_2	hydrogen gas
HAC	halogenated aliphatic compound
HDPE	high-density polyethylene
HEAST	Health Effects Assessment Summary Tables
HHEM	Human Health Evaluation Manual
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraaxocine
IAAP	Iowa Army Ammunition Plant
IRIS	Integrated Risk Information System
K	potassium
LAP	Joliet Army Ammunition Plant
LNAPL	light, non-aqueous-phase liquid
MAFB	McClellan Air Force Base
MCAGCC	Marine Corps Air Ground Combat Center
MCE	methylene chloride extractable
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
MEK	methyl ethyl ketone
MGP	manufactured gas plant
MNA	Monitored Natural Attenuation
Mn_4^+	manganese ion
N	naphthalene
N_2	nitrogen gas
NA	not available
NAPL	nonaqueous-phase liquid
NCEA	National Center for Environmental Assessment
ND	non detectable
NFESC	Naval Facilities Engineering Service Center
NG	no growth
NH_4^+	ammonium ion
NO_3^-	nitrate ion
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NRMRL	National Risk Management Research Laboratory
NRWQC	National Recommended Water Quality Criteria
NS	not specified
NTIS	National Technical Information Service
O_2	oxygen gas
O&M	operations and maintenance
P	phosphorus
PAH	polycyclic aromatic hydrocarbon

PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxins
PCDF	polychlorinated dibenzo-furan
PCE	perchloroethene
PCL	Protective Concentration Levels
PCP	Pentachlorophenol
PLFA	phosphilipids fatty acid
PO_4	phosphate ion
ppm	parts per million
PRG	Preliminary Remediation Goal
PVC	polyvinyl chloride
RAGS	Risk Assessment Guidance for Superfund
RCRA	Resource Conservation and Recovery Act
R&D	research and development
RDX	cyclotrimethyle netrinitramine
REACH-IT	Remediation and Characterization Innovative Technologies
RfD	reference dose
RI/FS	Remedial Investigation/Feasibility Study
R_I	radius of influence
RIMS	Remediation Information Management System
RMX	hexahydro-1,3,5-triaza-1,3,5-trinitrocyclohexane
ROD	Record of Decision
SABRE	Simplot Anaerobic Bioremediation Ex-Situ
scfm	standard cubic feet per minute
SMC	Stauffer Management Company
SO_4^{2-}	sulfate ion
SPLP	Synthetic Precipitation Leaching Procedure
SSL	soil screening level
SVE	soil vapor extraction
SVOC	semivolatile organic compound
SWRCB	State Water Resources Control Board
T&E	Test and Evaluation
TAC	Texas Administrative Code
TCA	trichloroethane
TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin
TCE	trichloroethylene
TCLP	Toxicity Characteristic Leaching Procedure
TNRCC	Texas Natural Resource Conservation Commission
TNT	trinitrotoluene
TPH	total petroleum hydrocarbon
TRRP	Texas Risk Reduction Program
TSD	treatment, storage and disposal
UHC	underlying hazardous constituents
USCG	United States Coast Guard
U.S. EPA	United States Environmental Protection Agency
UST	underground storage tank
UTS	universal treatment standard

VC	vinyl chloride
VOC	volatile organic compound

EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD) has devoted considerable effort over the last two decades to advancing the understanding of appropriate applications of bioremediation. Over the years, research direction has transitioned from substantial emphasis on mechanistic studies to a greater emphasis on evaluation of bioprocesses in the field. The initial research impetus provided the background information necessary for successful field applications, and was accomplished collectively through in-house research studies and cooperative research projects with public and private research institutes. The field efforts are conducted through the Bioremediation in the Field Program, supported by EPA/ORD, EPA's Office of Solid Waste and Emergency Response (OSWER), and the EPA Regions through the Superfund Innovative Technology Evaluation (SITE) Program and Cooperative Research and Development Agreements (CRADAs) with companies. This two-phase program has resulted in the development of cost-effective technical approaches to site cleanup that have been validated in the field.

Remedial activities have been conducted on groundwater, soils, sediments, and landfills with a range of contaminants, including chlorinated solvents, polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, oils, and many others. These activities range from catalyzing a shift in the nation's remedial approaches to groundwater cleanup using bioremediation to employing biotreatment technologies to remediate the Exxon Valdez oil spill, this country's largest cleanup effort.

As with other treatment strategies, the effectiveness and cost of biotreatment technologies are both site- and contaminant-specific. Because of the potential advantages offered by bioremediation, there remains a strong interest in the continued development of biotreatment processes. There are many cases where bioremediation can be employed with relative confidence. The aerobic degradation of petroleum hydrocarbons and low-molecular-weight aliphatic and aromatic hydrocarbons is well understood and has been applied at hundreds of sites using bioventing, biosparging, land treatment, biopile treatment, or composting. Bioslurry reactors also have been used historically, but tend to be less widely used than these other alternatives due to their higher capital costs and lower throughput rates. Regulatory approval for the aerobic biotreatment of these contaminants can be readily obtained, and the above processes can be applied with confidence to meet treatment goals. For such easily degraded contaminants, treatability tests can be minimized or even eliminated at most sites.

Whereas the biological treatment of easily degraded contaminants is relatively well understood and accepted, a large number of contaminants remain for which there are no readily available bioremediation technologies and for which biotreatment remains challenged. Reports of new and previously undocumented biotransformation pathways for recalcitrant contaminants continue to appear in the literature and suggest that new biodegradation pathways and mechanisms will continue to be discovered. Examples include recent reports of the anaerobic degradation of benzene and PAHs under sulfate-reducing conditions (Coates et al., 1996, 1997), anaerobic oxidation of dichloroethylene (DCE) and vinyl chloride (VC) (Bradley and Chapelle, 1996, 1997), the ability to stimulate anaerobic PCB dechlorination by the addition of surrogate polybrominated biphenyl compounds to soils or sediments (Bedard et al., 1998), and the complete dechlorination of polychlorinated biphenyl (PCBs) (Bedard and van Dort, 1998). These studies and others provide an optimistic future for the biodegradation of environmentally persistent contaminants, and reflect the need for further research for the development of new and innovative bioremediation strategies and technologies to address recalcitrant contaminants and increasingly challenging site conditions.

1.0 INTRODUCTION

This report is a critical review of biological treatment processes for remediation of contaminated soils. The focus of this review is on cost and performance of biological treatment technologies demonstrated at full- or field-scale. Contaminants of concern include primarily organic chemicals and, to a lesser extent, inorganic chemicals. The report was prepared by Battelle for EPA under Contract 68-C-00-185, Task Order 13. Primary authors were Dr. Victor S. Magar, Dr. Bruce Alleman, Dr. Andrea Leeson, Mr. James Abbott, and Ms. Regina Lynch.

Soils may be contaminated with a wide range of organic (e.g., petroleum hydrocarbons, organic solvents, pesticides and herbicides, dioxins and furans, polychlorinated biphenyls [PCBs], and energetic compounds) and inorganic (mostly metals) compounds. Much of the contaminant residue in terrestrial environments is found in surface soils, vadose-zone soils, and the capillary fringe. Their presence may threaten human or ecological receptors through a variety of exposure routes including direct contact with contaminated soil media, transport to the groundwater with further transport to a receptor, and aboveground volatilization. Conventional physical treatment processes have focused on physical removal of these contaminants from the vadose zone through excavation or soil vapor extraction (SVE) with *ex-situ* vapor treatment. Excavated soils commonly require treatment prior to disposal.

Biological treatment (or biotreatment) has been used to treat contaminated soils at Superfund sites for many years. As with other treatment strategies, the effectiveness and cost of biotreatment technologies are both site-specific and contaminant-specific. Because of the potential advantages offered by bioremediation, there remains a strong interest in the continued development of biotreatment processes.

There are many cases where bioremediation can be employed with relative confidence. The aerobic degradation of petroleum hydrocarbons and low-molecular-weight aliphatic and aromatic hydrocarbons is well understood and has been applied at hundreds of sites using bioventing, land treatment, biopile treatment, or composting.

Bioremediation of some contaminant waste streams has gained preapproval from the EPA as a "presumptive remedy." Since the enactment of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), the Superfund remedial and removal programs have found that certain categories of sites have similar characteristics, such as types of contaminants present, disposal practices performed, or environmental media affected. Based on information acquired from evaluating and cleaning up these sites, the Superfund Program has taken the initiative to develop presumptive remedies to accelerate future cleanups at similar sites. The presumptive remedy approach can be used to streamline remedial decision-making for corrective actions conducted under the Resource Conservation and Recovery Act (RCRA).

Presumptive remedies are preferred technologies for common categories of sites, based on EPA's experience and its scientific and engineering evaluation of alternative technologies. The objective of the presumptive remedy initiative is to use the Superfund Program's experience to streamline site characterization and expedite the selection of cleanup actions. Over time, presumptive remedies are expected to ensure consistency in remedy selection and reduce the cost and time required to clean up similar types of sites. In general, presumptive remedies are expected to be used at all appropriate sites except where unusual site-specific circumstances are present. Conditions at a site also may justify considering other technologies along with the presumptive remedy. These potential alternatives may then be combined with other components of the presumptive remedy to develop a range of alternatives suitable for site-specific conditions.

The primary presumptive remedy for treating organic contamination of soils, sediments, and sludges at wood-treater sites is bioremediation. Bioremediation has been selected as the primary presumptive remedy for these wastes because the EPA believes that it effectively treats wood-treating wastes at relatively low costs, and because it has been selected most frequently to address organic contamination at wood-treater Superfund sites. Bioremediation at wood-treater sites may be accomplished with *ex-situ* or *in-situ* processes. However, at some wood-treater sites, *ex-situ* bioremediation may be able to achieve higher performance efficiencies than the *in-situ* processes due to increased access and contact between microorganisms, contaminants, nutrients, water, and electron acceptors.

Bioremediation of wood-treater sites is generally inexpensive at $50 to $150/cu yd of treated soil. Expected removal efficiencies are as follows (EPA, 1995):

- *Ex situ*: 64% - 95% for PAHs; 78% - 98% for chlorophenols
- *In situ*: 51% for PAHs; 72% for pentachlorophenol (PCP).

Efficiency can be limited by lack of indigenous microbes, the presence of toxic metals and/or highly chlorinated organics, low permeability soils, pH outside of the 4.5-8.5 range, winter weather, and excessive or insufficient rainfall. Studies on the bioremediation of creosote contamination indicate that biotreatment processes work well on 2-, 3-, and often 4-ring compounds, but generally not as well on 5- or 6-ring compounds (EPA, 1995). However, despite these limitations, bioremediation of wood-treater sites successfully meets the EPA's CERCLA criteria for overall protection of human health and the environment; long-term effectiveness and performance; reduction of toxicity, mobility, or volume; short-term effectiveness; implementability; cost; and compliance with Applicable or Relevant and Appropriate Requirements (ARARs).

While biotreatment is accepted as a presumptive remedy for wood treating wastes, this does not imply its use as a presumptive remedy for other organic waste streams. Furthermore, the Presumptive Remedy Program does not specify the type of biotreatment technology that should be used for wood-treater sites; rather, this determination should be based on historical data and the type of waste stream being considered. While use of a presumptive remedy helps streamline the technology selection process, providing significant potential for cost and timesavings, it does not ensure that the process will meet treatment goals.

For the last decade, EPA's National Risk Management Research Laboratory (NRMRL) in Cincinnati, OH has evaluated the biotreatment of PAH-contaminated soils using land treatment, bioslurry treatment, composting treatment, and biopile treatment, and has amassed comprehensive information on the biodegradation of PAHs in soils. Most of this work has been done at pilot scale at EPA/NRMRL's Test and Evaluation (T&E) Facility. Other processes, such as the combination of soil washing and biotreatment for PCP-contaminated soils have been evaluated.

EPA/NRMRL is currently evaluating all of these processes in the field at a former manufactured gas plant (MGP) facility in Bedford, IN. The goal of this ongoing demonstration project is to evaluate several bioremediation technologies for meeting PAH cleanup goals as an alternative to conventional thermal and "dig and haul" strategies.

The primary objective of the Bedford project is to compare the performance of three active bioremediation treatments with natural attenuation on site soil with moderate PAH concentrations. The active treatments include phytoremediation, *ex-situ* land treatment, and *ex-situ* biopile/composting treatment. Besides these three active treatment technologies, two other *ex-situ* technologies, bioslurry treatment and chemical oxidation with biotreatment, are being evaluated at the site as a secondary objective to determine their effectiveness for reducing PAH concentrations in heavily contaminated soil.

Figure 1-1 is an overview picture of the Bedford site, showing several of the bioremediation technologies in operation. SVE was used at the site early in the study to reduce benzene concentrations to below risk levels before soil was used for chemical oxidation.

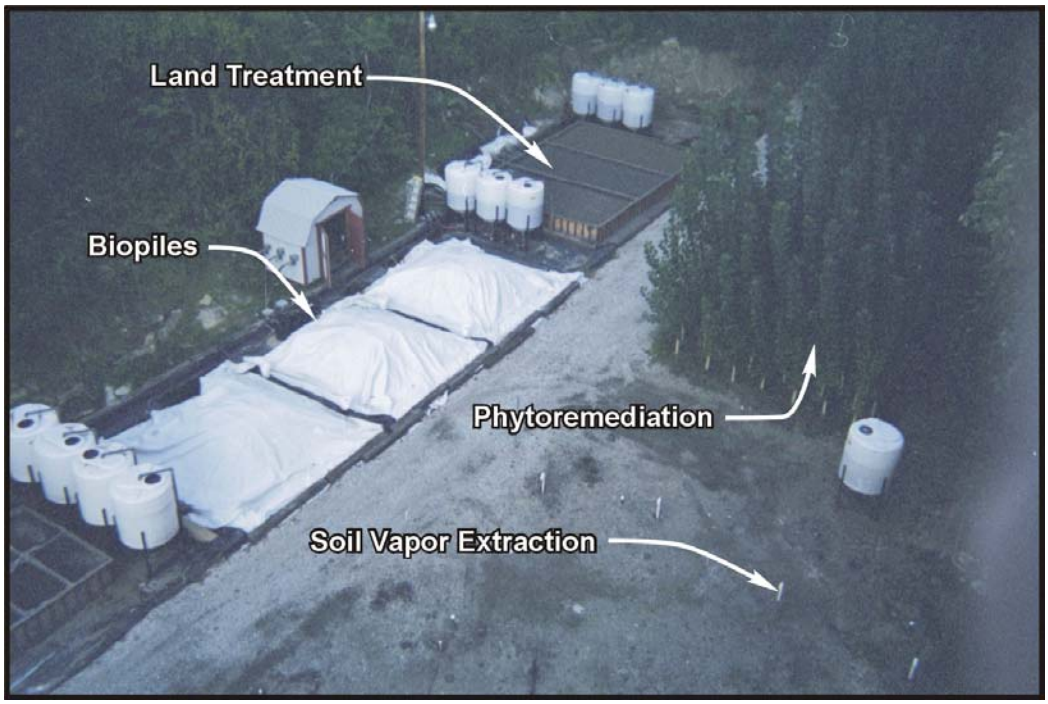


Figure 1-1. Treatment Technologies at Bedford MGP Site

Each of the four primary objective treatment technologies was replicated in nine treatment blocks in a randomized arrangement for statistical evaluation. Phytoremediation and natural attenuation were each operated and monitored for 3 years in nine *in-situ* treatment plots. *Ex-situ* biopile/composting treatment and land treatment systems were operated and monitored for three 1-year periods, treating three treatment plots per year.

Results from this large field-scale study are not yet available. However, the extent of this study alone demonstrates the dedication and interest of EPA/NRMRL to thoroughly research and advance bioremediation field efforts.

Despite the research of EPA and others, there is uncertainty regarding how widely bioremediation technologies are being used for full-scale treatment of contaminated soils, and how effectively they are being applied. The purpose of this report is to summarize cost and performance data from a wide variety of sites where bioremediation has been employed at full scale to treat contaminated soils, assess its effectiveness, compare the cost and performance of various biotreatment technologies, and outline future directions for additional research.

1.1 MAGNITUDE AND EXTENT OF SOILS, SEDIMENT, AND GROUNDWATER CONTAMINATION

Biotreatment of contaminated soils is the primary focus of this report. Data are provided in this section to help the reader become more aware of the overall scope of soil, sediment, and groundwater remediation efforts in the U.S., and and the general nature of the contaminants involved.

1.1.1 Common Contaminants of Concern (COCs)

Table 1-1 summarizes the data available as of 1996 indicating the status of sites remaining to be remediated under major federal and state programs in the United States. These programs are as follows:

- CERCLA (i.e., Superfund)
- RCRA Corrective Action (CA)
- RCRA Underground Storage Tank (UST)
- Cleanup activities by Department of Defense (DoD)
- Cleanup activities by Department of Energy (DOE)
- Cleanup activities by Civilian Federal Agencies (CFA)
- Cleanup activities by state agencies.

Table 1-2 shows the relative amounts of the different media and contaminants present at sites for four of these programs. The media types considered are groundwater (GW), soil, and sediment, and the contaminant types are volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and metals. As indicated by the table, many of the sites in all of the programs involve both soil and groundwater contamination and contamination by organics and metals. A more detailed breakout of the different types of contaminants found at various sites is shown in Table 1-3, and the distribution of contaminants found most often at Superfund sites with completed Records of Decision (RODs) is provided in Figures 1-2 and 1-3. Figure 1-2 illustrates the frequency of major contaminant subgroups at National Priority List (NPL) sites with RODs. Figure 1-3 shows the 12 contaminants most commonly found needing remediation at NPL sites. As indicated by these tables and figures, there is a wide range of chemical contaminants present and many of the sites contain mixtures of several different classes of contaminants.

Table 1-1. Status of Remediation Sites as of 1996

Program	Sites Remaining to be Remediated	Estimated Date of Completion	Estimated Cost to Remediate (Billions, in 1996 $)
Superfund	547	Not available	7
RCRA CA	3,000	2025	39
RCRA UST	165,000	Not available	21
DoD	8,336	2015	29
DOE	10,500	2070	63
CFA	>700[(a)]	Varies with agency	15
States	29,000[(b)]	Varies with state	13
Total	>217,083	Not applicable	187

(a) Number of facilities, some of which contain more than one contaminated site.
(b) Number of sites needing attention, but some sites may not require remediation.
Source: U.S. EPA, 1997, EPA/542/R-96/005

Table 1-2. Media and Contaminant Types at Remediation Sites as of 1996

Program	Percent of Media Types at Sites in Program[a]			Percent of Contaminant Types at Sites in Program[b]		
	GW	Soil	Sediment	VOCs	SVOCs	Metals
Superfund	76	72	22	71	61	65
RCRA CA	82	61	6	67	30	46
DoD[c]	71	67	6	65	69	43
DOE[d]	72	72[e]	NA[e]	38[f]	NA[f]	55

(a) Media type percentages total to greater than 100 because many sites have more than one type of contaminated media.
(b) Contaminant type percentages total to greater than 100 because many sites have more than one type of contaminant.
(c) DoD sites also involve contamination from fuels (22%), explosives (8%), and radionuclides (1%).
(d) DOE sites also involve contamination from radionuclides (90%).
(e) DOE media type data include soil and sediment under soil.
(f) DOE contaminant type data combine VOCs and SVOCs.
Source: U.S. EPA, 1997b, EPA/542/R-96/005

Table 1-3. Summary of Contaminant Types Found at Remediation Sites[a]

	Percent of Sites with Specific Contaminant Types									
	VOCs			SVOCs					Inorganics	
Program	Halogenated	BTEX[b]	Other Nonhalogenated	PAHs	PCBs	Explosives	Pesticides	Other	Metals	Miscellaneous[c]
Superfund	64	53	30	36	22	NS[d]	24	62	65	NS
RCRA CA	60	11	32	18	6	NS	6	20	46	15
DOD	49	22	44	16	6	8	15	32	69	49

(a) Percent of sites with specific contaminant types total to greater than 100 because many sites have more than one type of contaminant.
(b) BETX = benzene, ethylbenzene, toluene, and xylenes.
(c) Includes nonmetallic toxic elements, inorganic cyanides, and radionuclides.
(d) NS = not specified.
Source: U.S. EPA, 1997b, EPA/542/R-96/005

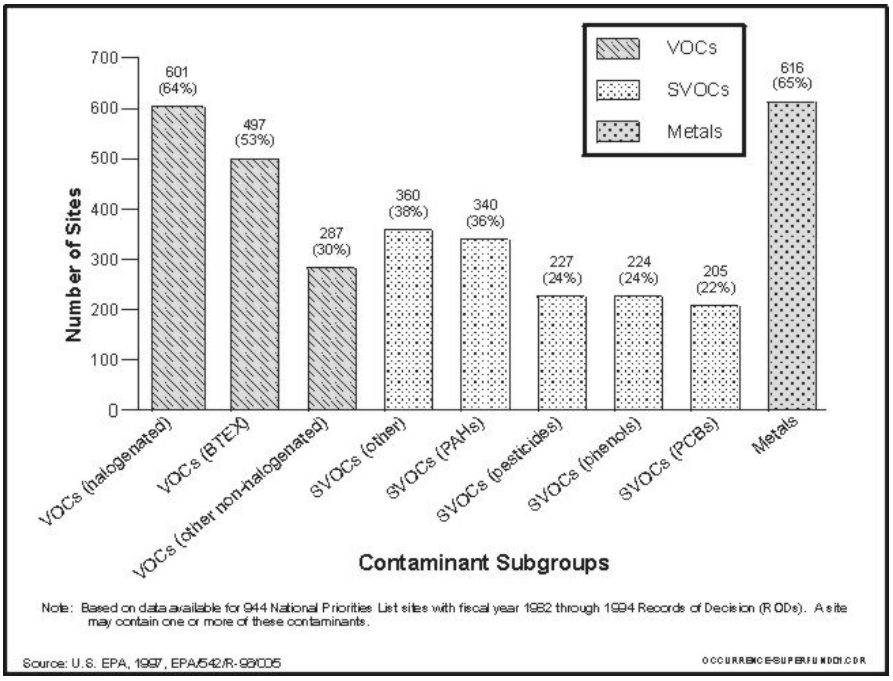


Figure 1-2. Frequency of Occurrence of Major Contaminant Subgroups at NPL Sites with RODs

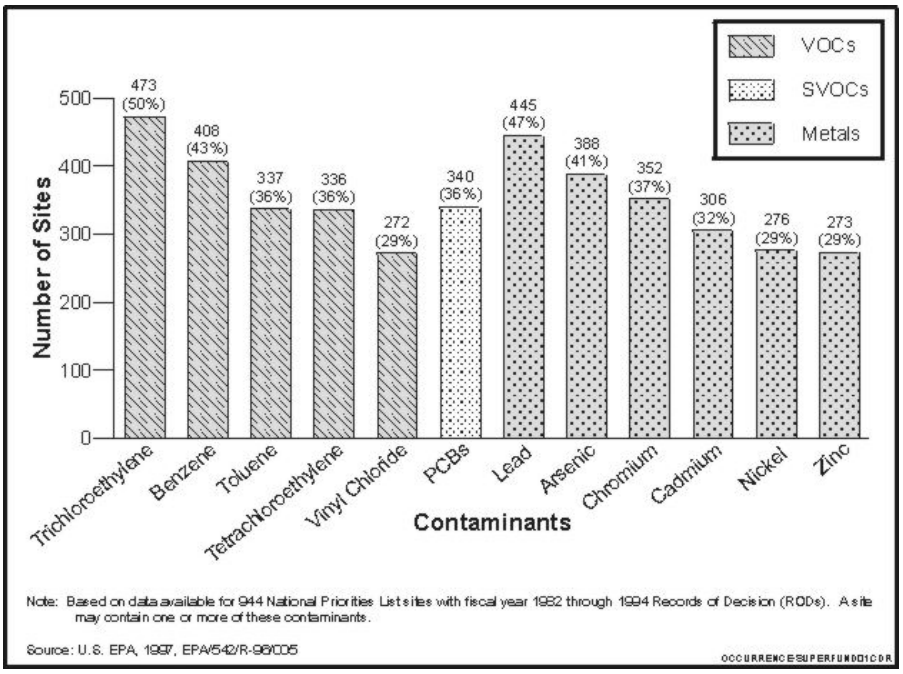


Figure 1-3. Frequency of Occurrence of the Most Common Contaminants at Superfund Sites

1.1.2 Sources of Soil Contamination

Soil contamination is primarily the result of inadequate practices for handling and storing hazardous or toxic solids or liquids (e.g., spills and leaks) and/or managing waste materials. The large number of contaminated sites related to these practices is illustrated in Table 1-4, which summarizes the main classifications of DoD sites requiring cleanup. Similarly, contamination remediated under the RCRA UST program often results from inadequate monitoring and maintenance that allowed stored liquids to leak from buried storage tanks. Many of the contaminated sites resulted from practices that were legal, and in some cases, considered to be fully adequate at the time the practice was in use. The failure of these practices became known only after extensive groundwater and soil contamination was found long after the waste materials had been placed in or discharged to the site.

Table 1-4. Most Common Types of DoD Sites Needing Cleanup

Classification of Site	Number of Sites in Classification	Percent of Sites in Classification
USTs	1,199	14.4
Spill Area	1,029	12.3
Landfill	940	11.3
Surface Disposal Area	700	8.4
Storage Area	569	6.8
Disposal Pit/Dry Well	535	6.4
Ordnance Area	496	5.9
Fire/Crash Training Area	230	2.8
Surface Impoundment/Lagoon	223	2.7
Other	2,415	29.0
Total	**8,336**	**100**

Source: U.S. EPA, 1997, EPA/542/R-96/005

National Pollution Discharge Elimination System (NPDES) requirements have decreased the allowable contaminant levels in individual point source discharges from industrial plants and municipal water treatment plants, but the number of discharge points can increase in many areas of the country due to growth. Efforts are also under way to reduce the inputs attributed to surface runoff and combined sewage overflow, but these reductions also may be offset by growth. The relative contribution of different contaminant types from point sources compared to those from nonpoint sources is an open question and undoubtedly varies substantially depending on the industrial and urban land-use mixture in a watershed.

1.2 SOIL TREATMENT GOALS

Soil treatment goals are discussed to provide preliminary estimates of the acceptance criteria for cleanup using biological treatment methods. Groundwater goals are also briefly discussed to indicate the degree of cleanup required to protect groundwater from contamination leaching out of soils.

1.2.1 State and Federal Standards

This section provides a general background of the regulatory framework for setting cleanup goals or guidance for soils and sediment. Groundwater cleanup goals are also discussed because soil treatment goals may be set based on requirements for groundwater protection. In addition to the standards and goals discussed in this section, site-specific risk assessment and standards promulgated by local jurisdictions (e.g., area water boards) often affect soil cleanup criteria. The various standards and goals overlap, so a site-specific analysis of ARARs is needed to identify the appropriate cleanup criteria for site

soils. Site-specific risk assessment should include a definition of the conceptual model for contaminant transport and applicable pathways and an evaluation of criteria required under the applicable regulatory program (e.g., the nine criteria for CERCLA sites).

1.2.1.1 Resource Conservation and Recovery Act (RCRA) Landban Requirement

Landban requirements specify treatment standards that must be achieved prior to land disposal of hazardous waste (40 CFR 268.40). These requirements consist of treatment standards for each RCRA waste code and universal treatment standards (UTSs) for the underlying hazardous constituents (UHCs). The treatment standards for specific waste codes are specified in terms of total concentration, leachable concentration, or required technology depending on the waste code and the nature of the waste (i.e., wastewater or nonwastewater). The UTSs define the maximum allowable total or leachable concentrations of the underlying hazardous constituents in hazardous waste. Landban treatment standards were developed based on the performance of the Best Demonstrated Available Treatment Technology (BDAT) for each waste type and hazardous constituent.

The landban requirements were developed using data collected from the application of specific technologies applied to specific RCRA wastes. These RCRA wastes are more uniform in physical and chemical properties than are contaminated soils. The particular challenges associated with the treatment of soil were recognized and resulted in the development of alternative treatment standards specifically applicable to land disposal of contaminated soil. The alternative treatment standard for soil requires at least a 90% reduction from the measured concentrations of UHCs in soils, but levels are not required to meet goals that would be lower than 10 times the UTS.

1.2.1.2 EPA Region 3 Preliminary Remediation Goals (PRGs)

Region 3 PRGs are risk-based guidelines used to screen sites not yet on the NPL, respond rapidly to citizen inquiries, and spot-check formal baseline risk assessments (Hubbard, 1999). These PRGs were developed primarily for screening chemicals during a baseline risk assessment and do not constitute regulation or guidance. The exposure equations are taken from EPA's Risk Assessment Guidance for Superfund (RAGS) Human Health Evaluation Manual (HHEM) (U.S. EPA, 1991b, 9285.7-01B) using exposure factors recommended in RAGS (U.S. EPA, 1991a, 9285.6-03) or supplemental guidance from the Superfund Program. PRGs are calculated for consumption of tap water, inhalation of ambient air, consumption of fish, and industrial and residential exposure to soil. The target cancer risk is $1x10^{-6}$, and the target hazard quotient is 1.0. Reference doses (RfDs) and cancer slope factors (CSFs) are taken from the Integrated Risk Information System (IRIS) (U.S. EPA, 1998b, IRIS), Health Effects Assessment Summary Tables (HEAST) (U.S. EPA, 1997c, HEAST), and provisional values from EPA's National Center for Environmental Assessment (NCEA). The PRGs have the following important limitations:

- Transfers from soil to air and water are not considered.
- Cumulative risks from multiple contaminants and media are not calculated.
- Dermal risk is not included.
- Inhalation risk due to water vapor is calculated using a very simple model (effects of confined areas or enhanced vaporization [e.g., showering] are not included).

1.2.1.3 EPA Region 9 Preliminary Remediation Goals

The Region 9 PRGs are developed for the following media and pathways:

- Groundwater (ingestion from drinking and inhalation of volatiles)
- Surface water (ingestion from drinking and inhalation of volatiles)

- Residential soil (inhalation of particles, inhalation of volatiles, and dermal absorption)
- Industrial soil (inhalation of particles, inhalation of volatiles, and dermal absorption).

Exposure from the direct ingestion of soil is calculated using the method presented in RAGS HHEM (U.S. EPA, 1991b, 9285.7-01B). Exposure from inhalation of vapors and particulate from soils are calculated using the revisions to the RAGS HHEM developed for the soil screening guidance document (U.S. EPA, 1996c, EPA/540/R-95/128). Soil dermal exposure is calculated using chemical-specific dermal adsorption values for arsenic, cadmium, chlordane, 2,4-D, dichlorodiphenyltrichloroethane (DDT), lindane, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), PAHs, polychlorinated biphenyls (PCBs), and chlorophenols as recommended in the Supplemental Dermal Guidance to RAGS (U.S. EPA, 2001). A default dermal absorption factor of 10% for semivolatile organic compounds is recommended, but default dermal absorption values for other chemicals (VOCs and inorganics) are not recommended. Exposure from groundwater and surface water ingestion and inhalation is calculated based on the RAGS HHEM. Inhalation of volatile chemicals from water is considered only for chemicals with a Henry's Law constant greater than or equal to 1×10^{-5} atm-m^3/mole and with a molecular weight of less than 200 g/mole. Exposure factors are primarily those recommended in RAGS (U.S. EPA, 1991a, 9285.6-03) supplemented by more recent guidance from the Superfund Program and the California EPA's Department of Toxic Substances Control (DTSC). The target cancer risk is 1×10^{-6}, and the target hazard quotient is 1.0. RfDs and CSFs are taken from IRIS (U.S. EPA, 1998b, IRIS) and HEAST (U.S. EPA, 1997c, HEAST), and provisional values are taken from EPA/NCEA.

Soil screening levels (SSLs) for the protection of groundwater are calculated for 100 of the most common contaminants at Superfund sites. These generic SSLs were calculated using the default values and standardized equations presented in the Soil Screening Guidance (U.S. EPA,1996c). SSLs are tabulated for dilution/attenuation factors (DAFs) of 20 and 1. DAFs are generic estimates to account for typical natural processes that reduce contaminant concentrations as groundwater migrates from the source zone. A DAF of 1 would indicate site conditions such as shallow groundwater, fractured media, karst topography, or source size greater than 30 acres that would typically cause little or no attenuation. In contrast, a DAF of 20 would account for contaminant dilution and attenuation during transport through the saturated zone, which would provide an accurate reflection of actual contaminant threat to groundwater resources. Also included in the PRG table are California EPA PRGs for specific chemicals where California values may be more restrictive than the federal values.

1.2.1.4 U.S. Environmental Protection Agency Soil Screening Guidance

EPA developed generic SSLs as preliminary screening values to help standardize and accelerate the evaluation and cleanup of contaminated soils at sites on the NPL with anticipated future residential land-use scenarios (U.S. EPA, 1996c, EPA/540/R-95/128). Generic SSLs were calculated at 110 for ingestion, inhalation, and groundwater exposure. Ingestion exposure includes direct ingestion of soil and dermal exposure for PCP, the only compound with sufficient data to support the calculation. The soil ingestion calculation uses the methods and data described in the RAGS. Calculation of the inhalation dose considers both contaminant vaporization from soil and generation and inhalation of contaminated dust. The inhalation calculation uses a volatilization factor and dispersion modeling approach developed during preparation of the soil screening guidance document. Calculation of SSLs for the groundwater exposure pathway considers leaching from the contaminated soil into the groundwater, migration of the groundwater, and direct ingestion of the groundwater. Groundwater modeling is based on linear equilibrium partitioning between soil and water and a simple water balance approach to determine a DAF. The target cancer risk is 1×10^{-6}, and the target hazard quotient is 1.0. RfDs and CSFs are taken primarily from IRIS (U.S. EPA, 1998b, IRIS) and HEAST (U.S. EPA, 1997c, HEAST) supplemented by a variety of other sources.

1.2.1.5 Texas Risk-Reduction Rule Guidance

The Texas Natural Resource Conservation Commission (TNRCC) has developed a risk-based system for site cleanup under its Texas Risk Reduction Program (TRRP). The required methods for the risk assessment are described in detail in 30 Texas Administrative Code (TAC) 350 to establish a protocol for risk-based site cleanup that is acceptable to the TNRCC. The approach follows a three-tiered system similar to that developed by the American Society for Testing and Materials (ASTM) for risk-based corrective action guides. The regulations include detailed descriptions of methods to define the appropriate exposure pathways and to calculate Tier 1 and Tier 2 cleanup goals. Equations are provided for determining risk-based cleanup criteria for carcinogens and noncarcinogens for the media and exposure routes shown in Table 1-5. These equations are used to calculate Tier 1 Protective Concentration Levels (PCLs) based on a target cancer risk is $1x10^{-6}$ and the target hazard quotient is 1.0. The Tier 1 PCLs were calculated for each media and exposure route combination and for residential and industrial scenarios for exposure to soil along the combined pathways of ingestion, inhalation of vapors and particulates, and dermal contact, and, for the residential scenario only, ingestion of vegetables.

Table 1-5. Cleanup Criteria Equations Provided in Texas Regulations

Source Media	Exposure Route	Exposure Media
Groundwater	Ingestion	Potable groundwater
Groundwater (Class 3)	Exposure to Class 3 groundwater	Class 3 groundwater
Groundwater	Inhalation of vapors	Ambient (outdoor) vapor
Groundwater	Discharge to surface water	Surface water
Surface soil	Inhalation of vapors and particulates	Ambient (outdoor) air
Surface soil	Dermal contact	Surface soil
Surface soil	Ingestion of soil	Surface soil
Surface soil	Ingestion of garden vegetables grown in contaminated soil	Vegetables
Subsurface soil	Inhalation of vapors	Ambient (outdoor) air
Subsurface soil	Leaching to groundwater	Groundwater

Source: 31 TAC 335 Subchapters A and S.

1.2.2 Groundwater Standards

This section provides summaries of federal and state standards and guidelines applicable to cleanup of contaminants in groundwater. These standards and guidelines may influence soil cleanup criteria at sites where soil cleanup is required to protect groundwater. A common soil cleanup criterion, particularly for risk-based corrective actions, is ensuring that soil cleanup goals are protective of groundwater. Usually, determining the leachate concentration from contaminated soils and relating those concentrations to groundwater cleanup goals identifies the soil cleanup goals.

1.2.2.1 Federal Maximum Contaminant Levels (MCLs)

MCLs are enforceable standards developed under the authority of the Safe Drinking Water Act and define the maximum permissible level of contaminants in water that is delivered to any user of a public water system. Maximum contaminant level *goals* (MCLGs) are distinguished from MCLs in that MCLGs are nonenforceable goals for drinking water contaminant concentrations. These goals are based on protection of human health for drinking water, and they allow an adequate margin of safety for public use (U.S. EPA, 1996d, EPA/822/B-96/002). MCLs are set at levels that also should protect human health but may have other factors that influence the selection of levels. For example, while MCLs are as close to the

MCLGs as feasible, they also may take into account available treatment technologies and the costs to large public water systems. MCLGs, on the other hand, are strictly health-based goals.

1.2.2.2 National Recommended Water Quality Criteria (NRWQC)

The NRWQC are nonenforceable guidelines developed and published by EPA as required by Section 304(a)(1) of the Clean Water Act (CWA) (U.S. EPA, 1999a, EPA/822/Z-99/001). These guidelines are developed to reflect the latest scientific knowledge based solely on data and scientific judgements on the relationship between contaminant concentrations and adverse effects to human health and the environment. Cost and feasibility of meeting the guidelines in ambient water are not considered during the process of setting the guidelines. Guidelines have been set for 157 contaminants based on adverse effects to human health and toxicity to freshwater and saltwater organisms.

1.2.2.3 California Maximum Contaminant Levels

California MCLs are similar to the federal MCLs, but include lower limits on some chemicals that are specifically applicable to drinking water in California.

1.2.2.4 California Ocean Plan Limits

The California Ocean Plan sets forth limits or levels of water quality characteristics for ocean water to ensure reasonable protection of beneficial use (SWRCB, 1997). The total discharge of waste materials shall not cause violation of these limits. Standards include water quality objectives for ocean water describing acceptable bacterial characteristics, physical characteristics, chemical characteristics, biological characteristics, and radioactivity; general requirements for management of waste discharge to the ocean; and quality requirements for waste discharges to the ocean, including contaminants in groundwater migrating into the ocean. These numerical discharge limits for chemical contaminants are based on protection of marine aquatic life or protection of human health.

1.2.3 Application of Risk-Based Cleanup Criteria

There is growing support for the application of risk-based corrective actions to clean up petroleum contaminants at UST sites EPA, 2002 (http:/www.epa.gov/swerust1/rbdm/rbdmfaq5.htm; last viewed 9/25/02). Risk assessment is required for CERCLA and RCRA CA during site characterization and remedy evaluation to determine the level of risk (Begley, 1996). In the early history of the CERCLA and RCRA CA processes, if the risk assessment indicated excessive risk, cleanup criteria were set based on the site background or practical limits of available technology (Begley, 1996). However, using risk assessment to set cleanup criteria based on site-specific pathways analysis, considering the planned future land use for the site, has been gaining acceptance (Begley, 1996).

