# CONTAMINANTS AND REMEDIAL OPTIONS AT SOLVENT-CONTAMINATED SITES

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### **NOTICE**

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency (U.S. EPA) under contract. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as a U.S. EPA document. Mention of trade names or commercial productions does not constitute endorsement or recommendation for use.

### **FOREWORD**

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (U.S. EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural resources to support and nurture life. These laws direct the U.S. EPA to perform research which defines environmental problems, measures their impacts, and searches for solutions.

The Risk Reduction Engineering Laboratory (RREL) is responsible for planning, implementing, and managing research, development, and demonstration programs. Further, the RREL provides an authoritative, defensible engineering basis in support of U.S. EPA policies, programs, and regulations with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research, and it provides a vital communication link between the researcher and the user community.

This guidance document was prepared to assist federal and state remedial project managers, local agencies, private cleanup companies, and support contractors that may plan and implement remedial actions at National Priorities List (NPL) and other solvent-contaminated sites. The primary purpose of this document is to provide guidance on carrying out concurrent remedial action planning and accelerating project implementation for the cleanup of solvent-contaminated sites. It is also designed for use in conjunction with the U.S. EPA's guidance document on conducting remedial investigations and feasibility studies (Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA). This guidance document will provide the user with a systematic approach to remedial actions for solvent-contaminated sites. However, many unique and potentially hazardous conditions at NPL sites require very specialized considerations.

E. Timothy Oppelt, Director Risk Reduction Engineering Laboratory

### ABSTRACT

This document provides information which facilitates the selection of treatment technologies and services to meet established cleanup levels at solvent-contaminated sites. It does not provide risk-assessment information or policy guidance related to the determination of cleanup levels. It will assist federal, state, or private site removal and remedial managers operating within the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), or state rules. This document is designed for use with other remedial guidance documents issued for RCRA, CERCLA, and/or other state mandated cleanup activities to accelerate the remediation of solvent-contaminated sites.

Solvents are organic compounds; they are common contaminants found at Superfund sites. They are used in a variety of industrial and commercial processes, including chemical and product manufacturing, and as cleaning agents. The improper use, storage, and handling of solvents have resulted in soil, sediment, and sludge contamination, secondary contamination of underlying soils, and potential groundwater pollution. Most solvents are amenable to many remediation methods, but the same characteristics which assist remediation also allow solvent transport through the environment which in turn potentially exposes humans to toxic compounds.

The remedial manager faces the challenge of selecting remedial options which will achieve established cleanup levels. Often, more than one technology is implemented in the remediation strategy of a solvent site in order to meet its cleanup goals. Three general options exist: immobilization, destruction, and separation/concentration. Separation/concentration technologies prepare pesticides for further remediation by destruction or immobilization technologies. The remedial manager also adds pre- and post-treatment components with the principal technology(ies) into treatment trains. In the Remedial Options section of this document, treatment trains are outlined, and examples are given to emphasize their importance to a remedial strategy.

Section 2, Contamination at Solvent Sites, discusses solvent uses, their characteristics, and their behavior in the environment. Section 3, Remedial Options, details innovative and emerging technologies and proven treatments. It includes a discussion about the implementation and selection of the cleanup technology, names criteria for the selection of a remediation strategy, and introduces the concept of high-energy destruction techniques to reach more stringent contaminant residual levels. The technology performance data provided can assist the remedial manager to narrow the options to those most likely to succeed in achieving site-specific cleanup goals in the most cost effective and permanent way possible.

Additionally, this remedial aid document provides an extensive bibliography, organized by relevance to each section, which complements the information offered in these pages.

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### ABBREVIATIONS AND SYMBOLS

ACL Alternate Concentration Limit

AFB Air Force Base

Ag Silver

APC air pollution control APEG alkali polyethylene glycol

ARARs Applicable or Relevant and Appropriate Requirements

As arsenic

ATTIC Alternative Treatment Technology Information Center

Ba barium

BCDP base-catalyzed decomposition process
BDAT best demonstrated available technology
BTEX benzene, toluene, ethylbenzene, xylene

BTU British thermal unit

CARD CLP analytical results database

Cd cadmium

CEC cation exchange capacity

CERCLA Comprehensive Environmental Response, Compensation, and Liability Act

CFB circulating fluidized bed CLP Contract Laboratory Program

CN cyanide CO<sub>2</sub> carbon dioxide

C-N-P carbon-nitrogen-phosphorous COE U.S. Army Corps of Engineers

Cr chromium

CT carbon tetrachloride
DCA dichloroethane
DCE dichloroethylene

DNAPL, dense nonaqueous-phase liquid

DOE Department of Energy
DOI Department of the Interior
EDB ethylene dibromide

EPA United States Environmental Protection Agency

EPRI Electric Power Research Institute

Fe iron

FWEI Foster Wheeler Enviresponse, Inc.

g gram

GAC granular-activated carbon

GC/MS gas chromatography/mass spectrometry

H<sub>2</sub>O water

HCl hydrogen chloride HDPE high-density polyethylene

HELP hydrologic evaluation of landfill performance

Hg mercury K potassium

### **ABBREVIATIONS AND SYMBOLS (Continued)**

 $K_h$  Henry's law constant  $K_{oc}$  adsorption coefficient

K<sub>ow</sub> octanol/water partition coefficient KPEG potassium polyethylene glycolate

L lite

LEEP low energy extraction process

LLNL Lawrence Livermore National Laboratory

LNAPL light nonaqueous-phase liquid LTTA low temperature thermal aeration LT3 low temperature thermal treatment

MC methylene chloride
MDL method detection limit
MEK methyl ethyl ketone

mg milligram

MIBK methyl isobutyl ketone

MPEG methoxypolyethylene glycolate

MSWRMB Municipal Solid Waste & Residuals Management Branch

NaPEG sodium polyethylene glycolate NAPL nonaqueous-phase liquid NPL National Priority List

NWWA National Water Well Association

OERR Office of Emergency and Remedial Response

ORD Office of Research and Development PAH polycyclic aromatic hydrocarbons

Pb lead

PCB polychlorinated biphenyls

PCE tetrachloroethylene
PCP pentachlorophenol
ppb parts per billion
ppm parts per million
PVC polyvinyl chloride

RCRA Resource Conservation and Recovery Act

RF radio frequency

RFI RCRA Facility Investigation

RI/FS remedial investigation/feasibility studies

RO reverse osmosis

RREL Risk Reduction Engineering Laboratory

ROD Record of Decision

SCAR Superfund chemical analysis results

Se selenium

SITE Superfund Innovative Technology Evaluation

S/S solidification/stabilization
SVE soil-vapor extraction
TCA trichloroethane
TCE trichloroethylene

TCLP Toxicity Characteristic Leaching Procedure

TPH total petroleum hydrocarbons

USEPA United States Environmental Protection Agency

# **ABBREVIATIONS AND SYMBOLS (Continued)**

USITC United States Internal Trade Commission underground storage tank ultraviolet

UST UV

VC vinyl chloride

VOCs volatile organic compounds

### **ACKNOWLEDGMENTS**

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### SECTION 1 INTRODUCTION

#### **PURPOSE**

This document provides federal, state, and local Remedial Project Managers (RPMs), On-Scene Coordinators (OSCs), private cleanup companies, and support contractors with data concerning solvent contaminants. Sources and types of solvent contaminants, their characteristics, and their behavior in the environment will be named, and remedial options, i.e., principal proven and innovative technologies selected for solvent sites will be described. It is designed for use with other remedial guidance documents issued for Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and/or state cleanups to accelerate solvent site cleanup. The authors assume the reader is familiar with the appropriate policy issues (RCRA, CERCLA, state), risk assessment, and the determination of cleanup guidelines.

A 1992 review of the record of decision (ROD) summary database revealed over 400 sites where solvents were identified as a site contaminant. Remedial managers typically can expect sites to contain mixtures of solvents, other organics, and metals. Within this document, solvents are divided into halogenated and nonhalogenated species. Table 1-1 lists solvents commonly found at solvent-contaminated sites.

This text emphasizes source identifications: primary, such as a surface spills, and secondary, such as a subsurface migration from the primary source. "Source" in this use can mean the following:

- Process or equipment generating the contamination
- Contaminated soil, sludge, or sediment migrating from contamination
- Migrated surface/subsurface water contamination

This approach allows the remedial manager to target remediation in terms of contaminated zones. For example, the remedial manager may consider the relative practicality of remediating a highly contaminated surface zone versus a deeper, less contaminated zone. The manager may achieve significant contaminant and exposure reductions at a lower cost by remediating a more accessible zone before a less accessible one.

TABLE 1-1. SOLVENTS COMMONLY FOUND AT SOLVENT-CONTAMINATED SITES

BDAT Class	Class Description	Specific Contaminants Found at Solvent- Contaminated Sites
W01 <sup>(1)</sup>	Halogenated non-polar aromatics	1,2-Dichlorobenzene Chlorobenzene
WO4	Halogenated aliphatics	1,1,2,2-Tetrachloroethane 1,1,1-Trichloroethane (TCA) 1,1,2-Trichloroethane 1,1-Dichloroethane 1,2-Dichloroethane 1,2-Dichloropropane Dichlorodifluoromethane Carbon tetrachloride Chloroethane Chloroform Chloromethane Ethylene dibromide Methylene chloride (MC) Tetrachloroethylene (PCE) Trichloroethylene (TCE) Trichlorofluoromethane Vinyl chloride (VC) 1,1-Dichloroethene 1,2-Dichloroethene (trans-1,2-dichloroethene)
W07	Heterocyclics & simple nonhalogenated aromatics	Benzene Ethylbenzene o-Xylene p-xylene Styrene Toluene m-Xylene
W09	Other polar organic compounds	1,4-Dioxane Acetone Cresols Phenol Cyclohexanone Ethyl acetate Isobutanol Methanol Methyl ethyl ketone (MEK) Methyl isobutyl ketone (MIBK) Tetrahydrofuran

<sup>(1) &</sup>quot;W" codes obtained from Summary of Treatment Technology Effectiveness for Contaminated Soil, EPA/540/2-89/053 (1).

First, this strategy should mitigate the most toxic/mobile materials, and later, the less toxic/mobile ones. The remedial manager also should consider the risk to human health when determining the remediation strategy and how to control contaminant migration.

The remedial manager can anticipate the presence of sediment and sludge. Natural water bodies such as ponds and streams can become contaminated directly as holding ponds/lagoons, or secondarily by the migrating of solvent compounds. Usually, pretreatment dewatering allows sediment to be processed as a soil. Sludge from lagoon bottoms and processing equipment also requires treatment; however, the options for treating sludge are more limited.

### ORGANIZATION

Specifically, this document is concerned with the treatment of soils contaminated with solvents; the technology descriptions address soil remediation. It identifies the most important uses of solvents, presents factors to predict their behavior in the environment, and identifies treatment options to remediate solvent-contaminated sites.

The Remedial Options section describes the four principal treatment groups for the solvent media/contaminant matrix.

- Immobilization technologies minimize migration, either through construction of physical barriers, through chemical reaction, or by a combination of physical and chemical means.
- Destruction technologies use thermal, chemical, or biological mechanisms to alter toxicity.
- Separation/concentration technologies use physical or chemical processes to separate contaminants from the associated media without altering the contaminant's toxicity or mobility.
- Water-treatment technologies treat surface water, groundwater, and the process residuals from the applied technology groups.

The presentation of the technologies in this document is not an indication of the relative importance or success of the technology. The Remedial Options section stresses the use of treatment trains to achieve cleanup levels. It also introduces the concept of high-energy destruction techniques to reach stringent contaminant residual levels versus lower energy techniques for less rigorous cleanup requirements. The remedial manager can use the technology performance data to narrow the options to those most likely to succeed in achieving site-specific cleanup goals.

Descriptions of remedial options include innovative and emerging technologies as well as proven treatments. The Water-Treatment section options provide only a brief overview of remedial techniques because they have already been discussed in other U.S. EPA publications referenced in Section 3 - Remedial Options - Water Treatment.

### **Treatment Trains**

Generally, no single technology can remediate an entire solvent site; remediation often requires a combination of control and treatment options to achieve toxicity reduction and/or contaminant immobilization. This treatment train concept combines incremental or sequential control and treatment technologies to achieve site-specific objectives and acceptable residual contaminant levels. The technical data and technology-specific considerations addressed in the Remedial Options section aids in the selection of alternatives that will maximize the benefits of the treatment train approach at a particular site.

### Cleanup Levels

Cleanup levels are usually determined by risk assessment and compliance with applicable or relevant and appropriate requirements (ARARs). Although this document does not discuss the process for establishing cleanup levels, the remedial manager faces the challenge of selecting remedial options that meet these established cleanup levels. Two available options are destruction or immobilization. Separation/concentration technologies prepare solvent waste matrices for either destruction or immobilization.

Cleanup goals are more stringent for remediation technologies selection when they are based on carcinogenic compounds and/or residential exposures because of the increased health risks and potential for contact with the contaminants. For stringent cleanup levels, the selected remedial option will probably require high-energy input, such as incineration or pyrolysis. When less stringent cleanup levels are acceptable, a low-energy technology such as soil vapor extraction may be more appropriate.

The Remedial Options section of this document focuses on technologies that can meet a required cleanup levels. Many factors can influence a cleanup level, including the toxicity of contaminants, location and future use of the site, and hydrogeology. Several criteria also influence the remedy choice, including feasibility, ease of implementation, and cost.

### **Stages of Technology Development**

The technologies discussed in this document are in different developmental stages: proven, innovative, and emerging. Some, such as incineration and capping, have been proven at commercial scale. Others, such as microbial degradation and soil flushing, are less proven, or innovative, and will require site-specific treatability tests to ensure they can meet the established cleanup levels. Emerging technologies, such as horizontal barriers, have yet to be shown effective in site remediation. The descriptions provided in the Remedial Options section will familiarize the manager with the newer technologies. This section also offers performance data and treatability study results (where available) for contaminants found at solvent sites or for analogous compounds.

### COMPLEMENTARY BIBLIOGRAPHY

For the remedial manager who wishes to delve into specific topics, a comprehensive bibliography, organized to correspond with each section, is provided in Section 4 of this document.

### **IMPORTANT REFERENCES**

The authors assume the remedial manager is already familiar with appropriate policy issues (RCRA, CERCLA, state), risk assessment, the determination of cleanup levels, and (as appropriate) with the references listed below.

### **Policy**

Corrective Action for Solid Waste

Management Units at Hazardous Waste

Management Facilities; Proposed Rule.

55 FR 145, July 27, 1990<sup>(2)</sup>.

Proposed Subpart S rule which defines requirements for conducting remedial investigations and selecting and implementing remedies at RCRA facilities.

### **Technical**

Guidance for Conducting Remedial
Investigations and Feasibility Studies
Under CERCLA (3) EPA/540/G-89/004.

Guide for Conducting Treatability

Studies Under CERCLA (currently under revision) (4) EPA/540/2-91/13a.

Provides the user with an overall understanding of the remedial investigation/feasibility study (RI/FS) process.

Describes the necessary steps in conducting treatability studies to determine the effectiveness of a technology in remediating a CERCLA site. U.S. EPA Guide for Conducting Treatability
Studies Under CERCLA: Aerobic
Biodegradation Remedy Screening Guide (5)
EPA/540/2-91/13a.

U.S. EPA Guide for Conducting Treatability
Studies Under CERCLA: Soil-Vapor
Extraction <sup>(6)</sup> EPA/540/2-91/019a.

U.S. EPA Guide for Conducting Treatability Studies Under CERCLA: Soil Washing (7) EPA/540/2-91/002a.