1.2.3.1 Criteria for Ex-Situ Treatment of Soil

The alternative landban requirements for soil will play a role in setting cleanup criteria for excavated soil or dredged sediment at many sites. Contaminated soil, once it is excavated, is considered a solid waste and, therefore, must be evaluated to determine if it is also a hazardous waste. If the soil exhibits a hazardous waste characteristic or contains a listed hazardous waste, the applicable waste codes will be applied and the landban standards applicable to those codes and for UHCs must be met prior to land disposal. RCRA requirements apply directly to hazardous waste soils excavated at non-CERCLA sites or transferred off site from a CERCLA site. Landban requirements usually are considered as an applicable requirement for hazardous waste soil treated and managed at a CERCLA site. Additionally, landban requirements may be applied at a CERCLA site as a relevant and appropriate requirement for soil that is

not classified as RCRA hazardous, but has chemical characteristics that are similar to a RCRA hazardous waste.

Site-specific risk assessment can be used to set cleanup limits for soil treatment to supplement landban or when landban provisions do not apply (i.e., nonhazardous soil). Cleanup goals developed by various regulatory authorities provide a preliminary indication of risk-based goals, but include simplifying assumptions and do not cover all possible site conditions. For example, a construction worker who is assumed to work in a trench where groundwater and contaminant vapors accumulate will have a much shorter period of allowable exposure at higher concentrations compared to the allowable exposure from the inhalation of vapors emanating from the soil surface. Typically, cleanup criteria are determined by first calculating PRGs and/or site-specific risk-based limits. The lowest value for each contaminant, determined by each method, is then selected and used. Risk assessment may result in setting cleanup criteria that are lower than the landban requirements in special circumstances, such as where multiple contaminants in the groundwater or multiple pathways of exposure increase the risk above acceptable levels.

1.2.3.2 Criteria for In-situ Treatment of Soil

When soil is treated *in situ*, no solid waste is generated so the RCRA hazardous waste rules are not triggered. Therefore, cleanup criteria are set on a site-specific basis. As with excavated soils, risk assessment considering site-specific conditions and planned land use is gaining acceptance with regulatory authorities as an approach for setting cleanup criteria. The cleanup criteria for *in-situ* soil should consider the viable pathways for surface soil (e.g., ingestion, volatilization, and dermal exposure) and groundwater protection for surface and subsurface soil.

Ingestion, volatilization, and dermal exposure are not probable exposure pathways for subsurface soils, but infiltrating rainwater can leach contaminants out of soil and carry them downward into an aquifer. A simple approach for setting cleanup criteria for subsurface soil is the use of equilibrium modeling or leach testing of soil to estimate or measure the leachate concentration; this concentration is then compared to an accepted groundwater standard or a risk-based standard for groundwater consumption. Leach testing normally is done using an accepted regulatory test such as the toxicity characteristic leaching procedure (TCLP) or the synthetic acid precipitation leaching procedure (SPLP). For more complex situations, risk-based goals may be based on modeling of transport from the source soil to the groundwater consumer. A detailed transport modeling approach requires considerably more effort than does the simple leachate estimation approach.

MCLs are generally ARARs at CERCLA sites for cleanup of an aquifer if the groundwater, prior to the contamination, could have been used at some future date as a drinking water source (U.S. EPA, 1988, EPA/540/G-89/006). Similarly, RCRA standards require cleanup of groundwater at hazardous waste treatment, storage, and disposal (TSD) facilities to meet MCLs. A cleanup standard more stringent than MCLs may be needed in special circumstances, such as where multiple contaminants in the groundwater or multiple pathways of exposure increase the risk above acceptable levels.

If the aquifer is not suitable for use as a drinking water supply (e.g., low yield and/or high salt content), cleanup to MCLs may not be required. In this case, cleanup criteria may be set using risk-based standards alone or in conjunction with other ARARs.

1.2.3.3 American Society for Testing and Materials Guide for Risk-Based Corrective Action

ASTM has developed a standard guide for risk-based corrective action at petroleum release sites (ASTM E 1739) and a provisional guide for risk-based corrective action applicable to a broad range of contaminant types (ASTM PS 104-98). Both of these guides describe a three-tiered approach as follows:

- Tier 1 evaluation – a risk-based analysis using non-site-specific values for complete and potentially complete direct and indirect human exposure pathways and qualitative ecological screening evaluation
- Tier 2 evaluation – a risk-based analysis for human exposure pathways using the same methods applied in the Tier 1 evaluation, but with site-specific analysis of exposure pathways and qualitative or quantitative analysis of ecological risks
- Tier 3 evaluation – a risk-based analysis for human exposure pathways using complex modeling of contaminant fate and transport and a more quantitative analysis of ecological risks than Tier 2.

Moving from Tier 1 to Tier 3 reduces the degree of conservatism in the cleanup criteria, but involves increased effort. In particular, Tier 3 calculations typically require a much larger amount of effort than do Tiers 1 or 2. The guides include detailed descriptions of methods to define the appropriate exposure pathways and to calculate Tier 1 and Tier 2 cleanup goals based on a wide range of pathways. Equations are provided for determining risk-based cleanup criteria for carcinogens and noncarcinogens for the media and exposure routes shown in Table 1-6. These equations are used to calculate Tier 1 cleanup criteria for some example contaminants; however, the standards are intended to prescribe a method for calculating risk-based cleanup criteria, not to define the specific chemicals to focus on or the cleanup values to use.

Table 1-6. Cleanup Criteria Provided in ASTM Risk-Based Guides

Source Media	Exposure Route	Exposure Media
Air	Inhalation	Air
Groundwater	Ingestion	Potable
Groundwater	Enclosed space vapor inhalation	Indoor air
Groundwater	Vapor inhalation	Outdoor air
Surface soil	Ingestion of soil, inhalation of vapors and particulates, and dermal contact	Soil and air
Subsurface soil	Vapor inhalation	Outdoor air
Subsurface soil	Enclosed space vapor inhalation	Indoor air
Subsurface soil	Leaching to groundwater	Groundwater

Source: ASTME 1739-95

2.0 UNDERLYING PRINCIPLES OF BIOREMEDIATION

Bioremediation may be defined as a process in which a biological, especially microbial, catalyst acts on pollutant compounds, thereby remedying or eliminating the environmental contamination (Madsen, 1991). Successful bioremediation of soils results from a manipulation of the contaminated system that encourages biological activity that results in the conversion of the contaminant to a less harmful form (Turco, 1999). This section focuses on the microbiology of contaminant degradation in soils. As discussed in Section 1, soils may be contaminated with a wide range of organic (e.g., petroleum hydrocarbons, organic solvents, pesticides and herbicides, dioxins and furans, PCBs, and energetic compounds) and inorganic (mostly metals) compounds. Table 2-1 summarizes the effectiveness of different remedial activities for specific contaminant groups. While Table 2-1 provides a general idea of how contaminants have been effectively treated in the past, it should be noted that the efficacy of bioremediation technologies is based on many site-specific factors, and if a technology has successfully remediated a certain class of contaminants in the past, this does not guarantee future success. Conversely, if a technology is listed as 'demonstrated ineffective' in Table 2-1, this does not imply that the same technology will be ineffective at treating the given contaminant at future sites.

Table 2-1. Effectiveness of Treatment Technologies for Contaminant Groups

Treatment Technology	Contaminant Groups						
In Situ	**Chlorinated VOCs / SVOCs**	**Fuels and Oils**	**Creosote, PAHs**	**Metals**	**PCBs**	**Pesticides Herbicides**	**Explosives**
Bioventing, Aerobic		**19**	**1**				
Bioventing, Cometabolic / Enhanced	**2**	**6**					
Monitored Natural Attenuation		**2**		**1**			
Phytoremediation, Extraction				**2**			
Phytoremediation, Mineralization	**1**	**1**	**1**				
Slurry-Phase Biotreatment		**1**					
Ex Situ							
Biocell	**1**	**6**					**4**
Biopile	**1**	**6**	**4**				**1**
Bioreactor, Aerobic Slurry-Phase		**2**	**3**			**1**	**1**
Bioreactor, with Anaerobic Slurry-Phase						**1**	**3**
Composting (mainly windrows)	**1**	**1**	**2**		**1**	**1**	**4**
Daramend Process		**1**	**2**			**1**	**2**
Land Treatment, Active	**2**	**18**	**4**				
Cycled Land Treatment (with non-aerated / anaerobic phase)	**1**	**2**	**1**		**1**		

	Demonstrated Effective
	Somewhat Effective
	Demonstrated Ineffective
#	Number of Sites

It is important to understand the limitations as well as the potential advantages of the different biological processes for degrading these contaminants when considering bioremediation technologies for contaminated soils. For example, some contaminants are best degraded aerobically while others are degraded only under anaerobic conditions. Understanding the biodegradation mechanisms will help in the proper selection of a bioremediation technology. The degradation characteristics of the soil contaminants are divided into the following groups: organic compounds that are degraded aerobically or anaerobically as primary growth substrates (this may include halogenated and non-halogenated compounds); organic compounds that are degraded cometabolically; and halogenated organic compounds that are degraded anaerobically via reductive dehalogenation.

2.1 BIODEGRADATION OF PAHs AND PETROLEUM HYDROCARBONS

Hydrocarbons, including PAHs, are introduced into the environment primarily in fuels, oils, creosotes, coal tars, and other refined petroleum products. These hydrocarbons are weathered in soils through volatilization, dissolution, sorption, and biodegradation. Lighter-molecular-weight compounds tend to evaporate into the vadose zone and subsequently into the atmosphere, or dissolve in water that infiltrates soils. However, for high-molecular-weight compounds, these mechanisms tend to be minor (Prince and Drake, 1999) and they tend to be much more persistent in the environment. Through adsorption, the binding of hydrocarbon compounds to soils can make them unavailable for biodegradation (Prince and Drake, 1999); this is particularly true of the higher-molecular-weight compounds that tend to have a higher affinity for sorption to soils due to their higher degree of hydrophobicity. However, it is important to recognize that higher-molecular-weight PAHs are generally more potent toxicants, suggesting that it may be necessary to treat all PAHs to mitigate risk. Further, weathering of lower-molecular-weight PAHs and sorption of higher-molecular-weight PAHs may not significantly reduce toxicity.

With respect to the destruction and removal of hydrocarbons from the environment, the most important of the weathering phenomena is biodegradation. Hydrocarbons are biodegraded by a wide variety of microorganisms in a broad range of habitats, under aerobic and anaerobic conditions (Prince and Drake, 1999). Aerobically, bacteria that grow on hydrocarbons typically initiate oxidation by incorporating molecular oxygen into organic compounds by the action of enzymes known as oxygenases (Wackett and Householder, 1989) that destabilize carbon-carbon bonds and render the organic molecule more susceptible to degradation. A number of hydrocarbon compounds have been shown to be degraded and ultimately mineralized to carbon dioxide (CO_2) in this manner, including PAHs, such as acenaphthene, fluorene, dibenzothiophene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, and benzo[a]pyrene (Prince and Drake, 1999). However, biodegradation of PAHs and other petroleum hydrocarbons tends to be more difficult with increasing molecular weight, resulting in reduced degradation rates.

In some cases, the oxygenases show activity for other compounds, a process known as cometabolism. Because oxygenases tend to be relatively non-specific with respect to the types of organic compounds that they will react with, the fortuitous oxidation of some contaminants will occur via the degradation of a primary growth substrate. Methane monoxygenase is the most widely studied non-specific oxygenase, and is well known for its ability to cometabolically degrade trichloroethylene (TCE) and other chlorinated aliphatic hydrocarbons (CAH). In addition to cometabolically degrading selective CAH, methane monooxygenase also has been shown to convert naphthalene to 1- and 2-naphthols (Dalton et al., 1981). A wide variety of organic compounds can serve as primary growth substrates or as the cometabolically degraded substrate. While cometabolism has not been exploited as a bioremediation mechanism for PAHs and other petroleum hydrocarbons to date, it may occur in the environment where petroleum spills result in significant biological activity, resulting in anaerobic conditions and methane production through methanogenesis.

Anaerobically, PAHs and other petroleum hydrocarbons are more difficult to degrade and degrade much more slowly than under aerobic conditions. For some time, it was thought that PAHs could not degrade anaerobically, especially under extreme sulfate-reducing or other reducing conditions. However, naphthalene and acenaphthene have been shown to be biodegraded under nitrate-reducing conditions (Milhelcic and Luthy, 1991; Durant et al., 1995), and naphthalene and phenanthrene have been shown to be biodegraded under sulfate-reducing conditions (Coates et al., 1996). New degradation pathways are continuously being discovered, and this list is unlikely to exhaust the potential for anaerobic degradation of PAHs.

2.2 BIODEGRADATION OF EXPLOSIVES

Explosive compounds include the nitroaromatic compounds (trinitrotoluene [TNT], picrate, and tetryl) and the nitramines (nitroguanidine, hexahydro-1,3,5-triaza-1,3,5-trinitrocyclohexane [RMX], and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraaxocine [HMX]). TNT is historically the most commonly used of all military explosives. Military grades of TNT also contain as a sum up to 8% 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) (Major, 1999).

Biological mineralization of the nitroaromatics is difficult due to the electrophilic nature and the orientation of the nitro groups (Major, 1999), and mineralization by individual bacterial cultures may not be possible, or practical. The *meta* spacing of the three nitro groups leaves only two unsubstituted carbons on the ring, situated *meta* to each other. Biological aromatic ring cleavage normally requires placement of phenolic substituents oriented *ortho* or *para* to each other. It is likely that the *meta* orientation of the nitro groups inhibits the hydroxylation of adjacent carbons on the aromatic ring and, consequently, ring cleavage, resulting in the persistence of these compounds in the environment (Major, 1999). Thus, the aerobic biodegradation of nitroaromatic compounds tends to favor biotransformation more than mineralization, resulting in the potential production of a variety of amino-nitro compounds.

TNT has been mineralized in the laboratory. The white rot fungus *Phanerochaete chrysosporium* is able to mineralize TNT to CO_2 (Fernando et al., 1990; Tudor et al., 1990); however, under strictly aerobic conditions, reports of mineralization in nature are lacking. Anaerobic reduction of nitro substituents to amino substituents can occur biologically under reduced conditions (Funk et al., 1993), forming amino-dinitro-, nitro-diamino-, and triamino-toluene. Anaerobic consortia can be enriched to degrade TNT to aliphatic end products (Funk et al., 1993, 1994). Presumably, under these conditions the nitro groups of the nitroaromatic compounds are used as terminal electron acceptors.

The nitramine explosives of environmental interest include the cyclic nitramines cyclotrimethylenetrinitramine (RDX) and HMX because of their wide use as explosives due to their explosive power (1.5 to 2 times that of TNT) and rapid detonating velocity (1.3 times that of TNT) (Major, 1999). Most weapons-grade RDX contains some HMX as an impurity and vice versa. Under anaerobic conditions, the nitro substituents of RDX are reduced (McCormic et al., 1981, 1985) to nitroso groups, producing nitrosoamines. This is followed by a series of reactions that result in the cleavage of the heterocyclic ring to form common byproducts of this degradation process including various hydrozine, dimethylhydrazine, and dimethylnitrosamine intermediates. Because dimythylnitrosamine is much more toxic than RDX, accumulation of this compound presumably would require more stringent remedial action (Major, 1999).

Much less is known about HMX degradation. Under reducing conditions, HMX is known to biotransform similarly to RDX in which the nitro groups undergo reductions to nitroso groups. However, HMX reduction proceeds only to the formation of the mono and dinitroso products with retention of the intact ring system (Major, 1999).

2.3 BIOTRANSFORMATION OF PCBs

Most PCBs in the environment are dispersed at low concentrations in soil, air, water, and sediment; however, environmental PCB pools remain in soils or sediments at concentrations high enough to pose environmental or public health risks (Hickey, 1999). The family of PCBs contains 209 theoretically possible molecular conformations, called congeners. Each congener consists of a biphenyl molecule substituted with one to ten chlorine substituents. PCBs were produced as mixtures during the mid-twentieth century and sold for industrial applications under trade names such as Aroclor, Clophen, Fenclor, or Kanechlor (in the USA, Monsanto Corporation produced Aroclors). Approximately 189 of the 209 theoretically possible PCBs have been identified in Aroclors and other PCB mixtures (Jones, 1998). Of these, 36 have been identified as the most significant in terms of their toxicity potential or abundance (McFarland and Clarke, 1989). The PCBs with the greatest toxicity potential are those substituted in both the *para* positions and at least two *meta* positions, because these congeners are stereochemically similar to 2,5,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (Hickey, 1999; NRC, 2001).

The fate of PCBs is influenced by sorption, volatilization, and degradation, and the extent to which these processes affect PCB weathering depends strongly on the number and positioning of chlorines on the PCB molecule. Increased PCB chlorination results in increased hydrophobicity, and increased sorption.

Sorption is the dominant process influencing the fate of PCBs in soils, and is of particular significance with PCBs because it may attenuate biodegradation. PCBs strongly partition into soil or sediment organic matter, which has the potential beneficial effect of immobilizing them against leaching into groundwater. However, in the context of biodegradation, as for PAHs, desorption may be rate limiting by restricting the release of PCBs into the aqueous phase where they would be more bioavailable (Hickey, 1999).

The primary factors affecting PCB biotransformation are the number and pattern of chlorine substituents (Hickey, 1999; NRC, 2001). Aerobically, the *meta* cleavage pathway is the primary method by which bacteria degrade the biphenyl molecule. Bacteria use biphenyl and monochlorinated biphenyls for carbon, energy, and growth (Ahmed and Focht, 1973). However, biphenyl degraders are unable to use PCBs chlorinated on both aromatic rings because they are unable to assimilate halogenated aromatic or aliphatic acids. Consequently, PCBs substituted on both rings generally fail to support growth (Hickey, 1999). However, these PCBs may be degraded cometabolically, in which degradation of biphenyl or monochlorinated biphenyls supports bacterial growth, and PCBs chlorinated on both aromatic rings are degraded fortuitously by the biphenyl dioxygenase and other nonspecific enzymes. Both the number and location of chlorine substituents strongly affects the ability for PCBs to be degraded cometabolically. In general, the ability for bacteria to degrade PCBs decreases with increased chlorination, and congeners with five or more chlorines are relatively recalcitrant to aerobic biodegradation (Furukawa et al., 1983; Masse et al., 1984; Bedard et al., 1986). The chlorine substituent pattern also affects the metabolic byproducts of dechlorination and their ability to be degraded further by other bacteria.

Fungi also have been reported to degrade or transform PCBs while growing on a supplemental carbon source. PCB degradation by white-rot fungi and soil fungi is similar to that of aerobic bacteria in that it is most extensive for lower-chlorinated congeners. The white-rot fungus *Phanerocheate chrysosporium* mineralized PCBs in the laboratory for congeners with four or fewer chlorines (Dietrich et al., 1995), and the soil fungus *Aspergillus niger* degraded technical grade PCB mixtures with less than 42% chlorine by weight (Murado et al., 1976); more chlorinated congeners were not degraded.

Under anaerobic conditions, the primary metabolic pathway is reductive dechlorination, in which chlorine removal and substitution with hydrogen by bacteria results in a reduced organic compound with fewer chlorines (Mohn and Tiedje, 1992). Higher chlorinated biphenyls are preferentially dechlorinated over lower chlorinated congeners, and the step-wise replacement of chlorines with hydrogen atoms results in

the accumulation of mono-, di-, and trichlorobiphenyls (Quensen et al., 1988). In general, reductive dechlorination preferentially removes chlorines from the *meta* and *para* positions and replaces them with hydrogen atoms, resulting in substantial reductions in carcinogenicity and "dioxin-like" toxicity. In addition to lowering the overall toxicity of PCB-contaminated materials, the tendency of the PCB mixture to bioaccumulate is also reduced. For example, 2-chlorobiphenyl and 2,2-bichlorobiphenyl display an approximate 450-fold decrease in the tendency to bioaccumulate in fish compared with tri- and tetra-chlorinated PCBs (Abramowicz and Olson, 1995).

Bedard et al. (1998) and Bedard and Van Dort (1998) demonstrated that PCB dechlorination can be initiated using brominated biphenyl (BB) analogs of chlorobobiphenyl analogs. Anaerobic PCB dechlorination in Woods Pond (Lenox, Massachusetts) sediments was stimulated using bromophenols. Mono-, di-, tri-, tetra-, and pentabromophenols were added to sediment microcosms; all were completely dechlorinated to biphenyl. The PCB dechlorination primed by several brominated biphenyls was nearly twice as effective as that primed by chlorinated biphenyls (Bedard et al., 1998), where the most effective primers were 26-BB, 245-BB, 25-3-BB, and 25-4-BB. The 26-BB primed microcosms converted approximately 75% of the hexa- through nonachlorobiphenyls to tri- and tetrachlorobiphenyls within 100 days, and removed approximately 75% of the PCBs that are more persistent in humans.

2.4 BIOTRANSFORMATION OF CHLORINATED ALIPHATIC HYDROCARBONS

Halogenated aliphatic compounds are frequently used as solvents, degreasers, refrigerants, aerosols, and pesticides. The popularity of their use has resulted in their frequent release into the environment. The most common halogenated aliphatic compounds are the CAHs, which include the chlorinated ethenes (perchloroethene [PCE], TCE, dichloroethylene [DCE] isomers, and vinyl chloride [VC]), the chlorinated ethanes such as 1,1,1- and 1,1,2-trichloroethane (TCA), and 1,1- and 1,2-dichloroethane (DCA); and chloromethanes including carbon tetrachloride and methylene chloride. In soils, these compounds exist as sorbed or dissolved in light non-aqueous phase liquids (LNAPL). Because many of these compounds form dense NAPLs (DNAPL), they are not commonly present in soils as free-phase liquids, except possibly trapped in soil pores. The transformation reactions of CAHs in biotic and abiotic systems have been reviewed extensively (Vogel et al., 1987; Mohn and Tiedje, 1992; Fetzner and Lingans, 1994; Castro, 1998; and Reinhard et al., 1999). This discussion focuses on microbial transformations of CAHs under aerobic and anaerobic conditions.

Three primary microbial mechanisms are used for the degradation of CAHs; halorespiration (e.g., reductive dechlorination) where the CAH is used as an electron acceptor in the microbial electron transport chain; direct oxidation where the CAH is used as a substrate for energy and growth; and cometabolism in which the CAH is oxidized by non-specific enzymes used for bacterial growth on an alternative primary substrate (Reinhard et al., 1999).

Halorespiration is a reductive process in which the CAH is used as an electron acceptor, and in the process dehalogenated, resulting in chlorine removal and substitution with a hydrogen atom. For some compounds that cannot be oxidized under aerobic or anaerobic conditions, such as PCE, carbon tetrachloride, 1,1,2,2-tetrachloroethane, and some highly chlorinated PCBs, halorespiration is the primary biological mechanism for their microbial transformation. In the absence of halorespiration, many of these compounds would persist in the environment indefinitely. Limitations of halorespiration are that this process requires strict anaerobic conditions, the presence of an electron donor for carbon and energy, and the presence of bacteria capable of sustaining these reactions. Another limitation is that halorespiration rates tend to decrease with decreasing chlorination, and the presence of bacteria that can halorespire a parent compound does not necessarily imply that the dechlorination daughter products also can be halorespired. This results in the potential accumulation of dechlorination byproducts in the environment, such as the production of DCE and VC from PCE or TCE dechlorination. The accumulation of

dechlorination byproducts has historically been among the most significant limitations of implementing this technology in the field, especially for chloroethenes, because the byproduct VC is much more toxic than its parent compounds PCE, TCE, or DCE. However, as discussed below, recent studies have shown that VC and DCE can be degraded aerobically, providing a removal mechanism for these compounds should they accumulate in the environment.

Some CAHs can be oxidized under aerobic or anaerobic conditions where the CAHs are used as growth substrates (Reinhard et al., 1999). Specifically, evidence has been presented for the aerobic degradation of monochloromethane (Yokota et al., 1986) or dichloromethane (Rittman and McCarty, 1980); aerobic degradation of 1,2-DCA (Hage and Hartmans, 1999); and the degradation of VC (Bradley and Chapelle, 1996; Bradley et at., 1998) 1,2-DCE under aerobic (Bradley et al., 1998) and anaerobic (e.g., Fe-reducing, Mn-reducing, or methanogenic) conditions (Bradley et al., 1998; Bradley and Chapelle, 1996, 1997). The ability for bacteria to use VC and DCE isomers as growth substrates under aerobic or anaerobic conditions has opened the possibility for sequential anaerobic/aerobic treatment of chloroethenes, PCE and TCE could be dechlorinated to DCE and VC under anaerobic conditions, then mineralized to CO_2 and hydrogen chloride (HCl) under aerobic conditions. Thus, under properly controlled conditions where the complete dechlorination of PCE to ethene is ineffective, partial dechlorination to DCE and VC may be promoted followed by their degradation to CO_2 and HCl. While the engineering application of this approach has been limited, there is increasing evidence of the sequential anaerobic/aerobic dechlorination of chloroethenes in nature under natural conditions. Furthermore, this mechanism was promoted as the optimal condition for complete degradation of chloroethenes in the environment under Monitored Natural Attenuation (MNA) in the Air Force Center for Environmental Excellence (AFCEE) protocol for evaluating MNA of chlorinated solvents in groundwater (Wiedemeier et al., 1996).

The aerobic cometabolism of chlorinated ethenes has been studied extensively because of its potential for site cleanup. Cometabolism relies on the oxidation of a cosubstrate that is affected by oxygenaze enzymes known as mono- or dioxygenazes. The nonspecific nature of these enzymes means that they are often used for the oxidation of CAHs or other compounds other than the primary growth substrate. PCE and carbon tetrachloride are important exceptions to this process, and there is no evidence to date of their oxidation under aerobic or anaerobic conditions, cometabolically or otherwise.

It is generally accepted that cometabolism of CAHs does not provide energy or carbon for cell growth. In fact, cometabolism often results in the depletion of stored energy reserves in the cell (Alvarez-Cohen and McCarty, 1991). This implies that an organic cosubstrate other than the CAHs is required for biological growth and for the production of the necessary oxygenase enzymes that are used to degrade the CAHs. A variety of growth substrates have been used for cometabolic CAH degradation, including methane (Broholm et al., 1993), propane (Wackett et al., 1989), propene (Reij et al., 1995), aromatic compounds including phenol (Hopkins et al., 1993), toluene (Wackett and Gibson, 1988), and isopropylbenzene (Dabrock et al., 1992).

Important issues related to the engineering application of cometabolic CAH degradation include CAH intermediate toxicity (Alvarez-Cohen and McCarty, 1991; Fox et al., 1990) and competitive inhibition. Because CAHs are degraded by the same nonspecific enzymes responsible for the degradation of the growth substrate, competition between the CAH and the growth substrate is known to occur. Intermediate toxicity during CAH degradation and competition can reduce the degradation rates of both the growth substrate and the CAH. In addition, multiple CAHs can compete (Strand et al., 1990) or create toxic conditions that can affect CAH degradation rates (Bielefeldt, 1995).

2.5 BIOTRANSFORMATION OF HALOGENATED AROMATIC COMPOUNDS

Halogenated aromatic compounds (HACs) include all compounds containing halogenated aromatic rings, including aryl halides such as DDT, dioxins, and dibenzofurans. While the more volatile compounds such as hexachlorobenzene and pentachloroanisole (Simonich and Hites, 1995) may volatilize after they are released into the environment and become distributed globally, less volatile compounds such as *p,p'*-DDT [*p,p'*-dichloro-(bis)-1,1-diphenyl-1,1,1-trichloroethane] and its degradation products *p,p'*-DDD and *p,p'*-DDE [*p,p'*-dichloro-(bis)-1,1-diphenyl-1,1-dichloroethane] tend to remain in place in soils or sediments to which they are originally bound (Adriaens et al., 1999). Thus, the fate and biotransformation of HACs is of particular interest for soils where many of these compounds are retained.

Aerobic biodegradation pathways for bacterial and fungal growth on HACs have been reviewed extensively for halogenated phenols, benzoic acids, benzenes, pesticides, anilines, and herbicides (Rochkind-Dubinsky et al., 1987; Häggblom, 1992; Neilsen, 1990; Engesser and Fisher, 1991; Commandeur and Parsons, 1994; Adriaens et al., 1999). While the initial oxidation steps may be carried out by a variety of enzymes, only a limited number of intermediates are produced; they include dihydroxylated benzoic acids and substituted catechols. Further degradation of these metabolites via either *ortho* or *meta* ring fission leads to intermediates of central metabolic pathways such as the tricarboxylic acid cycle (Adriaens et al., 1999). Despite the success of aerobic bacteria to degrade a variety of HACs, not all HACs are easily degraded aerobically. HACs only serve as sources of carbon and energy for aerobic or anaerobic bacteria if they can be dehalogenated prior to or after ring fission. Alternatively, these compounds may be degraded cometabolically, a process during which enzymes or proteins break the aromatic ring but the bacteria are unable to derive carbon or energy from the HAC.

Under anaerobic conditions, reductive dechlorination represents the most common detoxification method for HACs (Mohn and Tiedje, 1992). There is increasing evidence that reductive dechlorination is an energetically favorable reaction in which bacteria use the HACs as electron sinks for energy (Dolfing and Harrison, 1992; Mohn and Tiedje, 1992, 1991, 1990; Holliger and Schraa, 1994). Alternatively, dechlorination reactions may be used by bacteria to detoxify contaminants or they may occur fortuitously cometabolically (Mohn and Tiedje, 1992). However, because HACs in the environment are often present at trace or ultratrace concentrations, little measurable energetic benefit can be expected to be obtained from halide respiration (halorespiration) (Adriaens et al., 1999), and transformation of HACs may be considered a form of secondary metabolism. This makes the engineered application of anaerobic dechlorination increasingly difficult for contaminated soils where HACs are present at trace concentrations. Whether microorganisms in soil matrices grow on aryl halides, degrade them via secondary metabolism, or transform them cometabolically, ultimately the metabolic pathways converge into one of three possible intermediates, substituted halocatechols or dihydroxybenzoates, which further degrade and serve as growth substrate for numerous microorganisms. However, in the environment, dechlorination and mineralization represent only one of a number of possible pathways for aryl halides; microbially mediated conjugation, polymerization, and reactions with natural humic substances also determine the fate of the aryl halides. The relative contribution of each of these processes depends largely on the chemical reactivity of the aryl halide, the physiochemical characteristics of the soil matrix, and the biological component of the soils (Adriaens et al., 1999).

The susceptibility of the aryl halide compound to oxidative or reductive microbial degradation depends largely on the oxidation state of the aryl compound. Increased chlorination results in a more oxidized form of the aryl compound. Thus, not surprisingly, highly chlorinated compounds are more susceptible to reductive dechlorination while they tend to be difficult or impossible to oxidize aerobically. (The difficulty for aerobic bacteria to oxidize highly chlorinated aryl halides also may be due to the unavailability of free adjacent carbons on the aromatic ring; it is generally observed that mono- and dioxygenases will not act on aryl halides with more than two chlorines per ring [Adriaens et al., 1999].)

As Gibbs free energy associated with lesser chlorinated compounds decreases (Dolfing and Harrison, 1992), oxidative reactions become more favorable (Adriaens et al., 1999). The position of the aryl halogen also exerts an influence on microbial processes, where certain *ortho*-, *meta*-, or *para*-chlorine positions are preferentially dechlorinated. For example, chlorobenzene dechlorination under anaerobic conditions generally requires the presence of adjacent halogens. Isolated halogens on chlorobenzenes, such as 1,3- or 1,4-dichlorobenzene or 1,3,5-trichlorobenzene are relatively recalcitrant to dechlorination (Fathepure et al., 1998).

The primary factor that determines which microorganisms will degrade aryl halides in soils is the availability of electron acceptors and an alternative carbon source. Bacteria will utilize electron acceptors in order of the most energetically favorable, beginning with oxygen respiration, followed in sequence by nitrate-, iron(III)-, manganese(IV)-, and sulfate-reduction, ending with methanogenesis. Aryl halide reductive dechlorination is strongly dependent on the prevailing electron acceptor process and the availability of an electron donor. Dechlorination of aryl halides is most favorable under methanogenic and sulfate-reducing conditions, although sulfate reduction also can be inhibitory to reductive dechlorination (Mohn and Tiedje, 1992; H@ggblom, 1992; H@ggblom and Young, 1995; Adriaens et al., 1999). Alternatively, the metabolism of aryl halides also varies depending on the primary electron acceptor process. H@ggblom et al. (1993) investigated the effects of nitrate, sulfate and carbonate (methanogenesis) as electron acceptors on anaerobic metabolism of monochlorinated phenols and benzoic acids in freshwater and marine sediments. The respective denitrifying, sufidogenic, and methanogenic enrichments all were capable of utilizing at least one chlorophenol or chlorobenzoate, but none was capable of utilizing all six compounds tested. The variety of reports of dechlorination and metabolism of chlorinated compounds under varying electron acceptor conditions indicates that generalities and subsequent predictions may be impossible to make at some sites, regarding the degradability of aryl halogens, without bench-scale testing using site-specific soils and environmental conditions.

2.6 BIOTRANSFORMATION OF DIOXIN-LIKE COMPOUNDS

Dioxins (e.g., polychlorinated dibenzo-*p*-dioxins [PCDDs], and polychlorinated dibenzo-furans [PCDFs]) are ubiquitous in the environment at subparts-per-million concentrations. In general, these compounds are unwanted byproducts of combustion and industrial synthesis, and very little is known about their fate in soils. Under reduced conditions, PCDD have been successfully dechlorinated to mono-, di-, and trichlorinated dibenzo-*p*-dioxins (Barkovskii and Adriaens, 1996, 1998). Aerobically, the lesser chlorinated congeners have been cometabolized to form hydroxylated chlorodiphenylethers and chlorocatechols (Klecka and Gibson, 1980; Fortnagel et al., 1990). Similarly to the biodegradation processes of PCBs, the overall fate of PCDD may be dependent on an anaerobic/aerobic sequence of reactions to completely mineralize these compounds and remove them from the environment (Adriaens et al., 1999).

3.0 EXISTING BIOREMEDIATION TECHNOLOGIES AND APPLICATIONS

This section describes existing soil bioremediation technologies. Table 3-1 shows the technologies that are discussed and categorizes them as conventional or emerging. For the purposes of this report, conventional technologies are those that have been deployed at full scale and can be implemented readily without further significant research and development. Emerging technologies are those that have not yet been significantly implemented at full scale but currently are undergoing or could undergo further research and development to bring them to the field. An abundance of cost and performance data are available for soil bioremediation using the conventional technologies. Not surprisingly, cost and performance data generally are unavailable for the emerging technologies. Furthermore, most of the conventional technologies may be considered emerging or even developmental in cases where they may be applied to complex soil conditions and increasingly recalcitrant contaminants.

Table 3-1. Technology Maturity

Technology	Stage of Development	
	Conventional	Emerging
Land Treatment	✓	
Biopile	✓	
Biocell	✓	
Composting	✓	
Bioslurry Reactors	✓	
Aerobic Bioventing	✓	
Cometabolic Bioventing		✓
Anaerobic Bioventing		✓
Phytoremediation		✓
Sequential Anaerobic/Aerobic Treatment		✓
Natural Attenuation		✓

Section 3.1 describes the conventional technologies with respect to their principles of operation, specifically, the biological aspect of the technology, target contaminants, advantages and limitations, and the technology cost and performance as reported in available literature. Section 3.2 describes emerging technologies with respect to their principles of operation and future directions. Cost and performance data are reported for these technologies where available, but in general little such data were found for these technologies in published reports and documents.

For this report, a review of existing cost and performance data was conducted using on-line searches of databases including the National Technical Information Service (NTIS), EPA, Federal Remediation Technologies Roundtable (FRTR), Remediation Information Management System (RIMS), EPA Remediation and Characterization Innovative Technologies (REACH-IT), Bioremediation in the Field Search System (BFSS), and Lexis-Nexis. These databases provided cost and performance data for large-scale demonstrations. However, they did not usually provide extensive technology descriptions or site information.

As much as possible, full-scale or large-demonstration-scale cost and performance data were obtained and are reported in this study. A detailed description of how these data were obtained and used for this report is provided in Appendix A. All applicable cost and performance information was input into a Microsoft Access database. Site-specific reports generated from the database are provided in Appendix B. Figure 3-1 is a “box and whisker” plot showing the range of costs per cubic yard of the various conventional

technologies identified in the literature and evaluated in this section. Table 3-2 shows the data used to generate Figure 3-1. In the box and whisker plot, the bottom and top edges of the box are at the 25th and 75th percentiles of the sample set; the horizontal line in the box is at the median (50th percentile); and the upper and lower whiskers drawn from the box show the most extreme data point within 1.5 interquartile ranges (i.e., 1.5 times the distance between the 25th and 75th percentiles). The data points with more extreme values are marked with a star on the plot. Each technology shows a wide range of costs, which may be influenced by a number of site-specific factors including technology performance; duration of remedial activities; and requirements for monitoring, pilot testing, and/or design, to name a few. The highest costs are associated with composting, biopile/biocells, and slurry-phase bioreactors, while the lowest costs are associated with bioslurping, conventional bioventing, and phytoremediation. The wide range of costs associated with biopile/biocells and land treatment is caused by application at a wide variety of sites under highly variable treatment conditions.