U.S. EPA Guide for Conducting Treatability
Studies Under CERCLA: Chemical
Dehalogenation (8) EPA/540/R-92/013a.

Handbook on In Situ Treatment of Hazardous Waste Contaminated Soils (9) EPA/540/2-90/002.

Summary of Treatment Technology Effectiveness for Contaminated Soil (1) EPA/540/2-89/053.

Technology Screening Guide for

Treatment of CERCLA Soils and Sludges (10)

EPA/540/2-88/004.

RCRA Facility Investigation (RFI)
Guidance (Volumes 1 through 4) (11)
EPA 530/SW-89-031.

Describes the necessary steps in conducting treatability studies specifically for aerobic biodegradation remedy screening.

Describes the necessary steps in conducting treatability studies for assessing the applicability of soil vapor extraction.

Describes the necessary steps in conducting treatability studies for assessing the applicability of soil washing.

Describes the necessary steps in conducting treatability studies for assessing the applicability of chemical dehalogenation.

Provides state-of-the-art information on in situ technologies for use on contaminated soils.

Presents information on a number of treatment options that apply to excavated soils, and explains the BDAT contaminant classifications.

Contains information on technologies which may be suitable for the management of soil and sludge containing CERCLA waste.

Recommends procedures for conducting an investigation, and for gathering and interpreting the data.

In addition, U.S. EPA has also published engineering bulletins on topics that discuss single technologies, including the following:

Chemical Dehalogenation Treatment: APEG Treatment
Chemical Oxidation Treatment
Air Stripping of Aqueous Solutions
Granular Activated Carbon Treatment
In Situ Soil-Vapor Extraction Treatment
In Situ Steam Extraction Treatment
In Situ Soil Flushing
Mobile/Transportable Incineration Treatment
Soil Washing Treatment
Solvent Extraction Treatment
Slurry Biodegradation

Thermal Desorption Treatment

U.S. EPA documents may be obtained from the National Technical Information System (NTIS). The U.S. EPA Publications Bibliography cross references U.S. EPA publication numbers and titles with NTIS order numbers, as well as price codes.

Much information is being collected in data bases for quick retrieval. Many of these can be found in the following documents:

The Federal Database Finder (12).

A comprehensive listing of federal databases and data files.

Technical Support Services for Superfund Site Remediation (13).

Identifies technical support services available to field staff.

Bibliography of Federal Reports
and Publications Describing Alternative
and Treatment Technologies for
Corrective Action and Site Remediation (14)

Contains references for documents and reports from U.S. EPA, COE, U.S. Navy, U.S. Air Force, DOE, and DOI.

Bibliography of Articles from
On-Line Databases Describing
Alternative and Innovative
Technologies for Corrective Action
and Site Remediation (15)

Provides information for U.S. EPA remedial managers and contractors who are evaluating cleanup remedies.

Alternative Treatment Technology Information Center (ATTIC) (16).

A compendium of information from many available databases. Data relevant to the use of treatment technologies in Superfund actions are collected and stored in ATTIC.

### REFERENCES

- U.S. EPA (U.S. Environmental Protection Agency). 1989. Summary of Treatment Technology Effectiveness for Contaminated Soil. Office of Emergency and Remedial Response, Washington, D.C. EPA/540/2-89/053.
- 2. "Corrective Action for Solid Waste Management Units at Hazardous Waste Management Facilities: Proposed Rule," 55 Federal Register 30798. (27 July 1990) n. page.
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# SECTION 2 CONTAMINANTS AT SOLVENT SITES

### HISTORICAL USES OF SOLVENTS

Solvents are usually organic substances (liquids) capable of dissolving or dispersing one or more other substances. They can be halogenated or nonhalogenated and are widely used in many industrial and commercial applications. Solvents are commonly and most importantly used in chemical feedstocks; as intermediates and carriers in chemical manufacturing; in surface cleaning and preparation; in paints, varnishes, and strippers; as extractant processes in chemical and food processing; in textile processing and dry cleaning; and in industrial manufacturing processes. They also are used as aerosol propellants, foam blowing agents, refrigeration brines, and flame retardants (1). The major solvent-using industries, which account for approximately 80 percent of their total use, are paint, allied product and industrial operations (especially surface cleaning), dry cleaning operations, and pesticide, pharmaceutical, and other organic chemical manufacturers (1).

The most common contaminants found in groundwater at Superfund sites are listed in Table 2-1 <sup>(2)</sup>. Halogenated and nonhalogenated solvents are two of the most common classes of these contaminants. The compounds presented are quite varied and include halogenated volatile organics (liquid solvents and gases), nonhalogenated volatile organics (ketones/furans and aromatics), halogenated semivolatile organics [polychlorinated biphenyls (PCBs), pesticides, chlorinated benzenes, and chlorinated phenols], nonhalogenated semivolatile organics [polycyclic aromatic hydrocarbons (PAHs) and nonchlorinated phenols], and inorganics (metals). A ranked list of the top 22 organic groundwater contaminants identified at Superfund sites is presented in Table 2-2; the 20 most frequently identified contaminants are shown in Table 2-3. Note that the tables contain many halogenated and nonhalogenated solvents — thus indicating their wide use.

# TABLE 2-1. CONTAMINANTS COMMONLY FOUND AT SUPERFUND SITES (GROUNDWATER)

Halogenated Volatile	Nonhalogenated Volatile	Halogenated Semivolatile	Nonnaiodenated Semivolatile
Organics	Organics	Organics	Organics
Liquid Solvents	Ketones/Furans	PCBs (b)	PAHS (e)
Carbon Tetrachloride	Methyl Ethyl Ketone	Aroclor 1242	Acenaphthene
Chlorobenzene	4-Methyl-2-Pentanone	Aroclor 1254	Anthracene
Chloroform	Tetrahydrofuran	Aroclor 1260	Benzo(a)anthracene
cis-1,2-Dichloroethylene (d)			Benzo(a)pyrene
1,1-Dichloroethane (a)	Aromatics	Pesticides	Benzo(b)fluoranthene
1,2-Dichloroethane			Benzo(ghi)perylene
1,1-Dichloroethylene	Benzene (g)	Chlordane	Benzo(k)fluoranthene
1,2-Dichloropropane (a)	Ethyl Benzene (g)	DDD	Chrysene
Ethylene Dibromide (g)	Styrene	DDE	Dibenz(a.h)anthracene
Methylene Chloride	Toluene (g)	TOO	Finoranthene
1,1,2,2-Tetrachioroethane	m-Xylene (g)	Dieldrin	Fluorene
Tetrachloroethylene	o-Xylene (g)		Indeno(1,2,3-cd)pyrene
trans-1,2-Dichloroethylene (d)	p-Xylene (g)	Chlorinated Benzenes	2-Methyl naphthalene
1,1,1-Trichloroethane			Naphthalene
1,1,2-Trichloroethane	Inorganics	1,2-Dichlorobenzene	Phenanthrene
Trichloroethylene		1,4-Dichlorobenzene	Pyrene
	Arsenic (As)		•
Gases	Cadmium (Cd) Chromium (Cr)	Chlorinated Phenols	Nonchlorinated Phenols
Chloroethane	Cyanide (CN)	Pentachlorophenol (w)	m-Cresol (e)
Vinyl Chloride	Lead (Pb)	2,3,4,6-Tetrachlorophenol	o-Cresol (e)
	Mercury (Hg)		p-Cresol (e)
	Selenium (Se)		2,4-Dimethylphenol (e)
			Phenol

<sup>(</sup>a) May be component of antiknock fluids added to fuel oils

Source: (3)

<sup>(</sup>b) Constituent in some oils, greases, dielectric liquids, and thermostatic fluids
(d) May be present in dye or lacquer solutions
(e) Constituent of crude oil fractions (including fuel and motor oils) and/or coal tar fractions (including creosote); creosote may be present as DNAPL
(g) Constituent in fuel oils (e.g., gasoline)
(w) Combined with fuel oil #2 or kerosene when used as wood preservative

<sup>\*</sup> Although normally not classified as a contaminant, iron may strongly impact the subsurface behavior of other contaminants and may govern which treatment processes can or cannot be used. Note: Some contaminants listed may be present in subsurface as biological or chemical degradation products of others.

TABLE 2-2. 22 MOST FREQUENTLY OCCURRING ORGANIC CONTAMINANTS IN GROUNDWATER

Rank	Groundwater Contaminant
1	Acetone
2	Bis(2-ethylhexyl)phthalate
3	Toluene
4	TCE
5	Chloroform
6	МС
7	1,2-DCE
8	1,1,1-TCA
9	Benzene
10	Tetrachloroethylene (PCE)
11	Xylenes
12	1,1-DCA
13	Ethylbenzene
14	Di-n-butylphthalate
15	Naphthalene
16	MEK
17	Chlorobenzene
18	1,1-DCE
19	Phenol
20	Carbon disulfide
21	VC
22	1,2-DCA

Source: Superfund Chemical Analysis Results (SCAR), Downloaded from the CLP Analytical Results Database (CARD) Published in 1988.

TABLE 2-3. 20 MOST FREQUENTLY OCCURRING SUBSTANCES REPORTED AT FINAL NPL SITES

Rank	Substance
1	1,1,2-TCE
2	Lead
3	Chromium and compounds
4	Toluene
5 :	Benzene
6	PCE
7	1,1,1-TCA
8	Chloroform
9	Arsenic
10	PCBs
11	Cadmium
12	Zinc and compounds
13	Copper and compounds
14	Xylenes
15	1,2-Trans-DCE
16	Ethylbenzene
17	Phenol
18	1,1-DCA
19	MC
20	1,1-DCE

Source: Final National Priorities List (NPL) Sites as of March 1991. This list contains substances documented during HRS Score Preparation.

### **Halogenated Solvents**

The largest use of halogenated solvents occurs in degreasing/cleaning metal surfaces; the second involves the use of tetrachloroethylene (PCE) for dry cleaning (I). Other important applications involve their use in extraction processes, adhesives, aerosol products, paint and coating solvents, and industrial solvent blends. The four most widely used chlorinated solvents are 1,1,1-trichloroethane (TCA), methylene chloride (MC), trichloroethylene (TCE), and PCE. Table 2-4 shows consumption of these four chemicals.

### Nonhalogenated Solvents

Nonhalogenated solvents account for 64 percent of total solvent consumption. They are used most often as ingredients and wash solvents in the paint and allied products. Nonhalogenated solvents are used as process solvents, in the manufacture of adhesives, and in cold-cleaning operations. Xylene, toluene, methyl ethyl ketone (MEK), methanol, acetone, ethyl acetate, and methyl isobutyl ketone (MIBK) are the most frequently used nonhalogenated solvents <sup>(4)</sup>.

### SOLVENT USES AND THEIR RESIDUES

Major uses for the most common halogenated and nonhalogenated solvent chemicals are summarized in Table 2-4. Priority solvent industrial end uses are presented by category in Tables 2-5 and 2-6. Yearly production of solvent chemicals is presented in Table 2-7.

TABLE 2-4. CONSUMPTION OF MAJOR SOLVENTS (108 LBS/YEAR)

				Use as a Solvent	ıt						
Surface Classification	Coatings	Adhesives	82	Decreasing	Process Solvent	Other	Total Solvent Use	Nonsolvent	Franci	Total	% Used Domestically
Halogenated (RCRA)											
1,1,1-Trichloroethane	12	99	ı	378	36	ı	. 486	72	42	909	<u>6</u>
Carbon Tetrachloride	-	:	ŧ	0 to 10³	ı	1	0 to 10³	610 to 620³	40	099	0 to 2
Chlorobenzene			1		113	:	113	155	0	268	42
Chloroform	ı	-	-	ı	0 to 10³	ŧ	0 to 10³	312 to 412³	13	426	0 to 2
Fluorocarbons ··· ·	-	-		- 1113 -	373	+ <b>1</b> + 1	148	880	32	1,060	14
Methylene Chloride	l	1	-	39	132	1135	284	167	49	490	89
Tetrachloroethylene	4	9		196	ţ	3491	555	363	43	865	64
o-Dichlorobenzene	1	-	-	LÓ	7	ı	12	36	٥	47	26
Trichloroethylene	7	0		136	3	ŧ	143	10	17	170	84
Subtotal:	23	99	١	870	330	462	1,761	2,598	236	4,585	38
Nonhalogenated (RCRA)									÷		
Acetone	186	ı	:	22	121	ı	328	1,516	87	1,930	17
Benzene	0	ı	,	0 to 30	1	-	0:-0	446³	15	1,460	-6
Cresols	ı	1	•	8	:	24	32	88	13	133	24
Cyclohexanone	٥	0	0	0	0	-	5 to 25	ı	575 to 595 <sup>3</sup>	900	4-1
Ethyl Acetate	06	:1	· 1	·	18	29	136	4	. 62	220	62
Ethyl Benzene	1	1	1	-	••	54	54	7,146		7,200	0.8
Isobutanol	26		1		20	:	46	120	6	175	26

TABLE 2-4. (Continued)

				Use as a Solvent	į						
					Process		Total Solvent	Nonsolvent		Total	% Used Domestically
Surface Classification	Coatings	Adhesives	inks	Degreasing	Solvent	Other	Use	Use	Export	Demand	as Solvent
Methanol	113		1	63	146	107	419	7,336²	•	7,764	េ
Methyl Ethyl Ketone	308	78	22	1	156	ı	464	23	73	260	83
Methyl isobutyl Ketone	66	0 to 10	0 to 10	-	12 to 27 <sup>3</sup>	ı	121 to 138³	0 to 10³	14	162	80 to 91
n-Butanol	138	0_		7	0.54	-	189	1,284	112	1,595	12
Nitrobenzene		•	ŧ	ŧ	19		19	946	-	965	2
Toluene	358	7.1	99	31	36		560	6,040		009′9	8,5
Xylene	426	67	1	26	62	82	829	28,969	;	29,627	8
Subtotal:	1,742	221	92	162	651	292	3,076	64,916	987	68,971	6.2
Total RCRA Solvents	1,765	287	92	1,032	881	754	4,827	ı	:	1 .	ı
Other Organic Solvents (non-RCRA) <sup>4</sup>	1,663	1	ı	813	1,129	208	3,361	1	:	ı	4
Total Solvent Usage	3,418	287	92	1,845	2,010	362	8,180	ŀ	:	ŧ	1
% Halogentated (RCRA)	6.0	23.0	0	47.2	16.4	48.0	21.4	l		1	ı
% Nonhalogenated (RCRA)	61.0	77.0	100.0	8.8	27.4	30.4	37.5	\$	1	!	

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Includes chanol, isopropanol, special naphthas, chylere glycols, hexane, and mineral spirits. Excludes use of chanol as a solvent in consumer applications.

<sup>&</sup>lt;sup>1</sup> Dry cleaning.

<sup>&</sup>lt;sup>2</sup> Automotive solvent chemicals - 278.

<sup>5</sup> Estimated.

<sup>- =</sup> Not reported

<sup>5</sup> Paint stringer

<sup>6</sup> Information in table is from sources from years 1982 through 1986.

TABLE 2-5. PRIORITY SOLVENT INDUSTRIAL END USES

		e Category by t Type	1	of Solvent se Category	
Use Category	Halo- genated	Nonhalo- genated	Halo- genated	Nonhalo- genated	Percentage of Total RCRA Industrial Solvent Usage
Adhesives	23.0	77.0	3.8	7.3	6.0
Dry Cleaning	100.0	0.0	19.9	0.0	9.5
Industrial Paint Stripper	100.0	0.0	6.5	0.0	2.4
Inks	0.0	100.0	0.0	3.0	2.0
Paint/Coatings	1.3	98.7	1.3	56.8	36.7
Process Solvent	37.5	62.5	18.8	18.0	18.4
Vapor Degreasing/Cold Clean- ing	84.3	15.7	49.7	5.3	18.9
Miscellaneous	100.0	0.0	0.0	9.6	6.1
Total Industrial Uses	36.3	63.7	100	100	100

Source: (4)

TABLE 2-6. END USES OF SELECTED CHLORINATED SOLVENTS IN 1987, BY PERCENTAGE

·	Methylene Chloride	Tetra- chloroethylene	Tri- chloroethylene	1,1,1- Trichloroethane	
Adhesives			. 1	10	
Aerosols	18			13	
Chemical inter- mediate	<b></b> .	33	5	6	
Cleaning/ degreasing	10	. 11	87	54	
Coatings/inks				8	
Dry cleaning	<del></del>	50		2	
Electronics	8	-		4	
Paint stripping	33		1		
Pharmaceuticals	4				
Plastics	16				
Textile process- ing				- <del>-</del>	
Urethane foam	5				

<sup>--</sup> Use is small, but has not been quantified.

Source: (5)

TABLE 2-7. PRODUCTION OF SOLVENT CHEMICALS

Chemical	Production (millions of pounds)	Year	Source
Carbon tetrachloride	645.608	85	6
Chloroform	587.606	89	: 7
Chloromethane	460,558.000	89	8
1,1-Dichloroethane	502.000	77	; 6
1,2-Dichloroethane	13,382.874	89	8
1,2-Dichloropropane	76.953	80	6
Ethylene dibromide	155.000	83	6
Methylene chloride	481.639	89	8
Tetrachloroethylene	482.238	89	8
1,1,2,2-Tetrachloroethane	201.000	77	6
1,1,1-Trichloroethane	783.334	89	8
1,1,2-Trichloroethane	720.000	77	6
Trichloroethylene	180.000	85	6
Chloroethane	670.204	76	7
Vinyl chloride	10,134.86	89	8
Dioxane	9.217	81	6
Tetrahydrofuran	172.567	89	8
Acetone	2,524.338	89	8
Methyl ethyl ketone	450.089	89	8
Methyl isobutyl ketone	170.845	89	8
Toluene	5,249.313	84	6
Ethylbenzene	9,235.984	89	. 8
Styrene	8,336.905	89	. 8
Xylenes	988,417.508	89	8
Chlorobenzene	298.848	89	· , 8
1,2-Dichlorobenzene	52.236	84	6

### Paint and Allied Products

The largest solvent end use occurs within the paint and allied products industry; this accounts for approximately 50 percent of industrial solvent use. More than 98 percent of solvent consumption involves nonhalogenated solvents; xylene, toluene, MEK, and acetone.

Waste solvent streams from the paint and allied products industry contain solvent concentrations varying from trace levels to over 90 percent <sup>(4)</sup>. Solvent-bearing coatings and ink wastes from tank and equipment cleaning operations consist of a blend of solvents with solids concentrations up to 10 percent. Approximately one-third of equipment cleaning solvents are reclaimed, resulting in annual solvent disposal of 7 million gallons <sup>(1)</sup>. Similar to the paint industry, the manufacturing of inks, adhesives, dyes, and various types of coatings and printing applications involves nonhalogenated solvents in component formulations and equipment cleaning.

### **Surface Cleaning**

The primary uses of solvents for surface cleaning are in the metal working and service-related industries. Degreasing operations involve removal of oils, greases, waxes, lubricants, tars, water, and oil from surfaces. In 1980, the total number of solvent degreasing units in use was estimated to be 1.1 million in 336,000 plants. Surface cleaning and degreasing operations are concentrated in California, Illinois, Massachusetts, Michigan, New Jersey, New York, Ohio, Pennsylvania, and Texas (1).

Halogenated solvents are the primary cleaning agents used in vapor degreasers. The most widely used degreasing solvent is TCA; fluorocarbons, TCE, MC, and PCE are also common.

Chlorinated solvent use in surface cleaning is declining. Significant remedial trends include the substitution of petroleum-based solvents or alkaline reagents in cold cleaning; improvement in equipment design and operating procedures to reduce solvent emissions; and use of heat-pump technology for energy conservation in vapor degreasers.

Spent solvent composition depends on the degreasing application and may contain up to 90 percent of the original solvent. Sludges from recovery processes generally contain from 10 to 50 percent of the original solvent; heavy metal fines and other organics also are present (1, 2).

### Dry Cleaning

Estimates of the number of dry cleaning establishments which use solvents range from 21,000 to 40,000. Approximately 70 percent use tetrachloroethylene with annual consumption of 349 million pounds. About 30

percent use petroleum solvents such as Stoddard's™ solvent, a petroleum distillate (1).

Solvents used in dry cleaning are filtered to remove suspended materials and color bodies to allow their reuse. Filter cartridges, which are drained, reclaimed, or disposed, are used in approximately 75 percent of dry cleaning facilities. Dry cleaning wastes contain about 50 to 60 percent solvents contaminated with soil, lint, dirt, and detergent <sup>(4)</sup> originating from distillation residues or spent filter cartridges.

### Production of Pesticides, Pharmaceuticals, and Other Organic Chemicals

Solvents are used in the production of pesticides, pharmaceuticals, and other organic chemicals as a reaction medium and in equipment cleaning. Nonhalogenated solvents are the most commonly used.

Methylene chloride and TCA are chlorinated solvents used in pesticide formulation. Their use has decreased significantly during the past decade mainly due to costs. Where practicable, chlorinated solvents have been replaced by aqueous emulsions, deodorized kerosene, other organic solvents, and dry flowable formulations. Use of TCE and PCE has been curtailed due to concerns about their toxicity; carbon tetrachloride-based fumigants are no longer manufactured.

These industrial production processes generate solvent wastes from equipment cleaning, solvent recovery still bottoms, and off-specification materials. Much of this material is reclaimed, either on or off site, or incinerated (1)

### SOLVENT PRODUCTION AND USES

### **Liquid Halogenated Solvents**

### Carbon Tetrachloride

Carbon tetrachloride is used as a chemical intermediate in chlorofluorocarbon production and as a reaction medium in the polymer technology <sup>(6)</sup>. Ninety-one percent of carbon tetrachloride is used to produce trichloromonofluoromethane (Fluorocarbon 11, or F-11) and dichlorodifluoromethane (Fluorocarbon 12, or F-12). The remaining carbon tetrachloride produced is exported or used as a nonsolvent chemical intermediate <sup>(4)</sup>.

Carbon tetrachloride was used formerly in metal degreasing, dry cleaning, agricultural grain fumigation, and the manufacturing of fluorocarbons for aerosols, refrigerants, and fire extinguishers <sup>(6, 7)</sup>. Because of its toxicity, this solvent was replaced by less toxic chlorinated hydrocarbons in metal and fabric cleaning applications <sup>(8, 9)</sup>. Fluorocarbons 11 and 12 were widely used as aerosols in personal-care items until they were banned for use as spray-can propellants.

### Chloroform

Approximately 93 percent of chloroform demand is as a chemical intermediate in the production of monochlorodifluoromethane (Fluorocarbon 22, or F-22) for use as a refrigerant <sup>(4)</sup>. Additionally, it is used in the preparation of dyes and pesticides and as an extractant in the production of penicillin, vitamins, and flavors; a general solvent for adhesives, resins, pharmaceuticals, and pesticides; a solvent for removing fat from waste products; and a dry cleaning spot remover <sup>(4, 6, 7, 10)</sup>.

### 1,1-Dichloroethane (1,1-DCA)

1,1-dichloroethane is used as an intermediate in the production of TCA. It is used also as a solvent, a high-coupling agent in antiknock gasoline, and a paint, varnish, and finish remover (8, 10).

### 1,2-Dichloroethane (1,2-DCA)

Approximately 83 percent of the 1,2-DCA produced is used for production of VC to make polyvinyl chloride (PVC) <sup>(8)</sup>. A second important use is as a starting material for production of PCE, TCE, 1,1-dichloroethylene, (1,1-DCE) and TCA. 1,2-dichloroethane also is used as a solvent, an additive in antiknock gasoline, a lead scavenger, and a fumigant <sup>(7, 10)</sup>.

### 1,1-Dichloroethylene (1,1-DCE)

1,1-dichloroethylene is used as an intermediate in production of "vinylidene polymer plastics" such as Saran and Velon (used in screens, upholstery, fabrics, carpets, etc.). It is copolymerized with VC or acrylonitrile to form various kinds of Saran. It also is used in the manufacture of 1,1,1-TCA, as a component of synthetic fibers, and in adhesives <sup>(7, 10)</sup>.

### 1,2-Dichloroethylene (1,2-DCE)

1,2-dichloroethylene is used as a low-temperature extraction solvent for organic materials such as dyes, perfumes, lacquers, thermoplastics, and heat-sensitive solutions such as caffeine. Additionally, it is used as a chemical intermediate in organic synthesis of chlorinated solvents and compounds (6, 7, 10).

### 1,2-Dichloropropane

1,2-Dichloropropane is used in solvent mixtures for cellulose esters and ethers, and as an intermediate for PCE and carbon tetrachloride, a lead scavenger for antiknock fuels, a solvent for fats, oils, waxes, gums, and resins, a soil furnigant for nematodes, a scouring compound, a metal degreasing agent, and an insecticidal furnigant (6, 7, 10).

### Ethylene Dibromide (EDB) (1,2-Dibromoethane)

Ethylene dibromide is used in fumigation operations for preplanting and on grains, fruits, and vegetables; as a scavenger for lead in antiknock fluids and fuels; as a general solvent; in the production of water-proofing agents,

fire extinguishing agents, and gauge fluids during the manufacture of measuring instruments; in organic synthesis during the production of dye, pharmaceuticals, and ethylene oxide production; and as a specialty solvent for resins, gums, and waxes <sup>(6, 7)</sup>.

### Methylene Chloride (MC) (Dichloromethane)

The most common industrial method of producing dichloromethane uses a vapor-phase process. The oldest method to produce it was to react natural gas with chlorine; chloromethane, chloroform, and carbon tetrachloride are formed as coproducts <sup>(8)</sup>.

Methylene chloride is used as a solvent in approximately 60 percent of its applications. It is used most widely as a solvent for paint removal. Other significant applications include its use in chemical processing, as an extractant in food processing and for oil dewaxing, as a metal degreaser, and in electronics. It is important as an extractant in naturally-occurring, heat-sensitive substances, and for cellulose acetate. As a nonsolvent, MC is used primarily in the production of aerosols, urethane foam blowing agents, polycarbonate insecticides and herbicides, and as a vapor-pressure depressant in consumer products. The urethane foam industry uses MC to clean foam heads and lines between production runs (4, 7, 10).

### 1,1,2,2-Tetrachloroethane (1,1,2,2-TCA)

Frimary solvent uses of 1,1,2,2-TCA include its use as a dry-cleaning agent and in metals cleansing and degreasing. Additionally, it is used in the manufacture of PCE, 1,1-DCE, artificial silk, leather, pearls, paint, varnish, and rust removers. Other applications include employment as a soil fumigant; as a herbicide; as a solvent for chromium chloride impregnated in furs; in the estimation of water content in tobacco and many drugs; and in the production of photographic films, resins, lacquers, and waxes <sup>(7, 10)</sup>.

### Tetrachloroethylene (PCE) (Perchloroethylene)

The dry-cleaning and textile-processing industries are the primary users of PCE. Textile processing involves PCE use in fabric scouring and as a carrier solvent for fabric finishes, water repellents, sizing, and desizing operations. A significant portion of solvent demand involves metal degreasing. Tetrachloroethylene is used when high melting waxes and greases are removed, higher cleaning efficiency is required, or when water is present on part surfaces. The solvent also is used in coatings and adhesives applications (4, 7, 10).

As a nonsolvent, PCE is used as a chemical intermediate in the production of fluorocarbon F-113 (42 percent) and for export.

### 1,1,1-Tetrachloroethane (1,1,1-TCA)

Currently, 1,1,1-TCA is the most widely used degreasing solvent in the United States. As a solvent, it is used mainly for cold cleaning, vapor degreasing, adhesive formulations, electronics equipment cleaning, process solvent,

and coatings. As a nonsolvent, 1,1,1-TCA is utilized for adhesive applications. 1,1,1-tetrachloroethane is used during liquid Drano<sup>™</sup> production, for photographic film processing, as a propellant, and during printed circuit board production. 1,1,1-tetrachloroethane is available in uninhibited and inhibited grades, and it uses such stabilizers as nitromethane, methylpyrole, 1,4-dioxane, butylene oxide, 1,3-dioxane, and secbutyl alcohol <sup>(4, 6, 7)</sup>.

#### 1,1,2-Tetrachloroethane (1,1,2-TCA)

1,1,2-tetrachloroethane is used as a chemical intermediate in the manufacture of 1,1-DCE, and as a solvent for chlorinated rubber, fats, oils, waxes, and resins <sup>(7)</sup>.

#### Trichloroethylene (TCE)

Trichloroethylene is used as a degreasing solvent for approximately 80 percent of its total demand <sup>(5)</sup>. Additional solvent uses involve paints, coatings, fats, waxes, resins, oils, rubbers, extraction of caffeine from coffee, and general solvent applications. It also is used to flush liquid oxygen in aerospace operations and as a chemical intermediate in pesticides and herbicides <sup>(4, 6, 7)</sup>.

Because TCE has a lower boiling point than PCE, it is preferred for use in vapor degreasing operations. Stabilized grades of TCE for use in vapor degreasing and other cleaning operations have been developed to remain effective through repeated distillations and in degreasing aluminum.

#### Chlorobenzene

Major solvent applications of chlorobenzene are pesticide formulation and toluene diisocyanate processing. Also, it is used as a degreasing and dye assist agent, and synthetic rubber solvent for dipping applications. Total solvent use for these applications represents 42 percent of its current demand. Nonsolvent uses involve the production of nitrochlorobenzenes, diphenyl oxide, and phenylphenols <sup>(4, 6, 10)</sup>.

#### Dichlorobenzene

Both 1,2-dichlorobenzene and 1,4-dichlorobenzene are produced almost entirely as by-products of monochlorobenzene production <sup>(7)</sup>. Dichlorobenzenes are produced by benzene chlorination. The most common products of this method are monochlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene <sup>(6)</sup>.

1,2-Dichlorobenzene is used as a process solvent for manufacturing toluene diisocyanates; in the production of 3,4-dichloroaniline; as an intermediate for dyes and some agricultural chemicals; in degreasing operations; in limited application as a heat transfer fluid; and as an ingredient in fumigants, herbicides, and metal polishes (4, 6, 10). As a nonsolvent, it is used in pesticides manufacturing.

1,3-Dichlorobenzene usually occurs as a contaminant of 1,2-dichlorobenzene and 1,4-dichlorobenzene

production, and is used as a fumigant and insecticide (7).

Historically, 90 percent of the total production of 1,4-dichlorobenzene has been used for making insecticides or air deodorants. Additinally, 1,4-dichlorobenzene is used in the manufacture of dyes and intermediates, pharmaceuticals, moth repellents, and as a soil furnigant (7).

#### **Gaseous Halogenated Solvents**

#### Chloroethane

Chloroethane is employed as an ethylating agent in the manufacture of tetraethyl lead, dyes, drugs, perfumes, and ethyl cellulose. Other uses involve application as a refrigerant; as an anesthetic; as a solvent for fats, oils, waxes, phosphorus, sulfur, acetylene, and many resins; in organic synthesis of perchloroethane, esters, and Grignard reagents; as a propellant in aerosols; and as an insecticide and alkylating agent (6, 7, 10).