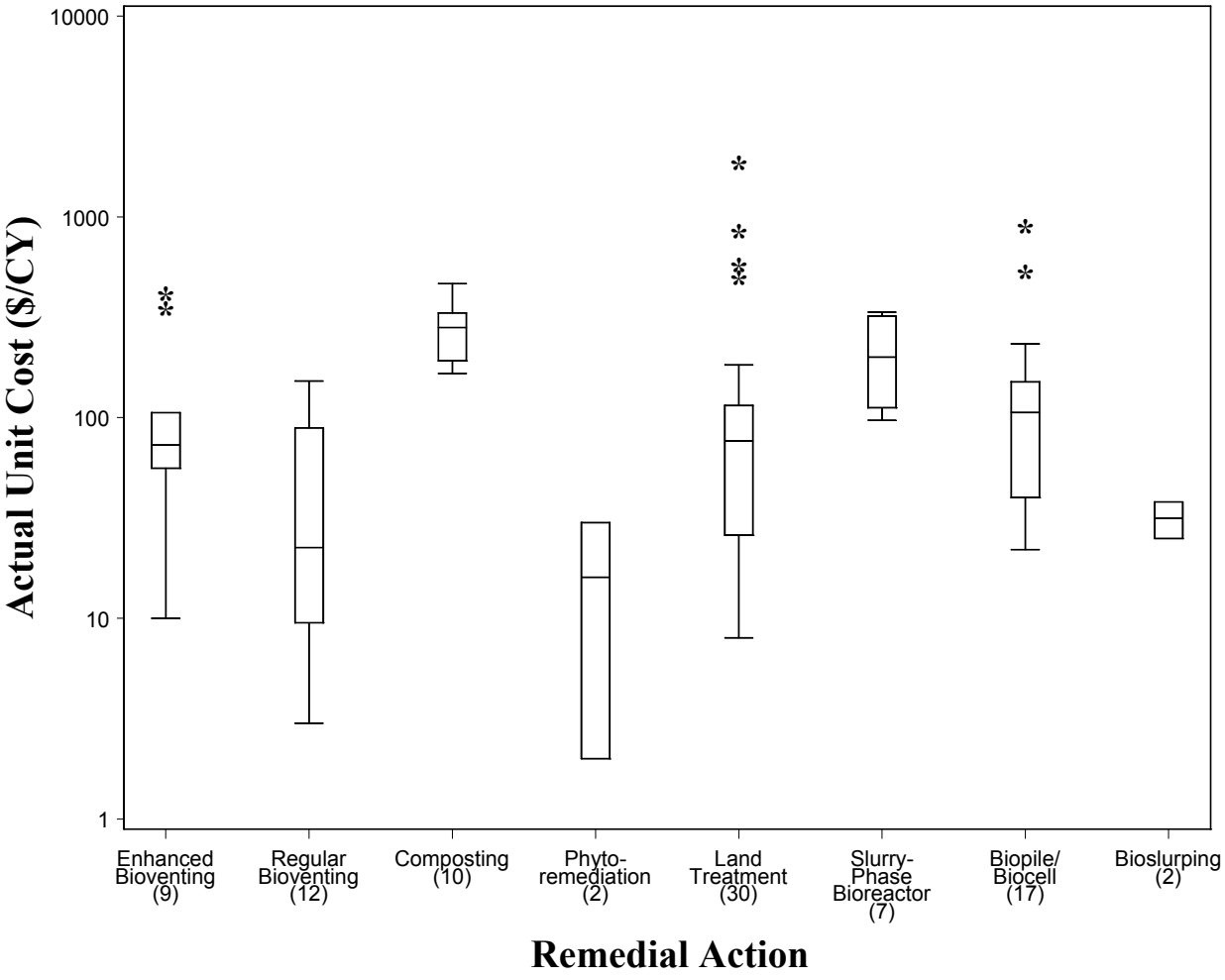


Figure 3-1. Cost per Cubic Yard for Remedial Actions Based on Cost and Performance Data Presented in Appendix B

Table 3-2. Costs per Cubic Yard for Remedial Actions: Data used to make Figure 3-1

	Cost per Cubic Yard for Remedial Technologies							
	Land Treatment (30 sites)	Biopile/ Biocell (17 sites)	Com-posting (10 sites)	Slurry-phase Bioreactor (7 sites)	Conventional Bioventing (12 sites)	Enhanced Bioventing (9 sites)	Bio-slurping (2 sites)	Phyto-remediation (2 sites)
Median	$77	$106	$281	$200	$23	$73	$32	$16
25th Percentile	$26	$40	$202	$112	$11	$56	$28	$9
75th Percentile	$115	$151	$332	$319	$86	$106	$35	$23
High Whisker[(a)]	$183	$233	$465	$335	$152	NA	NA	NA
Low Whisker[(a)]	$8	$22	$166	$97	$3	$10	NA	NA

(a) High and low whiskers represent the most extreme data point within 1.5 interquartile ranges, i.e., 1.5 times the distance between the 25th and 75th percentiles.

3.1 BIOREMEDIATION TECHNOLOGIES AND THEIR APPLICATIONS – CONVENTIONAL TECHNOLOGIES

This section describes conventional technologies with respect to their principles of operation, the types of contaminants for which they are appropriate, and cost and performance data reported in the literature. The technologies discussed in this section include land treatment, biopile/biocell treatment, composting, bioslurry treatment, conventional bioventing, and enhanced bioventing. The first four technologies are *ex-situ* processes, while the next two are *in-situ* processes. Bioslurping, an *in-situ* product recovery technology, is discussed within the bioventing section because the principal biological component of bioslurping is the venting of the vadose zone, comparable to bioventing. Phytoremediation is an *in-situ* technology discussed in Section 3.2.2.

3.1.1 Land Treatment

The term "land treatment" is used to refer to the technology of *ex-situ* treatment of contaminated soils, sediments, and sludges in engineered treatment cells or soil lifts designed to provide some level of process monitoring and control. Land treatment often includes the addition of nutrients, water, and externally cultured microorganisms, but not large-scale addition of organic materials. Land treatment has evolved from land farming as more stringent regulations limiting land application of wastes were enacted. Today, the technology is applied at full-scale to treat a wide range of contaminant types, with most success seen in treatment of total petroleum hydrocarbons (TPH), although land treatment of PAHs has shown good results as well.

3.1.1.1 Principles of Operation

Land treatment is typically conducted on a prepared pad that provides some containment and allows for desired levels of process monitoring and control. The treatment areas range from pads formed from asphalt or soil covered with impermeable liners to compacted clay. Because the units are exposed to the weather they are usually equipped with leachate collection and storage systems. Land treatment cells do not typically include forced aeration systems, and aeration occurs either passively from exposure to the atmosphere or through surface soil mixing or tilling. Figure 3-2 shows a field application of pilot land treatment that is hand-tilled, and Figure 3-3 is a schematic of full-scale land treatment.

Figure 3-2. Land Treatment

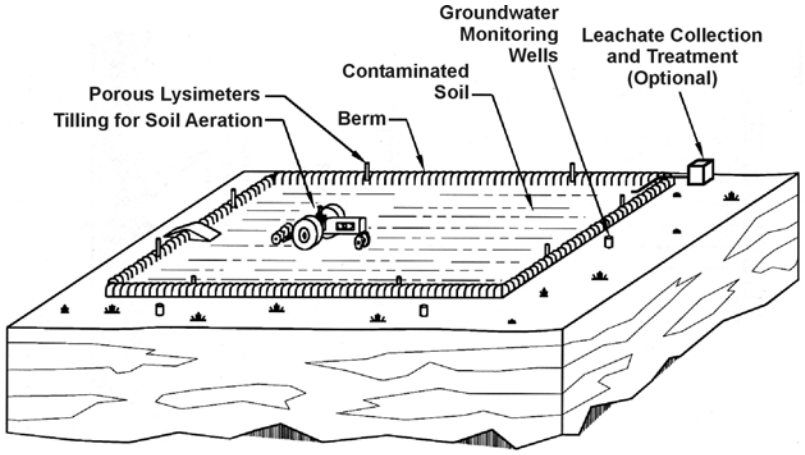


Figure 3-3. Land Treatment Schematic

Laboratory treatability tests are often conducted to determine the biodegradation potential of target contaminants and the need for amendments to optimize the biodegradation process. Typical amendments could include moisture, nutrients, pH adjustment, and/or microorganisms. Adding microorganisms, referred to as bioaugmentation, may increase both the rate and extent of contaminant removal and is being applied at many demonstration sites.

During land treatment, contaminated soil is excavated, screened to remove rocks and debris as necessary, mixed with appropriate amendments, placed into lifts in the treatment area, and then allowed to incubate to affect contaminant destruction. During incubation, the soil is routinely tilled, and the soil temperature, pH, and moisture are monitored and controlled as necessary. Soil tilling helps promote mixing, aeration, and bioavailability of contaminants for microbial degradation. Soil-gas oxygen levels can be monitored to ensure aerobic conditions. If oxygen becomes limiting, lift depths can be reduced and/or tilling frequency increased.

Monitoring land treatment performance requires collection of grab samples and analyses for target contaminants. Treatment is complete when the analytical results show that the cleanup goals have been

met or when sequential sampling and analyses show that no further treatment is being achieved. If the cleanup goals are attained, the soils can be used or discarded accordingly. If treatment stops short of achieving the cleanup goals, the soil may need to be treated further or disposed of according to pertinent restrictions. The potential uses for the treated soils and the requirements for handling soils that fail to meet the cleanup criteria must be determined prior to implementation of land treatment.

3.1.1.2 Target Contaminants

Land treatment usually is applied to treat compounds that are directly metabolized and cannot be easily removed through volatilization. The list of contaminants successfully treated with land treatment include:

- TPH
- BTEX
- Gasoline
- Diesel fuel
- JP-5 and other jet fuel
- Fuel oils
- PAHs (higher-molecular-weight compounds are more difficult to degrade)
- Creosote
- Coke wastes
- PCP and other chlorinated phenolics
- Non-chlorinated phenolics
- Chlorinated benzenes
- Certain pesticides
  - Dinosep
  - 2,4-D
  - 2,4,5-T.

3.1.1.3 Advantages and Limitations

The primary advantages of using land treatment include:

- The process is destructive with the contaminants being transformed into innocuous end products
- The system can be covered and left dormant over winter months during low biological activity
- Monitoring allows for control of contaminant migration
- The cost of land treatment is usually lower than alternatives such as incineration or hauling and disposal in a secured landfill
- Following remediation, the site can be converted to beneficial uses.

The primary limitations of land treatment include:

- Land treatment is land and management intensive
- Climatic conditions strongly affect biodegradation
- Lift depth is limited by depth of tilling
- Volatile emissions and/or dusts can be a nuisance and may pose a health threat
- Improper design and/or operation can result in an adverse environmental impact
- On-site waste storage is often required
- Site selection and permitting may be time consuming and public reaction may be negative.

3.1.1.4 Technology Cost Drivers

The major cost drivers for land treatment are as follows:

- Land treatment requires large treatment areas
- Soil type and composition affect aeration efficacy; permeable, low moisture soils are relatively easily aerated while silty/clayey soils with high moisture contents are difficult to aerate and require more extensive and more frequent tilling; presence of large rocks and debris can interfere with tilling efficiency and may require removal or prescreening
- Contaminant type and degradability impact the treatment duration
- Operations and maintenance (O&M) considerations include tilling frequency and extent, periodic water addition, and meeting nutrient requirements
- If treated soils cannot be returned to the site, additional post-treatment disposal costs may be incurred
- Volatile or dust emissions may require control measures.

3.1.1.5 Technology Performance and Cost

Land treatment has been applied at full scale at many sites including several Superfund sites. Data from a number of these case histories are summarized in Table 3-3. The data show that in most cases, land treatment was successfully applied with the treatment goals achieved and the sites closed. A few of the case histories indicated that the technology was not effective at achieving remedial goals and further treatment or controlled disposal of residuals was required.

Range of sites identified. Land treatment is applicable at a wide range of sites. It requires excavation of materials for treatment, and soils can be amended during processing for cell loading. The ability to economically excavate the soils is key to selecting the technology with depth limitations usually in the 25- to 30-ft below ground surface (bgs) range. More typically, the soils treated by land treatment come from less than 5 ft bgs. Contaminant type has more of an influence on the selection of this technology than hydrogeologic and/or soil characteristic constraints. The technology has not been used to treat inorganic contaminants nor contaminants that require a cosubstrate. Research into these uses is proceeding, but no successful applications have been reported in the literature.

Technology performance. Table 3-3 presents performance data for land treatment applications for a number of contaminant classes. The data show that treatment performance including treatment times and achievable levels are dependent on the contaminant type and concentrations. Other factors that affect performance include, but are not limited to, soil type, temperature, moisture, waste loading rates, application frequency, aeration, volatilization, and other site-specific factors.

Figure 3-4 presents box and whisker plots showing the range of starting concentrations (Figure 3-4a) and ending concentrations after treatment (Figure 3-4b) for various contaminants subjected to land treatment. The figures depict significant contaminant removals; not all the contaminants identified before treatment were necessarily monitored after treatment, resulting in fewer contaminants identified in Figure 3-4b than in Figure 3-4a. Table 3-4 shows the data used to create Figure 3-4.

Technology costs. Land treatment is a low-cost alternative to the more conventional thermal or physical/chemical treatment technologies with cost estimates typically ranging from $30 to $50/cu yd. Pretreatment costs include $25K to $50K for laboratory studies and up to $100K for pilot tests. The data in Table 3-3 show costs as high as $1,754/cu yd, with the higher costs associated with small treatment volumes and/or highly recalcitrant contaminants. Table 3-3 reflects an inability to gather complete data on

all sites either from a reluctance of site owners to impart the information or from missing site data. Additional site data on land treatment is available in Appendix B.

3.1.2 Biopile and Biocell Treatment

Biopiles and biocells are designed to treat contaminated soil that is excavated, mixed with appropriate soil amendments, placed in a heap configuration on a pad or prepared surface, and oxygenated through forced aeration. The main difference between the two treatments is that while a biopile is a free-standing pile of soil, biocells are contained by walls or sides (e.g., stacked hay bales or large metal dumpsters). The microbial processes promoted during biopile/biocell treatment are similar to land treatment, but the incorporation of forced aeration relieves the necessity for tilling and reduces space requirements. Biopiles and biocells exploit the activity of microorganisms that can thrive using the contaminant as a substrate for growth and obtaining energy. As such, they are most effective for treating readily degradable contaminants such as petroleum hydrocarbons. The goal of biopile/biocell treatment is to convert target contaminants to innocuous products, rendering the soils safe for on-site disposal or other beneficial uses.

The biopile/biocell treatment technology was developed by the Navy to treat petroleum hydrocarbons, and most of the earliest applications focused on various fuel compositions (see Table 3-3). Recent applications have expanded the application of biopiles and biocells to treat chlorinated solvents, creosote compounds, and PAHs. More sophisticated designs for applications that incorporate cometabolic or anaerobic metabolism are currently in the demonstration stage and have not yet been used for full-scale application. Such applications require relatively complex control systems to operate and maximize system performance. Nonetheless, these systems have the potential to expand the contaminant list for this technology to more effectively treat chlorinated solvents, PAHs, and explosives.

3.1.2.1 Principles of Operation

Biopiles and biocells are used to treat contaminated soil that has been excavated and cannot be placed back into the ground without contaminant removal and/or soil that must be detoxified prior to off-site disposal. Biopiles and biocells are constructed by mixing excavated soil with appropriate amendments (e.g., nutrients, chemical additives to adjust pH, or bulking agents to enhance aeration), then placing the mixture in a heap configuration on a platform or within a containment system. For small-scale temporary facilities, the biopiles and biocells can be constructed with a simple high-density polypropylene liner laid flat or within hay bale ‘walls’, and with a simple aeration and leachate collection system installed during construction. The more complex facilities include engineered concrete pads or boxes with built-in leachate collection and aeration systems.

Aeration systems are required to inject or pull air through the soil. The selection of the operating mode depends on the volatility of the contaminant and regulatory concern over vapor control. Aeration systems in cold weather climates must be heat traced to prevent freezing and maintain optimal microbial conditions, and therefore require knockout systems to remove moisture from the aeration plumbing. The piles and cells can be covered with plastic to minimize leachate; promote solar heating; and control runoff, evaporation, and volatilization.

Table 3-3. Summary of Site Characteristics at Land Treatment Installations*

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per cy)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Gila Indian Reservation	Closed	parathion; toxaphene	parathion: 2,000 mg/kg; toxaphene: 30,000 mg/kg	$9	NA	NA	NA	Biological treatment would have been successful if the neutralization after chemical treatment had been complete.	24
Rancho Vistoso Properties	Closed	petroleum (diesel)	43,000mg/kg	$56	7,000 mg/kg	Yes	438 mg/kg	NA	1
Technical Products, Inc.	Closed	1,2-DCE, 1,2-DCA, 1,4-dichlorobenzene, B, methylene chloride, TCE, T	1924 1,4-dichlorobenzene; 706 1,2-DCE; 612 1,2-DCA; 147 TCE; 236 B; 2273 T; 1120 methylene chloride	< $113	<1mg/kg all contaminants	Yes	<1mg/kg all contaminants	Contaminant reduction to acceptable limits occurs in 6-9 months, some sites remediated to closure levels within 3 months.	14
Chevron USA Products Company	Closed	BTEX, TPH	26,000 TPH; 8900 BTEX	$25	NA	NA	NA	NA	NA
Middle Mountain Silvex	Closed	2,4,5-trichlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid	2,4,5-T, 510mg/kg; 2,4-D, NA	$35	50mg/kg 2,4,5-T; NA 2,4-D	NA	NA	NA	NA
Popile Superfund Site	Active	BAP, PCP	BAP: 21; PCP: 200	$85	PAHs: 3mg/kg; PCP: <5mg/kg	NA	NA	NA	180-240
Navy Demo Camp Pendleton, CA	NA	TPH	29,000	NA	88	NA	NA	NA	NA
Matagorda Island Air Force Range	Closed	BTEX jet fuel, TPH	41.3 mg/kg BTEX jet fuel; 3400 mg/kg TPH	$87	30mg/kg BTEX jet fuel; 0.5mg/kg B; 70mg/kg E; 100mg/kg T; 100mg/kg TPH; 1000mg/kg X).	Yes	1mg/kg BTEX jet fuel; 0.4mg/kg benzene, Ethylbenzene, Toluene; 60mg/kg TPH; 10.4mg/kg Xylene	Tar and asphalt were not easily consumed; bioremediation proved successful in cleaning up BTEX and TPH contamination levels.	3 mo. (TPHs); all others NA
Northern Arizona	Closed	butyl benzyl phthalate, urea crystals	phthalate: 38,000mg/kg	$180	NA	NA	<90mg/kg phthalate	99% reduction	20
Mobil Station 18-566	Inactive	diesel/waste oil	660mg/kg	$38	100mg/kg	Yes	12mg/kg		0.5
Burgan oil Field	Active	Weathered crude oil	TPH, 67,000; PAHs, 26.5	NA	NA	Yes	TPH, 27,500, PAHs, 3.45.	TPH reduction 59% PAHs reduction 87%	8
Kohler Company manufacturing facility	Closed	kerosene (DRO)	1600	~ $26	100 DRO	Yes	ND	91% reduction DRO and 100% reduction PVOC	13

Table 3-3. Summary of Site Characteristics at Land Treatment Installations* (continued)

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per cy)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Poly-Carb	Inactive	cresol, phenols	cresol: 1,000; phenols: 8,000	$544	cresol:10; phenols: 20.	No	cresol: 20; phenols: NA	NA	14
Seabury Chevrolet	Closed	diesel/waste oil	36,000mg/kg	$8	7000mg/kg	Yes	400	NA	3
Tucson Rock and Sand, Inc.	Closed	diesel/waste oil	8,900mg/kg diesel, waste oil	$40	100mg/kg diesel, waste oil	Yes	40mg/kg diesel, waste oil	NA	3
Fort Greeley UST Soil Piles	Closed	Gasoline, diesel fuel, BTEX	3,000 mg/kg gasoline, 1,200 mg/kg diesel, 20 mg/kg BTEX	$76	100 mg/kg DRO; 50 mg/kg GRO; 0.1 mg/kg B; 10 mg/kg BTEX	Yes	Nondetectable levels of GRO	Reduced to below ADEC level A cleanup standards in all but two samples.	24
McKesson Envirosystems	Closed	N,N-dimethyl-aniline, A, aniline, BTEX, methanol, methylene chloride, TCE	13,072 mg/kg methanol; 1,830mg/kg N,N-dimethylaniline; 833mg/kg A; 11.5mg/kg B; 49mg/kg E; 827mg/kg methylene chloride; 17 mg/kg T; 140mg/kg TCE; 218mg/kg X.	$115	10 mg/kg for all contaminants.	Yes	N,N-dimethylaniline: 4.1; acetone: 1; aniline: 4.1; BTEX: 0.63; methanol: 1; methylene chloride: 0.63; TCE: 0.63.	NA	2
Vandalia Road Site	Inactive	PAHs	10,000	NA	NA	NA	NA	reduced total PAHs by 51%.	4
Bonneville Power Administration Ross Complex, Operable Unit A, Wood Pole Storage Area	Closed	PAHs, PCP	150mg/kg PAHs; 62 mg/kg PCP	$470	1mg/kg PAHs, 8 mg/kg PCP preferred. If not, <23mg/kg H PAHs, <126mg/kg PCP.	Met tier 2 treatment goals, not tier 1.	6.8 to 21.8 mg/kg H PAHs, 6.8 to 20.7mg/kg PCP	Land treatment could not meet Tier I cleanup goals for all soil at the site, so a gravel cap was installed.	2.75
Scott Lumber Company Superfund Site	Closed	PAHs, BAP	63,000mg/kg PAHs; 23mg/kg BAP	$1,754	500mg/kg total PAHs; 14mg/kg BAP	Yes	130mg/kg PAHs (6 mo.); 8mg/kg BAP	NA	6
Libby Superfund Site	Active	PAHs, PCP	Carcinogenic PAHs: 7,384; noncarcinogenic: 26,555; PCP: 2,700.	NA	carcinogenic PAHs: 88; naphthalene: 8; phenanthrene: 8; pyrene: 7.3; PCP: 37	NA	NA	NA	72
Brown Wood Preserving Superfund Site	Closed	PAHs (primary constituents in creosote)	208 mg/kg TCIC (total carcinogenic indicator chemicals)	$99	TCIC (total carcinogenic indicator chemicals) 100 mg/kg within 2 years	Yes	23 mg/kg TCIC	Cleanup goal achieved within 18 months using land treatment	18
Hayford Bridge Road	Active	PCB	100,000 mg/kg	$33	25 mg/kg	NA	NA	NA	24
Toote Mineral	Closed	TPH	500 mg/kg	$77	100 mg/kg	Yes	25 mg/kg	NA	2
Eastman Chemical Company	Closed	Petroleum	200 mg/kg BTEX; 1,500 mg/kg TPHs	NA	10 mg/kg BTEX; 100 mg/kg TPHs	Yes	1 mg/kg BTEX; 5 mg/kg TPHs	NA	4

Table 3-3. Summary of Site Characteristics at Land Treatment Installations* (continued)

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per cy)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Novartis Site	Inactive	Metolachlor	170mg/kg	$132	NA	Yes	1 mg/kg	NA	18
Handy Andy, Inc.	Closed	petroleum (benzene, BTX)	15.8 mg/kg BTEX; 0.056 mg/kg benzene	NA	11.705 mg/kg BTEX; 0.005 mg/kg benzene	Yes	<11.705mg/kg BTEX; <0.005mg/kg B	NA	18
Site 7, Savannah River Site	Active	TPH	17,000 mg/kg	$800	100 mg/kg	Yes	1 mg/kg	NA	6
Whitehorse Airport	Closed	TPH, BTEX	TPH: 3,900, BTEX: 480	$107	TPH: 2000; BTEX: 50	Yes	TPH: 9; BTEX: NA	NA	12
Former Golden Eagle Refinery	Closed	TPH, carcinogenic TPM	25,000mg/kg TPH; 20,000mg/kg carcinogenic TPM	NA	3,000mg/kg TPH, carcinogenic TPM	Yes	100mg/kg carcinogenic TPM, NA TPH	NA	NA
Domtar, Inc	Closed	chlorinated phenols, PAHs, TPH	chlorinated phenols: 700; PAHs: 2000; TPH: 8000.	NA	chlorinated phenols: 5; PAHs: 100; TPH:100	Yes	chlorinated phenols:1; PAHs: 35; TPH: 25	NA	6
Domtar Inc	Active	PAHs, naphthalene, BAP, benzo(a)anthracene, indeno(1,2,3-cd)pyrene, PCP, phenanthrene, pyrene.	PCP: 266; PAHs: 1182; naphthalene: 3.87; phenanthrene: 23.3; benzo(a)anthracene: 68.6; BAP: 35.7; indeno(1,2,3-cd) pyrene: 24.2; dibenzo(a,h)anthracene: 9.25; pyrene: 309.	NA	PCP: 5; PAHs, phenanthrene, pyrene: 100; naphthalene: 50; all others: 10.	Yes	NA	Reduced all contaminants to below treatment goal.	6
Hellman Lease	Closed	1)diesel; 2) kerosene, gasoline	7,000mg/kg diesel; 4,000mg/kg kerosene; 4,000mg/kg gasoline	NA	diesel, 1,000mg/kg TPH; kerosene, 100mg/kg TPH; gasoline, 100mg/kg TPH.	Yes	diesel, 10mg/kg; kerosene and gasoline, 5ug/kg	NA	3
Old Seattle Marketing Fuel Terminal	Active	TPH	2,660mg/kg (avg.)	NA	200 mg/kg TPH	Yes	200mg/kg TPH	NA	36-60
Great Falls International Airport	Closed	jet fuel	120,000mg/kg	NA	400mg/kg TPH	Yes	130 mg/kg	NA	5
Burlington Northern Tie Plant	Closed	PAHs	500,000 mg/kg	$183	36 mg/kg	NA	NA	NA	24
Idaho Pole Site	Active	Dioxins, PAHs, pesticides, phenols, oils	PCP: 3,800; TCDD: 0.0342	NA	PCDD/PCDF w/TCDD TE: 0.001; PCP: 48; B2PAHs: 15; DPAHs: 145.	NA	NA	NA	120
BN Somers Site	Closed	CPAHs	200	~ $20	57 mg/kg	NA	NA	NA	6
Montana Pole and Treating Plant	Active	PCP	70	~ $20	34 mg/kg	NA	NA	NA	3

Table 3-3. Summary of Site Characteristics at Land Treatment Installations* (continued)

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per cy)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Alcoa Land Treatment Unit (LTU) study	Active	PAHs, PCBs	PAHs, 1,662; PCB, 113	NA	NA	NA	PAHs, 124; PCB, 106 maximum concentrations	NA	Active, 2-3; Passive, 66+

B = benzene
T = toluene
E = ethylbenzene
X = xylenes
N = naphthalene
MEK = methylethylketone
BAP = benzo(a)pyrene
A = acetone
TCE = trichloroethylene
DCE = dichloroethylene
PAHs = polycyclic aromatic hydrocarbons
PCBs = polychlorinated biphenyls
TPH = total petroleum hydrocarbons
DCA = dichloroethane
CPAHs = carcinogenic polycyclic aromatic hydrocarbons
CB = chlorobenzene
NA = not available

*Eight sites included in Appendix B were not included in this table due to insufficient information. The excluded sites are Site ID Nos. 03-008, 05-012, 08-012, 08-013, 09-024, 09-025, 10-006, and 10-014.

Table 3-4. Concentrations of Contaminants of Concern Before and After Land Treatment: Data Used to Generate Figure 3-4

	Concentrations of Contaminants of Concern									
	Chlorinated VOC/SVOC		Pesticide, Herbicide		Fuel / Oil		BTEX		PAH, Creosote	
	Before Treatment (11 sites)	After Treatment (9 sites)	Before Treatment (3 sites)	After Treatment (24 sites)	Before Treatment (26 sites)	After Treatment (8 sites)	Before Treatment (12 sites)	After Treatment (8 sites)	Before Treatment (12 sites)	After Treatment (1 site)
Median:	612	1	2,000	18.5	8,450	1	125	28.5	2,500	106
25th Percentile	144	1.0	1,085	8	2,745	0.575	19	16.25	188	106
75th Percentile	767	1.0	16,000	147.5	25,750	1	297	98.5	10,095	106
High Whisker[(a)]	1,120	NA	30,000	200	43,000	NA	480	130	10,380	NA
Low Whisker[(a)]	52	NA	170	1	500	0.1	12	3	11	NA

(a) High and low whiskers represent the most extreme data point within 1.5 interquartile ranges, i.e., 1.5 times the distance between the 25th and 75th percentiles.

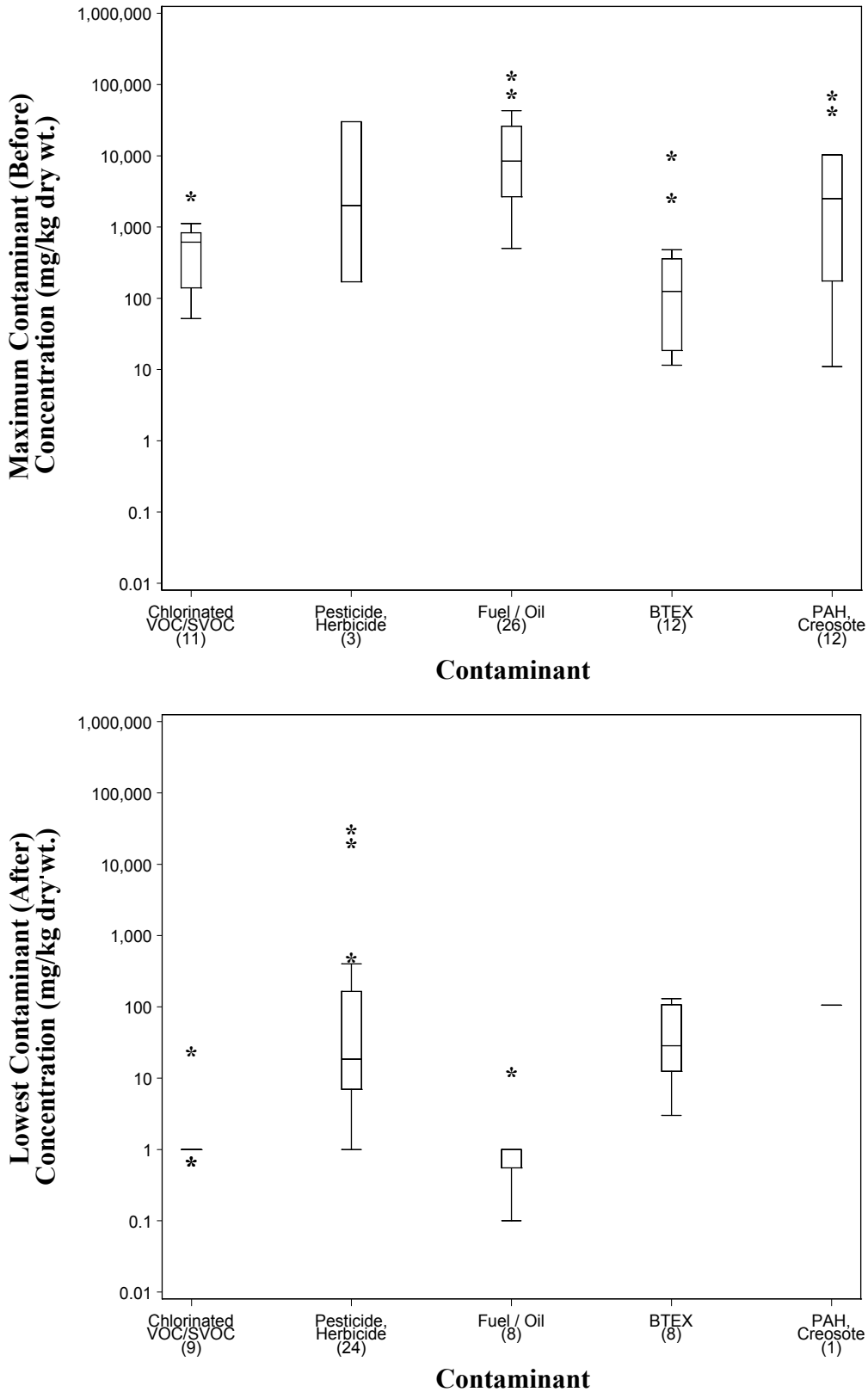


Figure 3-4. Box and Whisker Plots Showing Concentrations of Contaminants of Concern Before and After Land Treatment. (See Appendix B for data used to generate these plots.)

The basic underlying principle of biopile/biocell treatment is the promotion of aerobic biodegradation by microorganisms that are provided with a sufficient supply of oxygen as an electron acceptor and other amendments (e.g., nutrients) as necessary. The contaminants serve as growth substrates for the microorganisms that carry out the desired biological reactions. The contaminants and/or their degradation products can also supply other microorganisms with a needed nutrient/substrate that supports any number of symbiotic processes. As such, the contaminants must be both aerobically biodegradable and available to the microorganisms. For this reason, biopiles and biocells must be carefully constructed to optimize conditions for contaminant biodegradation by maximizing airflow and oxygenation of the pile and optimizing the distribution of additives such as nutrients.

The excavated soil can be mixed with bulking agents to increase the effective porosity, which will facilitate airflow. Unlike composting, the bulking agents are not added to supply carbon or nutrients, but simply to modify the texture of the soil so that the soil mass can be maintained aerobic through forced air movement. Nutrients, moisture, pH adjustment, and bioaugmentation can be applied during construction to enhance process performance by reducing the time required for cleanup and/or to lower the achievable level of treatment. The need for such amendments and the potential benefits that can be realized by adding them may be determined through laboratory treatability testing.

Biopile and biocell applications for contaminants that require cometabolism or anaerobic degradation are in the demonstration stage. These systems are more complex than the simple aerobic systems and require a higher level of monitoring and control. Figure 3-5 is a schematic of a biopile treatment system.

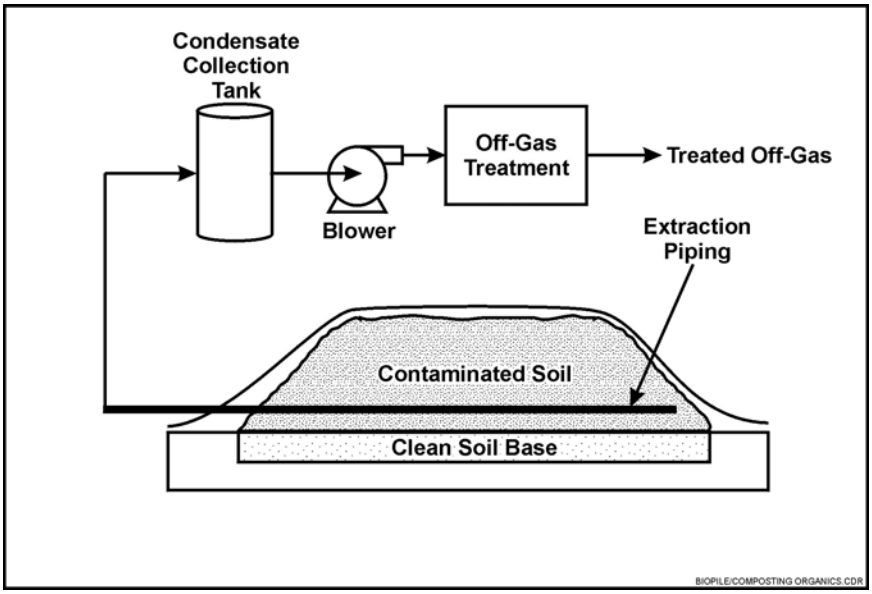


Figure 3-5. Biopile schematic

3.1.2.2 Target Contaminants

Currently, biopile/biocell treatment is applicable to compounds that are directly metabolized by the microorganisms that can survive within the soil matrix. Typically, it is more desirable to stimulate and promote the activity of indigenous microorganisms, but some success has been achieved using bioaugmentation with cultures that have known and desired metabolic capabilities. This success has

expanded the list of candidate contaminants, as well as enhanced the performance of the technology. Biopiles and biocells have been successfully used to treat the following contaminants:

- TPH
- Gasoline (more volatile constituents tend to volatilize, not biodegrade)
- JP-5 and other jet fuels
- Diesel fuel
- Motor oil
- Transformer oil
- PCP
- TNT
- PAHs (higher-molecular-weight compounds are more difficult to degrade)
- DCE and VC.

3.1.2.3 Advantages and Limitations

The main advantages associated with biopile and biocell treatment include the following :

- Systems are simple and easy to design
- Application is not limited by hydrogeologic constraints (beyond depth of excavation) or soil characteristics that limit *in-situ* technologies
- Contaminants are degraded to innocuous end products; ultimately CO_2 and water
- Forced aeration allows increased height, requiring less land space than other *ex-situ* biological treatment alternatives such as land treatment
- Nutrients, water, and microorganisms can easily be added and mixed during construction to accelerate the biodegradation process
- Simple design minimizes operation and maintenance requirements
- Biopiles (and, to a lesser extent, biocells) are relatively inexpensive due to low capital and O&M costs.

The primary limitations for biopile and biocell treatment are:

- Excavation is required
- Space is required for materials handling, soil preparation, and staging
- Controls may be required to prevent volatile emissions to the atmosphere
- Concentration reductions greater than 95% and residual concentrations below 0.1 ppm are very difficult to achieve
- Contaminants must be readily biodegradable under aerobic conditions
- Biopiles and biocells may not be effective for TPH at concentrations greater than 50,000 mg/kg.

3.1.2.4 Technology Cost Drivers

Major cost drivers of biopile and biocell treatment include:

- Biopiles are less land intensive than land treatment, but still require relatively large treatment areas
- Cell size and the volume of soil to be treated will impact the number of cells required; larger cells will require fewer cell units, but larger cells also are more difficult to construct and maintain

- Biopiles require frequent irrigation; leachate collection systems and treatment of leachate (if not returned to the biopile cell) will impact costs
- Volatile or dust emissions may require control measures
- Soils with low porosity may require bulking agents to increase the airflow through the pile; soil screening may be required to remove large rocks, debris, or other bulk objects
- O&M considerations include maintaining moisture levels via water amendments and maintaining nutrient levels and pH via nutrient and buffer amendments
- Biopiles require nutrient and/or buffering agents to control pH; such agents are difficult and expensive to administer once the biopiles are constructed
- If treated soils cannot be returned to the site, additional post-treatment disposal costs may be incurred.

3.1.2.5 Technology Performance and Cost

Biopiles and biocells have been in use for several years. Table 3-5 summarizes available data for biopile and biocell applications at 19 sites.

Range of sites identified. As the data in Table 3-5 reflect, biopiles and biocells have been used primarily at petroleum-contaminated sites. Because the soils can be amended during construction, the application of the technology is not limited by the hydrogeologic constraints that limit *in-situ* technologies. Typical criteria given for a successful biopile are:

- The contaminant must be biodegradable
- TPH values below 50,000 mg/kg can be tolerated; higher concentrations may be toxic
- Heterotrophic bacteria should be present at densities of > 1,000 colony forming units (CFU)/gram of dry soil
- Soil pH should be between 6 and 9
- Soil moisture should be maintained between 70% and 95% of field capacity.

Most of these variables can be adjusted during construction, and controlled during operation by adding selected amendments.

Technology performance. The time to achieve treatment depends on a number of factors including contaminant type, soil physical/chemical characteristics, the level of biological activity that can be obtained, and the climate for outdoor applications. Typical treatment times range from 3 to 6 months.

Figure 3-6 presents box and whisker plots showing the range of starting concentrations (Figure 3-6a) and ending concentrations (Figure 3-6b) for various contaminants subjected to biocell or biopile treatment. The figures depict significant contaminant removals; not all the contaminants identified before treatment were necessarily monitored after treatment, resulting in fewer contaminants identified in Figure 3-6b than in Figure 3-6a. Table 3-6 summarizes the data used to create Figure 3-6.

Technology costs. The costs for biopile and biocell treatments are dependent on the biodegradability of the contaminant, the cleanup goal, the cleanup procedure, other regulatory requirements such as off-gas treatment, and the volume of soil to be treated. Costs have been estimated to range from $25 to $70 per ton of contaminated soil treated. The Navy Facilities Engineering Service Center (NFESC) has estimated the cost of biopile treatment of fuel contaminants to be on the order of $40/cu yd. The costs shown in Table 3-5 are mostly within this cost range, although some costs range as high as $1500/cu yd. This high cost is due to the small size of the site; in addition, this particular study was a demonstration site to test the efficacy of biopile treatment only. Costs for full-scale deployment of this treatment tecnology would

not be as high. The information in Table 3-5 is not as comprehensive as would be preferred due to an inability to gather complete data on all sites, either from a reluctance of site owners to impart the information or from missing site data. Additional site data on biocell/biopile treatment is available in Appendix B.

3.1.3 Composting

Composting is an *ex-situ* technology designed to treat excavated soils contaminated with a range of recalcitrant contaminants. The process involves mixing the contaminated soil with bulking agents such as wood chips, straw, hay or alfalfa, and organic amendments such as cattle and/or chicken manure or vegetative wastes. The selection of the specific compost ingredients depends on the contaminants to be treated, the physical/chemical characteristics of the soil, and the availability of low-cost organic amendments. The goal is to select the proper bulking agents to achieve the desired porosity, and organic amendments that can provide the proper balance of carbon and nitrogen to promote biological activity in the compost. For most composting applications, it is necessary to provide amendments that will support thermophilic microbial activity.

Composting has been used to treat a wide range of contaminants in soils, and the use of the technology continues to increase as the basic understanding of the fundamentals of the biodegradation pathways of recalcitrant compounds and of the complex microbial interactions that occur during the composting process continues to increase. Composting has traditionally been used to treat a variety of solid wastes including wastewater sludge and the biodegradable fractions of municipal refuse with the primary goal being volume reduction. Composting contaminated soils differs from these traditional applications in that detoxification of contaminants sorbed to solid surfaces is desired, while volume reduction is not of primary concern. Although the ultimate goals are different, the two uses of composting are similar in that the intensive, usually thermophilic metabolic activity of a diverse and changing microbial population is promoted to achieve the treatment objective.

3.1.3.1 Principles of Operation

Composting is a biological remediation technology that exploits the intensive activity of a diverse range of microorganisms to degrade the target contaminants. The biological activity is enhanced through the addition of readily degradable substrates and a sufficient supply of nutrients. Composting is considered an aerobic technology because the compost is usually turned, mixed, or aerated to provide oxygen. However, the high level of microbial activity can deplete the oxygen between turning or aeration sequences creating anaerobic conditions in portions of the compost material, and microanaerobic zones can exist in organically rich portions of the compost. These anaerobic processes can be beneficial for promoting degradation of contaminants such as explosives or chlorinated organic compounds that are recalcitrant or only partially degrade under strict aerobic or anaerobic conditions. For contaminants that are readily mineralized under aerobic conditions, the development of anaerobic conditions is not desired, and turning, mixing, and/or aeration frequencies are adjusted to minimize this potential.

Table 3-5. Summary of Site Characteristics at Biopile/Biocell Installations*

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
BP Oil	Closed	Diesel	2100	$33	500 mg/kg	Yes	180	NA	9
Indiana Wood Treating	Closed	PAHs	4530 total PAHs; 666 carcinogenic PAHs	~ $222	500mg/kg total PAHs; 100mg/kg carcinogenic PAHs	Yes	58 total PAHs; 10 carcinogenic PAHs	NA	19
Hydro-Quebec/Verdun	Closed	PAHs	1000	~ $122	200mg/kg	Yes	50	NA	4
Biosites	Closed	PAHs, DRO, VOCs	DRO contamination <1000;1000-2000, 2000-3000	NA	DRO levels less than 250mg/kg	Yes	Unknown	Removes an average of 93% of contamination	3
Hydro-Quebec/Alma	Closed	PCP	100	~ $122	5mg/kg	Yes	1	NA	5
Boucherville Electrical Station	Closed	transformer oil	14,000	~ $150	5,000mg/kg	Yes	3,800	NA	11
Pueblo Chemical Depot	Closed	TNT, DNT, RDX	TNT: 3,800	$110	10 mg/kg	yes		NA	1.67
Dresherbrooke	Closed	TPH	1,250 TPH	$30	500 mg/kg	Yes	nondetectable	NA	3
Chevron Station #9-	Closed	BTEX, TPH	1,200 TPH; 21 B; 19 E; 99 T; 75 X(s)	$22	100mg/kg TPH	Unknown	NA	NA	18
Naval Fuel Depot Pt Molate	NA	Diesel, Fuel oil	TPH, 47,000	~ $52	TPH < 1,000 ppm	Yes	NA	Treatment has high success rate	4
IEI Site	NA	Fuels	TPH, 58,000	~ $52	TPH < 1,000 ppm	Yes	230	Reduced contaminants to well below treatment goal	2.25
Uran Oil Complex, Oil and Natural Gas Corp.	NA	Oil	TPH, 620,000	~ $52	TPH < 1,000 ppm	Yes	600	concentrations well below treatment goal	4
Joliet Army Ammo Plant (various)-- GRACE Biorem Technologies	NA	TNT, Tetryl	TNT, 3,000 avg; Tetryl, 7,500 avg	TNT: $476 Tetryl: $211	TNT, 50 ppm; Tetryl, 250 ppm	Yes, for Tetryl	TNT, 90; Tetryl, ND	97% TNT removal; 100% Tetryl removal	4
Joliet Army Ammo Plant (various)-- Institute of Gas Technology	NA	TNT, Tetryl	TNT, 3,000 avg; Tetryl, 7,500 avg	TNT: $1,578Tetryl: $1,240	TNT, 50 ppm; Tetryl, 250 ppm	No	TNT, 480; Tetryl, 1,875	84% TNT removal; 75% Tetryl removal	4
Mare Island NS	NA	Diesel, Fuel oil	1,670	NA	TPH, 100; BTEX, .005 (each) mg/kg	Yes for some cells	TPH, from < 100 to < 300	Varied	6

Table 3-5. Summary of Site Characteristics at Biopile/Biocell Installations* (continued)

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Yorktown Naval Weapons Station, Site 6	NA	TNT, RDX, HMX, TCE	TNT, 1,329; RDX, 319; HMX, 98; TCE, 2,332	NA	TNT, 15; RDX, 5; total VOCs 700	Yes	TNT, 2.9; RDX, 13.5; HMX, ND; TCE, 17	After 41 days of treatment. continued to 90 days.	3
Decommissioned Gas Plant	NA	Amines and salts	Amines, 15,000	$34	None reported	Yes	Below detection limit	Large concentration reduction	5 bio + 6 leaching
Abandoned tanks area	Active	TPH, BTEX, PAHs	TPH, 12,000; BTEX, <50; PAHs, < 100	NA	TPH, 500 mg/kg; BTEX, 50 mg/kg; PAHs, 60 mg/kg	Yes	TPH, 235; PAHs, ND	Below treatment goals at end of treatment; 87% reduction in TPH	6
Marine Corps Air Ground Combat Center (MCAGCC)	Closed	JP-5 jet fuel, Diesel	683, average	$40	None reported	Considered successful	56 average	On average, decreased by 92%	< 12

PAH = polycyclic aromatic hydrocarbons
DNT = dinitrotoluene
VOC = volatile organic compounds
DRO = diesel range organics
TPH = total petroleum hydrocarbons
TNT = trinitrotoluene
TCE = trichloroethylene
RDX = cyclotrimethylenetrinitramine
HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraaxocine
PCP = polychlorophenol
BTEX = benzene, toluene, ethylbenzene, xylenes

*Two sites included in Appendix B were not included in this table due to insufficient information. The excluded sites are Site ID Nos. 00-013 and 05-015.

Table 3-6. Concentrations of Contaminants of Concern Before and After Biocell/Biopile Treatment: Data Used to Generate Figure 3-6

	Concentrations of Contaminants of Concern							
	Chlorinated VOC/SVOC (2 sites)		Fuel / Oil (10 sites)		PAH, Creosote (3 sites)		Explosives (12 sites)	
	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment
Median:	1,216	9	12,000	233	1,000	50	3,000	285
25th Percentile	658	5	1,670	120	550	26	2,582	8
75th Percentile	1,774	13	47,000	525	2,765	54	7,500	2,081
High whisker[(a)]	2,332	17	58,000	1,000	4,530	58	NA	3,525
Low whisker[(a)]	100	1	683	1	100	1	98	1

(a) High and low whiskers represent the most extreme data point within 1.5 interquartile ranges (1.5 times the distance between the 25th and 75th percentiles).

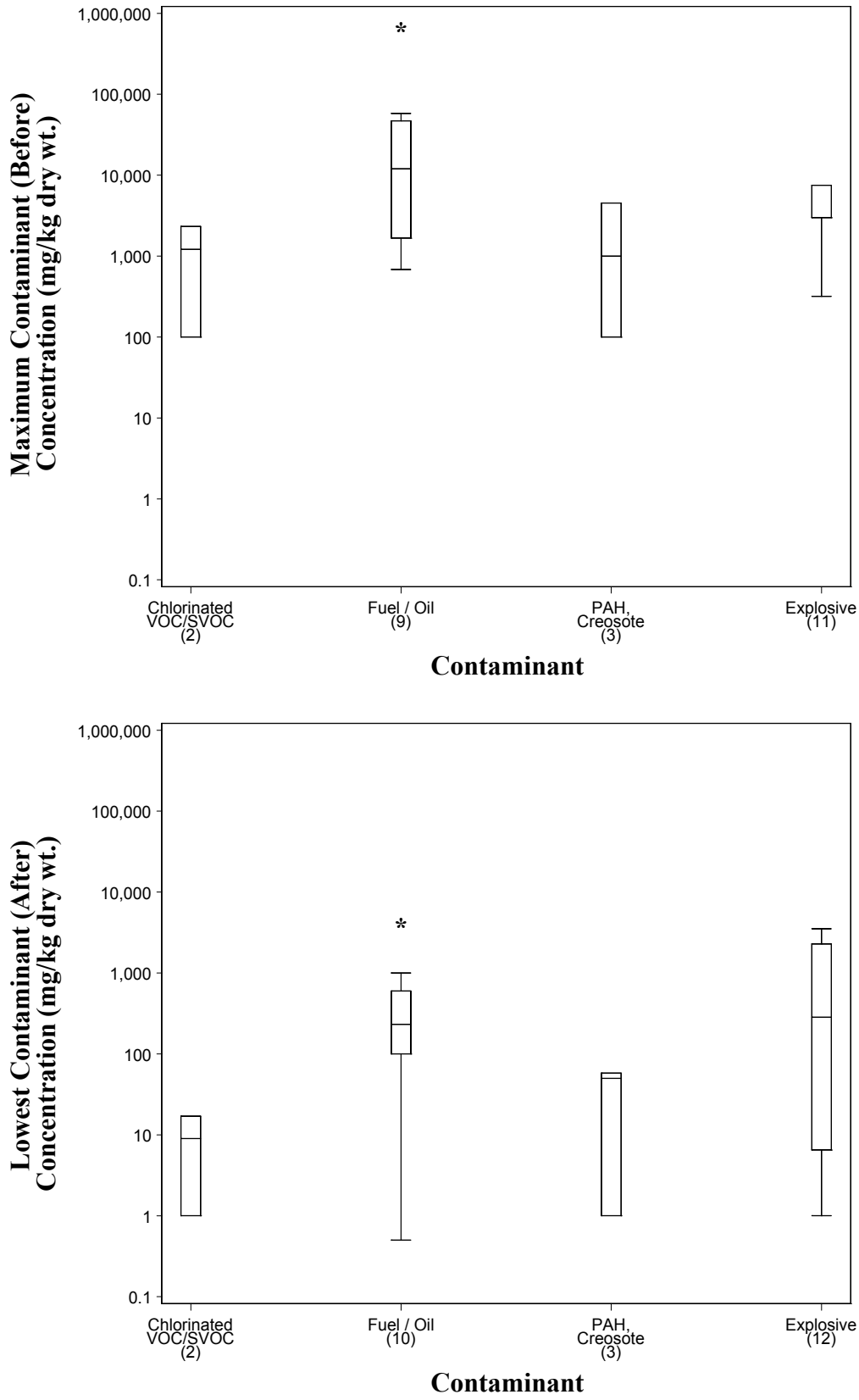


Figure 3-6. Box and Whisker Plots Showing Concentrations of Contaminants of Concern Before and After Biocell/Biopile Treatment. (See Appendix B for data used to generate these plots.)

The three configurations of composting include static pile, windrow, and in-vessel designs. Static piles are simple in design and operation and are similar to biopiles. They are often designed with forced aeration to control oxygen levels and maintain aerobic conditions. Air is pulled through the compost so that the off-gas can be treated for volatile organic compounds and/or odors as necessary. Windrow composting entails piling the soil on a containment pad with periodic turning to both keep the pile aerobic and to provide a high level of mixing. This serves to break up the compost and distribute both the contaminated soil and the nutrients. Because the piles are turned, windrows do not have forced aeration systems or vapor control capabilities and may not be appropriate for soils contaminated with VOCs that have the potential to volatilize to the atmosphere. In-vessel composting involves the use of enclosed reactors. This allows the operator to control the atmosphere and the mixing with minimal temperature disturbance. Vessels are typically designed with vapor control and more sophisticated monitoring systems than the static pile or windrow designs. However, in-vessel composting has a much lower throughput compared to static pile and windrow composting, which makes it the most expensive composting method. All composting systems require moisture monitoring and control. Figure 3-7 shows composting.

Figure 3-7. Composting

3.1.3.2 Target Contaminants

Composting is usually used to treat the more recalcitrant contaminants such as substituted- and higher-molecular-weight aromatic compounds. Compounds effectively removed by composting include contaminants associated with explosives such as TNT, RDX, HMX, and nitrocellulose; wood-preserving chemicals including PAHs and PCP; and certain pesticides. Degradation of these compounds is likely to benefit from the mixture of anaerobic and aerobic biological processes and the microbial complexity of composts. Other classes of compounds including petroleum hydrocarbons such as gasoline, diesel fuel, jet fuel, oil and grease, and chlorinated VOCs have been treated with composting. Often, these compounds are present when the technology has been designed to treat one of the more recalcitrant classes of contaminant, but removals nonetheless were substantial. Typically, these petroleum hydrocarbons and VOCs are better treated with an alternative technology such as biopiles, while composting is used to treat soils with more recalcitrant compounds that degrade too slowly to make the alternative technologies effective.

3.1.3.3 Advantages and Limitations

The primary advantages associated with composting include:

- Removal of recalcitrant compounds is more rapid than that achieved with biopile treatment
- End product can be humus-rich soil appropriate for commercial sale and/or reuse
- A wide range of soil textures can be treated through addition and mixing of compost bulking agents and amendments.

The primary limitations associated with composting include:

- Space requirements can be substantial
- Handling may require vapor control
- Volume of contaminated material can increase substantially due to addition of bulking agents
- Process can be susceptible to heavy metal or other toxin concentrations
- The contaminated soil in the compost mix is limited to approximately 30% by weight to achieve thermophilic conditions (EPA530-R-98-008, 1998c).

3.1.3.4 Technology Cost Drivers

Factors that drive the cost of composting include:

- Composting is less land intensive than land treatment, but still requires relatively large treatment areas
- Cell size will impact the number of cells required; larger cells will require fewer cells, but larger cells also are more difficult to construct and maintain
- Volatile, dust, or odor emissions may require control measures
- Soils with low porosity may require bulking agents to increase the airflow through the compost pile; soil screening may be required to remove large rocks, debris, or other bulk objects
- Composting may require nutrient amendments and water, in addition to bulking agents
- O&M considerations include turnover frequency, maintaining moisture levels via water amendments, maintaining nutrient levels and pH via nutrient and buffer amendments; thermophilic aerobic conditions also must be maintained, which may require amendments with biodegradable bulking agents.

3.1.3.5 Technology Performance and Cost

Composting of contaminated soil has been operating in the field for a number of years, and limited case history data are available. Table 3-7 summarizes performance and cost data collected for 10 composting applications. While these data are not complete in that they do not cover every composting application, the data contained in the table provide useful information regarding the status of the technology. Additional information on implementation of composting at full-scale sites can be found in Appendix B.

Range of sites identified. Composting is an *ex-situ* technology, and its application is not limited by the same constraints as many *in-situ* technologies. The material to be treated is mixed with bulking agents and other compost amendments that can be selected to adjust the porosity, moisture, pH, and other properties to desired conditions to maximize composting performance. Because the compost is "tailor made, " the technology can be applied to soils ranging from coarse sands and even gravels to the finest silts and clays, sediments, and other contaminated solids. The more crucial limiting factors for composting application are the depth of soil excavation, usually considered to be 20 to 30 ft bgs, and the

presence of toxic levels of contaminants or other compounds that can inhibit biological activity, such as heavy metals. The effects of such toxins must be determined on a case-by-case basis and is best done through laboratory treatability studies.

Technology performance. Composting has proven successful for treating soils contaminated with the explosives TNT, RDX, and HMX, achieving removals of up to 99.7%, 99.8%, and 96.6% in 40 days or less. Composting also has been shown effective for treating PAHs, PCP, and VOCs. At the Dubose Oil Products Co. Superfund Site in Florida, PAH, PCP, and VOC concentrations were reduced up to 91.3%, 77.3%, and >69.6%, respectively. Other examples of treatment performance are shown in Table 3-7. The data illustrate that, for the most part, the technology performed as expected and cleanup goals were achieved.

Figure 3-8 presents box and whisker plots showing the range of starting concentrations (Figure 3-8a) and ending concentrations after treatment (Figure 3-8b) for various contaminants subjected to composting treatment. The figure depicts significant contaminant removals; not all the contaminants identified before treatment were necessarily monitored after treatment, resulting in fewer contaminants identified in Figure 3-8b than in Figure 3-8a. Table 3-8 summarizes the data used to create Figure 3-8.

Technology costs. The costs of composting are strongly dependent on the volume of soil being treated and on the composition of the compost mix, primarily the percentage of contaminated soil that can be included. Typical costs for treating large volumes (> 20,000 cu yd) are reported to be on the order of $190/cu yd for windrow composting, and between $236 and $290 for aerated static pile and in-vessel composting. The costs for the examples presented in Table 3-7 are generally within this range or slightly higher. The information in Table 3-7 may be inadequate due to an inability to gather complete data on all sites, either from a reluctance of site owners to impart the information or from missing site data.

Composting can be cost competitive with physical/chemical and thermal remedial technologies. For instance, cost savings at Umatilla Army Depot were estimated at $2.6 million compared to the traditional treatment method of incineration (EPA530-F-97-045). The end product of the Umatilla effort was a humus-rich soil that was estimated to be worth $10/ton. This represented a total value of $150,000. The Army Corps of Engineers has estimated that the total cost savings of substituting composting for incineration at the remaining explosives-contaminated sites would be on the order of $200 million (EPA, 1997).

Table 3-7. Summary of Site Characteristics at Composting Installations*

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Burlington Northern Superfund Site	Inactive	PAHs, MCE hydrocarbons	17,871 total PAHs (1987); 89,000 MCE hydrocarbons (1993)	NA	8,632 total PAHs; 21,000 MCE hydrocarbons	Yes (PAHs), No (MCE hydrocarbons)	564 PAHs; 22,000 MCE hydrocarbons	The concentrations of total PAHs in the soil after treatment was less than the cleanup goal of 8632 mg/kg for all 9 treatment sessions. However, the cleanup goal for MCE hydrocarbons was not met in any of the 9 treatment sessions.	45
Pueblo Chemical Depot	Closed	TNT, DNT, RDX	TNT, 3,800: TNB, 60; TND, 38	$312	TNT, 3.8; TND, 3.2; TND, 2.1	yes	<0.5	To below action levels	0.5-1
Umatilla Army Depot Activity, Explosives Washout Lagoons, CERCLA Soils Operable Unit	Closed	TNT, RDX, HMX	TNT, RDX 2,000 ; HMX, 100	$181	30	Yes	4 TNT; 2 RDX; 5 HMX	Windrow composting performance after 40-day treatment generally reduced the levels of target explosives to below the cleanup goals.	1
Dubose Oil Products Co. Superfund Site	Closed	VOCs (TCE, benzene, toluene, xylene), PAHs, and PCP	38 VOC; 2.1 TCE; 69.6 xylene; 367 PAHs; 51 PCP	~ $465	<50 PAHs, <1.5 xylenes, <10 benzene, < 0.05 TCE	Yes	3.3 PAHs; 16.5 PCP; 0.03 xylene; 0.01 TCE	Each batch of soil was treated to less than the cleanup goals within 14-30 days.	7
Joliet Army Ammo Plant MFG OU	NA	TNT	NA	~ $332	NA	NA	NA	NA	NA
Joliet Army Ammo Plant (LAP) OU	NA	TNT, DNT, RDX, Tetryl, TNB	NA	~ $332	NA	NA	NA	NA	NA
Stauffer Mgt Co (SMC)	Active Treatment	Pesticides	chlordane, 48; DDD, 243; DDE, 11; DDT, 88; dieldrin, 3; molinate, 10; toxaphene, 779	$192	Chlordane, 2.3; DDD, 12.6; DDE, 8.9; DDT, 8.9; Dieldrin, 0.19; Toxaphene, 2.75; Molinate, 0.74	Yes for DDE, DDT, Dieldrin, Molinate	Chlordane, 5; DDD, 23; DDE, 7; DDT, 1; Dieldrin, ND; Toxaphene, 29; Molinate, ND	Reduced some contaminants to below treatment goals; all by ~90%	14
Tooele Army Depot, TEAD-81, SWMU 10	NA	TNT, DNT, RDX, HMX	TNT, 2,500; DNT, 5.9; RDX, 1,100; HMX, 257	$230	TNT, 94; RDX, 34; HMX, 18,000	NA	TNT, 0.1; RDX, 2.96; HMX, 4.45	Considered very effective	1.33
Former paper mill, Southwest Fill Area	NA	PCBs (mainly Arochlor 1248)	16	~ $166	None reported	NA	< 3	Up to 40% concentration decrease overall, most loss in less-chlorinated cogeners	12

Table 3-7. Summary of Site Characteristics at Composting Installations* (continued)

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Hawthorne Army Depot, Building 101-41	NA	TNT, RDX, HMX, ammonium picrate	explosives 60,000 - 120,000; PCP in wood chip amendment, 100	$250	Varied: TNB, 4; ammonium picrate, 7; RDX, 64; TNT, 233; HMX, 4,000	Yes	TNT, < 5; RDX, < 25; ammonium picrate, 0.4; PCP, ND (< 0.1)	Considered very effective	28 days

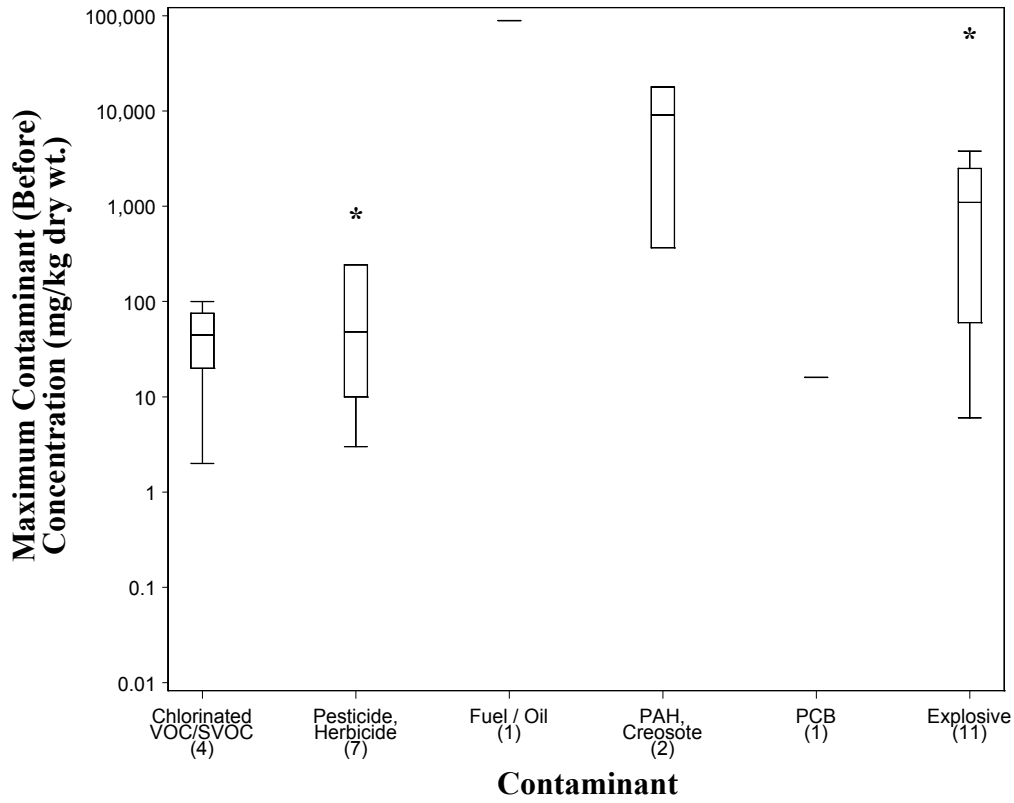
DDD = dichlorodiphenyldichloroethane
DDE = dichlorodiphenyldichloroethylene
TNB = trinitrobenzene
MCE = methylene chloride extractable
PAH = polycyclic aromatic hydrocarbons
TNT = trinitrotoluene
DNT = dinitrotoluene
RDX = cyclotrimethylenetrinitramine
HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraaxocine
VOC = volatile organic compounds
TCE = trichloroethylene
PCP = polychlorophenol
PCB = polychlorinated biphenyl
NA = not available

*One site included in Appendix B was not included in this table due to insufficient information. The excluded site is Site ID No. 05-014.

Table 3-8. Concentrations of Contaminants of Concern Before and After Composting Treatment: Data Used to Generate Figure 3-8

	Concentrations of Contaminants of Concern											
	Chlorinated VOC/SVOC		Pesticides Herbicides		Fuel / Oil		PAH, Creosote		PCB		Explosives	
	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment
Median:	45	0.1	48	5	89,000	22,000	9,119	284	16	3	1,100	3
25th Percentile	29	0.1	11	1	89,000	22,000	4,743	143	16	3	80	1
75th Percentile	63	9	166	15	89,000	22,000	13,495	424	16	3	2,250	5
High Whisker[(a)]	100	17	243	29	NA	NA	NA	564	NA	NA	3,800	NA
Low Whisker[(a)]	2	NA	3	1	NA	NA	NA	3	NA	NA	6	0.1

(a) High and low whiskers represent the most extreme data point within 1.5 interquartile ranges, i.e., 1.5 times the distance between the 25th and 75th percentiles.



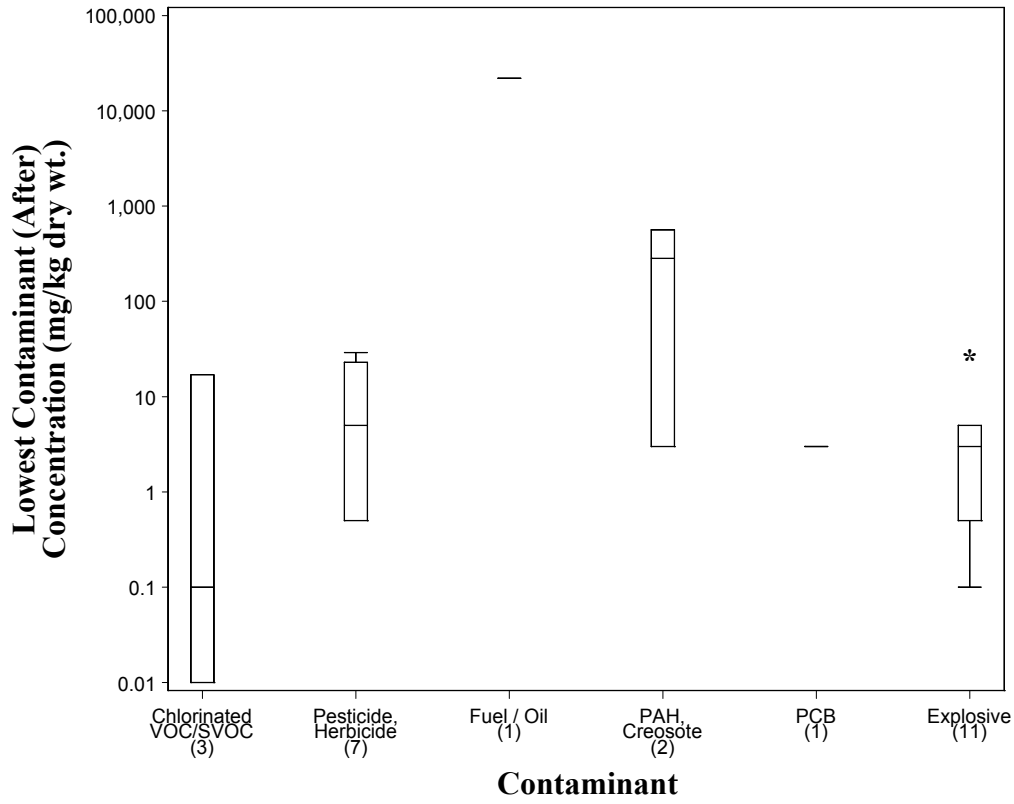


Figure 3-8. Box and Whisker Plots Showing Concentrations of Contaminants of Concern Before and After Composting Treatment. (See Appendix B for data used to generate these plots.)

3.1.4 *Ex-Situ* Bioreactors

Ex-situ bioreactors have a long industrial history and broad applicability. Groundwater pumped from contaminated aquifers is commonly treated using aboveground bioreactors. Off-gases from soil vapor extraction systems are often treated using vapor-phase bioreactors prior to discharge to the atmosphere. Municipal wastewater is most commonly treated using bioreactors, such as activated sludge or trickling filter systems. Residuals from activated sludge plants are usually treated in anaerobic digesters, a type of anaerobic bioreactor.

Bioreactors have more limited applicability to the treatment of soils and sediments. This is fundamentally due to the energy required to mix the media and mass transfer restrictions. Vapor and water require much less energy to mix than soils and sediments. Mixing typically is required to ensure that reactants or substrates are readily available to microbes and wastes are diluted and appropriately carried through the reactor system. The addition of water to soils to create a slurry enhances soil mixing and contaminant and nutrient mass transfer. The water acts as a lubricant for mixing and as a solvent to dissolve contaminants and nutrients and to suspend bacteria within the reactor. Bioslurry reactors are the most common *ex-situ* reactor configuration for soil remediation. Thus, the literature search for cost and performance data was restricted to bioslurry reactors.

Bioslurry treatment competes with land treatment and composting in the remediation technology selection process, and typically is chosen when mass transfer requirements or space limitations drive technology selection. Bioslurry reactors are used to degrade more recalcitrant compounds for which the reaction kinetics of a completely mixed system are more beneficial.

3.1.4.1 Principles of Operation

Bioslurry reactors include lagoons or vessels that contain a mixture of contaminated soil and water at a soil-to-water ratio ranging from 5% to 50% by weight. Slurries are used to accomplish the following objectives:

- Solubilize contaminants
- Improve mixing effectiveness
- Reduce mixing energy requirements
- Homogenize media
- Improve mass transfer.

Microbes that are indigenous to the soil or sediments, or exogenous cultures of microorganisms having desired metabolic capabilities, are used to biodegrade the target contaminants. Reactor design and operation may include manipulating the media through nutrient addition, aeration, mixing, pH control, and possibly temperature control to enhance conditions favorable for bacterial growth and enzyme production and activity.

Bioslurry reactors have been constructed using existing lagoons or ponds or aboveground mixing vessels. Contaminated soil is excavated from the site and loaded into the lagoon or aboveground vessel that will serve as the reactor. A bioslurry reactor is designed to apply sufficient mixing energy to suspend the bulk of solids and prevent excessive sedimentation. When existing lagoons or ponds comprise the reaction vessel, dredging equipment can be used to lift bottom sediments and achieve mixing.

Bioslurry reactors can be operated in continuous flow mode, like a continuous stirred tank reactor (CSTR), or in batch mode, depending on the nature of the contaminant and degradation process.

Regardless of the mode of reactor operation (continuous flow or batch), the mechanical action of slurry mixers helps to break up soil and aggregates, enhancing the distribution of air and nutrients and mass transfer throughout the reactor. Mass transfer refers to the transfer of contaminant mass from soils (e.g., sorbed, particulate, or pure phase contaminant in soils) to the aqueous phase, rendering the contaminants more bioavailable; mass transfer also can pertain to the distribution and transfer of nutrients to the aqueous phase for microbial bioavailability. The enhanced mass transfer of contaminants and nutrients in bioslurry reactors are attractive features of this technology that sets it apart from the variety of other *ex-situ* treatment alternatives such as land treatment, composting, and biopile/biocell treatment. Mass transfer is enhanced through mechanical agitation, which results in the breakdown of soil clumps into smaller particles and results in increased mixing between soil and aqueous phases. These actions increase the exposure of surface particles to water, from which contaminants can desorb and/or dissolve.

Process options for bioslurry reactors, largely dependent on soil and contaminant type, include:

- Batch or continuous flow modes
- Inoculation with prepared cultures
- Pretreatment (particle size reduction)
- Mixing with or without aeration (aerobic or anaerobic treatment)
- Nutrient addition
- Surfactant addition
- Residence time
- Solids content
- Cometabolite addition.

After treatment, the slurry typically is dewatered to separate solid (sludge) and liquid wastes. The methods of disposal of the sludge and liquid waste streams depends on their posttreatment characteristics. Secondary wastewater treatment can add significantly to soil treatment costs. Figure 3-9 shows an operating bioslurry reactor, and Figure 3-10 is a schematic of a bioslurry reactor.

Figure 3-9. Bioslurry Reactor

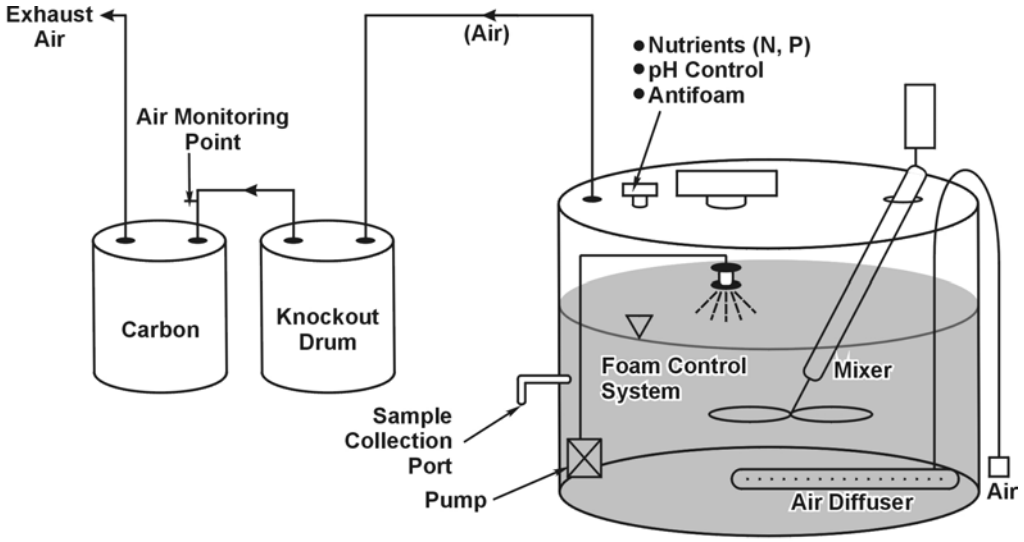


Figure 3-10. Bioslurry Reactor Schematic

3.1.4.2 Target Contaminants

Bioslurry reactors have a relatively broad applicability. Their primary restriction is to sites impacted with biodegradable contaminants. Contaminants that have been successfully remediated using bioslurry reactors include the following:

- Wood treating wastes
- PAHs
- Oil separator sludge
- Petroleum hydrocarbons
- Munitions and explosives
- Pesticides (not including highly chlorinated pesticides)
- PCBs
- DCE or VC.

Bioslurry reactors tend to be associated with relatively recalcitrant compounds because they tend to be more costly than other *ex-situ* treatment alternatives due to their slower throughput rates, more intensive mechanical requirements, and increased operation and maintenance requirements. Bioslurry reactors tend to be most commonly applied to sites with the following conditions:

- Sites with a high degree of soil and hydrogeologic heterogeneities that confound *in-situ* system design may be better suited for *ex-situ* treatment
- Sites with severe treatment time restrictions may benefit from improved treatment rates; the more rapid treatment kinetics of bioslurry reactors are mostly attributed to their enhanced mass transfer rates
- Sites with space restrictions may benefit from the smaller footprint provided by bioslurry reactors
- Sites with relatively recalcitrant compounds may benefit from bioslurry reactors, due to the potential for enhanced process control using bioslurry reactors.

The environmental contaminants for which bioslurry reactors are most applicable are compounds that are relatively difficult or slow to biodegrade using land treatment, composting, or biopile/biocell treatment, and that can benefit from enhanced mixing and process control. For example, higher-molecular-weight PAH compounds may be more degradable with this technology than with the more passive biotreatment processes. Bioreactors tend to be used most often on residual explosives, which have been shown to biodegrade only at a very slow rate. This is partly due to mass transfer limitations caused by the physical form of residual explosives in soil, which tend to occur in clumps and particles. In order to be biodegraded, individual molecules must interact with enzymes and other reactants. Highly viscous and semisolid materials such as explosives (e.g., TNT, RDX, and HMX) degrade more slowly, partly because the bioavailable molecules exist primarily on the outer surface of clumps of contaminants. One developing strategy for addressing this problem is to first dissolve explosives in a solvent, such as acetone, and then to treat the homogenized soil/contaminant mixture. This technique has been demonstrated on a pilot scale, and 2,000 ppm of TNT was remediated adequately within 5 days.

Process control may include operating under anaerobic, sequential anaerobic-aerobic, or strictly aerobic conditions. Explosives such as TNT, RDX, and HMX have been demonstrated to be susceptible to anaerobic biodegradation. Unfortunately, many of the degradation products of these biotransformations are no less toxic than the parent compound(s). Alternating anaerobic with aerobic processes may be effective at mineralizing these compounds due to the various conditions under which parent and daughter compounds have been found to degrade. This approach is easier to implement using a bioslurry reactor than land treatment or biopile/biocell treatment. However, this approach has not yet been widely implemented and requires further research and development, or at a minimum, pilot testing to demonstrate its effectiveness.

3.1.4.3 Advantages and Limitations

Bioremediation of contaminated soils, sludges, or sediments using bioslurry reactors offers the following advantages over many other remediation technologies:

- Contaminant bioavailability is enhanced
- Process control, including control of pH, temperature, and nutrients, is enhanced
- The contaminated solid and liquid fractions are fully contained, greatly enhancing treatment flexibility
- Volatile emissions are controlled (for constructed vessels only)
- Space requirements are reduced, particularly compared to land treatment, biopile/biocell treatment, and composting
- Bioslurry reactors may be mounted on trailers and transported for use at multiple sites, maximizing the utility of fixed costs.

Principal limitations of bioslurry reactors include the following:

- The physical nature of soil or sediment slurries make them extremely hard on machine parts (mixers, pumps, aerators, and other process control equipment incur costly wear and tear, resulting in increased repair and replacement costs)
- Mixing soil slurries is energy intensive, and, similar to activated sludge operations, aeration expenses can be a major cost constituent
- Post-treatment dewatering, secondary wastewater treatment, and solids disposal may be required, significantly increasing overall treatment costs

- Bioslurry reactors require more energy per unit soil treated than composting, biopiles, and land treatment
- Bioslurry reactors require more careful monitoring and more intensive O&M than the other land treatment options.