#### Vinyl Chloride (VC)

Primarily, VC is used in the production of polyvinyl chloride (PVC). It also is utilized in copolymers, adhesives for plastics, organic syntheses, and as a refrigerant <sup>(6, 7)</sup>.

#### **Liquid Nonhalogenated Solvents**

#### Acetone

Acetone is utilized as a solvent for fats, oils, waxes, resins, nitrocellulose, cellulose, acetylene, paint, varnish, lacquer, and many other substances. Other applications involve use in organic chemical manufacturing, dyestuffs, sealants and adhesives, acetylene gas storing, precision equipment drying and cleaning, paraffin purifying, tissue hardening and dehydrating, specification testing of vulcanized rubber products, smokeless-powder manufacturing, and nail-polish remover <sup>(4, 6)</sup>.

#### Benzene

Because of its toxicity, benzene is used currently as a solvent only when less hazardous compounds, such as toluene or xylene, cannot be substituted. Benzene was used previously as a solvent in cold cleaning, fabric scouring, and in the paint and coatings industry (4, 6, 10). Major nonsolvent uses involve production of ethylbenzene/styrene, cumene/phenol, cyclohexane, nitrobenzene/aniline, detergent alkylate, chlorobenzenes, maleic anhydride, and miscellaneous chemicals.

#### 1,4-Dioxane

1,4-Dioxane is used as a solvent for cellulose acetate, ethyl cellulose, benzyl cellulose, resins, oils, waxes,

oil- and spirit-soluble dyes, and many other organic and some inorganic compounds. Other solvent uses involve lacquers, paints, varnishes, cements, cosmetics, deodorants, fumigants, emulsions, and paint and varnish removers. It also is utilized as a wetting and dispersing agent in textile processing, dye baths, stain and printing compositions, cleaning and detergent preparations, polishing compositions, scintillation counters, and as a stabilizer for chlorinated solvents (6, 7, 10).

## Ethylbenzene

Ethylbenzene is employed in the conversion to the styrene monomer, the spray application of vinyl resing surface coatings, the manufacture of paints, varnishes, and other surface coatings, during the oven baking and drying of surface coatings, and as an intermediate in dye manufacture. Other applications include the production of acetophene, cellulose acetate, styrene, and synthetic rubber. Ethylbenzene is present in mixed xylenes and is a constituent of naphtha. It is used as an antiknock agent, especially in airplane fuels, and comprises 4.6 percent by weight in high octane gasoline (7, 10).

# Methyl Ethly Ketone (MEK) (2-Butanone)

2-butanone is used primarily as a solvent in vinyl nitrocellulose, acrylic and other coatings, and as a solvent in adhesives, magnetic tapes, printing inks, and lube oil dewaxing. Its most common nonsolvent use is as a chemical intermediate (4 percent). Other applications involve vegetable-oil extraction, azeotropic distillation in refineries, and cold cleaning <sup>(4, 6, 7, 10)</sup>. Because of its rapid drying capability and strong solvency for lacquer binders (nitrocellulose, acrylics, vinyls, etc.), MEK is the preferred solvent for thinning epoxy and PVC coatings and, occasionally, as a stripper <sup>(4,7)</sup>.

# Methyl Isobutyl Ketone (MIBK) (4-Methyl-2-Pentanone)

The primary use of MIBK is in solvent applications, especially in the coatings industry as a solvent in nitrocellulose lacquers. Additionally, 4-methyl-2-penatone is used for various coatings, adhesives, and inks. It is a good solvent for high solids coatings, such as acrylics, polyesters, alkyds, and acrylic/urethanes, because of its strong solvency, low density, and high electrical resistivity. 4-methyl-2-penatone is employed also as a solvent in pesticides or pharmaceuticals (tetracyclene antibiotics purification), as a rare-metal extractant, and as a denaturant. It may be blended with MEK for use in high-solids lacquers and vinyl-resin solutions (4, 6, 10).

#### Styrene

Major uses of styrene include the formation of polystyrene, resins, protective coatings (styrene-butadiene latex and alkyds), styrenated polyesters, rubber-modified polystyrene, and copolymer resins.

#### Tetrahydrofuran

Tetrahydrofuran is used primarily as a solvent for natural and synthetic resins, especially PVC and vinylidene chloride copolymers. It is used to cast PVC films, coat substrates with vinyl and vinylidene chloride, and solubilize

adhesives based on or containing PVC resins. A second major use is as an electrolytic solvent in the Grignard reaction-based production of tetraethyl and tetramethyl lead. Tetrahydrofuran also is used as an intermediate in production of polytetramethylene glycol <sup>(6, 7, 10)</sup>.

#### Toluene

The majority of toluene solvent uses involve the paints and coatings industry. It is used also in formulating adhesives, inks, pharmaceuticals, chemical processing, and cold cleaning. Toluene is used with other aromatics as a wash solvent and for thinning resins that are difficult to solubilize by aliphatics. Major nonsolvent uses are the production of benzene, toluene diisocyanate, benzoic acid, benzyl chloride, and other chemicals. Toluene also is used in aviation gasoline and high-octane blending stock, explosives (TNT), toluene sulfonates (detergents), and as a scintillation cocktail (4, 6, 7, 10).

## o-, m-, and p-Xylenes

Xylenes used during solvent applications are mixed xylenes which have been depleted in o-xylene and p-xylene. Xylene is used extensively in the paint and coatings industry as a wash solvent and a stripping and general solvent because of its ability to solubilize resins and lacquers, its lower cost compared to other solvents, and its rapid evaporation. This use accounts for about 58 percent of mixed xylene demand. Additional solvent applications involve adhesives, process solvent use, agricultural sprays, cold cleaning and fabric scouring, and miscellaneous uses <sup>(4)</sup>.

m-Xylene is used often as a solvent and as an intermediate for dyes and organic synthesis, especially isophthalic acid. Other applications include insecticides and aviation gasoline  $^{(7, 10)}$ . o-Xylene is used in the manufacture of phthalic anhydride, in vitamin and pharmaceutical synthesis, and in dyes, insecticides, and motor fuels  $^{(6,7)}$ . p-Xylene finds uses in the synthesis of terephthalic acid for polyester resins and fibers (Dacron, Mylar, Terylene), vitamin and pharmaceutical syntheses, and insecticides  $^{(7,10)}$ .

#### **Nonchlorinated Phenols**

#### o-, m-, and p-Cresols

Major solvent uses of cresols include utilization as an enamel solvent in producing magnetic wire, and as a cleaning compound and an intermediate in the production of phosphate esters, resins, antioxidants, perfumes, herbicides, and disinfectants. Additionally, cresols are used as ore flotation and textile scouring agents (4, 7, 10).

#### Phenol

Phenol is used as a selective solvent for refining lubricating oils and as an ingredient in the production of phenolic resins, epoxy resins (biphenyl-A), nylon-6 (caprolactam), 2,4-dichlorophenoxy acetic acid, adipic acid,

salicylic acid, phenolphthalein, PCP, acetophenetidin, picric acid, germicidal paints, pharmaceuticals, dyes, and indicators. Phenol also is employed as a laboratory reagent, slimicide, biocide, and general disinfectant (6, 7, 10).

#### BEHAVIOR, FATE, AND TRANSPORT

#### **Predicting Contaminant Behavior**

Physical and chemical properties of contaminants determine their fate in subsurface systems. This section deals with the properties that describe the physical state of solvents frequently found at Superfund sites as well as properties pertinent to their environmental fate and transport in the subsurface. Values of contaminant properties are found in Tables 2-8a and 2-8b.

- Boiling point is the temperature at which the vapor pressure of a liquid equals the atmospheric pressure.
   The boiling point of a substance at 1 atmosphere (760 mm Hg) is the normal boiling point of that substance.
- The melting point is the temperature at which a solid undergoes a phase change to a liquid. Solvents with melting points less than 30° C could be present as mobile nonaqueous phase liquids (NAPL). Those with melting points above 30° C are solids in the pure form or dissolved in water or an organic solvent.
- Henry's Law Constant (H) is the ratio of a compound's partial pressure in air to its concentration in water at a given temperature under equilibrium conditions. The larger the Henry's Law Constant, the more likely the contaminant will volatilize from an aqueous solution and be amenable to vacuum extraction treatment. Henry's Law Constants in the range of 10<sup>-3</sup> to 10<sup>-5</sup> atm-m³/mol indicate volatilization as an important transfer mechanism, with rapid volatilization at values greater than 10<sup>-3</sup> atm-m³/mol.
- Octanol/water partition coefficient (K<sub>ow</sub>) is the ratio of a contaminant's concentration in the octanol phase to its concentration in the aqueous phase in a two-phase octanol/water system. The coefficient is a measure of the tendency of a contaminant to partition into an organic phase or an aqueous phase. Contaminants with K<sub>ow</sub> values less than 10 are relatively hydrophilic, with high solubility in water, low soil sorption coefficients, and small bioconcentration factors. Hydrophobic compounds have K<sub>ow</sub> values greater than 10, and tend to accumulate in organic substances rather than water. Knowledge of the K<sub>ow</sub> value of a particular contaminant can help predict its tendency to sorb to subsurface solids or move with infiltrating water to reach groundwater.

TABLE 2-8a. SELECTED PROPERTIES OF CONTAMINANTS COMMONLY FOUND AT SUPERFUND SITES

Chemical	Melting Point (°C)	Boiling Point (°C)	Dynamic Viscosity (cp)	Kinematic Viscosity (cs)	Log K <sub>w</sub>	Log K <sub>∞</sub>
Halogenated Volatile Organics		1				
Liquid Solvents						'
Carbon Tetrachloride	- 23 <sup>(11)</sup>	- 22.6 <sup>(11)</sup>	0.965 (11)	0.605 (11)	2.83 (12)	2.64 <sup>(12)</sup>
Chloroform	- 64 <sup>(11)</sup>	- 63.5 <sup>(11)</sup>	0.563 (11)	0.379 (11)	1.97 (12)	1.64 (12)
cis-1,2-Dichloroethylene	- 81 <sup>(10)</sup>	. 60 ttoj	0.467 (11)	0.364 (11)	1.86 (12)	1.5 (12)
1,1-Dichloroethane	- 97.4 <sup>(51)</sup>	57.3 <sup>(11)</sup>	0.377 (11)	0.321 (11)	1.79 (12)	1.48 (12)
1,2-Dichloroethane	- 35.4 (11)	83.5 (11)	0.84 (11)	0.67 <sup>(11)</sup>	1.48 (12)	1.15 (12)
1,1-Dichloroethylene	-122.5 <sup>(11)</sup>	31.9 (11)	0.33 (11)	0.27 (11)	2.13 (12)	1.81 (12)
1,2-Dichloropropane	- 90 (11)	96.8 (11)	0.84 (11)	0.72 (11)	2.02 (12)	1.71 (12)
Ethylene Dibromide	9.7 (11)	131.36 (11)	1.676 (11)	0.72 ***	1.76 (12)	1.45 (12)
Methylene Chloride	- 97 <sup>(11)</sup>	40.5 (11)	0.43 (11)	0.324 (11)	1.25 (12)	0.94 (12)
1,1,2,2-Tetrachloroethane	-43 <sup>(11)</sup>	146.5 (11)	1.77 [11]	1.10 (11)	2.39 (12)	2.34 (12)
Tetrachloroethylene	- 22.7 (11)	120.97 (11)	0.89 (11)	0.54 (11)	3.14 (12)	1
trans-1,2-Dichloroethylene	- 50 (10)	48 (10)	0.404 (11)	0.64 (11)	2.09 (12)	2.82 <sup>(12)</sup>
1,1,1-Trichloroethane	- 32 (11)	74.08 (11)	0.858 (11)	0.647 (11)	2.49 (12)	
1,1,2-Trichloroethane	- 36 (11)	- 36.5 (11)	0.119 (11)	0.824 (11)	2.49 (12)	2.18 (12)
	-87 (15)	86.8 (11)		•		1.75 (12)
Trichloroethylene	- 87	00.8	0.570 (11)	0.390 (11)	2.42 (2)	2.10 (12)
Gases	120 4 (11)	12.5 (11)	0.70 (11)	0.040 (13)	4 40 1171	1 - 12
Chloroethane	-136.4 (11)	1	0.278 (11)	0.310 (11)	1.43 (12)	1'.17 <sup>(12)</sup>
Vinyl Chloride	-153.8 <sup>(11)</sup>	-13.9 (11)	0.252-100(11)	0.256 (11)	0.60 (12)	0.91 (12)
Nonhalogenated Volatile Organics						
Cydio						,
1,4-Dioxane	11.8 (11)	101.1 [11]	1.439150 (11)	1.397150 (11)	-0.27 (11)	log 17
Tetrahydrofuran	-108.5 (10)	66.0 <sup>(7)</sup>	0.55 (13)	0.618 (4)	0.46 <sup>(3)</sup>	log 1.77
Ketones/furans		1				
Acetone	- 94.4 (11)	56.5 (11)	0.331 (11)	0.418 (11)	-0.24 (11)	-0.43 <sup>(12)</sup>
Methyl ethyl ketone	- 86.4 (11)	79.6 (11)	0.40 (11)	0.497 (11)	0.29 (12)	0.65 (12)
Methyl isobutyl ketone	- 83 <sup>(11)</sup>	119.0 (11)	0.5848 (11)	0.729 (11)	1.25 (12)	1.38 (12)
Arometics		] : 				
Benzene	5.5 <sup>(11)</sup>	80.1 (11)	0.6468 (13)	0.7379 (11)	2.13 (12)	1.81 (12)
Ethyl benzene	- 94.97 <sup>(11)</sup>	136.19 (11)	0.678 (11)	0.782 (11)	3.15 <sup>(12)</sup>	2.83 (12)
Styrene	- 30.6 (11)	145.2 [12]	0.751 (13)	0.829 (13)	3.16 <sup>(12)</sup>	2.87 (12)
Toluene	- 95.1 <sup>(11)</sup>	110.8 <sup>(11)</sup>	0.58 (11)	0.669 (11)	2.73 <sup>(12)</sup>	2.41 (12)
<i>m</i> -Xylene	- 60 <sup>(11)</sup>	138.5 (11)	0.608 (11)	0.717 (11)	3.20 (12)	2.84 (12)
o-Xylene	- 25 <sup>(11)</sup>	144.4 (11)	0.802 (11)	0.932 (11)	3.12 <sup>(12)</sup>	2,84 (12)
ρ-Xylene	13 (11)	138.6 (11)	0.635 (11)	0.763 ( <sup>11)</sup>	3.15 <sup>(12)</sup>	2.84 [12]

TABLE 2-8a. (Continued)

Chemical	Melting Point (°C)	Boiling Point (°C)	Dynamic Viscosity (cp)	Kinematic Viscosity (cs)	Log K	Log K <sub>∞</sub>
Chlorinated Benzenes		1				
Chlorobenzene	- 45 <sup>(10)</sup>	131.7 (11)	0.756 (11)	0.683 (11)	2.84 <sup>[12]</sup>	2.2 (12)
1,2-Dichlorobenzene	- 17 <sup>(10)</sup>	180.5 <sup>(11)</sup>	1.302 (11)	0.997 (11)	3.38 <sup>(12)</sup>	3.06 (12)
1,4-Dichlorobenzene	53 <sup>(10)</sup>	174.56 (11)	1.258 (11)	1.008 (11)	3.39 <sup>(12)</sup>	3.07 (12)
Nonchiorinated Phenois						
m-Cresol	12 <sup>(10)</sup>	, 201 <sup>(12)</sup>	nd	nd	1.96 (14)	1.43 (15)
o-Cresol	31.0 <sup>(10)</sup>	191.0 (11)	4.49 <sup>400 (11)</sup>	4.37 <sup>40C(11)</sup>	1.95 <sup>(14)</sup>	1.23 (15)
p-Cresol	34.8 <sup>(10)</sup>	· 201 (12)	nd	nd	1.94 [10]	1.28 (15)
Phenoi	41 (10)	181.7 (12)	3.02 <sup>(f1)</sup>	3.87 <sup>(11)</sup>	1.46 <sup>(12)</sup>	1.15 (12)