3.1.4.4 Technology Cost Drivers

Major cost drivers of the slurry-phase biotreatment process include:

- The physical nature of soil or sediment slurries makes them extremely hard on machine parts (mixers, pumps, aerators, and other process control equipment incur costly wear and tear, resulting in increased repair and replacement costs)
- Excavation of contaminated media is required, except for lagoon implementation
- Post-treatment dewatering, secondary wastewater treatment, and solids disposal may be required, significantly increasing overall treatment costs
- Sizing of materials prior to putting them into the reactor can be difficult and expensive
- Heterogeneous soils and clayey soils can create serious materials handling problems. In the case of free phase contaminants, preventative removal is mandatory
- Bioslurry reactors may require careful monitoring, operation, and maintenance
- Costs are proportional to throughput, which for bioslurry reactors is relatively slow.

3.1.4.5 Technology Performance and Cost

The use of bioslurry reactors is relatively limited because of the high capital and operating costs of this technology, especially compared with alternative *ex-situ* biotreatment technologies. Cost and performance summaries of these sites are provided in Table 3-9.

Figure 3-11 presents box and whisker plots showing the range of starting concentrations (Figure 3-11a) and ending concentrations after treatment (Figure 3-11b) for various contaminants subjected to bioslurry treatment. The figures depict significant contaminant removals; not all the contaminants identified before treatment were necessarily monitored after treatment, resulting in fewer contaminants identified in Figure 3-11b than in Figure 3-11a. Table 3-10 summarizes the data used to create Figure 3-11.

Table 3-9. Summary of Site Characteristics at Bioslurry Installations

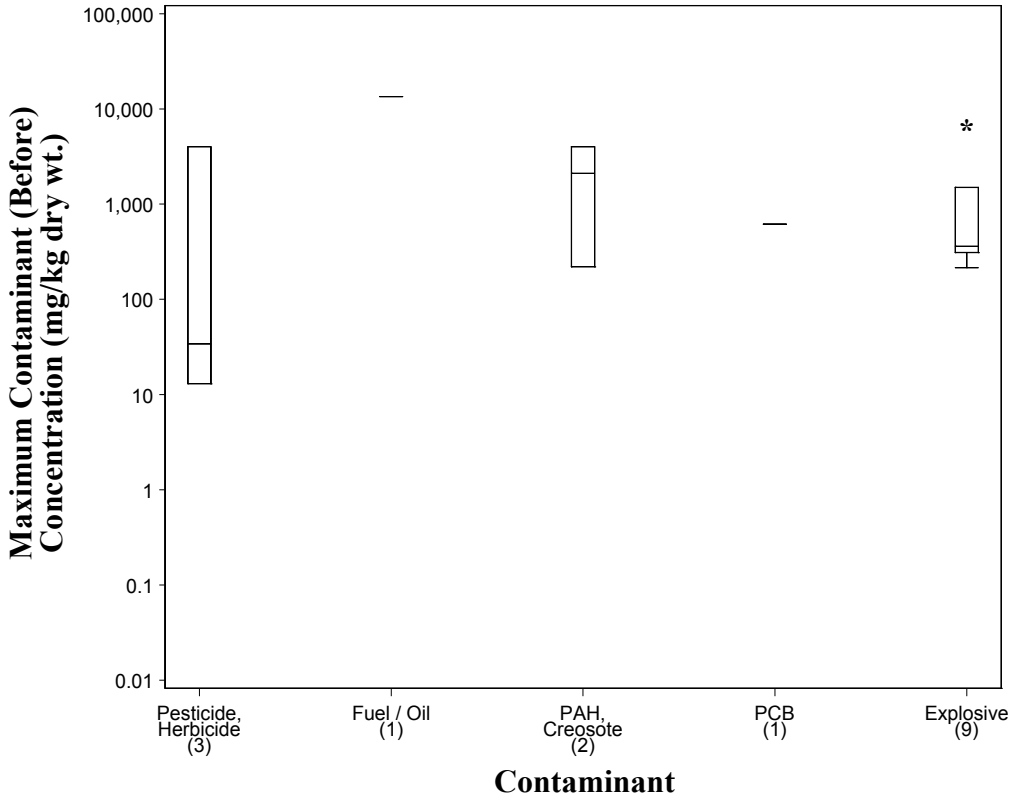
Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
La Cie Huntsman du Canada	Closed	oil and grease	13,500	$112	1000	Yes	420	NA	3
French Ltd. Superfund Site	Closed	PAHs, BAP, PCBs, vinyl chloride, arsenic	616 PCBs; 750 pentachlorophenol; 400 BAP.	$200	9 BAP; 23 PCBs; 43 vinyl chloride, 7 arsenic, 14 B	Yes	B: ND; BAP: ND	NA	22
Southeastern Wood Preserving Superfund Site	Closed	PAHs	4,000	$318	<950 total PAHs; <180 BAP-equivalent carcinogenic PAHs;	Yes	634 total PAHs; 152 BAP equivalent	Total PAHs efficiency 93%; 67% for BAP-equivalent	36
Iowa Army Ammunition Plant	Inactive	TNT, RDX	TNT: 1,500; RDX: approx. 270.	$335	TNT: 196; RDX: 53	Yes	NA	TNT below treatment levels in 8 weeks. RDX removal occurred afterTNT.	2
Eko Tec Site	Closed	Creosote	PAHs, 220	NA	total PAHs = 50; BAP and benzo(a)antracene = 10	Yes	PAHs, 27; others <10	All contaminants to below treatment goal	1
Yorktown Naval Weapons Station	NA	TNT, RDX	> 450	NA	TNT, 30; RDX, 100	Yes	TNT < 30; RDX, <100	Considered very effective	1
Joliet Army Ammo Plant OU; Group 61	NA	TNT, DNT, TNB, RDX, HMX	TNT, 6,226; DNT and TNB, 360; RDX, 310, HMX, 215	$320	TNT, 20	NA	TNT, <20 to <50; DNT <10 to <100; TNB, RDX <10	> 99% removal in all reactors	2.5
Navajo Indian Reservation Superfund Site	NA	Toxaphene	4,000	NA	NA	NA	180	NA	NA
Bowers Field	Inactive	Dinoseb, Nitroaniline, other pesticides and herbicides	Dinoseb, 34.2 maximum; Nitroanaline, 13.3 average	$97	Dinoseb contamination reduced by at least 95%.	Yes	Dinoseb, < 0.03; Notroaniline, < 0.75; DDT, malathion, parathion, < 0.75	Removed >99.8% dinoseb; > 88.6% parathion; other herbicides unchanged	0.75
Weldon Spring Ordnance Works	Inactive	TNT	TNT, 1,500	$112	TNT contamination reduced by at least 95%.	Yes	TNT, 8.7	99.4 % removal of TNT	9

ND = non-detectable
NA = not applicable
BAP = benzo(a)pyrene
PAH = polycyclic aromatic hydrocarbon
PCB = polychlorinated biphenyl
TNT = trinitrotoluene
RDX = cyclotrimethylenetrinitramine
TNB = trinitrobenzene
HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraaxocine
DNT = dinitrotoluene
DDT = dichlorodiphenyltrichloroethane

Table 3-10. Concentrations of Contaminants of Concern Before and After Bioslurry Treatment: Data Used to Generate Figure 3-11

	Concentrations of Contaminants of Concern									
	Pesticide, Herbicide		Fuel / Oil		PAH, Creosote		PCB		Explosives	
	Before Treatment (3 sites)	After Treatment (6 sites)	Before Treatment (1 site)	After Treatment (1 site)	Before Treatment (2 sites)	After Treatment (2 sites)	Before Treatment (1 site)	After Treatment (1 site)	Before Treatment (9 sites)	After Treatment (11 sites)
Median:	34	0.8	13,500	420	2,110	331	616	23	360	30
25th Percentile	24	0.8	13,500	420	1,165	179	616	23	310	10
75th Percentile	2,017	0.8	13,500	420	3,055	482	616	23	1,500	77
High whisker[(a)]	4,000	NA	NA	NA	NA	NA	NA	NA	NA	100
Low whisker[(a)]	13	NA	NA	NA	NA	NA	NA	NA	NA	9

a) High and low whiskers represent the most extreme data point within 1.5 interquartile ranges, i.e., 1.5 times the distance between the 25th and 75th percentiles.



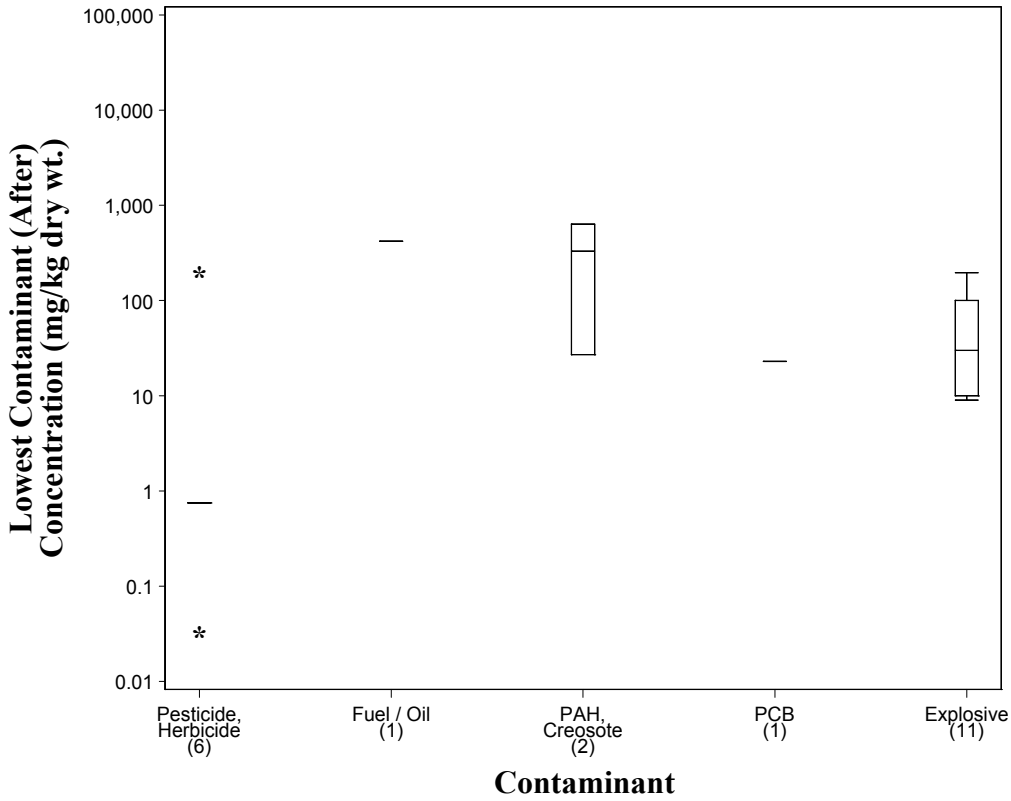


Figure 3-11. Box and Whisker Plots Showing Concentrations of Contaminants of Concern Before and After Bioslurry Treatment. (See Appendix B for data used to generate these plots.)

The following case studies are reported as examples of bioslurry reactor treatment of soils.

French Limited Superfund Site, Crosby, TX. The French Limited Superfund Site in Crosby, TX (French site) was an industrial waste disposal facility at which more than 70 million gallons of petrochemical industry wastes were disposed in an unlined disposal lagoon from 1966 to 1971. This project is the first reported application of a bioslurry reactor at a Superfund site. The bioslurry reactor was constructed about and within the existing disposal lagoon. A commercial system (MixFlo™) was used to aerate the system with pure oxygen and control volatile emissions from the lagoon surface. The system was designed to treat approximately 300,000 tons (2.7×10^8 kg) of subsoil underlying a layer of tarry sludge. The tarry sludge was removed prior to treatment of the subsoil in the bioslurry reactor.

Performance and factors. Table 3-11 lists the primary contaminants and their respective cleanup goals. For treatment, the lagoon was subdivided into two smaller lagoons, which were treated separately. The residence time of liquid and solid media in the lagoons was about the same as the total treatment time (10 and 11 months). The aerator consisted of a 3,400-hp (2.5-megawatt) motor supplying 2,500 lb (1,100 kg) of oxygen per hour over the treatment time. The system achieved a mass throughput of approximately 500 tons/day.

Table 3-11. Cleanup Goals for Primary Contaminants at the French Site

Contaminant	Cleanup Goal (mg/kg)
Benzo (a) pyrene	9
Total PCBs	23
Vinyl chloride	43
Arsenic	7
Benzene	14

Superfund Preliminary Site Closeout Report French Limited Site Crosby, Texas, September 1994. CERCLIS TXD-980514814, p. 6.

The ROD specified bioremediation of the lagoon subsoil, but also listed arsenic (an elemental heavy metal) as a primary contaminant. The reported concentration results showed that arsenic concentrations in soil decreased over treatment time, but it is unclear what effect biodegradation processes had on this contaminant. Nevertheless, the sediments in both lagoons were cleaned to below target levels within 11 months of operation.

Cost range. The costs directly attributable to treatment activities were $26,000,000, resulting in a mean cost of about $90/ton ($99/1,000 kg) of soil treated. Total costs, which included project management, pilot studies, and post-treatment activities, amounted to $49,000,000, yielding a total cost of $163/ton ($180/1,000 kg).

Southeastern Wood Preserving Superfund Site, Canton, MS. The Southeastern Wood Preserving Superfund Site in Canton, MS, evolved from wood-preserving operations from 1928 through 1979. Three unlined surface impoundments were used for wastewater treatment. Approximately 4,000 mg/kg of PAHs were found to exist in bottom sediment sludges from the impoundments. The material to be treated was classified as an RCRA K0001-listed hazardous waste. Unlike the French site, engineered slurry reactors were constructed on site, and media was moved to the reactors for treatment.

Performance and factors. Four bioslurry reactors were operated in batch mode. Each reactor was circular, with a 38-ft (11.6 m) diameter and a height of 24 ft (7.3 m), resulting in an operating volume of 180,000 gallons (680 m^3). Each batch consisted of about 170 cu yd (130 m^3) of material. In total, 14,140

tons (1.3 x 10^7 kg) or 10,500 cu yd (8,000 m^3) of material were treated. The bioslurry reactors were aerated at a rate of approximately 350 standard cubic feet per minute (scfm) (165 L/s) with a batch residence time ranging from 8 to 29 days. Air was used for aeration at the Southeastern Wood Preserving site, while the French site system used pure oxygen. Table 3-12 lists the average treatment efficiency of the bioslurry reactors for removal of PAHs. When initial operations revealed that cleanup goals for specific PAHs (pyrene and phenanthrene) were not being achieved in the design reactor residence time of 30 to 35 days, the cleanup goals were modified to specify total and carcinogenic PAHs, instead of specific PAHs. This was done by obtaining a variance under 40 CFR 268.44. Hence, cleanup goals were eventually obtained when the goals were adjusted to meet the performance efficiency of the bioreactors. Nonetheless, this approach was accepted. The system achieved a mass throughput of approximately 50 tons/day.

Table 3-12. Efficiency of Bioslurry Reactors for Removing PAHs at the Southeastern Wood Preserving Site

Constituent	Cleanup Goal (mg/kg)	Average Initial Concentration (mg/kg)	Average Final Concentration (mg/kg)	Average Removal Efficiency (%)
Naphthalene	NA	48	6	88
Benzo(a)pyrene	NA	98	79	19
Carcinogenic PAHs	NA	1,095	376	66
Benzo(a)pyrene equivalent	180	433	150	65
Total PAHs	950	8,621	655	92

Cost range. The costs directly attributable to treatment activities were $2,400,000, resulting in an average cost of about $170/ton ($190/1,000 kg) of soil treated. Total costs, which included project management, pilot studies, and post-treatment activities, amounted to $2,900,000, resulting in a total cost of $205/ton ($230/1,000 kg).

SABRE™ Process. Another application of bioslurry reactors is exemplified by the J.R. Simplot Company's Simplot Anaerobic Bioremediation *Ex-Situ* (SABRE™) Process. This approach includes the addition of proprietary amendments to the slurry and has been used to remediate explosives in soil. Two applications are summarized below.

Site descriptions. Soils from the Iowa Army Ammunition Plant (IAAP) were treated in a concrete trench lined with high-density polyethylene (HDPE). The trench was approximately 50 ft (15 m) long and 8.3 ft (2.5 m) wide and was filled with a 40% soil slurry comprising 40 cu yd of contaminated soil. The primary contaminants were the explosives TNT and RDX.

Soils impacted with explosives TNT and RDX from Yorktown Naval Weapons Station, VA, also were treated using the SABRE™ process. At the Yorktown site, a double-lined bioremediation cell was used to treat 1,900 cu yd (1,500 m^3) of contaminated soil, including preliminary pilot tests followed by full-scale treatment.

Performance and factors. At the IAAP site, TNT degraded first, followed by RDX. TNT was reduced from an initial concentration of about 800 mg/kg to below the cleanup standard of 196 mg/kg within approximately 8 weeks. RDX was reduced from its initial concentration of approximately 260 mg/kg to below its cleanup standard of 53 mg/kg within approximately 10 weeks.

At the Yorktown site, treatment times for both pilot- and full-scale treatment were 30 days. Table 3-13 lists the maximum concentrations of various explosives in soil and the respective cleanup goals achieved at the Yorktown site.

Cost range. At the IAAP site, treatment costs were projected to be in the range of $300 to $350/cu yd ($390 to $460/$m^3$). The Yorktown soils were treated for a cost of $398/cu yd ($520/m^3).

Table 3-13. SABRE™ Process Effectiveness at Yorktown Site

Explosive	Maximum Concentration (mg/kg)	Cleanup Goal Achieved (mg/kg)
TNT	35,000	30
RDX	5,400	50
HMX	11,000	3,900

3.1.5 Conventional Bioventing

Conventional bioventing is the process of aerating soils to stimulate *in-situ* biological activity and promote bioremediation. Conventional bioventing typically is applied *in situ* to the vadose zone and is applicable to any chemical that can be aerobically biodegraded. To date, it has been implemented primarily at petroleum-contaminated sites. A typical conventional bioventing system is illustrated in Figure 3-12. Although bioventing is related to the process of SVE, the primary objectives of these two bioremediation technologies are different. SVE is designed and operated to maximize the volatilization of
low-molecular-weight compounds; biodegradation is not typically a design objective. In contrast, bioventing is designed to maximize biodegradation of aerobically biodegradable compounds, regardless of their molecular weight, while minimizing volatilization. The major distinction between these technologies is that the objective of SVE is to optimize removal by volatilization, while the objective of bioventing is to optimize biodegradation while minimizing volatilization and reducing the capital and utility costs required for vapor treatment. Although both technologies involve venting of air though the subsurface, the differences in objectives result in different design and operating conditions for the two remedial systems.

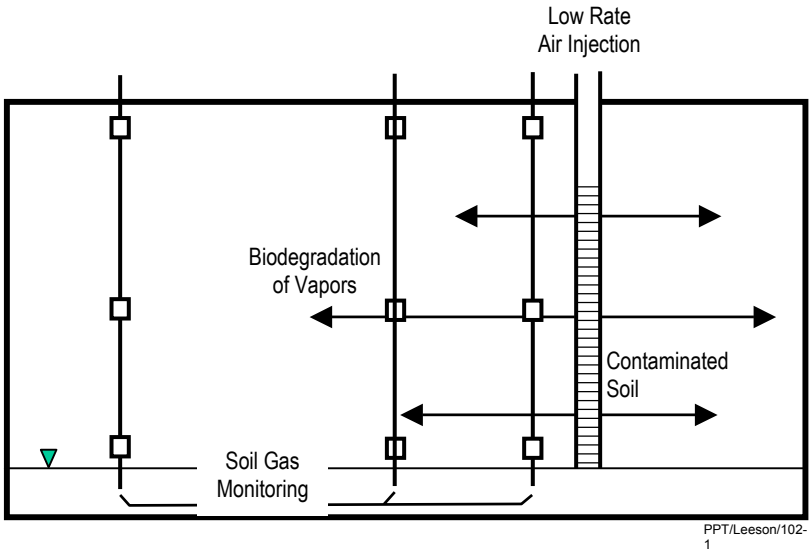


Figure 3-12. Schematic of Typical Conventional Bioventing Process

3.1.5.1 Principles of Operation

Conventional bioventing is a relatively simple technology involving minimal equipment including a blower for air injection, vent wells screened throughout the contaminated zone, soil-gas monitoring points, and associated monitoring equipment. Figure 3-13 shows a typical conventional bioventing system. Four primary characteristics impact the applicability and/or effectiveness of bioventing. These include soil-gas permeability, contaminant distribution, zone of oxygen influence, and microbial activity.

Figure 3-13. Conventional Bioventing System

Assuming that contaminants amenable to bioventing are present, geology probably is the most important site characteristic for a successful conventional bioventing application. Soils must be permeable enough to allow sufficient soil-gas flow to provide adequate oxygen for biodegradation, on the order of 0.25 to 0.5 vapor pore volumes per day. Soil-gas permeability is a function of soil structure, particle size, and soil moisture content. Typically, permeability in excess of 0.1 darcy is adequate for sufficient air exchange. Below this level, bioventing certainly is possible, but field-testing may be required to establish feasibility. When the soil-gas permeability falls below approximately 0.01 darcy, soil-gas flow is primarily through either secondary porosity (such as fractures) or through any more permeable strata that may be present (such as thin sand lenses). Therefore, the feasibility of conventional bioventing in low-permeability soils is a function of the distribution of flowpaths and diffusion of air to and from the flowpaths within the contaminated area.

Another important factor affecting the feasibility of conventional bioventing is contaminant distribution throughout the site. Difficulties in applying bioventing arise when significant quantities of the

contaminant are in the capillary fringe or below the water table due to groundwater fluctuations. Treatment of the capillary fringe by screening air injection wells below the water table is possible; however, the ability of bioventing to aerate the capillary fringe and underlying water table has not been evaluated. Limited oxygenation is expected to occur in saturated soils. If significant contamination exists below the water table, dewatering should be considered as a means of exposing any contaminated soil to injected air. Alternatively, a combination of air sparging (air injection beneath the water table) and bioventing may provide more efficient air delivery to the capillary fringe.

An estimate of the oxygen radius of influence (R_I) of air injection wells is an important element of conventional bioventing design. This parameter is used to design full-scale systems, specifically to space air injection wells, size blower equipment, and ensure that the entire site receives a supply of oxygen-rich air to sustain *in-situ* biodegradation. The radius of oxygen influence is defined as the radius to which oxygen has to be supplied to sustain maximal biodegradation. This definition of radius of influence is different than is typically used for SVE, where radius of influence is defined as the maximum distance from the air extraction or injection well where vacuum or pressure (soil-gas movement) occurs. The oxygen radius of influence is a function of both air flowrates and oxygen utilization rates, and therefore depends on site geology, well design, contaminant concentration and microbial activity. As microbial activity increases, the effective treated area will decrease. Therefore, it is desirable to estimate the oxygen radius of influence at times of peak microbial activity and to design the bioventing system based on these measurements.

Finally, conventional bioventing is dependent on providing microorganisms optimal conditions for active growth. Several factors may affect a microorganism's ability to degrade contaminants; however, those that impact the bioventing process significantly include availability and type of electron acceptors and moisture content.

One of the most important factors that influences the biodegradability of a compound is the type and availability of electron acceptors. For example, following a hydrocarbon spill, anaerobic conditions typically predominate in the subsurface because of oxygen depletion from microbial activity. While hydrocarbons may undergo limited biodegradation under anaerobic conditions (Bilbo et al., 1992; Mormile et al., 1994), in general, aerobic conditions are more suitable for relatively rapid remediation of petroleum hydrocarbons. Therefore, oxygen supply is critical to the success of a conventional bioventing system. In field studies, oxygen has been found to be the most important factor in determining the success of a bioventing system (Leeson and Hinchee, 1996; Miller et al., 1991).

Soil moisture content may impact conventional bioventing by its effect on microorganisms or soil-gas permeability. Microorganisms require moisture for metabolic processes and for solubilization of energy and nutrient supplies. Conversely, soil moisture content directly affects soil permeability, with high moisture contents resulting in poor distribution of oxygen. In practice, soil moisture has been found to directly limit biodegradation rates only where bioventing has been implemented in very dry desert environments. A more common influence of moisture is that excess moisture has led to significant reductions in soil-gas permeability (Leeson and Hinchee, 1996).

A fairly recent improvement to conventional bioventing technology is enhanced, or cometabolic, bioventing. Cometabolic bioventing, which utilizes the addition of gas-phase additives to the injected oxygenated air in order to enhance biodegredation, is discussed in detail in Section 3.1.6.

3.1.5.2 Target Contaminants

Any aerobically biodegradable compound can potentially be degraded through bioventing. To date, conventional bioventing has been applied primarily to petroleum hydrocarbons; however, bioventing of

PAHs (Lund et al., 1991; Hinchee and Ong, 1992; Alleman et al., 1995) and bioventing applied to an acetone, toluene, and naphthalene mixture (Leeson et al., 1994) have been implemented successfully.

The key to conventional bioventing feasibility in most applications is biodegradability versus volatility of the compound. If the rate of volatilization greatly exceeds the rate of biodegradation, bioventing is unlikely to be successful, as removal occurs primarily through volatilization. This will occur most often in those cases where the contaminant is a fresh, highly volatile fuel. An unsuccessful conventional bioventing application is unlikely to occur due to a lack of microbial activity. If conventional bioventing is operated in the injection mode, volatilized contaminants may be biodegraded before reaching the surface, unlike an extraction mode. Figure 3-14 illustrates the relationship between a compound's physicochemical properties and its potential for bioventing.

In general, compounds with a low vapor pressure[1] cannot be successfully removed by volatilization, but can be metabolized by microbes if they are aerobically biodegradable. High vapor pressure compounds are gases at ambient temperatures. These compounds volatilize too rapidly to be easily biodegraded in a bioventing system, but typically are a small component of fuels and, due to their high volatility, will attenuate rapidly. Compounds with vapor pressures between 1 and 760 mm Hg may be amenable to either volatilization or biodegradation. Within this intermediate range lie many of the petroleum hydrocarbon compounds of greatest regulatory interest, such as benzene, toluene, ethylbenzene, and the xylenes. As can be seen in Figure 3-14, various petroleum fuels are more or less amenable to conventional bioventing. Some components of gasoline are too volatile to easily biodegrade, but, as stated previously, typically are present in low overall concentrations and are attenuated rapidly. Most of the diesel constituents are sufficiently nonvolatile to preclude volatilization, whereas the constituents of JP-4 jet fuel are intermediate in volatility.

To be amenable to conventional bioventing, a compound must 1) biodegrade aerobically at a rate resulting in an oxygen demand greater than the rate of oxygen diffusion from the atmosphere, and 2) biodegrade at a sufficiently high rate to allow *in-situ* biodegradation before volatilization. Practically, this means that low vapor pressure compounds need not biodegrade as rapidly as high vapor pressure compounds for bioventing to be successful. The actual feasibility of bioventing is very site-specific; therefore, Figure 3-14 should not be used as absolute, but rather as a general guideline.

Of the petroleum hydrocarbons, BTEX generally are the compounds that are regulated most stringently. Typically, these compounds degrade very rapidly during bioventing, and, at most sites, are degraded to below detection limits within 1 year of operation of a bioventing system. This trend was illustrated in a study at Tyndall Air Force Base (AFB) and has been confirmed at numerous bioventing sites (Leeson and Hinchee, 1996). At Tyndall AFB, two test plots were conducted with initial hydrocarbon concentrations of 5,100 and 7,700 mg/kg. After 9 months of bioventing, TPH was reduced by 40% from the initial concentration. However, the low-molecular-weight compounds such as BTEX were reduced by more than 90%. The low-molecular-weight compounds were preferentially degraded over the heavier fuel components, which is consistent with previous research (Atlas, 1986).

Bioventing generally is not considered appropriate for treating compounds such as PCBs and chlorinated hydrocarbons. However, through a cometabolic process, it may be possible to enhance the degradation of compounds such as TCE through bioventing.

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[1] For the purposes of this discussion, compounds with vapor pressures below approximately 1 mm Hg are considered low, and compounds with vapor pressures above approximately 760 mm Hg are considered high.

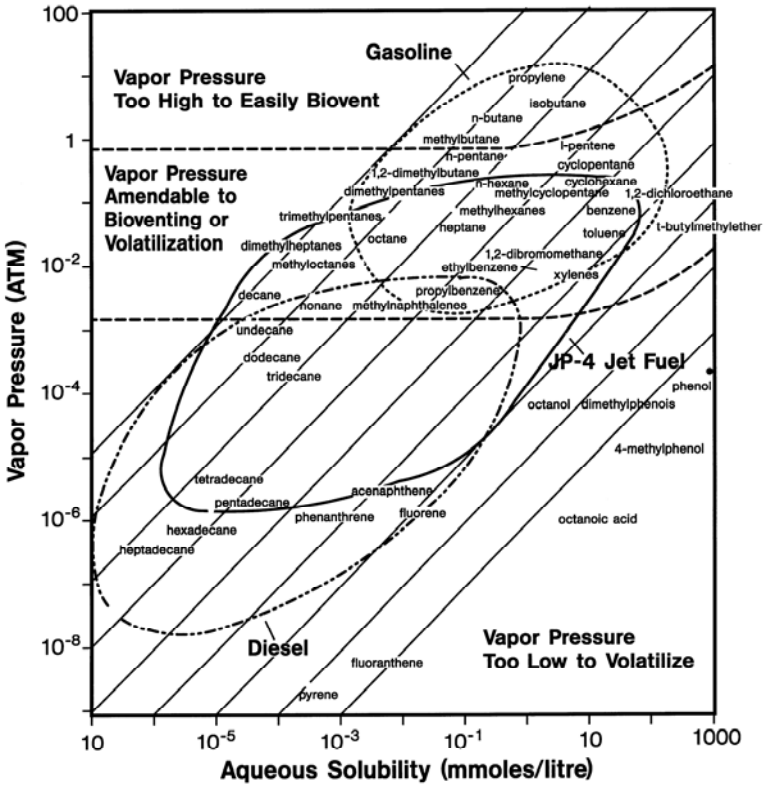


Figure 3-14. Relationship Between Organic Physicochemical Properties of Organic Compounds and their Potential for Conventional Bioventing (Leeson and Hinchee, 1996)

3.1.5.3 Advantages and Limitations

The primary advantage of implementing conventional bioventing over other comparable technologies is the cost savings. Conventional bioventing is a relatively simple technology, and this translates into significantly reduced costs. In addition, conventional bioventing is an *in-situ* technology that results in minimal disturbances to sites. Given that many sites that are amenable to bioventing are in high-traffic areas, such as gasoline stations, this is a significant benefit, as business can continue uninterrupted once installation is complete. Finally, the microbial aspect of conventional bioventing results in two benefits: nonvolatile contaminants can be removed (unlike during SVE), and contaminants are biotransformed to innocuous byproducts instead of transferring the contaminants to another matrix.

The primary limitation of conventional bioventing is the time involved to complete remediation. While BTEX components may be removed rapidly, the heavier-molecular-weight compounds may take several years to be removed. This long time frame may not be acceptable for all sites. Also, bioventing is not applicable to all sites, depending on contaminant volatility, biodegradability, soil permeability, and site use restrictions.

3.1.5.4 Technology Cost Drivers

Major conventional bioventing cost drivers include:

- Capital equipment costs will increase with increasing site size, including blower size and capacity, well installation frequency, and well depth

- Depth of contamination will impact the drilling requirements and the material costs for well installation; depth also impacts energy costs when air needs to be blown across larger depth intervals
- More permeable soils require less energy to force air through the soil matrix; also, more permeable soils lead to a more uniform air distribution and consequently more uniform biodegradation
- Off-gas capture generally is not recommended because air flow should be commensurate with biodegradation rates; however, at high risk sites where off gas could impact human activity, off-gas capture and treatment may be required, significantly increasing treatment costs.

3.1.5.5 Technology Performance and Cost

Table 3-14 provides a summary of various full-scale conventional bioventing installations, including information on contaminant type and concentrations, target cleanup levels, and status of site cleanup (See Appendix B for the data used to generate Table 3-14). Figure 3-15 shows box and whisker plots for contaminants treated using conventional bioventing, as reported in Appendix B. Figure 3-15a presents the range of contaminant concentrations before treatment, and Figure 3-15b illustrates their range after treatment. Table 3-15 illustrates the data used to generate Figure 3-15. Information provided in the tables and figures in this section is not as comprehensive as desired due to an inability to gather complete data on all sites, either from a reluctance of site owners to impart the information or from missing site data. Of the 22 conventional bioventing sites shown, five sites achieved their treatment goals, three sites achieved some of their treatment goals, two sites did not meet any of their treatment goals, and sufficient information was not available for 12 of the sites to determine whether or not treatment goals were achieved.

At the USCG Support Center, BTEX was removed to below detection limits, but TPH remained well above the treatment goal of 100 mg/kg. Initial TPH concentrations were approximately 2,900 mg/kg, and the bioventing system was operated for 18 months. In order to meet treatment goals for this site, the biodegradation rate required may be calculated as follows:

$$\frac{(2{,}900\ \text{mg/kg} - 100\ \text{mg/kg})}{18\ \text{months} \times \frac{30\ \text{days}}{\text{month}}} = 5.2\ \text{mg/kg/day} \qquad (1)$$

The actual concentration achieved at the end of 18 months was approximately 1,450 mg/kg, indicating a much slower average biodegradation rate of approximately 2.7 mg/kg/day using the same equation as shown above. Both of these biodegradation rates fall within a normal range of 1 to 20 mg/kg/day (Leeson and Hinchee, 1996), and indicates that the bioventing system was not operated for a long enough time period to achieve the TPH treatment goals.

A similar situation occurred at Vanier Gas Station, Canada, where treatment goals for benzene, toluene, and xylene were not achieved although concentrations were reduced. At this site, though, the system was operated only for 111 days. Most evidence indicates that this would not be sufficient time to achieve complete removal, even of the more biodegradable BTEX compounds.

At Sorel Gas Station, the conventional bioventing system was operated for 475 days, but only small amounts of removal were achieved. No information was available on soil type at this site; however, air was injected below the water table, possibly indicating a significant amount of contamination present in the capillary fringe. Water-saturated soil would not be amenable to bioventing and this could explain the lack of degradation at this site. However, without additional site information, it is difficult to determine the causes for not achieving the treatment goals.

Of the remaining 10 sites, information on attaining treatment goals was not available. At four of these sites, this is due to the fact that the systems are still active at the time when data for these sites were collected. Four of the sites have been closed indicating that treatment goals were met, but not reported in an attainable format. The remaining two sites are now inactive (Greenwood Chemical Superfund Site, and Site ST-20, Eielson AFB). At the Greenwood Chemical Superfund Site, the system was installed as part of a research study and was not intended to be operated until contaminants were completely removed. At Site ST-20, the initial system was installed as a research project and was to be expanded to the entire site once funding was received. Given that this expansion has not occurred, it is probably because the Base is still awaiting funds to expand operation at this site.

Table 3-14. Summary of Site Characteristics at Conventional Bioventing Installations*

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
George AFB, OU 3 FT19a	Active treatment	BTEX, TPH	TPH, 65,000; B 22; T 210; E 59; X 610	$14	< 25 ft: TPH, 10; B, T, E, 0.005; X, 0.015. Soil 25-100 ft, TPH 10, BTE 0.3 X 1.0.	Expected to reach by 2003	TPH, 14,000; B, 2.9; T, 68; E, 34; X, 266	Considered effective	36
Greenwood Chemical	Inactive	A, T, N, CB, B, 1,2-DCA	A: 47; T: 630; N: 120; CB: 4.6; B: 9.4; 1,2-DCA: 2.4	$27	NA	NA	A: 0.012; T: 0.002; N: 0; CB: 0; B: 0; 1,2-DCA: 0.007	A: >99; T: >99; N: >98; CB: >98; B: >99; 1,2-DCA: >90	15
Sorel Gas Station	Closed	BTEX	B; 41; E: 31; T: 280; X: 650.	NA	B: 5; E: 50; T: 230; X: 50	No	B:14; E: 66; T: 230; X: 290	NA	12.5
Vanier Gas Station	Inactive	BTEX	B: 36; E: 76; T: 250; X: 520.	$82	B: 5; E: 50; T: 30; X: 50.	E: yes, others: no.	B: 6.1; E: 11; T: 68; X: 80.	NA	4
Elmendorf Air Force Base	Active	BTEX, TRPH	E: 94. T: 87, X 430,. TRPH: 5340	NA	NA	NA	E: 52. T: 41; X: 240; TRPH: 3900	NA	NA
Hill AFB (8 areas at site)	Active	BTEX, TRPH	B1.2; T: 1150; E: 5840. X: 17,300; TRPH: 32,200.	NA	B: 0.2; T: 100; E: 70; X: 0.36; TRPH: 30.	Yes, except TRPH	B: 0.64. T: 0.38. E: 2. X: 5.8. TRPH: 12,000	NA	NA
Robins Air Force Base	Closed	BTEX: TRPH	B: 1.3; E: 220; T: 59; TRPH: 9000; X: 39.	NA	Site Specific	NA	B: ND; E: 0.11; TRPH: 1,900; X: 1	NA	NA
BLDG 30, 406, 528, and a POL Area of Offutt AFB	Active	BTEX; TRPH	B: 2000; X: 38,000; T: 7,100; E: 4100	NA	Site Specific	Yes	B: 0.0042; X: 0.0029; T: ND; E: 0.019 TRPH: 4.3	NA	NA
Sites, D-10; FC-2, S-4, Kelly AFB	Active	BTEX; TRPH	30 B; 884 total BTEX in all four sites; 5430 TRPH	NA	NA	NA	T: 8; TRPH: 920; X: 12	NA	NA
East 15th Street Service Station	Active	diesel	5500	NA	100	NA	NA	NA	NA
Site 5, Savannah River Site	Active	diesel	100	$4	100	NA	NA	NA	NA
NASA/Wallops Flight Facility	Closed	Diesel oil, furnace oil	6970 TPH	$146	50	Yes	NA	NA	NA
Lowry Air Force Base	Closed	Heating oil, BTEX	14,000 TRPH	NA	500 TPH; 500 TRPH; <100 BTEX	NA	NA	NA	24+
Site 280, Hill AFB	Active	JP-4 jet fuel, TPH, BTEX	5040 TPH; 11,200 Soil-gas TPH	NA	NA	NA	2,600 ppm (Soil-gas TPH)	Evidence of hydrocarbon degradation	48+

Table 3-14. Summary of Site Characteristics at Conventional Bioventing Installations* (continued)

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
IRP Site ST-49, Eglin AFB	Active	Petroleum; VOC	2430	$96	50 VOC	Yes	0	NA	60
USCG Support Center, Elizabeth City, NC	Inactive	TPH (JP-4), BTEX	346 BTEX; 2,954 TPH	NA	<100 TPH	No	0, BTEX; 1,457, TPH	98% benzene, 60% TPH.	18
Los Angeles Air Force Base	1&2 Closed, 3 Inactive	TRPH	(1) 1580; (2) 11,800; (3) 14000	NA	Site Specific	Yes	NA	NA	NA
Site 914, Hill Air Force Base	Closed	JP-4 jet fuel, TPH, BTEX	10,000 TPH	$152	38.1 TPH	Yes	< 6	NA	15
Eielson Air Force Base Source Area ST 20	Inactive	JP-4 jet fuel, TPH, BTEX	1,500 TPH	$13	200 TPH; 2lbs/day in extracted soil gas	NA	NA	NA	36+
Fort Bliss, Bldg. 675	Active treatment	BTEX	1,350 avg	$6	NA	NA	690 in first year	NA	12
Tyndall Air Force Base	Unknown	TPH	> 1,000	$30	NA	NA	TPH, < 30	NA	
Fort Carson Bldg. 8200	Active treatment	TPH, BTEX	TPH, 1,350 avg; BTEX, 17 avg	$18	NA	NA	TPH, reduction rate 170 mg/kg/year	NA	12
Fort Rucker SWMU 14	Closed	TPH, BTEX	TPH, 25,000 avg; BTEX, 10 avg	$3	NA	NA	TPH, 16.9; BTEX, ND	Effective	12

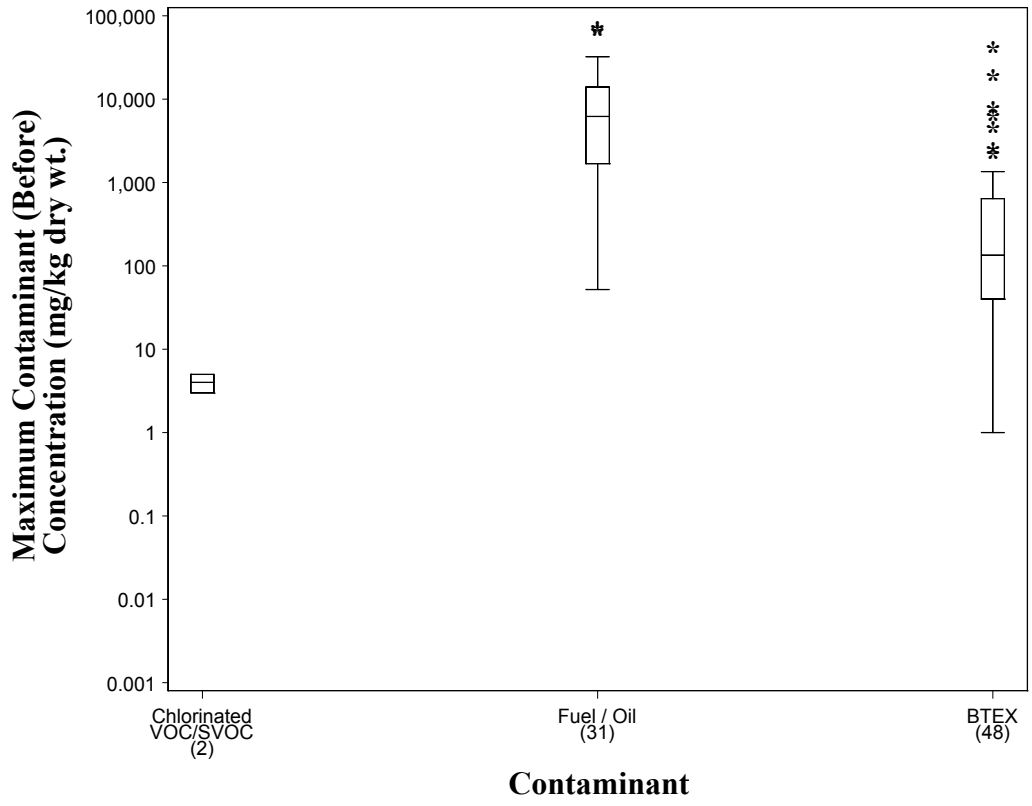
B = benzene
T = toluene
E = ethylbenzene
X = xylenes
A = acetone
CB = chlorobenzene
N = naphthalene
TPH = total petroleum hydrocarbons
DCA = dichloroethane
TRPH = total recoverable petroleum hydrocarbons
VOC = volatile organic compound
NA = not available

*One site included in Appendix B was not included in this table due to insufficient information. The excluded site is Site ID No. 08-006.