TABLE 2-8b. SELECTED PROPERTIES OF CONTAMINANTS **COMMONLY FOUND AT SUPERFUND SITES** 

Chemical	· Water Solubility . (mg/l)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m³/mol)	Liquid Density (g/cc)	Vapor Specific Gravity
Halogenated Volatile Organics	•				
Liquid Solvents	Ţ				
Carbon Tetrachloride	800 (12)	91.3 <sup>(11)</sup>	0.0302 (12)	1.5947 (11)	5.5 <sup>(11)</sup>
Chloroform	8,000 (12)	160 (33)	0.0029 *(12)	1.485 (11)	4.12 (11)
Cis-1,2-dichloroethylene	3,500 (10)	200 <sup>(19)</sup>	0.0076 *(10)	1.284 (11)	3.34 (11)
1,1-Dichloroethane	6,600 <sup>(11)</sup>	182 *(11)	0.0043 *(11)	1.175 (11)	3.44 (11)
1,2-Dichloroethane	8,690 (12)	83.35 (11)	0.00091 *(12)	1.253 (11)	3.4 (11)
1,1-Dichloroethylene	400 (12)	500 (11)	0.021 *(12)	1.214 (11)	3.25 (11)
1,2-Dichloropropane	2,700 (12)	39.5 (11)	0.0023 *(12)	1.158 (11)	3.9 (11)
Ethylene Dibromide	3,400 (10)	11 (11)	0.000318 (16)	2.172 (11)	6.48 (11)
Methylene Chloride	20,000 (12)	350 111	0.0020 *(12)	1.325 (11)	2.93 (11)
1,1,2,2-Tetrachloroethane	2,900 [12]	6 <sup>(11)</sup>	0.00038 *(12)	1.600 ""	5.79 <sup>(11)</sup>
Tetrachloroethylene	160 (12)	14 (11)	0.0153 (12)	1.625 (11)	5.83 (11)
Trans-1,2-dichloroethylene	150 (12)	265 (11)	0.384 *(12)	1.257 (11)	3.34 (11)
1,1,1-Trichloroethane	4,400 (12)	100 (11)	0.018 *(12)	1.325 (11)	5.45 * <sup>(11)</sup>
1,1,2-Trichloroethane	4,500 (12)	19 (11)	0.00074 (11)	1.4436 (11)	5.45 * <sup>(11)</sup>
Trichloroethylene	1,100 (12)	67.8 <sup>(11)</sup>	0.0091 *(12)	1.4649 (11)	4.53 (11)
Gases	ş			:	
Chloroethane	57,000 <sup>(18)</sup>	1,000 (11)	0.0111 (12)	0.8978 (11)	2.22 (11)
Vinyl Chloride	1,1000 (18)	2,300 (11)	O.695 (16)	0.9121 (11)	2.15 (11)

<sup>(</sup>c) calculated (\*) value at 25°C

TABLE 2-8b. (Continued)

Chemical	Water Solubility (mg/l)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m <sup>3</sup> /mol)	Liquid Density (g/ce)	Vapor Specific Gravity
Nonhalogenated Volatile Organics	1				
Cyclic	ı			1	
1,4-Dioxane	miscible**(11)	38.09*(11)	4.80 E-6*(18)	1.035 (11)	2.22 (11)
Tetrahydrofuran	miscible (11)	45.6 *(14)	O.00011 <sup>(3)</sup>	0.8892 (10)	nd
Ketones/furans					
Acetone	miscible (12)	181.72 (11)	0.0000397+(12)	0.791 (11)	2.0 (11)
Methyl Ethyl Ketone	28,600 [12]	71.2 (11)	0.0000274 (2)	0.805 <sup>(11)</sup>	2.5 (11)
Methyl Isobutyl Ketone	17,000 (12)	16 (11)	0.000155 (13)	0.8017 (11)	3.45 (11)
Aromatics					
Benzene	1,780 (12)	76 <sup>(11)</sup>	0.00548 (12)	0.8765 (11)	2.77 (11)
Ethylbenzene	152 (12)	7.1 <sup>(11)</sup>	0.0066 (12)	0.8670 (11)	3.66 (11)
Styrene	300 (12)	5 <sup>(10)</sup>	0.00261 (12)	0.9060 (13)	4.26 (12)
Toluens	515 <sup>(12)</sup>	22 <sup>(11)</sup>	0.0067 (12)	0.8669 (11)	3.14 (11)
m-Xylene	173 *1121	g <sup>(11)</sup>	0.0070 (12)	0,8642 (11)	3.66 (11)
o-Xylene	152 (12)	7 <sup>(11)</sup>	0.00527 [12]	0.880 (11)	3.7 (11)
p-Xylene	198 (12)	9 (11)	0.0071 (12)	0.8610 (11)	3.66 (11)
Chlorinated Benzenes				······································	
Chlorobenzene	500 <sup>(12)</sup>	8.8 (11)	0.00303 (12)	1.106 (11)	3.9 (11)
1,2-Dichlorobenzene	100 112)	0.0019 (12)	0.0019 (12)	1.306 (11)	5.1 <sup>(n)</sup>
1,4-Dichlorobenzene	59 (12)	0.0031 (12)	0.0031 (12)	1.288 (11)	5.07 <sup>(11)</sup>
Nonchlorinated Phenois					
m-Cresol	23,500 (10)	0.153 (14)	0.000038 [14]	1.038 (10)	nd
o-Cresol	31,000 40°C (10)	0.245 (14)	0.000047 (14)	1.0273 (14)	3.72 (11)
p-Cresol	24,000 40°C [10]	0.108 (14)	0.00035 (14)	1.0347 (10)	nd
Phenol	84,000 (10)	0.529 <sup>(18)</sup>	7.80 E-07°	1.0576 (16)	3.02 (11)

<sup>(</sup>c) calculated (\*) value at 25°C (\*\*) miscible in all proportions

- Adsorption coefficient (K<sub>∞</sub>) is the ratio of the mass of contaminant adsorbed per unit weight of organic carbon in soil to the concentration of the contaminant in solution at equilibrium. The adsorption coefficient describes the tendency of a contaminant to partition between solid and solution phases of a water-saturated or unsaturated soil. Sorption affects mobility, volatilization, hydrolysis, and biodegradation potential of a contaminant.
- Aqueous solubility is the maximum amount of the compound that will dissolve in pure water at a specific temperature. It is expressed in units of mg/L, g/L, parts per million (ppm), or weight percent (WT %). Highly soluble contaminants are easily distributed in water and tend not to sorb to subsurface solids. These chemicals are amenable to removal by pump-and-treat methods and are usually biodegradable.
- Specific gravity is the ratio of the density of a substance to the density of a reference substance at a specific condition. The reference for the specific gravity of liquids is usually water at a temperature of 4°C. Contaminants with specific gravity greater than 1 potentially will migrate under the influence of gravity through saturated and unsaturated subsurface materials. These contaminants are called dense nonaqueous-phase liquids (DNAPLs); examples include TCE and PCE. Compounds with specific gravity less than 1 tend to float on the water table. These contaminants are called light nonaqueous-phase liquids (LNAPLs); examples include gasoline and fuel oils. Highly soluble compounds with specific gravity less than 1 may dissolve completely in groundwater; examples include acetone and MEK.
- Vapor specific gravity is the ratio of the vapor density of a pure compound to that of air at the same temperature and pressure. The vapor specific gravity of air is 1. The vapor specific gravity can be determined using the ideal gas law and is equal to the ratio of the molecular weight of the compound to the molecular weight of air.
- Vapor pressure of pure compounds is the pressure exerted by the vapor of a substance under equilibrium conditions. It provides an indication of the extent to which the contaminant will volatilize. The higher the vapor pressure, the greater the tendency for volatilization. Contaminants with high vapor pressures are more amenable to vacuum extraction treatment technologies.
- Dynamic viscosity is the ratio between applied shear stress and shear rate. The mobility of a contaminant in pure form is inversely proportional to its dynamic viscosity.
- Kinematic viscosity is the ratio of a contaminant's dynamic viscosity to its density. The lower the kinematic viscosity, the greater the tendency to migrate downward. In the case of groundwater contamination by DNAPLs, the lower the kinematic viscosity of the DNAPL, the more likely it will penetrate finer-grained layers in the subsurface.

#### Transport

Subsurface contamination by halogenated or petroleum solvents exists initially as a separate phase within the soil pores. Over time, the solvents dissolve into the aqueous phase, adsorb to the subsurface solids, and volatilize to the atmosphere. However, significant NAPLs can remain on the soil and aquifer solids as either residual saturation or continuous-phase liquid. A review by Mercer and Cohen (17) on properties, models, characterization, and remediation of immiscible fluids in the subsurface is a recommended reference.

Contaminant flow may occur through a number of mechanisms. Volatilization from residual saturation or bulk liquid into the unsaturated pore spaces produces a vapor plume. Migration of this vapor plume is independent of groundwater movement (18, 19) and may occur due to both advection and diffusion (20). Advection is the process by which the vapor plume contaminants are transported by the movement of air and may result from gas pressure or gas density gradients (20). Diffusion is the movement of contaminants from areas of high vapor concentrations to areas of lower vapor concentrations. The vapor plume is enriched with compounds of high vapor pressure and lower aqueous solubility.

For compounds with vapor densities greater than air, density-driven flow of the vapor plume may occur due to gas density gradients (20). Toluene, ethylbenzene, xylenes, chlorobenzene, naphthalene, and phenols are less dense than water and unlikely to move by density-driven flow. However, they may be capable of diffusive transport, causing vapor plumes to move away from residual saturation in the unsaturated zone (21). Residual saturation is the portion of the liquid contaminant that remains in the pore spaces due to capillary attraction after the DNAPL moves through the soil (22). Volatilization from contaminated groundwater also may produce a vapor plume of compounds with high vapor pressures and high aqueous solubilities. Dissolution of contaminants from residual saturation or bulk liquid into water may occur in either the unsaturated or saturated portions of the subsurface with the contamination then moving with the water. Contaminant dissolution from nonaqueous phase liquid under laminar flow conditions typical of aquifers is mass transfer limited, requiring decades for dissolution and producing a dilute waste stream of massive volume (23,24).

#### Transport of DNAPLs in the Unsaturated Zone

Halogenated aliphatic hydrocarbons introduced into the unsaturated portion of the subsurface potentially exist in four phases (25):

- Air phase: contaminants present as vapors
- Solid phase: contaminants adsorbed or partitioned onto the soil or aquifer material
- Water phase: contaminants dissolved into the water according to their solubility
- Immiscible phase: contaminants present as DNAPLs

One or more of the three fluid phases (gaseous, aqueous, immiscible) may occupy the pore spaces in unsaturated zone. Sorbed DNAPLs are considered immobile, but slow desorption of TCE from the organic mathematical cone has been reported [26].

Residual saturation is the portion of the bulk liquid retained by capillary attraction in the porous media (25). The DNAPL is no longer a continuous phase, but is present as isolated residual globules. Dense nonaqueous-phase liquid held in residual saturation is immobile under normal subsurface pressures; further migration will occur only by dissolution into water or by vapor movement (18). The residual-phase saturation acts as a source of contamination to infiltrating water in the unsaturated zone. Dissolution of the DNAPL bulk liquid or vapor readily occurs as water percolates through the unsaturated soil material, producing saturated solutions even with low flow rates (18). Particle grain size and degree of saturation are soil physical properties important for controlling residual saturation (26, 27).

Vapor movement of NAPLs is independent of groundwater movement (18,19). Vapor transport of contaminants may be due to both advection and diffusion. Gas-phase advection may result from gas pressure or gas density gradients (20). For example, upward diffusion of dichloromethane in a dry, uniform sand has been shown to take three times longer than the time required for downward diffusion (18).

Because the vapor-specific gravity of DNAPLs is greater than that of air, their vapors move downward, potentially contaminating soil and groundwater. The magnitude of density-driven flow depends on the contaminant's saturated vapor density, and the extent of partitioning from the gas phase into the aqueous and solid phases (20). Interactions with the pore spaces can lead to differential retardation of the vapor flow (19). For example, a study found greater volatilization of chloroform, 1,2-DCA, 1,1,2-TCA, TCE, and PCE from water than from soil, suggesting a diffusion limitation through air-filled pores (28).

Because DNAPLs are more dense than water, vertical migration of pure liquid through soils, aquifers, and unsaturated materials occurs until reaching a zone of lower permeability. When reaching a zone of low permeability such as a clay lens, DNAPLs will collect at the boundary of the low permeability zone and flow horizontally through the more permeable material. When the DNAPL reaches an area where it can flow vertically because of increased permeability, it will flow further into the underlying stratigraphic units. Eventually the DNAPL material will permeate the low permeability zone and flow through it as well, although at a much slower rate than the high permeability zones (25).

# Transport of DNAPLs in the Saturated Zone

The saturated zone containing DNAPL is a three-phase system consisting of the solid, water, and immiscible hydrocarbon <sup>(25)</sup>. No gaseous phase exists due to the water-filled pores. The DNAPLs can sink within an aquifer until an impermeable layer is reached. They then collect in pools or ponds in depressions on top of the impermeable layer, and can undergo lateral migration. Both vertical and lateral migration continues until residual saturation is

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reduced or an impermeable depression is reached that immobilizes the DNAPL. Any DNAPL present as residual saturation is mobile only by dissolution of the contaminant into the water. Although DNAPL sorbed onto aquifer solids is usually considered immobile, slow release of TCE from long-contaminated soils has been observed in column studies (29).

#### **Transport of LNAPLs**

Similar to denser-than-water solvents, contamination of petroleum-derived solvents in the unsaturated zone exists in four phases: vapor in the pore spaces; sorbed to subsurface solids; dissolved in water; or as NAPL.

The nature and extent of transport is determined by the interactions between contaminant transport properties (density, vapor pressure, viscosity, and hydrophobicity) and the subsurface environment (geology, aquifer mineralogy, and groundwater hydrology). Vapor-phase transport usually results in a relative enrichment of the more volatile compounds. This evidence of contamination migrating in a hydraulically upgradient direction by vapor-phase transport has been observed at a subsurface fuel spill (19). The observers found that the enrichment of groundwater [by aliphatic hydrocarbons of high-vapor pressures and low solubilities relative to the more soluble volatile aromatics compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX compounds)] increased with distance from the source. This enrichment is characteristic of vapor-phase transport. At another site, high concentrations of aliphatic hydrocarbons (compared to BTEX compounds) were observed in wells surrounding a gasoline spill (29). Vapor-phase transport of the aliphatic hydrocarbons — with subsequent dissolution in the groundwater — may explain why the aliphatic rather than the aromatic components of the gasoline were found in groundwater distant from the spill location.

After a spill occurs, the NAPL migrates vertically in the subsurface until residual saturation depletes the liquid or the capillary fringe above the water table is reached. Some spreading of the bulk liquid occurs until pressure from the infiltrating liquid develops sufficiently to penetrate to the water table. The pressure of the infiltrating liquid pushes the spill below the surface of the water table. Bulk liquids less dense than water spread laterally and float on the surface of the water table, forming a mound that becomes compressed into a spreading lens. The concentration of constituents dissolving from the contaminant liquid into the water under the floating product remains relatively uniform regardless of the distance from the spill (19). However, as the plume of dissolved constituents moves away from the floating bulk liquid, interactions with the aquifer solids affect dissolved concentrations. Compounds more attracted to the aquifer material move at a slower rate than the groundwater and are found closer to the source; compounds less attracted to the aquifer material move most rapidly and are found in the leading edge of a contaminant plume.

#### Solubility and Sorption

Most solvent sites are contaminated by a mixture of several chemicals. The presence of other contaminants can affect the partitioning behavior, and therefore, the fate and transport of individual contaminants by altering their

aqueous solubilities. The effect of organic cosolvents on the sorption and aqueous solubility of hydrophobic organic chemicals by soils was studied by Rao et al. (30) and Pinal et al. (31). The hydrophobic chemicals studied were diuron, anthracene, naphthalene, biphenyl, fluoranthene, and pyrene. Nonpolar, partially miscible organic solvents such as toluene, p-xylene, and TCE did not influence sorption by soils significantly when present as a cosolvent/cosolute in the aqueous phase, or as a separate liquid phase. However, polar, partially miscible organic solvents with high aqueous solubilities, such as nitrobenzene and o-cresol, were found to decrease sorption and enhance solubility of the hydrophobic chemicals significantly. The presence of a completely miscible organic solvent, such as methanol or dimethyl sulfoxide, increases the solubility of the partially miscible organic solvents, resulting in increased solubility and decreased sorption of the hydrophobic organic chemicals.

Recent work by Ball and Roberts (32) tested long-term sorption of PCE and tetrachlorobenzene on aquifer material containing low organic carbon. The long-term sorption of PCE and tetrachlorobenzene exceeded the predictions of hydrophobic partitioning into soil organic matter by more than an order of magnitude.

#### **Locating Free Liquids**

### **Soil-Gas Monitoring**

Soil-gas monitoring is a valuable tool for determining contaminant vapors in the subsurface and detecting groundwater plumes (33, 34). Halogenated and petroleum-derived hydrocarbon solvents commonly found at Superfund sites are amenable to soil-gas analysis because of their volatility. The more soluble solvents such as acetone, tetrahydrofuran, 1,4-dioxane, MEK, MIBK, phenol, and cresols are potentially amenable to soil-gas analysis if they result from a leak or spill in relatively dry soil. Chlorobenzenes and dichloropropane are detectable by soil-gas techniques only where probes can sample near contaminated soil or groundwater.

Compounds with high Henry's Law Constants may be present in the unsaturated zone as a result of volatilization <sup>(35)</sup>. Identification of other gases, e.g., carbon dioxide, methane, oxygen, and nitrogen, in both the unsaturated and saturated zones is useful in determining subsurface microbial activity and redox conditions.

### LNAPL

Subsurface contamination by residual-phase NAPLs serves as a continuous contaminant source to infiltrating waters and fluctuating water tables. Most petroleum-derived solvents are less dense than water and exist as floating pools on the water table when in contact with groundwater. Detection of floating pools in monitoring wells is an indication of LNAPL contamination <sup>(36)</sup>.

LNAPL Sites: Soil-gas monitoring is important in identifying LNAPL sites. Reliance on visual identification in core samples is not advised due to the heterogeneous distribution or potentially low residual contamination. Chemical analysis can measure the total contaminant concentration on the subsurface solids, but cannot determine

More volatile LNAPL compounds readily partition into the air phase. A soil gas sample collected from an area contaminated by vapor-phase transport typically contains relatively greater concentrations of the more volatile compounds than one contaminated by groundwater transport (19). Vapor-phase transport occurs with subsequent dissolution in groundwater. Aqueous-phase contaminants with high Henry's Law Constants can be expected to volatilize into the pore spaces.

#### DNAPL

Hazardous waste sites that contain residual or continuous-phase chemicals with densities greater than that of water and which are found below the water table are termed DNAPL sites. Identification of DNAPL sites is important to site characterization because these sites can have complex contamination distributions that are difficult to locate and remediate.

DNAPL Sites: The most common DNAPLs are chlorinated solvents, such as PCE, TCE, and 1,1,1-TCA, used in degreasing and cleaning operations. At some sites, chemicals other than DNAPLs may have been used, resulting in a waste mixture. For example, petroleum-derived solvents plus chlorinated solvents and other contaminants are common mixtures. DNAPL sites may also contain creosote, pesticides, or PCBs.

Direct evidence of DNAPL contamination is free-product detection in a monitoring or pump-and-treat well. Normally, this direct evidence is quite difficult to obtain. Absence of free product is not evidence that DNAPL does not exist at the site. DNAPL accumulates at the bottom of the well in a thin layer. Recovering the DNAPL requires bottom-of-the-well sampling devices. If the sand pack or filter pack extends below the bottom of the well screen, the DNAPL may be found at the bottom of the sand pack and cannot be recovered.

The extent of residual saturation or continuous-phase DNAPL may be small compared to the spacing of monitoring wells; direct interception by monitoring wells may be insufficient. Direct evidence of DNAPL is difficult to obtain even when intercepted by monitoring wells. At most sites, indirect evidence of DNAPL contamination is more economical and efficient. Both direct and indirect evidence are used to determine if a site contains DNAPL (37).

The possible presence of DNAPL compounds can usually be determined from a detailed history of site activities and land use. Types of activities associated with DNAPL sites are solvent manufacturing, recycling, and packing; any activity involving metal working or engine maintenance; dry cleaning; electronics manufacturing; industrial waste storage or disposal; and many others. The DNAPL below the water table frequently results from small routine solvent leaks, spills, releases, or disposals. Although the quantity lost routinely seems small compared to inventory, the impact to groundwater may be significant.

Other indirect evidence is concentrations of DNAPLs in monitoring wells as low as 1 percent of the solubility of the DNAPL chemical. Values near the solubility limit of a chemical would be unusual due to dilution of DNAPL dissolving from residual saturation into less contaminated groundwater. Saturated concentrations of DNAPL cannot be observed unless monitoring wells are installed within or close to residual saturation or continuous-phase product.

The direction of DNAPL migration below the water table is controlled by gravity, geological structure, and permeability, not by the direction of groundwater flow. The DNAPL identified in monitoring wells upgradient or across gradient may be used as indirect evidence of DNAPL location. Uncontrolled disposals in locations not identified previously as disposal areas may also account for DNAPL in upgradient monitoring wells. Migration of DNAPL vapors also can cause upgradient groundwater contamination also, but normally this contamination is shallow.

Identification of DNAPL dissolved in groundwater at depths well below the water table is additional indirect evidence of DNAPL contamination. It is necessary at DNAPL sites to determine maximum depth of contamination, especially in fractured rock materials that allow DNAPL to migrate to great depths. However, determination of maximum depth of DNAPL contamination is difficult in fractured rock aquifers.

Soil gas monitoring identifies residual saturation in the vadose zone due to the high vapor concentrations close to the DNAPL. Location of residual saturation may identify entry location of DNAPL below the water table. These locations are identified frequently by locally erratic or isolated high concentrations. The DNAPL located only below the water table will not produce high concentrations of vapor in the vadose zone. High concentrations of DNAPL at the water table only, but not at depth, is an indication of soil vapor contamination.

Feenstra et al. <sup>(36)</sup> describes a method for NAPL determination using the results of chemical and physical analyses of the soil, and fundamental principles of chemical partitioning in unsaturated or saturated soil. The method allows determination of residual NAPL in subsurface environments. Additional information concerning DNAPL sites may be found in Mercer <sup>(17)</sup>, Feenstra et al. <sup>(36)</sup>, Feenstra <sup>(37)</sup>, Villaume <sup>(38)</sup>, and Mackay et al. <sup>(59)</sup>.

#### **Transformations**

# Biological and Chemical Reactions of Solvent Chemicals

Solvent chemicals are subject to biological and chemical reactions when introduced into the subsurface. Halogenated aliphatic compounds may undergo abiotic (hydrolysis and chemical dehalogenation) and/or biological reactions in subsurface environments. Although petroleum-derived solvents are quite degradable biologically, they are relatively resistant to chemical transformations. Abiotic transformations are nonbiological reactions, and they are usually elimination or hydrolysis reactions. Alkaline hydrolysis reactions are abiotic transformations that occur

at pH values greater than 7.

Microbial transformations are broadly classified into aerobic and anaerobic processes. Aerobic conditions occur in the presence of oxygen, in which bacteria use oxygen as a terminal electron acceptor during respiration. Complete aerobic biodegradation converts organics to carbon dioxide, water, and other organic products (depending upon the constituent of the starting material). Transformation products of biological and chemical reactions of halogenated solvents are shown in Table 2-9.

Anaerobic conditions occur in the absence of molecular oxygen and include two major classes of reactions. Anaerobic fermentation reactions transform organics into intermediate organic products. In anaerobic respiration, microorganisms may use other alternative electron acceptors to oxidize organics in the absence of molecular oxygen. The most common alternate electron acceptors include nitrate (with the microbial process termed dentrification), sulfate (sulfate reduction), and carbon dioxide (termed methanogenesis due to the production of methane). Methanogenic refers to strictly anaerobic conditions in which bacteria produce methane, typically from carbon dioxide.

In addition to these fundamental microbial processes, a variety of other microbial transformations may take place. Of particular interest for transformation of certain solvents is reductive dehalogenation (reductive dechlorination for chlorinated solvents), in which halogen atoms are selectively removed from organic molecules leaving lower halogenated or nonhalogenated organic products. Reductive dehalogenation also results in the cometabolic transformation of chlorinated solvents where they are transformed by microorganisms while oxidizing other substrates.

The occurrence of these biological processes depends upon the specific organic substrates, the types of microbial populations present, and the environmental conditions. These factors should be understood in evaluating the fate of solvents in the environment.

TABLE 2-9. COMPOUNDS FORMED FROM TRANSFORMATION OF  $\mathrm{C_1}$  AND  $\mathrm{C_2}$  HALOGENATED HYDROCARBONS

Compound	Products	Condition	References
1,1-Dichloroethylene	Vinyl chloride	Anaerobic	48,49,50,51
	Carbon dioxide	Anaerobic	49
	Chloroacetylene	Alkaline hydrolysis	43
1,2-Dichloroethylene	Vinyl chloride	Anaerobic	51
	Carbon dioxide	Anaerobic	52,53
cis-	Chloroethane (92%)	Anaerobic	48
<b>.</b>	Vinyl chloride (8%)	Anaerobic	48
trans-	Vinyl chloride	Anaerobic	48,50
Trichloroethylene	1,2-Dichloroethylene	Anaerobic	50
	25 times more cis-	Anaerobic	51
	than trans-1,2-Dichloroethylene	4	
	50% to all cis- above	Anaerobic	53
	trans-1,2-Dichloroethylene One measure of more trans- than	·	
	cis-1,2-dichloroethylene	A	
	1,1-Dichloroethylene	Anaerobic	54
	Vinyl chloride	Anaerobic Anaerobic	51
	Carbon dioxide	Anaerobic soil column	50,51,54
	Carbon dioxide	Anaerobic soil column	40 55
		cometabolism	33
	Carbon dioxide	Aerobic column,	56
		methane cometabolism	
Tetrachloroethylene	Trichloroethylene	Anaerobic	51,53,54
	25 times more cis-	İ	
	than trans-1,2-Dichloroethylene	Anaerobic	51
	70% to all cis- above		
	trans-1,2-Dichloroethylene	Anaerobic	53,54
	1,1-Dichloroethylene	Anaerobic	51
	Vinyl chloride	Anaerobic	51
	Trichloroethylene Dichloroethylene	Methanogenic column	40
	Vinyl chloride	Methanogenic column	40
	Carbon dioxide (24%)	Methanogenic column  Methanogenic column	40
•	Ethylene	Anaerobic	40 57
	Vinyl chloride	Anaerobic	11
1,1-Dichloroethane	Chloroethane	Anaerobic	51
•	Carbon dioxide	Anaerobic	42
	Vinyl chloride	Alkaline hydrolysis	43
1,2-Dichloroethane	Carbon dioxide	Anaerobic	52
š	Carbon dioxide	Aerobic	58
	Chloroethanol	Aerobic	43
	Vinyl chloride	Alkaline hydrolysis	43
	Ethylene glycol	Neutral hydrolysis	43
1,1,2,2-Tetrachloroeth-	1,1,2-Trichloroethane	Anaerobic	
ane	Trichloroethylene	Aerobic	43
1,1,1-Trichloroethane	1,1-Dichloroethane	Anaerobic	49,51,53,54
	Chloroethane	Anaerobic,	50
	Carbon dioxide	Anaerobic	49
	Methylene chloride	Anaerobic	51
	1,1-DCE (26% product)	Abiotic	49,59
	Acetic acid	Abiotic	49
	Vinyl chloride 1,1-Dichloroethylene	Abiotic	49
	171 Dictiloroeutylene	Abiotic	60

TABLE 2-9. (Continued)

Compound	Products	Condition	References
1,1,2-Trichloroethane	Chloroacetic acid	Aerobic	61
	Glyoxylic acid	Aerobic	61
	Vinyl chloride	Aerboic	61
	1,2-Dichloroethylene	Alkaline hydrolysis	43
Chloroform	Methylene chloride	Anaerobic	51
	Carbon dioxide	Anaerobic	52
	Methane (9%)	Anaerobic	52
	Carbon dioxide (98%)	Methanogenic	52
	Methane 1-2%)	Methanogenic	52
Carbon tetrachloride	Chloroform	Anaerobic	51,53,54
	Methylene chloride	Anaerobic	51
	Carbon dioxide	Anaerobic	52
	Carbon dioxide (99%)	Methanogenic	52
	Methane (0-2%)	Methanogenic	52
	Chloroform	Denitrifying	62
	Carbon dioxide	Denitrifying	62
Ethylene dibromide	Bromomethane	Abiotic	45,63
•	Ethylene glycol	Abiotic	63
	Ethylene (2 mo.)	Abiotic	64
	Bromide ion (2 mo.)	Aerobic	64
	Carbon dioxide	Aerobic	65
Methylene chloride	Carbon dioxide	Aerobic	66
	Carbon dioxide	Anaerobic	66
.Vinvl chloride	Ethylene	Anaerobic	52
	Methane	Anaerobic	52
	Chloromethane	Anaerobic	52
	Carbon dioxide	Anaerobic	52
Vinyl chloride	Carbon dioxide	Aerobic	67

Source: Adapted from Mallon, 1989 (29)

#### **Chemical Transformations**

Transformation reactions can be classified as oxidation and reduction substitution (hydrolysis), or dehydrodehalogenation (chemical dehalogenation) (40). Oxidation and reduction reactions require external electron transfer, while substitution and dehydrodehalogenation reactions do not. Although biological transformations are usually dominant, both abiotic and slow biological transformation reactions can be important due to the long residence times of contaminants in aquifers with slow-moving groundwater.

Hydrolysis results from the introduction of a hydroxyl group (-OH) from water or hydroxide to a carbon atom and displaces an atom such as chlorine <sup>(41)</sup>. In this reaction, the halogen is removed from one carbon atom with removal of a hydrogen atom from an adjacent carbon.