Table 3-15. Concentrations of Contaminants of Concern Before and After Conventional Bioventing: Data Used to Generate Figure 3-15

	Concentrations of Contaminants of Concern							
	Chlorinated VOC/SVOC		BTEX		Fuel / Oil		PAH, Creosote	
	Before Treatment (2 sites)	After Treatment (2 sites)	Before Treatment (48 sites)	After Treatment (35 sites)	Before Treatment (31 sites)	After Treatment (17 sites)	Before Treatment (1 site)	After Treatment (1 site)
Median:	4	0	134	6	6,190	960	120	0
25th Percentile	3	0	41	0	2,055	30	120	0
75th Percentile	4	0	635	59	13,600	2,600	120	0
High whisker[(a)]	5	NA	1,350	80	25,000	3,900	NA	NA
Low whisker[(a)]	NA	NA	1	NA	52	4	NA	NA

(a) High and low whiskers represent the most extreme data point within 1.5 interquartile ranges, i.e., 1.5 times the distance between the 25th and 75th percentiles.



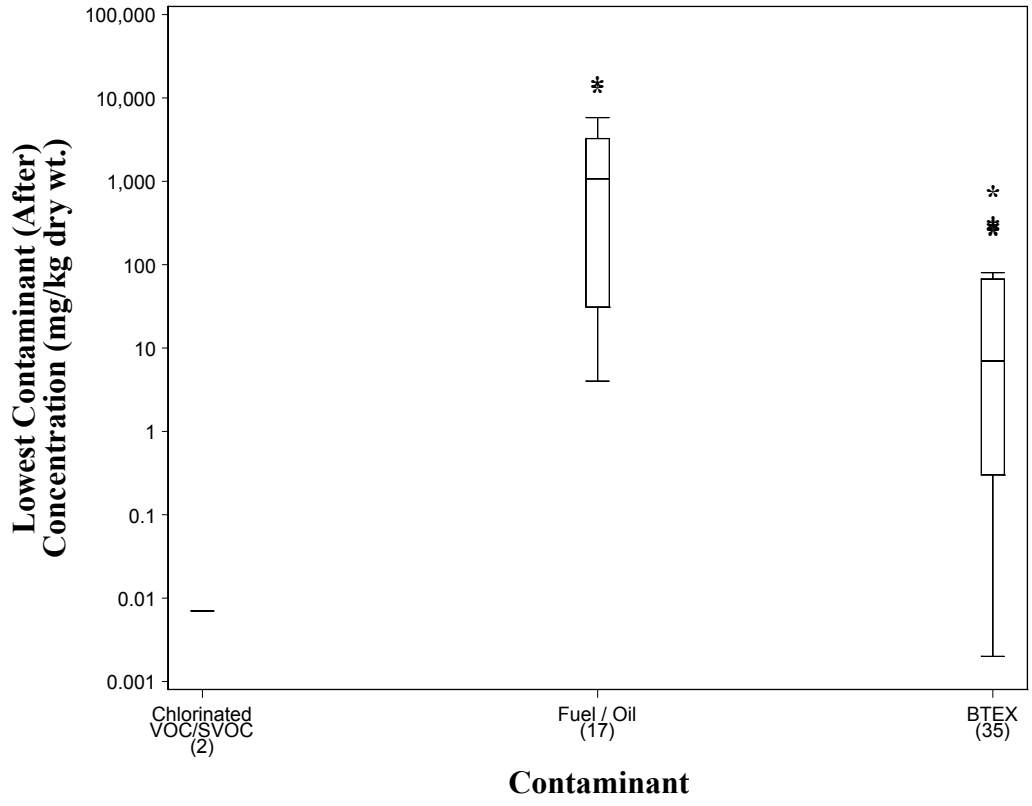


Figure 3-15. Box and Whisker Plots Showing the Range of Contaminant Concentrations Before and After Conventional Bioventing (See Appendix B for data used to generate these plots)

Overall, conventional bioventing performance has been shown to be highly effective and reliable if sufficient time is provided to complete removal. Problems with system performance occur when bioventing systems are viewed as being identical to SVE systems, requiring relatively short time periods to complete remediation. While BTEX compounds will be removed within this time period, the higher-molecular-weight compounds are unlikely to be significantly impacted. Further research is necessary on chlorinated solvent remediation to adequately assess system performance when treating these compounds.

Based on U.S. Air Force and commercial applications of this technology, the total cost of *in-situ* soil remediation using conventional bioventing technology is $10 to $60/cu yd (Downey et al., 1994). At sites with over 10,000 cu yd of contaminated soil, costs of less than $10/cu yd have been achieved. Costs greater than $60/cu yd are associated with smaller sites or those using amendments, but bioventing still can offer significant advantages over more disruptive excavation options. O&M costs are minimal, particularly when on-site personnel perform the simple system checks and routine maintenance that are needed. Table 3-16 provides a detailed cost breakdown of remediation of 5,000 cu yd of soil contaminated with an average concentration of 3,000 mg of JP-4 jet fuel per kg of soil.

Table 3-16. Typical Full-Scale Conventional Bioventing Costs (Downey et al., 1994)

Task	Total Cost ($)
Site Visit/Planning	5,000
Work Plan Preparation	6,000
Pilot Testing	27,000
Regulatory Approval	3,000
Full-Scale Construction	
Design	7,500
Drilling/Sampling[1]	15,000
Installation/Startup	4,000
2-Year Monitoring	6,500
2-Year Power	2,800
Soil Sampling at 2 Years	13,500
Total	**90,300**

[1]Assumes four air injection wells drilled to a depth of 15 ft.

Ward (1992) compared costs of conventional bioventing to other *in-situ* bioremediation technologies (Table 3-17). Costs shown in Table 3-17 reflect actual costs for these three technologies at fuel spills at Traverse City, Michigan. Even though the area treated through bioventing was larger than that treated with hydrogen peroxide or nitrate, total costs for bioventing were significantly lower than for the other technologies.

Table 3-17. Cost Comparison of *In-Situ* Bioremediation Technologies Utilized at Fuel Spill Sites (Ward et al., 1992)

Task	Total Costs ($/m^3 of Contaminated Earth)		
	Hydrogen Peroxide Addition	Nitrate Addition	Conventional Bioventing[1]
Construction[2]	45	118	26
Labor/Monitoring	72	96	40
Chemicals	500	30	0.44
Electricity	24	12	6.8
Total	**641**	**256**	**73**

[1]Values reflect only first 4 months of demonstration.
[2]Prorated to a 5-year service life on buildings, pumps, and blowers.

3.1.6 Enhanced Bioventing

Enhanced, or cometabolic, bioventing is a variation of conventional bioventing that involves the addition of a cometabolic substrate within an air stream. Addition of nutrients (N, P, and K) may also be required. The cometabolic substrate promotes aerobic growth and the subsequent cometabolic degradation of the contaminant of interest. As an aerobic process, cometabolic bioventing can use compressed air and the growth substrate is provided as a vapor at low percent levels. As far as physical appearance and schematic views, cometabolic bioventing looks the same as conventional bioventing. The only difference is that instead of injecting air alone into the subsurface, a cometabolic substrate (i.e., propane or methane) is also injected.

3.1.6.1 Principles of Operation

Cometabolism is a biological process that involves the fortuitous degradation of CAHs by bacteria during the degradation of an organic cosubstrate. For the purposes of this application, this discussion focuses on the cometabolism of CAHs. Bacteria that grow on hydrocarbons typically initiate oxidation by incorporating molecular oxygen into organic compounds by the action of enzymes known as oxygenases (Wackett and Householder, 1989). Two types of oxygenases, monooxygenases and dioxygenases, are involved in the cometabolic oxidation of CAHs. The mono- and dioxygenases are relatively nonspecific with respect to the type of organic compounds that they will attack, and bacteria that use these oxygenases for the degradation of a growth substrate often accidentally attack secondary substrates, such as CAHs.

A variety of growth substrates have been used to stimulate cometabolic CAH degradation, including aromatic compounds (e.g., toluene and phenol), methane, butane, propane, and propene. Ammonia oxidation is also known to stimulate cometabolic CAH degradation. Among the organic cosubstrates, methane, butane, propane, and propene are gaseous carbon compounds under ambient conditions and can be introduced with air to supply both carbon and oxygen for biological growth. Each of these gaseous compounds is nontoxic and biodegrades rapidly under aerobic conditions. Because this is an aerobic process, cometabolic bioventing does not require the displacement of oxygen in the vadose zone. In fact, the primary differences between cometabolic bioventing and conventional bioventing are the addition of the cometabolic cosubstrate at low percent levels and subsequent monitoring requirements. Consequently, cometabolic bioventing can use much of the same equipment and methods as conventional bioventing. Some exceptions include enhanced safety regulations, such as the use of steel pipe instead of PVC pipe to carry the mixed gas stream, aboveground monitoring for potentially explosive gases, and

other similar safety measures. The emphasis on safety cannot be overstated. The use of flammable or potentially flammable gas mixtures in vadose zone soils presents significant, unique safety concerns if any cometabolic growth substrate has not degraded before air exits the vadose zone.

3.1.6.2 Target Contaminants

Chloroethenes, chloroethanes, and chloromethanes are the most extensively studied compounds for cometabolism; exceptions include PCE and carbon tetrachloride, neither of which can be oxidized aerobically. A typical application of cometabolic bioventing could be the addition of methane or propane to promote the growth of methanotrophs or propane-degrading bacteria, respectively, and the cometabolic degradation of TCE or lower chlorinated ethenes.

3.1.6.3 Advantages and Limitations

Cometabolic bioventing has several advantages over conventional remediation technologies, combining the benefits of bioventing with the added value of cometabolic activity. Specific advantages include:

- The cometabolic component allows for enhanced biodegradation of CAHs, thus reducing vapor emissions and potentially increasing the degree of remediation attainable. Cometabolism achieves mineralization of the CAHs and does not result in the production of toxic byproducts or the transfer of contaminants to another matrix such as granular activated carbon (GAC), as is the case with SVE combined with off-gas treatment using GAC.

- Conceptually, cometabolic bioventing is a simple process that uses commercial, off-the-shelf equipment. The bioventing component requires standard air compressors or blowers that can deliver air to the subsurface efficiently and at relatively low flowrates. To enhance cometabolism, the process requires the addition of a gaseous cosubstrate (such as methane or propane) that is widely available and for which no special preparation is needed before use.

Limitations of cometabolic bioventing do exist and require thorough evaluation prior to the wide-scale implementation of this technology. Some uncertainties about long-term effectiveness remain, as is the case with any technology, but proper monitoring and evaluation can mitigate these uncertainties. Specific limitations include:

- Similar to most remedial technologies, the effectiveness of cometabolic bioventing can be limited by soil heterogeneities at a site (i.e., differing permeabilities). In fact, minimal differences in soil permeabilities may lead to areas within a site that are not treated as rapidly as more permeable portions of the vadose zone.

- Cometabolic bioventing uses potentially explosive gas mixtures that require extra safety precautions to protect workers and the public.

- The use of cometabolic growth substrate should be tested in the laboratory before field testing to ensure that a bacterial population is present to catalyze the desired reactions for this process.

- Very high CAH concentrations could be inhibitory to the growth of bacteria.

- Off-gas control may be required when injecting air into the subsurface to ensure that CAHs are not volatilized and released into the atmosphere.

Although the above challenges can be overcome technically, the driving force will be the economics of the process and the potential to develop a cost-effective process that can compete with conventional technologies such as excavation and SVE.

3.1.6.4 Technology Cost Drivers

Major cometabolic bioventing cost drivers are similar to conventional bioventing cost drivers, except for the addition of a cometabolic growth substrate. Major cometabolic bioventing cost drivers in addition to bioventing cost drivers include:

- The cost of the cometabolic growth substrate and additional plumbing and capital costs to support the addition of the growth substrate

- Pilot tests (as needed) to demonstrate the efficacy of the cometabolic process

- Explosive growth substrates (e.g., methane, propane, or butane) require unique safety features to prevent explosive conditions; these may include flame or spark resistant materials, preventative measures to ensure that explosive conditions to not exist above ground,and automatic shutdown controls in the event of a system failure, to name but a few.

3.1.6.5 Technology Performance and Cost

EPA/NRMRL, the Environmental Security Technology Certification Program (ESTCP), and Battelle are testing the use of cometabolic bioventing using propane as the primary growth cosubstrate to promote the biodegradation of TCE in vadose zone soils at Hill AFB, UT. Performance and cost data are not yet available for this site.

ESTCP, Battelle, and Oregon State University employed cometabolism to treat TCE-contaminated groundwater at McClellan AFB (MAFB), CA. Although this site involved the treatment of groundwater and saturated soils, it is presented here as an example case study of the treatment of CAHs using cometabolism (Lynch et al., 2001). Furthermore, because propane and CAH contaminants enteredhe vadose zone during the sparging process, cometabolic degradation in the vadose zone also hadthe potential to enhance CAH removal from the site. The MAFB pilot demonstration usedpropane and methane as growth substrates to treat TCE-contaminated groundwater. Performance of this technology at MAFB is summarized below:

- For the first 500 days of treatment, propane was added as the cometabolic substrate. However, there was no sign of propane degradation or cometabolic CAH degradation in the vadose zone throughout the propane feed period, despite the presence of active propane degradation and cometabolism in the saturated zone.

- Methane was used as the substrate from approximately day 500 to day 550. In several monitoring points, propane, TCE, and *c*-DCE were depleted concurrently with methane, and in one well TCE and *c*-DCE were reduced to below detection limits, indicating degradation of these compounds by cometabolism.

- Microcosm studies demonstrated that propane-degrading bacteria was present at the site. The fact that these bacteria were present and cometabolism did not occur in the vadose zone suggests the following observations:

- The presence of propane-, methane-, or other substrate-degrading bacteria does not necessarily imply that cometabolic CAH degradation will ensue. CAH degradation rates varied widely in microcosms using soils from different sites despite the presence of active propane degradation in all microcosms.

- Microcosm and other pilot-scale studies are integral to successful implementation of cometabolic bioventing due to the need to establish the presence and activity of indigenous, substrate-degrading bacteria.

While these results show that cometabolism can be used for site restoration, it also reinforces the fact that site-specific microcosm testing is required to verify the presence of microorganisms and microbial processes of interest. Until this technology becomes widely used, field pilot testing is warranted to adequately demonstrate the process viability for any given site.

Table 3-18 provides a summary of various full-scale enhanced bioventing installations, including information on contaminant type and concentrations, target cleanup levels, and status of site cleanup (See Appendix B for the data used to generate Table 3-18). Figure 3-16 shows box and whisker plots for contaminants treated using enhanced bioventing, as reported in Appendix B. Figure 16a presents the range of contaminants before treatment, while Figure 16b illustrates their range after treatment. Table 3-19 illustrates the data used to generate Figure 3-16. Information provided in the tables and figures in this section reflects an inability to gather complete data on all sites, either from a reluctance of site owners to impart the information or from missing site data.

Table 3-18. Summary of Site Characteristics at Enhanced Bioventing Installations

Site Name	Site Status	Contaminants of Concern	Maximum Contaminant Concentrations (mg/kg dry weight)	Unit Cost (per CY)	Numerical Treatment Goals (mg/kg dry weight)	Treatment Goals Achieved	Concentration Achieved (mg/kg dry weight)	Treatment Effectiveness	Treatment Duration (Months)
Former Bulk Terminal	Closed	Diesel	33,000	$56	100 TPH	Yes	10	NA	24
NY State Dept.	Active	DCE, A, MEK, TCE	20 TCE; 4.8 DCE; 7.4 MEK; 15 A	$390	TCE: 1.5, DCE: 0.6; MEK: 0.6; A: 0.2	Yes	< 0.005 TCE and DCE; < 0.05 MEK and A	NA	5
Northrop-Hawthorne	Closed	TRPH	20,000	$18	100	NA	NA	NA	NA
BNRR Fueling Pump House	Closed	No. 2 diesel fuel, TPH, BTEX	52,000 TRPH	$10	NA	Yes	5,000 TRPH; 73 total BTEX (benzene ND)	60%	24
Oakland Chinatown	Closed	BTEX; TPH	BTEX: 100; TPH: 5000	$90	0.05 BTEX; 100 TPH	Yes	50 TPH	NA	18
Turtle Wax Car Wash	Closed	B, BTEX	29,393 BTEX; 181 B	$60	16 BTEX; 0.25 B	Yes	14 BTEX;0.16 B	NA	48
US Coast Guard Air Station	Closed	Gasoline, JP-4 jet fuel	NA	$73	NA	NA	<0.1 JP-4; <0.2 gasoline	60% fuel removed in 4 months.	4
van Oss	Closed	Mineral oil	< 5,000	$106	900	Yes	< 490	all below goal.	10

B = benzene
T = toluene
E = ethylbenzene
X = xylenes

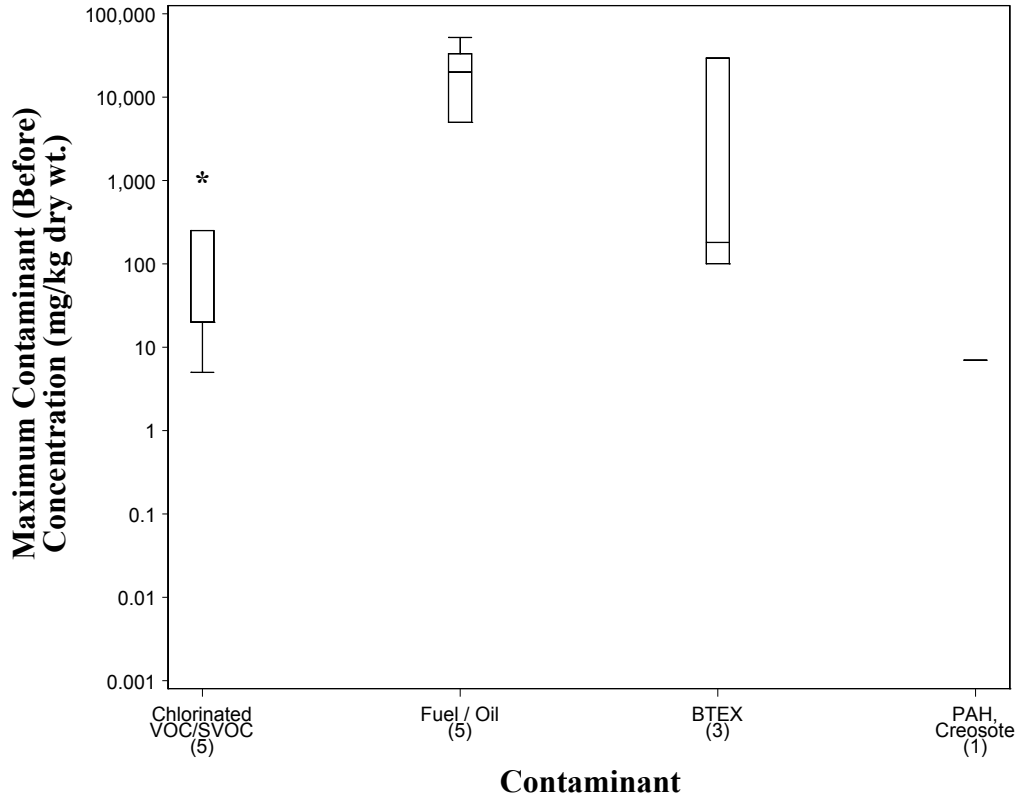
A=acetone
MEK = methyl ethyl ketone
DCE = dichloroethylene
TCE = trichloroethylene

TRPH = total recoverable petroleum hydrocarbons
TPH = total petroleum hydrocarbons

Table 3-19. Concentrations of Contaminants of Concern Before and After Enhanced Bioventing: Data Used to Generate Figure 3-16

	Concentrations of Contaminants of Concern							
	Chlorinated VOC/SVOC		BTEX		Fuel / Oil		PAH, Creosote	
	Before Treatment (5 sites)	After Treatment (5 sites)	Before Treatment (3 sites)	After Treatment (4 sites)	Before Treatment (5 sites)	After Treatment (6 sites)	Before Treatment (1 site)	After Treatment (1 site)
Median:	20	0.25	181	7	20,000	30	7	0
25th Percentile	7	0.01	104	0.2	5,000	3	7	0
75th Percentile	250	0.25	14,787	29	33,000	380	7	0
High whisker[(a)]	NA	NA	29,393	NA	52,000	490	NA	NA
Low whisker[(a)]	5	NA	100	NA	NA	NA	NA	NA

a) High and low whiskers represent the most extreme data point within 1.5 interquartile ranges, i.e., 1.5 times the distance between the 25th and 75th percentiles



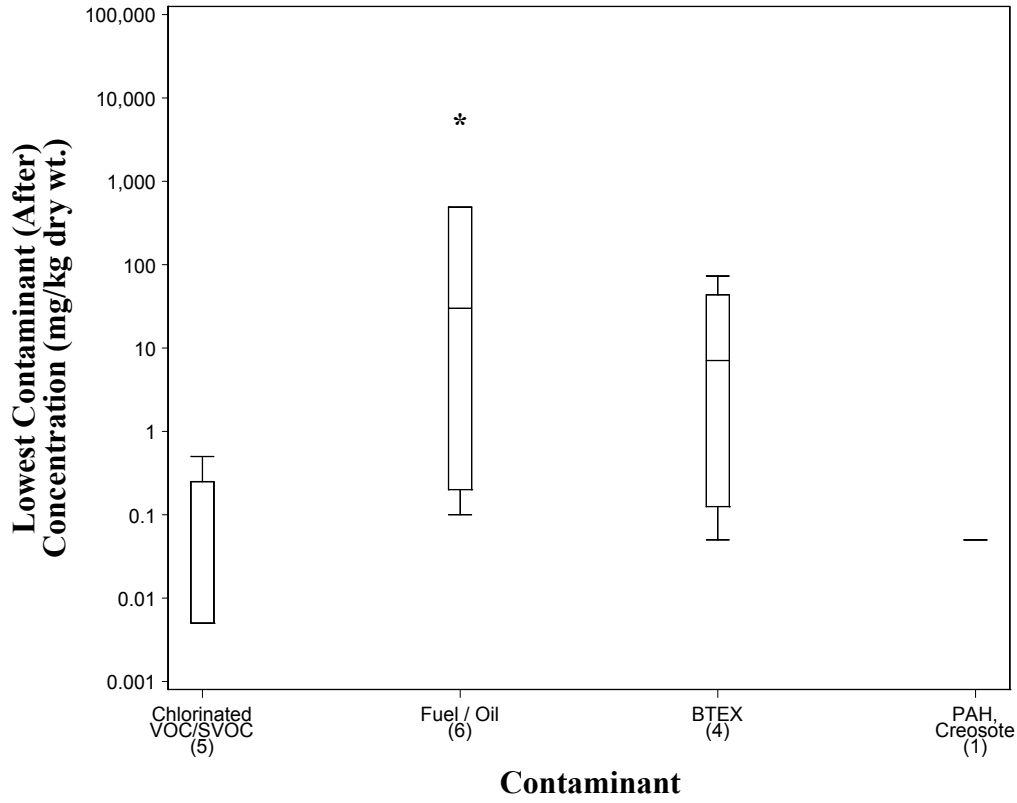


Figure 3-16. Box and Whisker Plots Showing the Range of Contaminant Concentrations Before and After Enhanced Bioventing (See Appendix B for data used to generate these plots).

3.1.7 Bioslurping

Bioslurping is primarily used for rapid and effective removal of LNAPL floating on the water table and is applicable to most hydrocarbon releases that result in a significant layer of free-phase petroleum product. The technology consists of applying a strong vacuum capable of supporting multiphase extraction from aquifer sediments. Free product, groundwater, and soil vapor are extracted together through a manifold system and separated above ground. Free product is typically recycled, and water and vapor streams usually require treatment prior to discharge. An operating bioslurping system is shown in Figure 3-17, and Figure 3-18 is a schematic illustrating how bioslurpers work.

Figure 3-17. Bioslurping

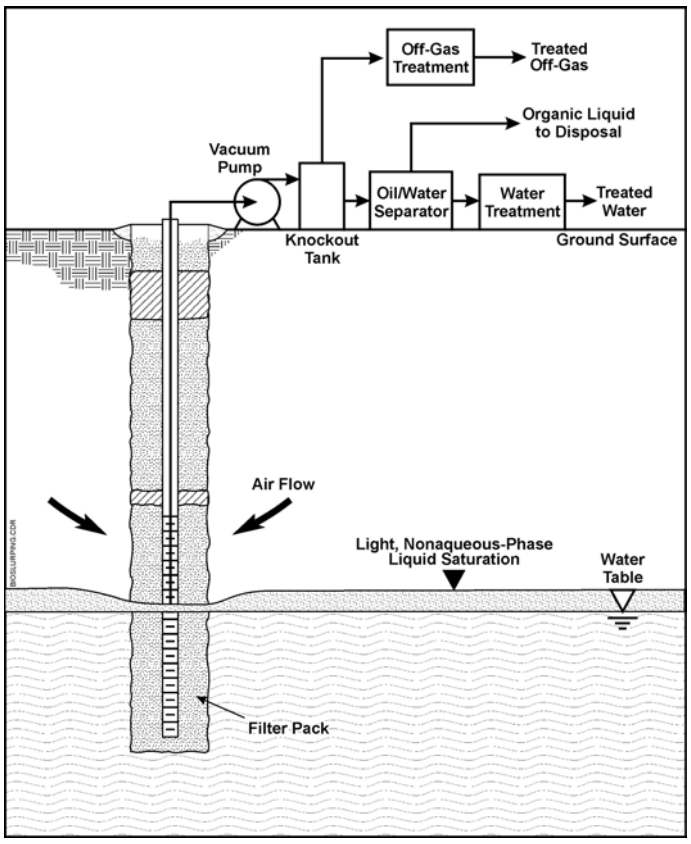


Figure 3-18. Bioslurping Schematic

Bioslurping is described here because the soil vapor convection imposed by a bioslurping system creates an oxygen-rich environment in the vadose zone concomitant with free product removal and performs as a bioventing system above the water table. Indeed the "bio" component of bioslurping is bioventing. (The "slurping" moniker is derived from the liquid extraction process that typically occurs in slugs, much like slurping liquid from a straw in an almost-empty glass.) After recoverable free product has been removed from the water table, a bioslurping system is easily transformed into a standard bioventing system to bioremediate residual soil contamination. While bioslurping systems are designed with free product removal as the primary objective, life cycle designs incorporate the likely eventual conversion of the system to bioventing only.

3.2 BIOREMEDIATION TECHNOLOGIES AND THEIR APPLICATIONS – EMERGING TECHNOLOGIES

This section describes emerging technologies with respect to their principles of operation and the types of contaminants for which they may be appropriate. General cost and performance data reported in the literature are provided, if available, but because these technologies have not yet evolved to significant full-scale use, full-scale cost and performance data are generally not available in the literature. The technologies discussed in this section include anaerobic bioventing**,** phytoremediation, sequential anaerobic/aerobic treatment, and natural attenuation.

3.2.1 Anaerobic Bioventing

Anaerobic bioventing is the injection of anaerobic (i.e., oxygen-free) gases into the vadose zone to establish an anaerobic environment by displacing the oxygen-rich soil gas. Common gases used for this purpose include nitrogen (N_2) and argon (Ar). The anaerobic gas is infused with hydrogen (H_2) gas to supply an electron donor and promote reductive dechlorination of the chlorinated hydrocarbons. Practical applications of anaerobic bioventing include remediating vadose zone soils contaminated with PCE or TCE, such as those commonly found at dry-cleaning facilities.

Technology Description. Anaerobic bioventing is comparable to aerobic bioventing with the exception that a gaseous blend that promotes anaerobic conditions is injected into the vadose zone in lieu of air or pure oxygen (O_2). As with conventional bioventing, gaseous uptake must be monitored. In the case of anaerobic bioventing, H_2 takes the place of oxygen and H_2 utilization rates are measured in place of oxygen utilization rates. The goals of anaerobic bioventing are to reduce O_2 in the soil in the pore spaces of the contaminated vadoze zone through displacement with an inert gas, and to lower the redox level and promote reductive dechlorination by providing an electron donor in the form of H_2.

If the electron donor is molecular hydrogen, the sequential reactions are as follows for PCE dechlorination to DCE:

$$\mathrm{PCE} + \mathrm{H_2} \rightarrow \mathrm{TCE} + \mathrm{HCl} \quad (2)$$

$$\mathrm{TCE} + \mathrm{H_2} \rightarrow \mathrm{DCE} + \mathrm{HCl} \quad (3)$$

Similar dechlorination reactions can be expected for other halogenated hydrocarbons including aliphatic and aromatic compounds. Further dechlorination of DCE to VC and ethene may be possible, but are likely to involve reduced dechlorination rates and consequently longer bioventing requirements. Longer acclimation periods also could be expected for DCE and VC dechlorination than for PCE and TCE dechlorination. Alternatively, DCE and VC could be degraded aerobically or cometabolically. Although this approach has not yet been tested, aerobic degradation of the PCE and TCE dechlorination byproducts could be promoted by exchanging the anaerobic gas for air or pure O_2 after the reductive dechlorination process becomes rate limiting.

Advantages and Limitations. Anaerobic bioventing has several advantages over conventional remediation technologies, combining the benefits of bioventing with the added value of anaerobic dechlorination. Specific advantages are described in the following paragraphs:

- Reductive dechlorination of CAHs should reduce vapor emissions and potentially increase the degree of remediation attainable.

- Aerobically recalcitrant compounds can be treated *in situ*, without relying on extraction and off-gas treatment and disposal. Contaminants can be reduced to nontoxic byproducts through careful application of the anaerobic process to ensure complete dechlorination, or through anaerobic/aerobic sequencing to promote the dechlorination of higher-chlorinated compounds and the subsequent aerobic degradation of the dechlorination byproducts.

- This is an emerging technology that has the potential to offer a cost-effective means of cleaning up chlorinated hydrocarbons in vadose zone soils. Because this approach has many similarities to that of aerobic bioventing, conventional bioventing equipment and knowledge can be used to develop this technology and apply it in the field. The exception is that extra safety precautions

must be taken when working with compressed H_2 gas in the field. Additional work is needed to develop a more economical way to scrub O_2 from air.

Limitations of anaerobic bioventing exist and require thorough evaluation prior to the wide-scale implementation of this technology. Some uncertainties about long-term effectiveness remain, as is the case with any technology, but proper monitoring and evaluation can mitigate these uncertainties. Specific, disadvantages include the following:

- Similar to most remedial technologies, the effectiveness of anaerobic bioventing can be limited by soil heterogeneities at a site (i.e., differing permeabilities). In fact, minimal differences in soil permeabilities may result in non-uniform distribution of injected gases. This nonuniform distribution may lead to areas within a site that are not treated as rapidly as more permeable portions of the vadose zone, or in zones that remain aerobic.

- Reductive dechlorination of CAHs generally requires an acclimation period for bacterial growth or to otherwise stimulate the dechlorination process. Sequential acclimation periods may be required for parent compounds and their daughter products. The length of an acclimation period may be able to be predicted using laboratory microcosms, but differences in the field should be anticipated.

- Incomplete dechlorination can result in the production of undesirable byproducts; in the case of PCE treatment, dechlorination can result in the production of DCE isomers and VC.

- Anaerobic bioventing uses potentially explosive gas mixtures that require extra safety precautions to protect workers and the public.

- Because anaerobic bioventing is in a relatively young stage of development, its potential for cost savings remains unknown.

- The use of anaerobic bioventing requires further field testing to demonstrate its effectiveness. Site-specific pilot testing also may be required.

- Very high CAH concentrations could be inhibitory to the growth of anaerobic bacteria.

- Off-gas treatment and control may be required when injecting gases into the subsurface to ensure that CAHs are not volatilized and released into the atmosphere. Controlling the rates of gas injection will minimize the need for off-gas treatment and control.

Although the above challenges can be overcome technically, the driving force will be the economics of the process and the potential to develop a cost-effective alternative that can compete with conventional technologies such as excavation and SVE.

Performance. EPA NRMRL and Battelle are testing anaerobic bioventing in the field at Salina, KS, and at Hill AFB, UT. There are strong indications that the injection of a N_2/H_2 gas mixture into the vadose zones of these sites displaced the O_2 in the soil gas and lowered redox potentials. As of the writing of this report, additional performance data were unavailable.

3.2.2 Phytoremediation

Phytoremediation is an emerging treatment technology that utilizes plants, plant microbial systems, soil amendments, and agronomic techniques to remove, stabilize, and/or degrade environmental contaminants. Figure 3-19 shows a phytoremediation plot in the field at an MGP site in Bedford, IN. The technology takes advantage of the natural hydraulic and metabolic processes of plants, resulting in a technology that is passive and driven by solar power. Phytoremediation may be employed exclusively or in tandem with conventional treatment technologies to remediate soil and groundwater contaminated with heavy metals, pesticides, chlorinated solvents, explosives, crude oil, PAHs, and landfill leachate.

Figure 3-19. Phytoremediation

Phytoremediation is a broad term that describes a number of mechanisms that are defined by plant systems. These mechanisms described below are illustrated schematically in Figure 3-20. Phytoremediation may involve plant uptake of contaminants, or it can exploit enhanced biological activity associated with the rhizosphere. In general, these two treatment modes are governed by the physical characteristics of the contaminant(s) of concern. The water solubility and soil sorption capacity are two major chemical characteristics that influence the phytoremediation of pollutants. Water-soluble inorganic pollutants and those organic pollutants with intermediate log K_{ow}s (approximately 1-4 L/g) are taken up by roots and are considered to be good targets for phytoremediation. Organic pollutants that fall outside this range are not readily taken up by plants and are targets for extracellular plant enzymes or microbiota associated with the rhizosphere. The following phytoremediation mechanisms are described below:

- Phytostabilization
- Phytoaccumulation/phytoextraction
- Phytotransformation/phytodegradation
- Hydraulic control
- Rhizodegradation
- Rhizofiltration.

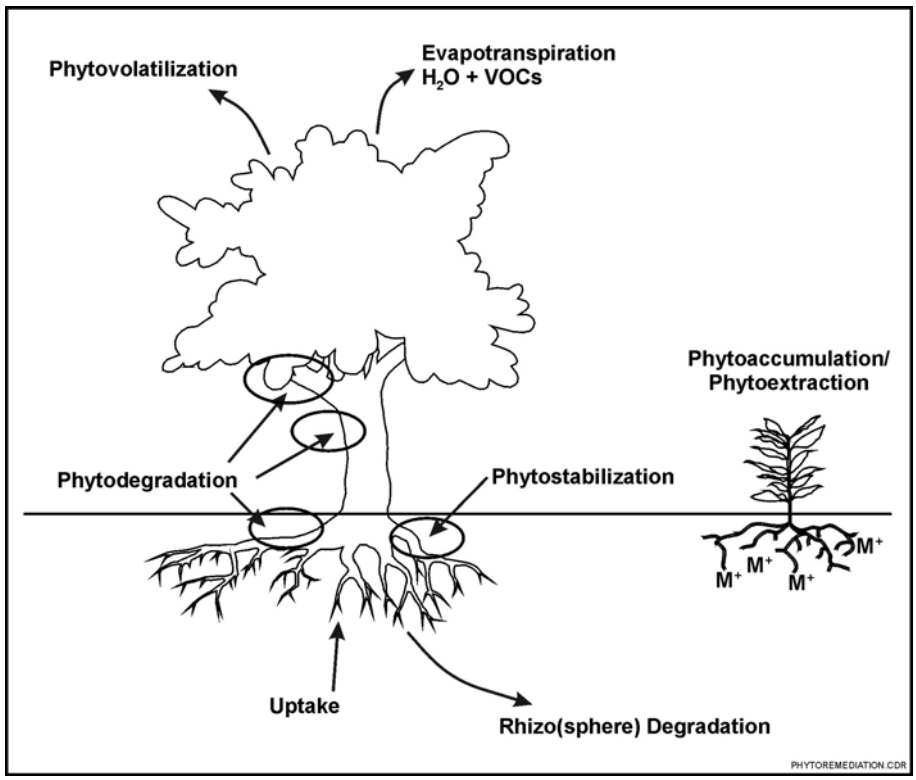


Figure 3-20. Phytoremediation Schematic

Phytostabilization is the use of plants to increase sequestration of contaminants (heavy metals and hydrophobic organics) in soil. Soil sequestration occurs as plants alter water flux and reduce contaminant mobility. Plants and microbial enzymes bind contaminants into soil (humification). Plants also incorporate free contaminants into plant roots (lignification) and prevent wind and rain erosion.

Phytoaccumulation/Phytoextraction uses specific plant species to absorb unusually large amounts of metals. This mechanism is typically used for remediation of soils and groundwater contaminated with heavy metals (Pb, Cd, Zn, As, Cu, Cr, Se, and U). Uptake plants may be harvested and later ashed.

Phytotransformation/Phytodegradation is the process where plant enzymes completely mineralize or partially break down contaminant compounds such as herbicides (atrazine, arochlors), aromatics (BTEX), chlorinated aliphatics (TCE), nutrients (NO_3, NH_4, PO_4), and ammunition wastes.

Hydrologic Control (organic pumps)/phytovolatilization is the use of plants to control the migration of contaminants in groundwater by exploiting their natural hydraulic properties. This application can result in chemical uptake and transpiration of chemicals through the leaf tissue.

Rhizodegradation is the process whereby plant roots excrete sugars, acids, and alcohols that microorganisms in the rhizosphere utilize for food. Through biostimulation or cometabolism, microorganisms subsequently degrade organic contaminants such as pesticides, aromatics, and PAHs.

Rhizofiltration utilizes plant root systems developed hydroponically to remediate contaminated waste streams that are directed through the root mass; alternatively, plant root systems may be encouraged to develop *in situ* in contaminated saturated zones to uptake contaminants from contaminated waste streams

or leachate beds. Rizofiltration typically is used for heavy-metal-contaminated water and landfill leachates.

Each of these mechanisms has been demonstrated with varying levels of success. Most sites involve more than one mechanism, and most studies, particularly field studies, cannot easily distinguish between the different mechanisms that contribute to overall site remediation. Of the mechanisms described above, phytostabilization, phytoaccumulation/phytoextraction, phytotransformation/phytodegradation, and rhizodegradation may be used for soils treatment. However, while hydrologic control and rhizofiltration are confined to groundwater or surface water wastes, they also may contribute to lessening the amount of contaminant infiltration through soils.

3.2.2.1 Advantages and Limitations

Phytoremediation can be a cost-effective treatment because it is an *in-situ* technology that is passive and solar driven. It can be employed for a wide variety of environmental contaminants and provides an aesthetically pleasing site appearance. It is a relatively unobtrusive application with site soils remaining in place, and, unlike chemical treatment technologies, will not alter soil characteristics.

The technology is limited to the ability of the plants of choice to be subjected to abnormal environments where contaminant concentrations must remain below the toxicity threshold to maintain a healthy plant population. For applications that involve contaminant uptake through plant root systems or for applications that utilize the rhizosphere, roots must be able to reach to the vicinity of contamination, which at some sites and for some plants may be limited to surface soils. Several growing seasons may be needed so that the plant(s) of choice may reach a level of maturity required for the remedial process.

There is growing concern about the use of non-native species for phytoremediation. Native species or species that will not threaten the existing biodiversity in the vicinity of the site should be used. This restriction could limit the optional selection of plants to meet site-specific cleanup requirements.

3.2.2.2 Technology Performance

Unfortunately, insufficient field data are available to evaluate phytoremediation performance. For those field studies that have been completed, phytoremediation has not been an effective remedial strategy for soils under most circumstances. While phytoremediation seems to be a good technique for hydraulic control of groundwater, it does not appear to be an effective stand-alone technology for cleanup of contaminated soils. At sites where there is no danger of contaminated soils impacting the population, phytoremediation may be a good long-term option for eventual cleanup. The fact that phytoremediation has not worked well to date to remediate soils limits its use in the field at full scale, and keeps phytoremediation in the emerging technology category of this report. The following four issues generally must be addressed to gain regulatory acceptance of phytoremediation at a site (Rock and Sayre, 1999):

- Provide site-specific evidence for the effectiveness of phytoremediation using site soils and contaminants; this includes laboratory and/or greenhouse evidence

- Adequate containment of contaminated soils must be assured; plants must establish themselves to a point where they contain/degrade the contaminants of interest.

- Site monitoring must address the fate of contaminants in soils and plants; monitoring the efficacy of an innovative treatment such as phytoremediation tends to be more extensive than is required for more conventional technologies

- If phytoremediation is attempted, but does not succeed, an adequate backup plan with a high chance of success must be in place.

To implement phytoremediation at field scale, the current database must be expanded to show contaminant-specific field rates and extent of activity of the various phytoremediation mechanisms. More information is needed that outlines specific data on plants and their interactions with contaminants under different climatic conditions. In addition, regulators need a standardized monitoring system. Currently, there is no consensus from the scientific community as to what parameters should be considered critical measurements (Rock and Sayre, 1999).

Numerous research teams, private companies, and government agencies have been working to advance phytoremediation for soil applications. A variety of contaminant applications have been investigated over recent years. One of the more extensively studied forms of phytoremediation is phytoextraction. Private companies and industry have implemented phytoextraction in the field. One such company, formally known as Phytotech Inc., dedicated its practice to the application of lead remediation using *Brassica juncea* to achieve high metal accumulation rates. In a Brownfield demonstration in Trenton, NJ, Phytotech used *B. juncea* combined with soil amendments to reduce the average soil surface lead concentrations by 13%. The target soil concentration of 400 mg/kg was achieved in approximately 72% of the treated area in one cropping season (Blaylock et al., 1999). Another pilot-scale demonstration was conducted to extract uranium from contaminated soil at a former DOE facility in Ashtabula, OH (no data available) (Zodrow, 1999). Additional site-specific case studies can be found in Appendix B.

Bench-scale research has shown that plants are capable of enhancing the mineralization rate of a variety of herbicides, such as atrazine and methoxychlor (Burken and Schnoor, 1996; Kruger et al., 1997). Soils in the rhizosphere of Kochia plants were shown to degrade atrazine by 62% after 36 days over that of nonvegetated controls. Other rhizospheric soils capable of atrazine degradation included mush thistle, catnip, foxtail barley, witchgrass, and lambsquarter (Elsevier, 1996). Others have shown the ability of plants to facilitate the degradation of other hazardous organic compounds in the rhizosphere including 2,4-D, Diazinon, PAHs, and TCE (Anderson et al., 1993; Shann, 1995).

Researchers at Kansas State University conducted greenhouse studies to determine the effect of the rhizosphere on PAH-contaminated soil. The rate of PAH removal was compared in rhizosphere soil, nonrhizosphere soil, and sterile soil. Non-rhizosphere soil contained no roots but was spiked with root exudate to mimic the carbon contribution to the rhizosphere that normally occurs in whole root systems. The results showed that after 180 days soils with plants had more than twice the mineralization rate than soils without plants, indicating that the presence of plants is a necessary part of the phytoremediation process. Simple exudation of organic compounds did not fully mimic the presence of roots (Banks et al., 1996).

Others have found that vegetation can be actively used to promote microbial degradation of TCE (Walton and Anderson, 1990; Brigmon et al., 1999). Significantly higher levels of TCE-degrading cultures were found in the rhizosphere of TCE-contaminated soils than in nonvegetative contaminated soils. This increase in TCE degradation in the rhizosphere indicates that plant root/microbial interaction had a significant role in enhancing TCE removal.

Researchers have found that red mulberry (*Morus rubra L.*) roots release phenolics into soils and that these compounds can serve as carbon sources for the growth of PCB-degrading bacteria (Hedge and Fletcher, 1996).

3.2.3 Sequential Anaerobic/Aerobic Treatment

For soils, anaerobic biodegradation involves the dechlorination of halogenated hydrocarbons, such as PCBs, dioxins and furans, and pesticides. Anaerobically, these compounds undergo microbially catalyzed reductive dechlorination, which removes chlorine substituents from the more highly chlorinated congeners and replaces them with hydrogen atoms. Reductive dechlorination is a well-understood process that has been studied extensively in the laboratory for soils and sediments contaminated with PCBs, chlorinated pesticides, and CAH. For PCBs, it has seen limited field application due to limitations in the extent of PCB dechlorination, and because destruction removal efficiencies usually are insufficient to meet treatment goals for PCBs. However, by shifting the congener distribution to less chlorinated analogs, the overall toxicity of the mixture is typically reduced and the mixture becomes more susceptible to aerobic degradation. For pesticides and herbicides, anaerobic/aerobic sequential treatment faces similar problems with respect to achieving cleanup goals. For CAHs, anaerobic or ex situ processes have difficulty competing with more conventional technologies like SVE.

In general, PCB reductive dechlorination preferentially removes chlorines from the *meta* and *para* positions and replaces them with hydrogen atoms, resulting in substantial reductions in carcinogenicity and "dioxin-like" toxicity, which tends to coincide with meta-chlorinated PCBs. In addition to lowering the overall toxicity of PCB-contaminated materials, the tendency of the PCB mixture to bioaccumulate is also reduced, as discussed previously. For example, 2-chlorobiphenyl and 2,2-dichlorobiphenyl display an approximately 450-fold decrease in the tendency to bioaccumulate in fish compared with tri- and tetra-chlorinated PCBs (Abramowicz and Olson, 1995).

3.2.3.1 Advantages and Limitations

The primary advantage of anaerobic/aerobic processing for soils contaminated with recalcitrant compounds like PCBs is that it may be used to address soils contaminated with relatively highly chlorinated PCB congeners that cannot be degraded aerobically. Another potential advantage may be its applicability to soils with high organic and/or moisture contents, where oxygen depletion and anaerobic conditions can be promoted readily.

The primary limitation of anaerobic/aerobic processing for soils is that PCBs degrade slowly and biodegradation of PCBs has not yet been demonstrated to consistently meet treatment goals, usually in the range of 50 mg/kg or less. Because this technology has yet to be proven consistently reliable, it is not often used for full-scale treatment. If used, it must be preceded by a site-specific, field-scale treatability study to demonstrate its effectiveness.

3.2.3.2 Technology Performance

Several approaches have been attempted to enhance the microbially catalyzed reductive dechlorination of PCBs. Researchers have attempted to stimulate dechlorination by amending microcosms with carbon substrates (e.g., fatty acids). Although in some cases this resulted in shortened lag times or increased initial rates of dechlorination, the overall extent of PCB dechlorination was not significantly increased (Abramowicz and Olson, 1995). Others have attempted to stimulate dechlorination by adding individual polychlorinated or polybrominated congeners to microcosms. The process is designed to selectively enhance populations of organisms that can use the supplied congener as an electron acceptor. In one instance, this strategy reduced 79% of hexa- through nonachlorobiphenyls in sediments contaminated with Aroclor 1260; the resulting dechlorination products were predominately tri- to pentachlorobiphenyls (Abramowicz and Olson, 1995). This approach may not be applicable to *in-situ* remediation efforts due to the potential regulatory resistance encountered at the prospect of adding polyhalogenated biphenyls to a contaminated site, but it may be appropriate for *ex-situ* applications.

The use of anaerobic biodegradation as a stand-alone treatment for PCB-contaminated sites would likely be hampered by regulatory treatment goals that are generally based on mass removal, not toxicity reduction. Although anaerobic dechlorination may provide greater toxicity reduction than aerobic PCB biodegradation, it is less likely to be used at a contaminated site because it does not produce the same level of PCB mass removal. The discrepancy in mass removals can be partially explained by the fact that a mass reduction of only 34.45 g is observed for each mole of chlorine atoms removed via reductive dechlorination, while a 233.45 g mass reduction (about seven times more) is observed for each mole of trichlorobiphenyl destroyed aerobically. To optimize the reduction of both PCB toxicity and mass removal, researchers have begun investigating the utility of following anaerobic biodegradation with an aerobic biodegradation step.

Sequential anaerobic-aerobic biodegradation is a two-step process in which soils contaminated with large-molecular-weight chlorinated PCBs are first incubated anaerobically to reductively dechlorinate the more heavily chlorinated compounds. The anaerobic incubation is followed by aerobic incubation intended to degrade the resulting mass of lower-chlorinated congeners. In principle, this process should permit a significantly greater PCB mass removal compared to anaerobic or aerobic processes alone because the anaerobic process is confined primarily to relatively highly chlorinated PCBs (i.e., PCBs with four or more chlorines), while the aerobic process is confined to the relatively low chlorinated PCBs (i.e., PCBs with three or fewer chlorines).

Evans et al. (1996) conducted a study of sequential anaerobic-aerobic treatment of PCB-contaminated soil collected from a capacitor bank at a power substation; PCB concentrations were approximately 100 mg/kg, and the congener pattern resembled weathered Aroclor 1248. A 19-week anaerobic incubation period resulted in a 50% reduction of the *meta*-substituted chlorines (from 1.5 to 0.75 *meta*-chlorines/biphenyl), but little change in the *para*-chlorination pattern, yielding mostly *para*- and *ortho*-substituted PCBs. (Longer incubations of up to 60 weeks did not yield significantly more dechlorination than the 19-week period.) Inoculation with *Pseudomonas* sp. LB400 and aerobic incubation for 19 weeks followed the anaerobic incubation period. During the aerobic incubation period, all dichlorobiphenyls and a large fraction of the tri-, tetra-, and pentachlorobiphenyls were degraded, resulting in a 70% overall decrease in total PCB concentrations using sequential anaerobic/aerobic treatment. Without anaerobic treatment, aerobic treatment alone resulted in a 67% PCB concentration reduction, leaving primarily tetra- and pentachlorobiphenyls. The fact that the vast majority of congeners in Aroclor 1248 are susceptible to aerobic degradation skews data in favor of the aerobic incubation for this particular aroclor. Nonetheless, results showed that microcosms undergoing aerobic treatment alone contained a higher proportion of penta- and hexachlorobiphenyls. Only 1% of the congeners in Aroclor 1248 contain six or more chlorine atoms. Anaerobic dechlorination, on the other hand, is more effective for the more highly chlorinated congeners. Thus, for some sites where lower-chlorinated PCB congeners predominate, it may be more effective to undergo solely aerobic degradation.

Shannon et al. (1994) demonstrated a 9% decrease in the PCB mass concentration after 12 weeks of anaerobic incubation, followed by an additional 72% decrease after aerobic incubation resulting in a total mass reduction of 81%. However, this study did not compare results of sequential anaerobic/aerobic treatment with aerobic-only treatment.

Although no full-scale field demonstrations of PCB bioremediation have been documented, a few pilot-scale field demonstrations have been conducted with varying degrees of success. General Electric (GE) conducted the first field-scale attempt to bioremediate PCBs at a former racing drag strip in New York contaminated with Aroclor 1242. Initial PCB concentrations at the site ranged from 50 to 525 ppm in a 5-m × 12-m area rototilled to a depth of 20 cm and inoculated with *Pseudomonias putida* Strain LB400, an aerobic PCB-degrading bacterium. The area was dosed with 200 L LB400 (2×10^9 cells/mL). PCB biodegradation was first detected after 8 to 10 weeks, and the maximum reported PCB loss was

approximately 25% in the top 3 cm of soil after 18 weeks; no degradation was observed in the control plots that did not receive LB400. This reduction was only about half of what was expected based on bench-scale treatability studies conducted in the laboratory using site soil. Researchers speculated that environmental factors such as temperature and moisture content in the soil hampered treatment effectiveness due to high summer temperatures at the site (McDermott et al., 1989). The heat dried the soil and likely desiccated the bacteria; LB400 cell counts on the soil were virtually zero only 2 days after inoculation during the hottest weather.

In 1991, GE attempted another PCB bioremediation field study with Hudson River sediments in an *in-situ* bioslurry using caisson reactors with added inorganic nutrients, biphenyl, and oxygen; the study duration was 73 days. The initial concentration of PCBs in the sediments was 39 ppm, and a 37 to 55% reduction in PCB concentrations was observed; repeated inoculation with a purified PCB-degrading bacterium failed to improve biodegradative activity. A possible explanation for the low destruction was low bioavailability of the PCBs. The authors speculated that the resistant PCB fraction was in a sorbed state and would have to diffuse through the organic matrix before it became desorbed and bioavailable (Harkness et al., 1993).

PCB-contaminated sludge from the Madison, WI Metropolitan Sewerage District was applied to test plots in eight combinations to study the effects of PCB sludge concentration, sludge loading rate, and sludge application methods on performance (Gan and Berthouex, 1994). PCB concentrations ranged from 25 to 75 mg/kg for untreated soils, with approximately 85% of the untreated PCBs being 2-, 3-, 4-, and 5-chlorinated PCBs. Most PCB congeners showed significant decrease in their soil concentrations over time, although the more highly chlorinated PCBs were more persistent in the sludge than the lower chlorinated PCBs. Biodegradation was thought to be the primary removal mechanism based on results of active versus control plots, and analysis of leachate data from the plots. A simple first-order model was used to describe the disappearance of PCBs in the surface soils of the sludge-amended farmland. The half-lives of 2-Cl, 3-Cl, and 4-Cl congeners ranged from 7 to 11, 5 to 17, and 11 to 58 months, respectively. A total of 24 congeners (mostly 6-, 7-, and 8-Cl PCBs) appeared to remain stable in the soils.

3.2.4 Natural Attenuation

Natural attenuation is a remedy-of-choice that allows natural biological, chemical, and physical processes (biodegradation, dispersion, diffusion, weathering, etc.) to slowly minimize or “attenuate” contaminant concentrations. While the use of natural attenuation has become extremely popular in recent years for the remediation of contaminated groundwater (Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, &UST Sites. Directive 9200.4-17P. EPA, 1999b), there is very little information in the literature documenting the use of this technology for treatment of contaminated vadose-zone soils. Most of the available literature on natural attenuation of soils pertains to metals, which are susceptible to physical and chemical (i.e., abiotic) reactions with the soil matrix that can “stabilize” the metals through sorption and precipitation reactions. These stabilization reactions render the metals less mobile and ultimately less bioavailable. There is virtually no literature documenting the use of intrinsic bioremediation as a remedy for vadose zone soils contaminated with organic contaminants. Figure 3-21 is a schematic presentation of how natural attenuation works in groundwater.

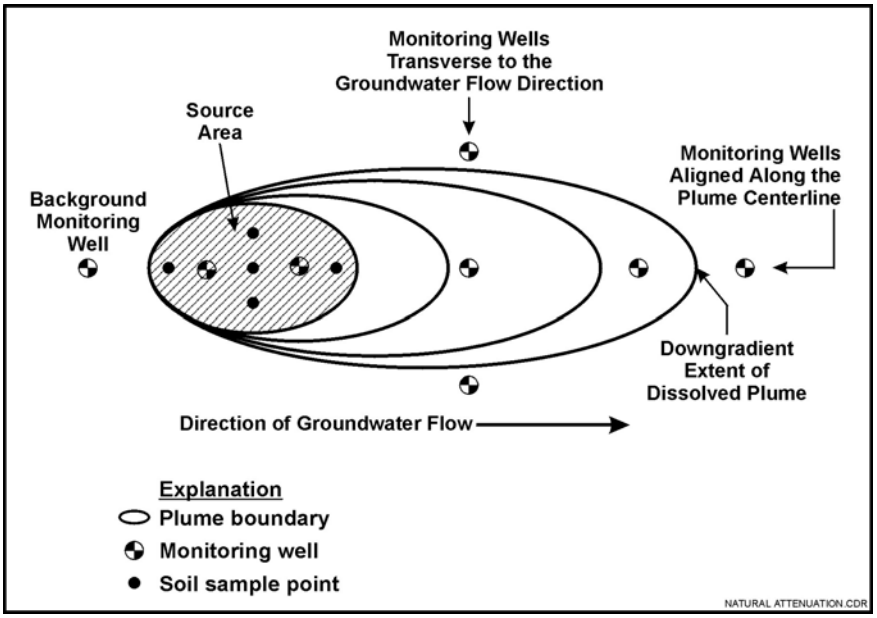


Figure 3-21. Groundwater Natural Attenuation Schematic

PAHs and other high-molecular-weight compounds undergo a variety of weathering processes, including dissolution and dilution into the aqueous phase, sorption and sequestration, volatilization, and biotransformation. It is important to understand the mechanisms involved in those weathering processes to understand the potential for natural attenuation of contaminated soils, and to understand the impact of weathering processes on the risks posed by the contaminants. The popularity of natural attenuation for groundwater contaminants is due in part to the fact that the most mobile contaminants tend to be the most readily biodegradable contaminants with regard to petroleum hydrocarbons. Octanol-water partition coefficient, K_{ow}, has been shown to be negatively correlated with solubility and biodegradability; chemicals with low K_{ow} values tend to be transported through the soil and enter the groundwater, where they may be degraded, whereas chemicals with high K_{ow} values tend to remain sorbed onto soils (Brady et al., 1999). Poorly soluble organic compounds are often resistant to intrinsic biodegradation by virtue of the fact that it is difficult for them to readily reach reaction sites in the microbial cells (Haider,1999). So while poorly soluble compounds tend to be degraded slowly, they also tend not to be very mobile and tend to remain associated with soils.

While weathering of soils has been investigated historically, little information is available regarding its ability to remediate a site through natural attenuation. Contaminant weathering in soils can occur to provide a permanent contamination reduction. Weathering includes such mechanisms as dilution, volatilization, biodegradation, and sequestration. However, these mechanisms do not affect all contaminants equally. PAH weathering tends to preferentially remove the lower-molecular-weight PAH compounds that are more easily degraded or mobilized (two- or three-ringed compounds).

Another potential explanation for the paucity of documented soil-natural-attenuation case studies is the phenomenon of decreasing bioavailability with time. Prolonged contact of organic contaminants with soils causes sorbed chemicals to become increasingly less available for microbial biodegradation (Alexander, 1994), presumably due to sequestration or penetration of the chemical into biologically inaccessible sites (Adriaens et al., 1999; Linz and Nakles, 1997). Microorganisms are typically present in pore sizes between 0.25 µm and 6 µm in diameter; the 0.25-µm diameter is the smallest size limit for entry of bacteria, while sizes in excess of 6 µm allow for entry of protozoa that feed on bacteria (Adriaens et al., 1999). Thus, sequestration may limit the microbial bioavailability of organic contaminants and the

ability for natural attenuation to result in the permanent destruction and removal of these contaminants from soils. Figure 3-22 shows that the amount of a contaminant mineralized by microorganisms is lower in soils that have been in contact with the contaminant for a longer period of time. Thus, compounds with the greatest tendency to sorb to the soil matrix tend to be biodegraded the slowest.

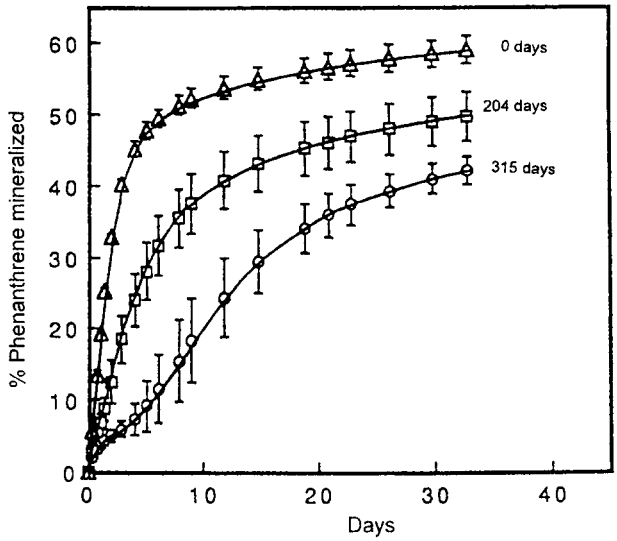


Figure 3-22. Illustration of Decreased Biodegradability of Aged Phenanthrene in Soil (from Adriaens et al., 1999; originally from Hatzinger and Alexander, 1995)

In addition to being sequestered, certain organic chemicals such as pesticides can also form soil-bound residues, which also limits their degradability by microorganisms. These complexes form as a result of attachment of the compounds to reactive sites on the surface of organic colloids or by their incorporation into the structure of humic and fulvic acids (Adriaens et al., 1999).

Limited microbial bioavailability should not be confused with reduced toxicity. The risk posed by sorbed compounds may not decrease simply because they are less likely to desorb in the environment. Thus, the sequestration of inorganic and organic contaminants may reduce the ability of microbes to biodegrade or transform these contaminants in the environment, but may have little overall impact on the toxicity of the contaminated medium.

Despite these limitations, natural attenuation may be a viable treatment technology for soil-bound contaminants, but more research is required to demonstrate its effectiveness and to develop a protocol for the investigation and demonstration of this technology. For metals, this may take the approach of demonstrating that they have become irreversibly sorbed into crystal lattices and thus effectively isolated from soil, groundwater, and biota, as suggested by Brady et al. (1999). For organic contaminants, the study of natural attenuation would require the investigation of weathering phenomena such as dissolution, adsorption, sequestration, and biodegradation.

3.3 EXISTING BIOREMEDIATION TECHNOLOGIES SUMMARY

This section reviews the following conventional bioremediation technologies for their effectiveness to treat contaminated soils: land treatment, biopile treatment, composting, bioslurry reactors, enhanced bioventing, and conventional bioventing. Emerging technologies including phytoremediation, sequential anaerobic/aerobic treatment, natural attenuation, and anaerobic bioventing also were reviewed with

respect to the state-of-knowledge required for their application in the field. In an effort to focus on actual cost and performance information, and to gauge the extent of their application at full scale, a variety of on-line and off-line data bases were reviewed for existing case studies. The summary of this case study search is presented in Appendix B and was used to evaluate the specific technologies.

The cost of various conventional treatment technologies can vary greatly from site to site, depending on site-specific contaminants and conditions. Table 3-20 shows the primary types of equipment used for the conventional technologies discussed in Section 3.1, and Table 3-21 identifies factors that commonly impact biological treatment costs negatively.

Table 3-20. Primary Equipment Used for Conventional Bioremediation Technologies

Technology	Typical Equipment Types
Land Treatment	• Containment pad • Leachate collection and management system • Tilling equipment • Leachate collection and treatment system
Biopile/Biocell	• Soil pile support pad or container • Aeration pipes and blowers • Off-gas treatment equipment • Leachate collection and treatment system • Nutrient feed and chemical stabilizer system
Composting	• Mixing equipment for organic additives • Organic additives and bulking agents • Soil pile support pad and aeration pipes and blowers for windrow turning machine or composting reactor (depending on method) • Off-gas treatment equipment (for static pile or in-vessel treatment)
Slurry-Phase Bioreactors (soil and sediment)	• Soil/sediment mixing equipment • Bioreactor with aeration components • Clarifier • Off-gas treatment system • Nutrient feed and chemical stabilizer system
Bioventing	• Air injection wells • Blowers • Soil-gas monitoring points • Off-gas treatment equipment (if required)

Table 3-21. Factors That Tend to Increase Costs for Conventional Bioremediation Technologies

Cost Factor	Comments
Concentration of contaminants	Higher concentrations increase the time needed for treatment.
Presence of higher-molecular-weight organics	Higher-molecular-weight organics (e.g., PAHs) tend to increase treatment time.
Area or volume requiring treatment	Increased area or contaminated volume requires increased capital expenditures. However, unit costs typically decrease with increased volume to be remediated.
Depth of contamination	Deeper contamination increases the amount of well drilling required for bioventing or excavation requirements for *ex-situ* applications.
Complex geology	Complex interbedding of high and low permeability layers can be difficult to treat, possibly increasing the density of wells needed or the length of treatment time for bioventing or increased mixing requirements and treatment time for *ex-situ* applications.
Low soil permeability	Treating low permeability soils decreases the radius of influence of in situ technologies, requiring an increase in the treatment density for *in-situ* treatment.
Presence of recalcitrant contaminants	Relatively recalcitrant contaminants may require increased treatment time or alternative treatment strategies, or may preclude biological treatment entirely.
Presence of halogenated organics	Halogenated contaminants may require anaerobic pretreatment to reduce the level of chlorination, and may require increased off-gas control measures.

3.3.1 Applicability of Bioremediation for Contaminated Soils

To date, bioremediation's greatest successes have been with technologies that exploit the use of aerobic processes for the biotreatment of organic contaminants, especially for petroleum hydrocarbons, which have been shown to degrade under a wide variety of environmental conditions. Each of the aerobic bioremediation processes have been shown to be capable of meeting cleanup goals for petroleum hydrocarbons such as BTEX, TPH, and many PAHs. The use of composting is fairly well accepted for more complex waste streams such as soils contaminated with explosives or larger-molecular-weight PAHs. The following criteria must be met to ensure the efficacy of aerobic bioremediation to meet treatment goals for contaminated soils:

- The contaminant of interest must be able to be degraded (preferably mineralized) biologically; if the contaminant is not mineralized, biotransformation should not result in the production of toxic byproducts
- Bacteria must be present that are capable of biodegrading the contaminant
- If bacteria are not immediately available for contaminant degradation, a suitable acclimation period should be provided, or the soils may be augmented with known contaminant-degrading bacteria (both of these processes should be pilot tested before implementing at full scale)
- Nutrients required for biodegradation must be readily available
- The contaminant must be bioavailable; for hydrophobic contaminants that are strongly sorbed to soils, bioavailability is likely to be a rate-limiting step toward complete remediation

- Soil chemical conditions, such as alkalinity and pH, must be suitable for bioremediation

- A suitable electron acceptor must be abundantly available; for aerobic processes, this means ensuring that oxygen is not limiting (in water, DO $ 2 mg/L; in soil gas O_2 > 5%)

- Adequate time for acclimation must be provided to promote bacterial growth for contaminant degradation; this may involve weeks or months, depending on the contaminant and the media chemical and microbiological characteristics; for some sites, preferential degradation of easily degraded compounds may necessitate prolonged acclimation periods before the more recalcitrant contaminants of interest are degraded.

While bioremediation is well understood and well accepted for the aerobic treatment of easily degraded petroleum hydrocarbons, the challenge for bioremediation increases significantly for more recalcitrant contaminants and/or more complex site conditions. Large-molecular-weight PAHs, PCBs, chlorinated aromatic and aliphatic compounds, dioxins, pesticides and herbicides, and nitroaromatic compounds all present unique obstacles for biological treatment, particularly with respect to the ability of bacteria to degrade and ultimately mineralize these various contaminants. It is common for these compounds to be biotransformed and not degraded or mineralized, often resulting in the production of potentially toxic byproducts, some of which can be equally or more toxic than their parent compound.

The addition of bacteria cultivated for the degradation of a specific compound (bioaugmentation) has been used to promote faster and potentially more complete degradation, but has seen limited use in the field, most likely because it has not yet been proven to be a reliable strategy. The fate of bacteria added to a complex soil medium is unpredictable. Furthermore, such bacteria may favor the degradation of more readily degradable contaminants before they degrade the contaminant of interest.

There has long been interest in anaerobic processes to biotransform or degrade more recalcitrant compounds, particularly halogenated and nitro-substituted compounds. Anaerobic processes are seeing increased field applications and continue to be investigated in the laboratory and the field. Anaerobic treatment systems tend to be more difficult to control and maintain than are aerobic systems, and, for certain compounds, anaerobic systems catalyze the incomplete biotransformation of contaminants and require subsequent degradation using aerobic bacteria. In some cases, such as the dechlorination of highly chlorinated PCBs to lower chlorinated PCBs, dechlorination can have a significant detoxification effect (NRC, 2001); yet even this may be insufficient for site restoration if cleanup requirements are based on total PCB removal and not on a congener-specific treatment approach to detoxify soils. In other cases, such as in the production of VC from chloroethene or chloroethane dechlorination, the daughter product may be more toxic than its parent compound. Consequently, anaerobic bioremediation often may require post treatment that may include aerobic or physical/chemical treatment processes. Anaerobic/aerobic sequenced technologies have significant potential for remediation of recalcitrant contaminants, but continued research is needed to bring them to the marketplace. Despite its obstacles, anaerobic treatment has substantial promise for treating soils, either solely or in combination with aerobic treatment, particularly if it can be employed *in situ*, as would be the case for *in-situ* anaerobic bioventing.

In addition to anaerobic bioventing, cometabolic bioventing is gaining interest as an aerobic approach to treat certain halogenated aliphatic contaminants. Cometabolic bioventing provides another alternative for vadose zone remediation and complete destruction of CAHs that do not require anaerobic conditions.

3.3.2 Bioremediation Advantages and Disadvantages

Perhaps the greatest advantages and attractions of bioremediation are that 1) contaminants can be degraded to nontoxic byproducts and some can be mineralized, resulting in the complete removal of the

contaminant from the environment; 2) bioremediation uses natural means to achieve contaminant removal; and 3) bioremediation is perceived as relatively inexpensive and environmentally friendly. The fact that bioremediation can detoxify contaminants using natural methods means that contaminants are not displaced to another medium, such as activated carbon, that could require further treatment, and they are not discarded in a landfill. A primary disadvantage of landfill disposal is that the original owner retains ownership of the contaminated medium indefinitely. Thus, a technology such as bioremediation that can detoxify or destroy contaminants on site is very attractive because of its ability to reduce or eliminate liability for contaminants.

The perception that bioremediation is a relatively low-cost treatment alternative probably stems from the fact that most bioremediation technologies rely on low-tech and low-cost methods. Aeration, for example, rarely requires the use of pure oxygen and can be affected by simply blowing air through the soil media using conventional blowers. While nutrient addition and bioaugmentation are difficult *in situ*, *ex-situ* nutrients (and bacteria) can be added and mixed with soils during excavation and stockpiling or during construction of the treatment system. Some of the most significant cost impacts on bioremediation systems are sampling and O&M. Because biotreatment is often a relatively slow process, O&M costs tend to escalate when treatment operations are prolonged from weeks to months, or to years. Minimizing O&M through careful design and management can have a significant impact on reducing overall treatment costs for biotreatment processes. While the reported costs for bioremediation range from less than $50/cu yd to more than $1,000/cu yd, bioremediation treatment costs should be competitive with physical/chemical treatment processes; bioremediation treatment alternatives that greatly exceed physical/chemical treatment costs may be inappropriately targeting recalcitrant contaminants or conditions not well suited for bioremediation.

The most significant disadvantage of bioremediation is that, in general, it is much less predictable than most physical/chemical and thermal technologies, often necessitating pretreatment or field pilot-scale studies. The reason for this is that the site-specific bacterial population, physical conditions, and nutrient availability for the degradation of a specific contaminant cannot easily be predicted. For example, while extensive research has been conducted to demonstrate the ability of bacteria to biodegrade PAHs, the actual rate of PAH biodegradation and the potential for certain large-molecular-weight PAHs to be recalcitrant to biodegradation cannot be predicted without treatability testing. Thus, at some sites PAH degradation may be relatively rapid, requiring months of biotreatment, while at other sites PAH degradation may require years or may not be achieved at all. Fortunately, treatability studies are practiced widely and can easily be implemented at a relatively low cost. Their greatest disadvantage is that they may take a long time and have the potential to significantly delay site restoration. Under a climate of wanting to remove wastes rapidly, many site owners are unwilling to take time to conduct a treatability test, which itself is unpredictable, and often prefer the more predictable results of physical/chemical or thermal treatment alternatives.

4.0 IMPLEMENTATION OF BIOREMEDIATION TECHNOLOGIES

Bioremediation testing and implementation follow similar steps for testing and implementation of any remedial process, namely, site characterization, treatability testing for technology screening/selection, and pilot-scale testing. While the specific data needs of bioremediation technologies differ, there are many common parameters that affect the implementation of any remedial technology and these must be known to effectively select an appropriate alternative. The following sections summarize the general approach for implementing the bioremediation technologies described in this report

4.1 SITE CHARACTERIZATION

Before selecting any remedial approach, it is necessary to perform some level of site investigation to characterize the contamination, delineate the horizontal and vertical extent of the contamination, define the hydrogeologic conditions including the depth to the water table and the soil stratigrahy, and determine key soil characteristics such as pH, moisture, texture, and permeability. Site characterization for successful implementation of bioremediation technologies requires more investigation than do physical/chemical processes because a wide range of parameters may impact the desired metabolic activity of microorganisms in the soil environment. The parameters of importance depend on the type of contaminant being treated, the microbial process being exploited, and the selection of an *in-situ* or *ex-situ* approach. It is recommended that the following important screening parameters be measured in any site investigation where bioremediation is being considered.

- Contaminant type(s)
- Depth to groundwater
- Soil stratigraphy/texture
- Contaminant distribution
- pH and alkalinity
- Organic matter
- Nutrients (N, P, K)
- Soil gas O_2 and CO_2
- Electron acceptors
- Soil moisture
- Soil permeability
- Microbial populations

1. *Contaminant type(s):* It is important to determine not only the contaminant(s) of concern (COC) from a regulatory perspective, but also to know what contaminants and co-contaminants are present that may affect the microbial degradation of the target compounds. Co-contaminants can range from compounds that are preferentially degraded over the COCs and hence exert a demand for remedial reagents, to compounds that are inhibitory to the microorganisms that carry out the desired degradation reactions. An example of the latter case was observed at a wood preserving site in Minnesota where the degradation of the PAHs of interest was preceded by degradation of the carrier oil components in a creosote bioventing project (McCauley et al., 1999). This required the bioventing system to be operated for 3 years before any significant reduction in COCs occurred.

2. *Depth to groundwater:* Knowing the depth to groundwater and the amount that the depth fluctuates over time is important for designing any remedial approach and for screening technologies. Sites with shallow water tables (<3 – 5 ft) can pose problems with subsurface delivery of remedial reagents such as gas injection, and surface application of liquid solutions could be a concern due to mobilization of contaminants to the aquifer. Depending on site specifics, shallow water table sites

may be more suitable for *ex-situ* technology applications. Sites with deeper water tables are more appropriate for *in-situ* bioremediation if subsurface reagent delivery is possible. Sites that exhibit large water table fluctuations can pose challenges due to the cyclic saturated/unsaturated conditions that can impede reagent delivery and the potential for continuous smearing of contaminants when NAPL is present. In summary, knowing the depth to the water table is a crucial parameter for selecting and designing a remedial approach, and the limitations of this parameter on the potential for implementation of a specific technology are dependent on other site characteristics.

3. *Soil stratigraphy/texture:* Observations made during drilling or soil coring are used to define the stratigraphy for the site. Knowing the stratigraphy is important for understanding how the contamination is distributed in the soil and determining the potential for delivering remedial reagents. Less permeable soils such as silts and clays tend to slow the migration of contaminants and often contain more contaminants than the more permeable strata. The presence of more permeable strata can facilitate delivery of reagents; a high degree of silt and clay content in the soil can preclude such delivery. Contaminants held up in very tight soils are difficult to treat *in-situ* and depending on the depth and volume needing treatment may be candidates for *ex-situ* treatment. Fracturing technologies are being developed to "open up" tight soil formations to allow delivery of reagents.