Initial hydrolysis of halogenated aliphatic hydrocarbons produces alcohols, which, if halogenated, are further hydrolyzed to carboxylic acids or aldehydes. Chloroform is resistant to hydrolysis <sup>(42)</sup>. While only neutral hydrolysis occurs for carbon tetrachloride and TCA, chlorinated ethenes react with hydroxide under extreme conditions and exhibit no neutral hydrolysis <sup>(43)</sup>. Calculated rate constants for hydrolysis of halogenated ethenes are so small at environmental temperatures and pH conditions that their hydrolysis can be regarded as negligible <sup>(43)</sup>. The rate and pattern of hydrolysis of alkyl halides are sensitive to pH, temperature, and ionic strength of the water <sup>(44)</sup>. Hydrolysis is more likely than chemical dehalogenation for halogenated alkanes. Slower substitution reactions and longer half-lives occur with increased halogenation <sup>(40, 44, 45)</sup>. Alkanes, benzenes, halogenated aromatics, alcohols, phenols, and ketones are compounds that are chemically resistant to hydrolysis <sup>(41)</sup>. Lists of half-lives for some halogenated compounds are shown in Tables 2-10 and 2-11.

Dehydrodehalogenation is an elimination reaction in which alkenes are produced from alkanes, such as the formation of TCE from 1,1,2,2-tetrachloroethane (46, 47). In this reaction, a halogen is removed from one carbon and a hydrogen is removed from an adjacent carbon.

Elimination reactions generally are favored by higher temperatures and strong basic conditions which are not found in groundwater. An elimination reaction may compete with hydrolysis for organic compounds that contain good donor groups such as a halide <sup>(41)</sup>, resulting in both reactions occurring in groundwater. The formation of acetic acid from hydrolysis of TCA plus formation of 1,1-dichloroethylene from its dehydrodehalogenation from TCA is one example of this <sup>(42, 49)</sup>. These elimination and substitution reactions occur in a ratio of 1:3, independent of temperature and pH <sup>(69)</sup>.

TABLE 2-10. LABORATORY MEASUREMENTS OF HYDROLYSIS OR DEHALOGENATION HALF-LIVES OF HALOGENATED ALIPHATIC HYDROCARBONS

Compound	Half-Life (vear)	Conditions. Sediment Type. Etc.	Befarence
Trichloroethylene	0.9	Aerated water, dark, sealed, 25°C Water in sealed bottles, dark, estimated by extrapolation	Diling et al., 1975 Pearson and McConnell, 1975
Tetrachloroethylene	0.73 6	Aerated water, dark, sealed, 25°C Water in sealed bottles, dark, estimated by extrapolation	Diling et al., 1975 Pearson and McConnell, 1975
1,1-Dichloroethane			
1,2-Dichloroethane	. 20	Calculated from extrapolated rate constants, 20°C	Mackay and Vogel, 1985
1,1,1-Trichloroethane	0.5 >0.25 2.5 to 19 0.75 1.7	Aerated water, dark, sealed, 25°C Groundwater, sealed, pH 7, 20°C, to acetic acid, all abiotic processes Groundwater, sealed, pH 7, 20°C, to 1,1-dichloroethylene, all abiotic processes es Estimated for seawater at pH 8, 10°C (mostly dehalogenation) Calculated from extrapolated rate constants, 20°C	Diling et al., 1975 Vogel and McCarty, 1987b Vogel and McCarty, 1987a Pearson and McConnell, 1975 Mackay and Vogel, 1985
1,1,2-Trichloroethane	170 Not determined	20°C Hydrolysis rates of chlorinated ethanes with concentrated base: 1,1,2- trichloroethane>1,2-dichloroethane>1,1,1-trichloroethane>1,1-dichloroeth- ane	Mabey et al., 1983 Walravens et al., 1974
Chloroform	1.3 3500	Aerated water, dark, sealed, 25°C Extrapolated from high pH	Diling et al., 1975 Mackay and Vogel, 1985
Carbon tetrachloride	7000	Extrapolated from high pH	Mackay and Vogel, 1985
Ethylene dibromide	2.5	Half-live at 25°C extrapolated from higher temperatures (50 to 70°C), pH 7.5.	Vogel and Reinhard, 1986

Source: Mallon, 1989 (68)

TABLE 2-11. IN SITU OR ESTIMATED HALF-LIVES OF HALOGENATED ALIPHATIC HYDROCARBONS IN GROUNDWATER

Compound	Half-Life (year)	Conditions, Sediment Type, Etc.	Reference
Trichloroethyl- ene	0.6	Observed disappearance, Palo Alto Baylands Aquifer, injected groundwater recharge experiment	Roberts, 1985
	Fast	Waterloo, Ontario landfill	Reinhard et al., 1984
	2	Estimated from well sample data, Noordwijk Dump, The Netherlands	Zoeteman et al., 1984
Tetra-chloroeth- ylene	0.6	Observed disappearance, Palo Alto Baylands	Roberts, 1985
	0.1 to 1	Estimated from contamination data for groundwater in The Netherlands	Zoeteman et al., 1980
	Faster	Faster than Waterloo, Ontario landfill transport	Reinhard et al., 1984
1,1,1-Trichloro- ethane	0.6	Observed disappearance, Palo Alto Baylands Aquifer, injected groundwater recharge experiment	Roberts, 1985
·	1	Estimated from well sample data, Noordwijk Dump, The Netherlands	Zoeteman et al., 1980
Chloroform	0.6	Observed disappearance, Palo Alto Baylands Aquifer, injected groundwa- ter recharge experiment	Roberts, 1985
	0.1 to 1	Estimated from well sample data, Noordwijk Dump, The Netherlands	Zoeteman et al., 1980
Ethylene dibrom- ide	23 to 57	Estimated time from diffusion equations to reach 50% equilibrium of residual ethylene dibromide in Connecticut soils	Steinberg et al., 1987

Source: Mallon, 1989 (68)

#### **Microbial Transformations**

Microbial transformations include both aerobic and anaerobic processes by which microorganisms obtain energy for growth, and a variety of other transformation processes (i.e., reductive dechlorination or cometabolic transformations).

Microorganisms obtain energy from a variety of electron donors and acceptors under different redox conditions; the order of preference for electron acceptors is O<sub>2</sub> (aerobic metabolism), NO<sub>3</sub>. (denitrification), SO<sub>4</sub> (sulfate reduction), and CO<sub>2</sub>/carbonate (methanogenesis) <sup>(70)</sup>. The redox state of aquifer and soil solids is an important factor controlling microbial transformations and the geochemistry of many inorganic and organic compounds <sup>(71, 72)</sup>. Redox conditions determine the dominant electron acceptor of a subsurface system. Most pristine groundwaters are oxygenated <sup>(70)</sup>, but introduction of organic contaminants depletes available oxygen. Microorganisms then use alternate electron acceptors (NO<sub>3</sub>., SO<sub>4</sub>, and HCO<sub>3</sub>.) commonly found in shallow groundwater <sup>(72)</sup>. Many subsurface materials contain manganese oxides and iron oxyhydroxides, which also may act as electron acceptors in microbial processes <sup>(72)</sup>. Microbial reduction of these solid-phase minerals may account for oxidation of organic matter and mobilization of Fe<sup>2+</sup> and MN<sup>2</sup> in groundwater <sup>(72,73)</sup>.

#### **Transformations of Halogenated Solvents**

In oxygenated subsurface materials, chlorinated solvents, such as TCE, TCA, PCE, and others, are not ordinarily biodegradable and tend to persist in those environments (28, 70). In anaerobic environments, PCE, TCE, and TCA undergo reductive dehalogenation (53, 59, 74). Transformation products of TCE are dichloroethylenes and VC; those of TCA are 1,1-dichloroethane and chloroethane (48, 75, 59). [TCA also can be nonbiologically transformed to 1,1-dichloroethylene (1,1-DCE) by an elimination reaction, and to acetic acid by hydrolysis (69).] In addition, TCA also has a nonbiological fate, whereby 1,1-dichloroethylene is formed from the abiotic dehydrochlorination of TCA. Acetic acid is a second transformation product formed by abiotic processes with potential of further biodegradation of 1,1-DCE to VC (49, 59, 74). These reactions can occur in conditions of dilute aqueous solutions at neutral pH and 20° C common to groundwater. Transformation products of TCE and TCA are more mobile in groundwater than the parent compounds, and in the case of VC, more carcinogenic. With an estimated half-life between 0.9 to 2.5 years (40), TCE is resistant to hydrolysis.

Although aerobic biodegradation of TCE and related compounds does not occur under ordinary aerobic conditions <sup>(28)</sup>, recent work has shown bacteria that oxidize certain other organics including gaseous hydrocarbons (methane, ethane, propane, or butane) are also able cometabolically to oxidize TCE and other low molecular weight halogenated compounds <sup>(56, 76, 77, 78, 79)</sup>. Cometabolism is the biodegradation of an organic substance by a microbe that cannot use the compound for growth and, hence, must rely on other compounds for carbon and energy.

Use of alkanes such as methane, propane, or butane as primary substrates for co-oxidation of chlorinated compounds has advantages. First, the alkane serves as the primary source of carbon and energy needed to sustain a stable microbial community when the target pollutant is present in trace amounts as in the case of TCE in groundwater. These alkanes are commonly used, inexpensive industrial chemicals that are nontoxic to humans and easily biodegraded.

#### **Transformations of Petroleum-Derived Solvents**

Volatile aromatics such as benzene, toluene, ethylbenzene, and BTEX compounds are more soluble in water than the aliphatic and higher-molecular-weight aromatic constituents of petroleum products (80). The presence of these compounds in groundwater is therefore indicative of subsurface petroleum contaminants (81). Once released to the subsurface, petroleum compounds are subject to aerobic and anaerobic processes. Low-molecular weight alkanes and aromatics are readily biodegraded in oxygenated groundwater, and deplete the groundwater of available oxygen (82, 83). Reoxygenation of groundwater may occur through re-aeration from soil gases, groundwater recharge, and mixing with surrounding oxygenated groundwater (84, 85). Mixing processes in aquifers are not efficient. Although groundwater near the perimeter of the contaminant plume may be re-oxygenated, the interior of the plume will remain anoxic for a distance downgradient.

Anaerobic biological processes can account for most of the BTEX removal from the plume <sup>(86)</sup>. However, biogeochemical mechanisms that contribute to anaerobic processes in the subsurface are not well understood.

The impact of anaerobic microbial processes on the fate of monoaromatics, substituted aromatics, and chlorinated hydrocarbons in anoxic subsurface environments has been studied in laboratory and field situations (87, 88, 89). Field evidence of biotransformation of xylenes was observed in methanogenic landfill leachate with their preferential removals compared to other alkylbenzenes present (90).

Although aromatic hydrocarbons were thought to be recalcitrant to biological action without molecular oxygen (91) or oxygen-containing substituent groups (92), recent field and laboratory data indicate biotransformation of benzene and alkylbenzenes does occur under anoxic conditions (93, 94). The products of biotransformations of benzene and alkylbenzenes identified under anaerobic conditions included phenol o-, m-, and p-cresols, and various benzoic acids (94, 95). In other studies, at least 50 percent of toluene and benzene were metabolized anaerobically to carbon dioxide and methane by a mixed microbial population (96). Intermediates consistent with ring hydroxylation of benzene and toluene, and methyl oxidation of toluene (such as phenol, cresols, and aromatic acids) were identified.

Analyses of water downgradient from a crude oil spill at Bemidji, Minnesota, showed phenol plus aromatic, alicyclic, and straight- and branched-chain aliphatic organic acids that were not original constituents of the oil and were not found outside the contaminant plume (94). The source of the phenol and aromatic organic acids was thought

to be the result of anaerobic biodegradation of benzene and alkylbenzenes. Oxidized products of anaerobic transformations of benzene, toluene, xylenes, plus six additional substituted benzenes, were identified by gas chromatograph/mass spectrometer (GC/MS).

Styrene has been biotransformed to styrene oxide by aerobic microorganisms and fungi isolated from soil and water samples (97).

A variety of environmental factors also may affect transformation of solvents. Such factors may include nutrient levels, the presence of other chemicals, and certain hydrologic properties of the aquifer itself. Microbial degradation of m-cresol, toluene, and chlorobenzene were found to vary with transmissivity (a measure of the rate of groundwater flow through an aquifer) of subsurface layers (70). m-Cresol is an analog of naturally occurring organic matter that is degraded easily in all layers. Toluene and chlorobenzene degraded most rapidly in moderately transmissive uniform fine sand. Degradation of compounds that are components of naturally occurring organic matter, such as phenol, is rapid. Degradation rates of compounds that are not major components of naturally occurring organic matter, such as toluene, are more variable.

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# SECTION 3 REMEDIAL OPTIONS

#### CLEANUP GOALS AND REMEDIAL OPTIONS

The remedial manager must select treatment options to meet cleanup action levels; the two available options are immobilization or destruction. Separation/concentration technologies prepare solvent-contaminated matrices for either destruction or immobilization. The order in which the treatment technologies are presented in this document is not indicative of the importance or success of the technology.

To achieve stringent remediation objectives, a more energy-dependent remediation technology, such as incineration or pyrolysis, may be necessary. If less stringent cleanup levels are acceptable, a low-energy technology, such as soil vapor extraction, may be more appropriate. If only volatiles are present, separation or concentration technologies may apply. If dioxins are present, only thermal or dechlorination techniques may apply due to the more restrictive cleanup levels required. Sites with higher concentrations of volatile components will stress separation/concentration techniques. Sites with higher concentrations of semivolatile co-contaminants will rely most likely on destruction options to achieve desired cleanup levels. However, with further development, innovative technologies such as thermal desorption and soil washing may be considered in the future. The matrix, i.e., soil, sediment, or sludge, also affects the type of technology needed to treat the contaminants. Sludge and sediment can increase treatment and material handling costs.

Sites contaminated with pure solvent are not likely to be found. Thus, combinations of different technologies and pre- and post-treatment handling components, either used in series or simultaneously, may be required to meet cleanup levels. The selection of technology(ies) and treatment train components will be highly dependent on the concentrations and types of co-contaminants. The presence of metal co-contaminants, for instance, can make remediation more complex by requiring additional treatment. Metals require immobilization or solidification/stabilization (S/S) considerations of residuals from other treatments. Thus, depending on which classes of co-contaminants are present at the site, a treatment train may be required.

The appendix tables compare CERCLA solvent sites with the treatment combinations selected. A technology chosen as the principal component of a treatment train in one case — for example, incineration followed by S/S — might act as a secondary component (post-treatment) in a different treatment train — such as solvent extraction followed by incineration. The remedial manager must consider each element of the process, from excavation, materials handling, and primary treatment, to treatment of residual streams. One concern at

solvent sites is air emissions from organic volatilization. They may occur as a result of physical operations such as drilling, excavation, stockpiling, and handling; as a byproduct of chemical reactions during treatment, such as S/S; and from biological digestion processes.

Some technology descriptions that follow include a schematic diagram for an overall treatment process, from excavation to post-treatment.

# TYPICAL TREATMENT COMBINATIONS

The treatment combinations described below deal primarily with solvent-contaminated soil. The remedial manager may find sediment and sludge on site. Ponds and streams can become contaminated directly as holding ponds/lagoons or by migration of solvent compounds. Sludge from lagoon bottoms and processing equipment will require treatment. Sediment, which may also require treatment, contains a smaller particle size distribution and higher moisture content than soil. After pretreatment dewatering, sediment can be processed as a wet soil. In comparison to sediment, sludge contains highly concentrated contaminants in a noncohesive and unsupportive matrix. Sludge treatment options are more limited because dewatering the matrix is difficult.