4. *Contaminant distribution:* Defining the contaminant distribution in the subsurface is a prerequisite for selecting any remedial approach. Knowing vertical and horizontal extents of the contamination allows calculation of the volume of soil requiring treatment, the potential for, and extent of, excavation for *ex-situ* treatment, and designing the placements for injection/extraction and monitoring devices for *in-situ* treatment.

5. *pH and alkalinity:* Although microbial activity occurs over a wide pH range, the optimal pH for the majority of the soil microbial activity exploited for contaminant destruction is usually in the range of pH 6 to 8. The addition of certain reagents as well as enhancement of microbial activity can often cause a significant pH change, which in turn can adversely affect contaminant degradation. Measuring the pH and alkalinity provides a measure of how well the system is naturally buffered against such changes. If the buffering capacity is too low, buffer addition might be required. Buffer addition is more easily applied to *ex-situ* soil treatment as *in-situ* delivery often requires saturation of the soil, which can result in a decrease in the effective porosity and impede reagent delivery and/or cause problems with contaminant mobility.

6. *Organic matter (Total Organic Carbon):* Naturally occurring organic matter can affect degradation performance by imparting an oxygen demand, serving as an electron donor, or decreasing the effective bioavailability. Organic matter can interfere with the delivery of remedial reagents including both vapor-phase and liquid nutrients. Typically, high organic concentrations are found in shallower soils in areas with thick vegetation. Soils with high percentages of organic matter tend to hold water. Distribution of reagents throughout the subsurface can be difficult, and *ex-situ* treatment may be required.

7. *Nutrients (N, P, K):* Microbial activity in soils with low concentrations of essential nutrients can be limiting, slowing the degradation process and extending the time required for treatment. In some soils, nutrient concentrations can be limiting to the point that degradation does not occur. The primary nutrients, nitrogen (N), phosphorus (P), and potassium (K), can easily be measured to determine if nutrient-limiting conditions exist. Trace nutrients may be present in concentrations below analytical detection capabilities, but may still be present in sufficient quantities. Treatability studies are useful for evaluating nutrient limitations and can be designed to investigate various nutrient addition scenarios to optimize degradation and minimize chemical costs. Although nutrient-to-substrate ratios are often prescribed, care must be taken when adding nutrient salts so as not to

decrease the soil water potential to the point where microbial activity is adversely impacted. Nutrients are added easily to soils treated in *ex-situ* reactors; *in-situ* nutrient addition can be more challenging.

8. *Soil-gas oxygen and carbon dioxide:* O_2 and CO_2 concentrations in soil gas provide a good indication of the aerobic biodegradability of the contaminant, the presence/absence of indigenous microorganisms that can degrade the contaminant, and the need for O_2 delivery to promote the degradation by those organisms. A decreased ratio in the percent O_2 to the percent CO_2 in the contaminated soil compared to that in a non-contaminated background soil is a good indicator of increased biological activity and that the increased activity is due to the presence of the contaminant. Note, these ratios are not direct evidence that a specific compound of interest is being degraded if that compound is the sole contaminant. The ratios are considered reliable indicators of the biodegradation potential for the fuel hydrocarbon mixtures, fairly reliable for PAH mixtures such as creosote or MGP wastes, fairly reliable for mixtures of other directly aerobically metabolizable compounds such as certain halogenated benzenes and phenolics, and not so reliable for compounds that are only aerobically degraded cometabolically such as certain chlorinated solvents and/or other chloroorganics.

9. *Electron acceptors:* Biological degradation reactions involve the transfer of electrons. The molecule from which the electron is removed is termed the "electron donor," and the molecule to which the electron is transferred to is termed the "electron acceptor." Under different conditions, contaminants can serve as either electron donor or acceptors. The aerobic degradation of benzene is an example of the contaminant serving as the electron donor as electrons are transferred from the benzene to oxygen resulting in the formation of CO_2. It is important to know the electron acceptor concentrations in the soil under these conditions to calculate the amount of O_2 that needs to be added to promote the desired degradation. Anaerobic degradation of PCE via dehalorespiration is an example of the contaminant serving as the electron acceptor as electrons are transferred from hydrogen to PCE, resulting in the reductive dechlorination of the PCE to the lesser-chlorinated ethenes. In the case of PCE, H_2 generally serves as the electron donor. H_2 can be provided via direct gaseous H_2 injection, as in the case of anaerobic bioventing, or via the anaerobic fermentation of an organic substitute.

10. *Soil moisture.* Soil microorganisms, like all life forms, require water. This includes soil microbes that grow attached to soil particles as well as those suspended in the water bound to soil particles and within the interstitial spaces between soil particles. Typically, the water content of soil is measured as soil moisture, and optimal moisture content for biological activity is reported to be between 60% and 80% of field capacity. A more appropriate measure of water availability is the soil water potential that takes into account the salinity of the water. Measuring the water potential is more involved than measuring the soil moisture, but the data are more useful, especially when considering adding nutrient salts.

11. *Soil permeability:* Soil permeability provides a measure of the potential for effective delivery of remedial reagents to subsurface soils. Soil gas permeability is measured by injecting air at different flow rates and measuring pressure changes at radial distances from the point of injection. Soil liquid permeability can be measured by two methods, infiltration from the surface using a double ring infiltrometer where a constant head is maintained in two concentric rings and the rate of infiltration is measured in the center ring, or permeability in the subsurface using a modified slug test. The data from these tests can be used as a direct indicator of the ability to deliver reagents and may exclude *in-situ* treatment if soils are too tight. Soil gas permeability improves the reliability of designing well spacing and placement for technologies such as bioventing. Liquid injection is subject to gravity flow through preferential flow channels. This coupled with the fact that the diffusion of liquid reagents is limited makes liquid delivery in the vadose zone more challenging than vapor-phase delivery.

12. *Microbial populations:* Enumerating microorganisms from soils is by no means an exact science because of the difficulty in removing the cells from the soil particles coupled with the fact that many soil microorganisms are simply not culturable in the laboratory. Even though this may be a shortcoming from a quantification standpoint, it is possible to enumerate various classes of microorganisms as an indicator of the potential for promoting a desired biodegradative process. General plate counts (i.e., total heterotrophs) provide a general measure of the ability of microorganisms to survive in a soil, but provide no direct evidence of any biodegradation potential. Comparing these counts to counts from soil collected from an uncontaminated location at the site is sometimes used as indirect evidence and a very qualitative indicator of the impact of the contaminant on the microbial population. More specific plating techniques can provide better evidence of the potential for promoting microbial activity for a specific degradation process. This entails plating on specialized media with the contaminant included with any other essential co-substrates, electron donors, and/or other essential nutrients. These plating techniques can be used to isolate and enumerate microorganisms with specific metabolic capabilities and/or requirements. Phospholipids fatty acids (PLFA) analysis provides information on biomass concentration, metabolic activity level, and what types of microbes are present in a soil sample. This technique can be used to determine how environmental factors (temperature fluctuations, pollution, disturbances, etc.) affect a microbial population. Fatty acid methyl ester (FAME) analysis provides a microbial fingerprint which can be used to identify the bacterial strain present. Denaturing Gradient Gel Electrophoresis (DGGE) analysis uses DNA sequencing to identify specific organisms present in a sample. By using the 16S RNA gene and comparing DNA sequences using national databases, different bacterial species can be identified. FAME and DGGE analyses can separate contaminant microbes and aid in positive identification of specific microbes. Although microbial enumerations are often considered as an optional analysis, proper technique can provide valuable information for technology selection and design.

4.2 TECHNOLOGY SELECTION

Biotreatment technologies should be considered as viable remedial options for a wide range of contaminants under a wide range of environmental scenarios. The individual technologies that should be considered in the technology screening process are site specific as discussed below. The two governing factors that would exclude consideration of bioremediation are short treatment time requirements and contaminant biodegradability considerations. For the most part, bioremediation approaches can require more time than the more aggressive thermal and/or physical/chemical treatment technologies. This might not be true for *in-situ* applications where large volumes of soil are to be treated, but for smaller volumes or for *ex-situ* applications, biologically-based processes are usually slower. What makes the biological approaches attractive is that they:

- Result in contaminant destructions, not simply phase transfer or removal for off-site disposal
- Are often simple designs that require minimal energy input
- Are less costly than most other alternatives
- Allow on-site reuse of the soil.

Selection of a bioremediation approach is a stepwise process. The first step is to determine if an *in-situ* or *ex-situ* application is required. Generally, *in-situ* technologies are preferred, but site constraints such as soil permeability, depth to groundwater, and contaminant distribution may dictate the selection of an *ex-situ* approach. *Ex-situ* technologies are preferred when the ability to deliver remedial agents is limited, the remedial process includes reagents that could mobilize the contaminant (i.e., surfactants, buffers, or liquid nutrients), and/or more exact control of the remedial process is required (i.e., temperature, pH, moisture, nutrient concentration, or leachate control).

4.3 TREATABILLITY STUDIES AND PILOT-SCALE TESTING

Biological processes are affected by complex interactions of many environmental variables, and the potential for performance of any bioremedation technology is best assessed through treatability studies. These studies can be conducted in the laboratory or at small scale in the field. The goals of the treatability study are to determine if biological activity can be promoted to achieve the desired level of treatment for a specific site soil and contaminant, and to determine the degradation kinetics to provide a preliminary estimate of the time required to achieve treatment. Because treatability tests are relatively inexpensive and they can provide information that is useful for screening and selecting technologies, it is often recommended that they be conducted as part of any Remedial Investigation/Feasibility Study (RI/FS) where bioremediation is being considered. During that time, treatability studies allow the flexibility of investigating a range of environmental variables such as pH, alkalinity, temperature, and nutrient addition, all of which can affect degradative performance and be controlled in the field when using the appropriate technology. The data could prove useful for selecting *ex-situ* over *in-situ* approaches.

Pilot-scale testing is conducted when technologies require site-specific design data for full-scale implementation. Technologies that require more sophisticated engineering, such as bioslurry reactors, require pilot-scale testing to collect data necessary to size reactor system components and determine the energy input required to maintain the slurry in suspension. Less complex technologies can also benefit from pilot-scale testing. For example, the standard practice for bioventing combines the treatability test with the pilot-scale test to simultaneously collect data to calculate the soil-gas permeability and an initial biodegradation rate. The soil-gas permeability data are used to determine vent well spacing, while the initial biodegradation rate is used to determine an air exchange rate and to size the blowers. The initial degradation rate can be used to make a preliminary estimate of the time that will be required to achieve cleanup.

Both treatability and pilot-scale testing require the objectives of the tests to be clearly defined, the experiments/tests to be designed and conducted to collect the data needed to achieve those objectives, and a good quality assurance plan to ensure the validity of the data collected. Frequently, more detailed scientific and engineering data are collected for both scale-up considerations and to better understand the underlying microbial processes for system optimization.

4.4 FULL-SCALE DESIGN

Once treatability and/or pilot-scale testing is completed, full-scale designs can be completed that incorporate the data collected and take site hydrogeological and other logistical constraints into consideration. For many of the *ex-situ* bioremediation technologies, the volume of soil requiring treatment, the time required/allowed for treatment, and space constraints dictate many aspects of the full-scale design. For example, land treatment, biopile treatment, and composting are relatively simple designs, but often require more residence time than the more complex biotreatment designs such as bioslurry reactors and treating the same volume of soil in the same amount of time will require more space.

In-situ technologies are screened and selected based on the results of the treatability tests, and full-scale systems are designed based on hydrogeologic and contaminant distribution data collected during the site investigation and/or pilot testing. The location of injection wells/points as well as monitoring devices must take into account the soil permeability and the horizontal and vertical extent of the contamination. The injection equipment (i.e., pumps, blowers, etc.) is designed based on the number and size of the injection points and the kinetics of reagent utilization.

4.5 PROCESS OPTIMIZATION

The treatment conditions defined by treatability and/or pilot-scale testing serve as the initial design parameters for full-scale implementation. Optimizing the system involves tweaking the operational parameters to decrease the costs of operation and/or the time required to achieve cleanup concentrations. For example, aerobic technologies such as bioventing that promote contaminant degradation by providing O_2 achieve optimum performance when O_2 concentrations in the soil gas are maintained above 5% to 8%. At concentrations above this range, the degradation is zero order with respect to O_2 so no enhanced degradation is realized. Optimizing the system by decreasing the flow rate of the blower or operating in a pulsed mode to maintain the O_2 partial pressure at 5% rather than at ambient levels could reduce the energy costs. Data generated during periodic soil-gas measurements and respiration testing can be used to make such adjustments. An example of optimization of an anaerobic technology would involve adjusting the feeding strategy and hence the addition of the electron donor to minimize the amount of donor that is lost to methanogenesis. *Ex-situ* technologies might benefit from inoculating the soil with a small amount of soil from the previous reactor run by shortening the time of acclimation and therefore the run time. Controlling aeration to maintain the non-rate limiting O_2 concentration can decrease energy input and off-gas collection and treatment requirements. The process of system optimization requires periodic system monitoring and making adjustments to system operation to compensate for any changes during the treatment cycle.

4.6 CONTAMINANT DEGRADATION PLATEAUS

Biological degradation plateaus are temporary or semipermanent degradation endpoints that often occur during the biotreatment of environmental contaminants. They occur for a variety of physical, chemical, and microbiological reasons, usually resulting in residual contaminant concentrations that exceed target or expected degradation endpoints. The major reasons for degradation plateaus include:

1. Preferential microbial degradation of compounds that are more easily biodegraded than the target contaminants
2. Exhaustion of a cometabolic growth substrate
3. Limited contaminant bioavailability
4. Nutrient limitations
5. Predation of contaminant-degrading bacteria by opportunistic predators
6. Energetic limitations
7. Buildup of toxic intermediates.

This section briefly describes each of these biotreatment mechanisms and their potential for contributing to the occurrence of biodegradation plateaus.

4.6.1 Preferential Degradation of Easily Degraded Compounds

Bacteria rely on environmental compounds for carbon, energy, and nutrients for growth. The microbial degradation of organic compounds provides carbon necessary for growth, while oxidation/reduction reactions that involve organic and inorganic compounds provide energy. As a general rule, bacteria preferentially degrade the most energetically favorable compounds followed by compounds that are decreasingly energetically favorable. In other words, bacteria first metabolize compounds that provide the most carbon and/or energy for the least amount of work, provided that they have the necessary enzymes and exist under the necessary environmental conditions to metabolize those compounds. This phenomenon is often apparent in environmental media with contaminant mixtures, such as petroleum hydrocarbons. In the presence of TPH, for example, and because biodegradation of PAHs and other petroleum hydrocarbons tends to be more difficult with increasing molecular weight, bacteria

preferentially degrade lower-molecular-weight compounds like short-chain aliphatics and BTEX, followed by increasingly difficult-to-degrade compounds such as longer-chained aliphatic compounds and lower-molecular-weight PAHs (2- or 3-ring PAHs), again followed by the most difficult-to-degrade compounds like high-molecular-weight aliphatic compounds and the 4- to 6- ring PAH compounds. This leads to reduced degradation rates for the more difficult-to-degrade, higher-molecular-weight compounds, the apparent step-wise degradation of environmental contaminants, and the appearance of degradation lag times or plateaus for the more difficult-to-degrade contaminants. These degradation plateaus may show evidence of downward movement after bacteria exhaust the more easily degraded contaminants and begin to degrade the more difficult-to-degrade compounds. Figure 4-1 is a conceptual illustration of a typical contaminant plateau.

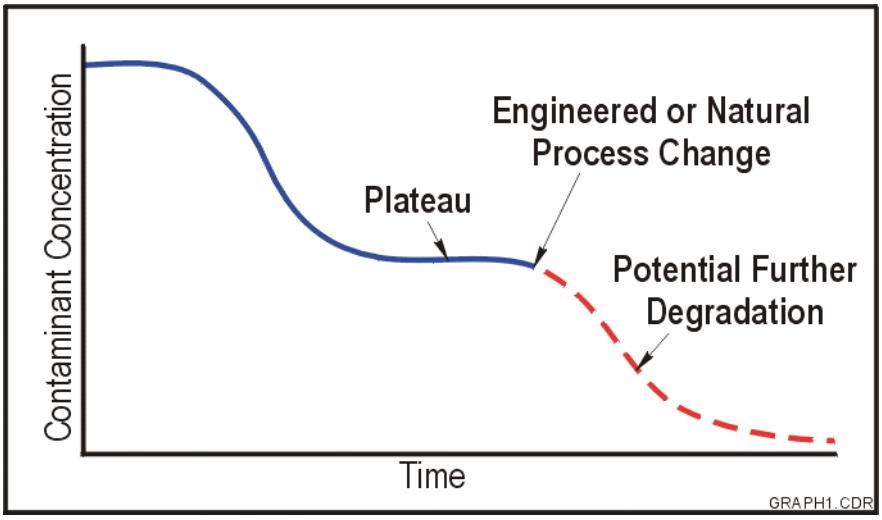


Figure 4-1. Contaminant Degradation Plateau

4.6.2 Exhaustion of a Cometabolic Growth Substrate

Aerobically, bacteria that grow on hydrocarbons typically initiate oxidation by incorporating molecular oxygen into organic compounds by the action of enzymes known as oxygenases (Wackett and Householder, 1989), which destabilize carbon-carbon bonds and render the organic molecule more susceptible to degradation. In some cases, nonspecific oxygenases show activity for other compounds, a process known as cometabolism. The oxidation of some environmental contaminants occurs through cometabolism, which involves the degradation of a primary growth substrate and the fortuitous degradation of the cometabolized contaminant. The best-known and most exhaustively researched examples of cometabolism involve the aerobic cometabolic degradation of low-molecular-weight chloroethenes (TCE, DCE, and VC) by methanotrophs (methane-degrading bacteria), utilizing the methane monooxygenase enzyme. In addition to cometabolically degrading selective chlorinated solvents, methane monooxygenase also has been shown to convert naphthalene to 1- and 2-naphthols (Dalton et al., 1981).

A wide variety of organic compounds can serve as primary growth substrates or as cometabolically degraded substrates. Although cometabolism has not been exploited as a bioremediation mechanism for PAHs or PCBs to date, many scientists believe it is a relatively common phenomenon in the environment and is likely responsible for a substantial portion of contaminant degradation at petroleum release sites. PAH compounds, specifically the high-molecular-weight compounds that prove very difficult for bacteria to metabolize, may be degraded cometabolically by nonspecific oxygenase enzymes of bacteria that

degrade 2- and 3- ring PAHs. Evidence for this phenomenon with PAHs is beginning to surface at the EPA's Bedford, IN site where multiple soil bioremediation technologies are being investigated.

At sites where cometabolism is primarily responsible for degrading a specific compound, degradation plateaus occur when the primary growth substrate is exhausted. Assume, for example, that compound B is cometabolically degraded along with compound A. The bacteria require compound A for carbon and energy, which they do not obtain from compound B. If compound A is exhausted first, the non-specific enzyme(s) responsible for compound B degradation will no longer be produced or activated, resulting in the termination of compound B degradation. The result is a residual compound B concentration plateau. Theoretically, compound B degradation will resume in the presence of more compound A, so that adding compound A to the medium may be a potential strategy to further stimulate compound B degradation.

4.6.3 Limited Contaminant Bioavailability

A prerequisite for the microbial degradation of any compound is that the compound be bioavailable. That is, for bacteria to metabolize a substrate, the bacteria (or its enzymes) and substrate must come into direct contact, and substrate mobility must permit its degradation. The adsorptive binding of hydrocarbon compounds to soils can make them unavailable for biodegradation (Prince and Drake, 1999); this is particularly true of the higher-molecular-weight compounds, which tend to have a higher affinity for sorption to soils due to their higher degree of hydrophobicity. The hydrophobic nature of many high-molecular-weight contaminants, including PAHs and PCBs, often renders these compounds unavailable to bacteria. Furthermore, prolonged contact of organic contaminants with soils may cause sorbed chemicals to become increasingly less available for microbial biodegradation (Alexander, 1994), presumably due to sequestration, the migration of the contaminant into biologically inaccessible sorption sites (Adriaens et al., 1999; Linz and Nakles, 1997). Contaminants with the greatest tendency to sorb to the solid matrix tend to be biodegraded the slowest.

Contaminants in soils may be categorized in three fractions: a readily bioavailable fraction, a moderately or slowly bioavailable fraction, and an unavailable fraction. The readily bioavailable fraction is biodegraded with minimal lag and may include a mobile, aqueous phase of the contaminant, a NAPL phase from which dissolution into the aqueous phase is not rate limiting, and a sorbed phase where desorption into the aqueous phase also is not limiting due to relatively weak sorptive forces. The moderately bioavailable fraction is represented by sorbed or NAPL phases that can desorb or dissolve into the aqueous phase, but for which desorption/dissolution are rate-limiting steps toward biodegradation. The unavailable fraction is represented by strongly sorbed or sequestered contaminants that for all practical purposes are insoluble. It is the moderately bioavailable and unavailable fractions that have the potential to create the appearance of degradation plateaus.

4.6.4 Nutrient Limitations

Nutrient limitations also can result in degradation plateaus. In addition to the need for carbon and energy, microbial contaminant degradation also requires macronutrients like nitrogen and phosphorus and micronutrients including metals and salts. Nutrient limitations can be determined through microcosm testing or pilot testing by comparing nutrient-amended soils with unamended controls. At McClellan AFB, for example, nitrogen limitations hindered propane degradation, which was being used to stimulate cometabolic TCE degradation. Background nitrogen in groundwater was available at 5 mg/L; this concentration was insufficient to support propane degradation when propane was added at 4% air (Lynch et al., 2001; Tovanabootr et al., 2001). The result was a degradation plateau for TCE cometabolic degradation. Because nitrogen could not easily be added to this *in-situ* application, propane gas concentrations had to be reduced so that nitrogen requirements would not exceed the nitrogen availability in groundwater.

4.6.5 Predation of Contaminant-Degrading Bacteria

Predation of contaminant-degrading bacteria can theoretically reduce their population, resulting in a degradation plateau. Environmental restoration technologies stimulate microbial contaminant degradation by adding amendments, nutrients, or growth factors that optimize the environment for contaminant-degrading bacteria. Creating such ideal environments for bacteria can result in the rapid proliferation of contaminant-degrading bacteria, and a subsequent proliferation of predator microorganisms that live off of contaminant-degrading bacteria. The result is a cyclic process where contaminants are degraded relatively rapidly followed by a rapid decline in the biological population resulting in reduced degradation rates. This may be followed by new bacterial growth and renewed contaminant degradation. In the environmental restoration field, this phenomenon has been most apparent with methanotrophic cometabolic processes in which the rapid and enormous proliferation of methanotrophic bacteria due to methane and oxygen addition to the environment results in a proliferation of opportunistic microorganisms that live off the methanotrophs. These opportunistic microorganisms lead to system failures where the target cometabolic process ceases to work.

4.6.6 Energetic Limitations and Buildup of Toxic Intermediates

Degradation rate and extent is governed by microbial thermodynamics. Thermodynamic equations depend both on the amount of energy that can be released by the contaminant degradation process as well as the relative concentrations of degradation substrates and byproducts. Bacteria may be limited in their ability to degrade contaminants to very low regulatory concentrations because they may be unable to gain sufficient energy for growth at low contaminant concentrations. Contaminant-degrading enzymes may have a relatively poor affinity for the contaminant of concern, also resulting in high concentration endpoints.

Inhibition phenomena also can hinder contaminant degradation. Such inhibition can include substrate or product inhibition, or competition among substrates for degradation. A well-known example of product inhibition occurs during anaerobic fermentation of organic compounds. In an anaerobic consortium of bacteria, syntrophic bacteria (syntrophs) comprise a unique group of bacteria that catalyze substrate oxidations via interspecies hydrogen transfer. The syntrophs produce H_2 via anaerobic fermentation of an organic substrate, and require the removal of the H_2 by methanogens, sulfate-reducing bacteria, or other hydrogen-utilizing bacteria. Some syntrophs, including *Syntrophomonas wolfei*, are able to convert the range of C-4 to C-8 compounds and some aromatic compounds such as benzoate and phenol to short-chain fatty acids, particularly acetate, and to H_2 and CO_2 (Balows et al., 1992). Others (e.g., *S. sapovorans* and *C. bryantii*) are able to use C-11 to C-18 compounds. Because fermentative bacteria often operate at conditions very close to thermodynamic equilibrium, excess production of acetate and H_2 is thermodynamically unfavorable. Thus, the efficiency of the organic carbon fermentation process depends on the efficient removal of acetate and H_2 by methanogens or sulfate reducers. The involvement of syntrophic bacteria in the anaerobic degradation of organic contaminants requires a well balanced, healthy biological system to maintain the contaminant degradation process and prevent the appearance of degradation plateaus.

5.0 FUTURE DIRECTION OF BIOREMEDIATION TECHNOLOGIES AND BIOREMEDIATION RESEARCH

This report reviews the state-of-the-art of bioremediation, primarily focusing on organic contaminants. Bioremediation has been and continues to be employed with relative confidence for a variety of waste streams that are amenable to microbial degradation. However, there are numerous waste streams that have proven difficult to remediate biologically. Continued research and development (R&D) is needed to identify environmentally and economically marketable biotechnology approaches for remediating recalcitrant wastes. This section focuses on future R&D needs to help identify contaminants, waste streams, and treatment technologies that require further development, and to identify those developmental requirements. The discussion of research needs is divided into three categories: 1) optimization of technologies that are proven in the marketplace,
2) development of emerging technologies to bring them to the marketplace, and 3) fundamental R&D approaches for waste streams for which there are no existing technologies.

5.1 OPTIMIZATION OF TECHNOLOGIES THAT ARE PROVEN IN THE MARKET PLACE

As summarized in Section 3, the aerobic degradation of TPH and of lower-molecular-weight aliphatic and aromatic hydrocarbons is well understood and has been applied at hundreds of sites using bioventing, land treatment, biopile treatment, composting, or bioslurry reactors. There is a wealth of information available to scientists and engineers to aid in the design and implementation of these technologies. For contaminants that are readily biodegraded aerobically, such as BTEX, low-molecular-weight TPH and PAHs, and some wood-treating wastes, these aerobic biotechnologies can be used "off-the-shelf," and laboratory or pilot-scale treatability tests can be minimized or even eliminated at most sites. In fact, EPA has designated bioremediation as a "presumptive remedy" for wood-treating waste streams. Thus, the regulatory approval for the aerobic treatment of such nonrecalcitrant contaminants can be readily achieved, and treatment can be conducted with confidence that these contaminants can be removed to meet treatment goals.

The confidence with which these technologies can be applied raises the question of where R&D can best be applied for these technologies. The following research needs may be applied generally to the aerobic technologies listed in this section.

1. *Process improvements*: Process improvements may include reduced O&M requirements, improved contaminant destruction and removal efficiencies, enhanced contaminant destruction and removal rates, and increased contaminant throughput rates.

2. *Increased target contaminant range*: While these technologies are available for readily degradable contaminants, there is a wide range of relatively recalcitrant contaminants that may require treatability testing before field implementation or for which these technologies may not yet be applicable. Such contaminants include larger-molecular-weight PAHs, PCBs (particularly Aroclor mixtures with a wide range of PCB congeners), dioxins and furans, some chlorinated solvents and pesticides, and explosives.

3. *Improved monitoring techniques*: A significant amount of O&M is expended on process monitoring. Improved monitoring may include the use of automated and/or remote sensors, improved statistical approaches for monitoring to minimize sampling requirements, and improved analytical methods.

4. *Nutrient requirements*: Nutrient addition has the potential to enhance contaminant degradation rates, and at some sites may be a limiting factor to contaminant degradation.

5.2 DEVELOPMENT OF EMERGING TECHNOLOGIES TO BRING THEM TO THE MARKETPLACE

R&D is still needed for emerging technologies to bring them to the marketplace for full-scale implementation. Much of the microbiology of these technologies is relatively well understood, and while there is a continuous need to better understand the microbiology, the engineering application of these technologies remains the limiting factor for bringing them to the marketplace. Emerging technologies include anaerobic treatment, anaerobic/aerobic sequencing, cometabolic bioventing, phytoremediation, bioaugmentation, and natural attenuation.

5.2.1 Anaerobic Treatment and Anaerobic/Aerobic Sequencing

Anaerobic treatment technologies show increasing promise for treatment of relatively recalcitrant contaminants including chlorinated solvents, chlorinated aromatics (including some pesticides and PCBs), petroleum hydrocarbons, nitroaromatics (including explosives), and heavy metals (Fathepure and Tiedje, 1999). Anaerobic treatment offers a wide range of alternative electron acceptors (i.e., NO_3^-, Mn_4^+, Fe^{3+}, $SO_4^=$, and CO_2 for methanogenesis) under which biodegradation can occur, and there is increasing evidence of contaminant degradation under these various electron acceptor conditions. While anaerobic treatment holds great promise for bioremediation, its application at full scale has been limited. A primary limitation of anaerobic treatment technologies is that they often result in biotransformation byproducts that may be more harmful than their parent compounds. For example, PCE or TCA dechlorination can result in the production of DCE isomers and VC; PCB dechlorination generally results in the accumulation of lower-chlorinated byproducts; and anaerobic degradation of nitroaromatic compounds generally results in their conversion to amino-aromatic byproducts. Thus, the use of anaerobic treatment for many of these contaminants is likely to require subsequent aerobic treatment. The use of dual treatment processes results in increased cost and O&M requirements. While anaerobic/aerobic treatment trains have been investigated in the laboratory, this approach has not yet been tried at full scale.

Another reason why anaerobic treatment technologies have not been widely used is that they often target relatively recalcitrant contaminants. Because aerobic treatment has been so effective in the treatment of petroleum hydrocarbon contaminants, much of the remediation efforts over the past decade have focussed on aerobic treatment technologies and on removing these easily degraded contaminants. Furthermore, compared to chlorinated solvents, PCBs, energetics, and metals, the suite of petroleum hydrocarbon contaminants tend to be much more easily accessed and targeted for treatment. For example, LNAPLs are much more easily treated than DNAPLs, which in some cases cannot even be characterized; PAH-contaminated soils are more easily handled than soils contaminated with PCBs and dioxins; and most petroleum hydrocarbons tend to be associated with point sources resulting from accidental releases, compared to nonpoint sources for energetic compounds and heavy metals. In light of the success of aerobic bioremediation of petroleum hydrocarbons, there is an increasing portion of R&D funding that is targeting more recalcitrant compounds, which by default will include anaerobic treatment technologies because of the numerous compounds that degrade more readily under anaerobic conditions. Thus, it is increasingly likely that anaerobic biological treatment will be used in the field in the near future.

Research needs for anaerobic treatment technologies include the following:

1. *Technology maturity*: Extensive literature is available on anaerobic processes, but little has been done to date to bring technologies to the marketplace. Thus, a broad area of R&D opportunities exists for expanding and transferring concepts developed in the laboratory to pilot-scale and, ultimately, full-scale use. For example, there is extensive knowledge of the ability of anaerobic cultures to reductively dechlorinate chlorinated solvents, but reductive dechlorination in the vadose zone has seen limited field use. The primary limitation of enhanced anaerobic dechlorination resides in the

ability to introduce a suitable electron-donating compound to the environment in the area of contamination particularly for *in-situ* soils.

2. *Control and treatment of anaerobic treatment byproducts*: The potential for byproducts to form using anaerobic processes introduces the possibility of the production of undesirable contaminants, even though the parent compound may be transformed microbially. Development of treatment methods to manage byproducts formed during anaerobic treatment is needed. The most likely biological treatment scenario is the sequential use of anaerobic and aerobic treatment.

3. *Nutrient requirements*: As with aerobic technologies, nutrient addition has the potential to enhance contaminant removal rates using anaerobic treatment approaches, and at some sites may be a limiting factor to contaminant degradation.

4. *Toxicity measurements*: Methods for measuring soil toxicity and reductions in soil toxicity due to biological treatment are needed. This is especially true for anaerobic PCB treatment. Certain congeners, especially higher chlorinated congeners and those that have dioxin-like characteristics, may be much more toxic than other congeners that are less chlorinated and do not behave like dioxins (NRC, 2001). For example, EPA's Integrated Risk Information System (IRIS) uses two different cancer slope factors for highly-declorinated PCB mixtures and lower-chlorinated PCB mixtures. A cancer slope factor at 2.0 $(mg/kg\text{-}day)^{-1}$ is stipulated for all PCB mixtures except those congeners with more than 4 chlorines, which comprise less than 0.5% of the total PCB mass (EPA/600/P-96/001F). The dioxin-like characteristics are associated mostly with *meta*- and *para*-chlorinated PCBs and the more highly chlorinated PCBs (four or more chlorines). *Meta*- and *para*-chlorinated compounds are the PAHs most susceptible to reductive dechlorination (NRC, 2001; Bedard & Quenger, 1985; Quensen et al., 1998). Thus, dechlorination has the potential to significantly detoxify soils, even though it does not reduce the molar concentration of PCBs in soils.

5. *Metals stabilization*: Anaerobic technologies may be used to stabilize certain metals in soils. Stabilization occurs when these metals are transformed as hydroxide or sulfide precipitates under anaerobic conditions. The long-term stability of these precipitates after the soils become aerobic is an important factor in using anaerobic treatment for metals and warrants further investigation.

5.2.2 Phytoremediation

Phytoremediation is gaining increased use for soils remediation. Phytoremediation research needs include the following:

1. *Contaminant fate and transport*: The fate and transport of contaminants during phytoremediation plays an important role in its application. Contaminants may be biotransformed in the rhizosphere due to increased biological activity. If plants transpire contaminants, they may be released into the atmosphere unaltered or they may go through various levels of transformation by plant enzymes. Alternatively, plants may simply act as a hydraulic barrier to rainwater infiltration and the dissolution of contaminants.

2. *Field implementation studies*: Field studies of phytoremediation are needed to demonstrate this technology at pilot or full scale. A variety of field demonstrations are in their infancy. As these demonstrations mature, more information about the efficacy of phytoremediation will be forthcoming.

3. *Types of plants that can be used for phytoremediation*: Fundamental studies on phytoremediation continue to be required to identify plants that can be used for this technology and contaminants that are amenable to phytoremediation.

5.2.3 Bioaugmentation

Bioaugmentation has been a potential tool for environmental engineers and scientists for a decade, but has seen limited application. The primary obstacles to bioaugmentation that require further R&D include:

1. *Bioaugmentation performance*: For many sites, cultivation of indigenous bacteria is more cost effective than growing and concentrating foreign bacteria for augmentation. Additional comparison of the performance of augmented soils vs. unaugmented soils is needed to better understand the potential improvements made by bioaugmentation.

2. *Culture stability*: The stability of externally cultivated bacteria is not well understood, particularly when cultivated bacteria are introduced into foreign environments after augmentation.

3. *Delivery methods*: Delivery methods for bacteria are not well developed, particularly for *in-situ* vadose zone applications. R&D to produce improved delivery mechanisms is needed to ensure efficient delivery in the area of contamination.

5.2.4 Natural Attenuation

Natural attenuation may be a viable treatment technology for contaminated soils, but more research is needed to demonstrate its effectiveness and develop methods to validate its use. Research needs include the following:

1. *Sorption/precipitation of metals*: For metals, studies on irreversible sorption or precipitation are needed to ensure the stability of metals in the environment.

2. *Contaminant weathering*: Weathering of organic contaminants should be investigated to identify the fate and transport of these contaminants in soils.

3. *Protocol development*: The development of analytical tools to assess the efficacy of natural attenuation is needed to establish a uniform, engineered approach. To date, an approach to assess natural attenuation of soils has not been established.

5.3 FUNDAMENTAL RESEARCH AND DEVELOPMENT NEEDS FOR RECALCITRANT WASTE STREAMS

A variety of relatively recalcitrant compounds and waste streams have proven difficult to biodegrade, resulting in their persistence in the environment. More fundamental research is needed to develop potential biological treatment approaches that can address these environmental concerns.

1. *Dioxin biological treatment*: Under reduced conditions, dioxins (PCDD or PCDF) have been demonstrated to dechlorinate to potentially less harmful daughter products. Aerobically, the lesser-chlorinated dioxins may be biodegraded to form chlorinated salicylates, catechols, or phenols, which may require further anaerobic or aerobic biotransformation. Thus, the sequence of biological reactions may be relatively complex for dioxins and requires further investigation.

2. *Biotreatment of other relatively recalcitrant contaminants*: Fundamental research continues to be needed for the variety of relatively recalcitrant contaminants in the environment for which there are few treatment alternatives. Among the list of recalcitrant contaminants are the dioxins, identified above, PCBs, large-molecular-weight PAHs, chlorinated solvents and aromatic compounds, and energetic (nitroaromatic) compounds.

3. *Bioavailability*: In addition to the complexity of dioxin biotransformation pathways is the fact that dioxins, while ubiquitous in the environment, usually exist at sub-parts-per-million concentrations. Their low concentrations, low aqueous solubilities, and high sorption affinity make them relatively unavailable (low bioavailability) for microbial degradation. Research is needed to develop bioremediation approaches for low-concentration or low-bioavailable contaminant waste streams, and to better understand the biological fate of these contaminants in the environment.

5.4 SUMMARY OF RESEARCH NEEDS

Biological treatment of soils has been remarkably successful over the last decade when applied to low-molecular-weight petroleum compounds and other contaminants that are easily biodegraded. Today, the environmental restoration field is at a critical juncture. The biological treatment of easily degraded contaminants is relatively well understood and accepted, but a large number of contaminants remain for which there are no readily available technologies and for which biological treatment remains challenged.

It is helpful to remember that about a decade ago it was thought that aroclor mixtures were among the most recalcitrant contaminants in the environment due to their low bioavailability and high degree of chlorination (Adriaens et al., 1999). However, since the late 1980s, it has been well documented that PCB toxicity can be reduced through reductive dechlorination and can be completely mineralized through the combination of anaerobic and aerobic treatments. Reports of new and previously undocumented biotransformation pathways for recalcitrant contaminants continue to appear in the literature. Examples include recent reports of the anaerobic degradation of benzene and PAHs under sulfate-reducing conditions (Coates et al., 1996, 1997), anaerobic oxidation of DCE and VC (Bradley and Chapelle, 1996, 1997), and the ability to stimulate anaerobic PCB dechlorination by the addition of surrogate polybrominated biphenyl compounds to soils or sediments (Bedard et al., 1998) and the complete dechlorination of PCBs (Bedard and van Dort, 1998). These studies not only have important implications for the biodegradation of the specific contaminants on which they reported, but also indicate that new biodegradation pathways and mechanisms continue to be discovered and provide an optimistic future for the biodegradation of environmentally persistent contaminants.

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APPENDIX A: DATABASE REPORT SUMMARY TABLES

and

APPENDIX B: DATABASE REPORTS

for

APPLICATION, PERFORMANCE, AND COSTS OF BIOTREATMENT TECHNOLOGIES FOR CONTAMINATED SOILS

on

CONTRACT NO. 68-C-00-185
TASK ORDER NO. 13

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NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
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