On-site remedial techniques for optimal recovery of pure compounds or mixture of compounds should precede implementation of the selected destruction technology. A physical separation option, such as soil-vapor extraction to lower the level of VOCs in the soil, should be considered for pretreatment at a solvent site to help prevent fugitive emissions during excavation. Soil-vapor extraction may offset excavation costs when emission controls are implemented.

Solvent-contaminated sites may contain highly mobile organic compounds. The most common solvent-contaminated sites contain BTEX and chlorinated solvents. Other hydrocarbon solvents and BTEX are low-solubility floating compounds, while chlorinated organics are low-solubility sinking compounds. Thus, groundwater contamination almost always constitutes an immediate concern. Remedial options for these sites always must include groundwater treatment.

Pretreatment by recovering solvent contamination (light nonaqueous-phase liquid - LNAPL) floating on top of an aquifer may reduce the contaminant load in many sites. The groundwater level is lowered by pumping a well placed in the middle of a spill area, thereby concentrating the relatively nonsoluble contaminant at the lowest point as it flows with the groundwater in the well. Then, LNAPL is collected.

There are many options for a remediation strategy. The subsections on destruction and separation/concentration technologies include tables which describe technologies and pre- and post- treatment handling techniques commonly used with them.

Frequently used materials handling procedures at hazardous waste sites include:

- Excavation and removal
- Dredging
- Size and volume reduction
- Dewatering
- Conveying systems

A wide range of equipment is available for conducting materials handling procedures. Due to the volatility of solvents, it may be necessary to enclose equipment under negative pressure with air pollution control. Further information about materials handling can be found in Survey of Materials Handling Technologies at Hazardous Waste Sites (1).

# <u>.</u>

#### **Treatment Costs**

When evaluating total treatment costs, the remedial manager must compare all elements of each train, including the principal components and costs of material handling through the final disposal of residuals. The treatment costs for well developed and field-tested technologies (such as incineration and bioremediation) can be quite reliable, but estimates for innovative and emerging technologies become increasingly less reliable. The following are some of the capital and operation and maintenance (O&M) costs typically considered when estimating how much a remediation will cost.

Direct costs include the following:

- Remedial action construction costs
- Component equipment costs
- Land- and site-development costs
- Building and services costs
- Relocation of affected population costs
- Disposal of waste material costs

Indirect capital costs include the following:

- Engineering expenses
- Contingency costs
- Project management costs

Operation and maintenance costs are those that must be incurred after construction but during the remediation phase to ensure continued efficiency of the treatment process. The major components of O&M costs include:

- Operating labor
- Maintenance materials and labor
- Auxiliary materials and energy
- Residuals disposal costs
- Purchased services
- Administrative costs
- Insurance, taxes, and licenses
- Maintenance reserve and contingency costs

#### IMMOBILIZATION TECHNOLOGIES

#### Containment Technology

Containment is a common component in the overall remediation of a solvent site. Initial on-site actions to establish containment provisions will accomplish the following:

- Minimize migration of contaminated groundwater from the site
- Prevent the increase of groundwater contamination due to water percolation and precipitation
- Control population exposure to contaminants
- Contain contaminants while remediation proceeds
- Reduce air emissions

Thus, containment control ranges from a surface cap that limits infiltration of uncontaminated surface water to subsurface vertical or horizontal barriers that limit migration of contaminated groundwater.

#### **Capping Systems**

Capping systems reduce surface-water infiltration, control population exposure, prevent erosion, control gas and odor emissions, improve aesthetics, and provide a stable surface over the waste. Caps can range from a simple native soil cover or plastic to a full RCRA Subtitle C composite cover. If a cap is temporary, knowledge of final remedial options may help in determining the type of cap to be used so as not to increase remedial costs later in the project. The following RREL computer models will assist the remedial manager in cap design.

- Hydrologic Evaluation of Landfill Performance (HELP) evaluates the rate of infiltration of surface water through capping material.
- F-COVER evaluates potential design problems in the individual capping elements.
- VegCov provides guidance on the selection of a vegetative cover.

RREL programs are available from the U.S. EPA Municipal Solid Waste & Residuals Management Branch (MSWRMB) at (513) 569-7871.

#### **Vertical Barriers**

Vertical barriers minimize the movement of contaminated groundwater off site or limit the flow of uncontaminated groundwater on to the site. Common vertical barriers include slurry walls in excavated trenches, grout curtains formed by injecting grout into soil borings, cement-bentonite filled borings or holes formed by withdrawing beams driven into the ground, and sheet-pile walls formed of driven steel.

Solvent compounds can affect caps and vertical barriers. The permeability of bentonite may increase significantly when it is exposed to high concentrations of water-soluble salts, electrolytes (sodium, calcium, heavy metals), strong organic/inorganic acids, and solvents having a very low dielectric constant. Specific gravity of salt solutions greater than 1.2 affects bentonite. In general, bentonite permeability does not change significantly if the leachate is at least 50 percent water and no separate-phase organic chemicals are present. High concentrations of solvents floating atop the groundwater can lead to degradation of the bentonite. In general, soil/bentonite blends resist chemical attack best if they contain only 1 percent bentonite and 30 to 40 percent natural soil fines. Treatability tests should be performed to evaluate the chemical stability of the barrier if these conditions are suspected.

Concrete and cement mortars can be vulnerable to attack from organic solvents and liquids. The presence of free-phase solvents in the groundwater can influence the integrity of a grout curtain. Therefore, chemical compatibility of the grout with the solvent should be evaluated prior to construction.

Carbon steel used in pile walls quickly corrodes in dilute acids, slowly corrodes in brines or salt water, and remains mostly unaffected in organic chemicals or water. The water-soluble salts reduce the service life of a steel sheet pile; corrosion-resistant coatings extend their anticipated life. Major steel suppliers will provide site-specific recommendations for cathodic protection of piling.

Geomembranes can be used to form vertical barriers in applications where chemical degradation of conventional grouts is anticipated. Geomembranes are used as liners in lagoons and landfills and significant

chemical resistance data about them is available. The geomembrane curtain can be placed as an outer protective component of a conventional slurry wall, or as the primary vertical curtain without the slurry wall component. Geomembrane curtains are commercially available in the form of interlocking high-density polyethylene (HDPE) panels. A hydrophilic polymer that swells in the presence of water is used to seal them. The impact of potential contaminants on the integrity of the HDPE and the seal must be determined using the EPA 9090 test prior to field use. In general, solvents will not degrade the physical properties of HDPE.

# **Horizontal Barriers**

Horizontal barriers underlie a sector of contaminated materials without removing the hazardous waste or soil. Grouting techniques reduce the permeability of underlying soil layers. Studies performed by the U.S. Army Corps of Engineers (COE) (2) indicate that conventional grout technology does not produce an impermeable horizontal barrier because it does not ensure uniform lateral placement of the grout. These same studies found greater success with jet-grouting techniques in soils that contain sufficient fines to prevent collapse of the wash hole and no large stones or boulders to deflect the cutting jet.

# **Implementation Costs**

Accurate costs have not been established for horizontal barriers since few have been constructed. Typical equipment costs range from \$1,200 to \$3,000 per day. Borehole spacing is a function of grout penetration; it is site specific. Typical borehole spacing ranges from 6- to 10-feet centers. Horizontal barrier costs for boring and injection may exceed \$80 per square foot. The cost of the grout is a relatively minor expense.

Construction costs for capping systems are shown in Table 3-1. Costs for vertical barriers are shown in Table 3-2.

**TABLE 3-1. CAPPING COSTS** 

Component	Installation	Total Cost (\$)
Bedding layer	On-site excavation, hauling, spreading, compaction	1.00 to 2.50/yd <sup>3</sup>
Gas collecting layer	Off-site excavation, hauling, spreading, and collector pipes Geonet alternative	12.00 to 18.00/yd²
Composite barrier: clay	On-site excavation, hauling, spreading, compaction Geosynthetic clay liner Add for off-site clay (<20 mile haul)	2.40 to 6.00/yd³ 0.85/ft² 8.00 to 14.00/yd³

**TABLE 3-1 (Continued)** 

Component	Installation	Total Cost (\$)
Composite barrier: geomembrane	Installed HDPE - 60 mil PVC - 40 mil	0.50/ft² 0.35/ft²
Drainage layer	Off-site excavation, hauling, spreading, and collector pipes Geonet alternative	12.00 to 18.00/yd² 0.40/ft²
Protective layer	On-site excavation, hauling, spreading, compaction	1.00 to 2.50/yd <sup>3</sup>
Vegetative layer	Topsoil hauling, spreading, and grading	10.00 to 16.00/yd <sup>3</sup>
Asphalt hardened cap option (4-6 in)	Delete protective and vegetative layers, hauling, spreading, rolling	4.00 to 6.00/yd²
Concrete hardened cap option (4-6 in)	Delete protective and vegetative layers, on- site mixing, hauling, spreading, finishing	6.00 to 11.00/yd <sup>2</sup>

**TABLE 3-2. VERTICAL BARRIER COSTS** 

Component	Depth	Cost (\$/ft²)
Soil/bentonite slurry wall	30 ft 30 to 50 ft 50 to 125 ft	3 to 7 6 to 11 9 to 15
Cement/bentonite slurry wall Vibrating beam	30 ft 30 to 50 ft	3 to 7 6 to 11
Injection grout	50 to 125 ft 30 ft 30 to 50 ft	9 to 15
Steel sheet-pile wall	50 to 125 ft	18 to 55 27 to 75 16 to 28

# S/S TECHNOLOGIES

S/S processes reduce the mobility of a contaminant, either by physically restricting its contact with a mobile phase (solidification) or by chemically altering/binding the contaminant to reduce its mobility (stabilization). Figure 3-1 depicts a schematic diagram of an S/S process. Stabilization can be achieved without solidification, while solidification usually includes stabilization. Solidification also refers to the use of binders for waste bulking to facilitate the handling of liquid wastes.

Binding agents fall into several classes. The most common are cementitious and pozzolanic materials, including Portland<sup>TM</sup> cement, fly ash/lime, and fly ash/kiln dust. Binding agents form a solid, resistant, aluminosilicate matrix that can occlude waste particles, bind various contaminants, and reduce permeability of the waste/binder mass. Proprietary agents added to the binder may improve specific properties of S/S-treated waste, such as strength, curing rate, contaminant binding, pore size, or waste dispersion.

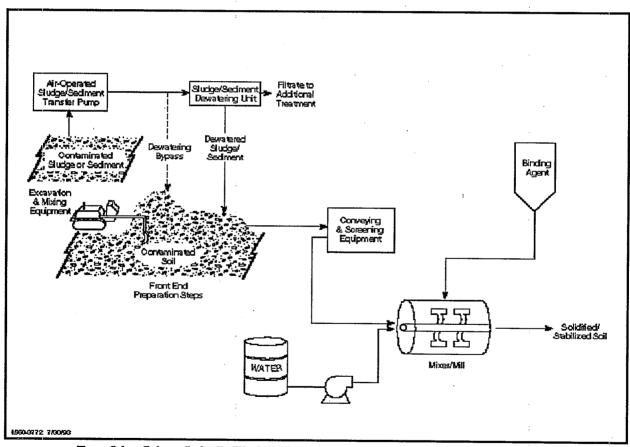


Figure 3-1 Schematic for Ex Situ Solidification/Stabilization of Contaminated Soils

Figure 1

### **Treatment Combinations**

Immobilization treatment usually does not apply to sites contaminated with organics only. However, when the contaminants are inorganics or volatile organics, S/S technology can be combined with other remediation processes in successful treatment trains such as soil vapor extraction (SVE) or biotreatment followed by S/S for in situ treatment, and solvent extraction, thermal desorption, or biotreatment followed by S/S for ex situ treatment. Data suggest that silicates used with lime, cement, or other setting agents can stabilize sludges and soils contaminated with solvents (3).

# **Technology Applicability**

Organic Compounds: Two considerations for organic compounds in S/S treatment are the immobilization of the organic contaminant and the potential effects of organic compounds on the solidification matrix or on immobilization of other contaminants.

Organic compounds at varying contaminant levels can retard or prevent setting of typical S/S matrices. Connor <sup>(4)</sup> found that many types of organics have adverse effects on set/cure times, cement hydration, and product properties. For example, unconfined compressive strength decreases with increasing organic content. To date, concentration levels for organics not treatable with conventional binder systems have not been established.

Owing to the relatively high vapor pressure of many solvents, S/S is not a preferred remediation method because of its inability to reduce the contaminant's mobility and because of the volatilization which occurs during curing. However, in three specific cases, S/S technology may be useful: (1) when used to control residual contamination (such as metals) following primary treatment for solvent removal or destruction, (2) when used to control low levels of semivolatile organics, and (3) when used to improve materials-handling properties of a liquid or sludge prior to remedial treatment.

Organic compounds, although present below cleanup action levels, may interact with a binder or inorganic contaminants. They can exert a negative influence on S/S treatment by forming complexes which hinder reactions that immobilize metals. Organic compounds that form anions at the particular pH level of the waste, such as alcohols and carboxylic acids, are most likely to bind with cationic metals. In addition, the organic compounds may be hydrophobic; thus, they can hinder the intimate waste-binder contact necessary for metals immobilization.

Organics may volatilize during mixing and the period between mixing and curing of waste in the S/S material handling process. Even organics with low vapor pressures can be dispersed into the air. Organic volatilization is enhanced when treatment produces heat, as with some cementitious binders. Volatilization must be addressed at sites containing benzene and low molecular weight solvents since they exert appreciable vapor pressures at 20° C.

Solidification, or waste bulking, sometimes facilitates the handling of organic-dominated wastes/sediments/sludges in preparation for off-site disposal/treatment or for interim management prior to on-site remediation. Two entries in the Alternative Treatment Technology Information Center (ATTIC) database describe this approach: solidification followed by RCRA capping. This process usually produces containment of NAPLs. The treatment agent is often a lime-containing waste, such as baghouse dust from limestone calcination or cement production (sometimes called kiln dust or fly ash) and fly ash from coal-fired power plants. As with S/S treatment, the possibility of organic volatilization must be considered in waste-bulking processes. There is no clear evidence that organics will volatilize in the bulking process, but prudence suggests testing for volatilization until sufficient scientific data can prove the practice safe.

Metals: Often, S/S has been applied to wastes and soils containing metals. Solvents and other contaminants such as metals commonly are found at the same site. Unlike organic compounds that can be destroyed, metals can only be changed in oxidation state, chemical species, and physical form. Thus, the goal of S/S is to convert the metal to a less mobile form and physically restrict its contact with water and air. Cementitious materials are the most common binders. In addition to solidification, calcium hydroxide in these binders can cause precipitation of many metals as sparingly-soluble oxyhydroxides. Additionally, metals can adsorb to the aluminosilicate matrix or replace cations normally present in the crystalline structures of cement.

The high alkalinity that favors precipitation of many metals can hinder immobilization if the metals form soluble anionic hydroxides at a high pH. Cadmium, for example, can precipitate at a moderately alkaline pH as cadmium hydroxide, but becomes increasingly soluble at a higher pH, owing to the formation of an anionic cadmium hydroxide. Because the pH for minimum solubility differs for each metal, one set of conditions may not cover all metal-insoluble hydroxides.

Sulfide agents can produce highly insoluble metal compounds with cationic metal species, such as copper. However, the stability of these compounds depends on the permanent exclusion of oxygen and other oxidizers from contact with the metal sulfide <sup>(5)</sup>. For some metals, the oxidation state also affects toxicity, for example, trivalent versus hexavalent chromium.

Another complication in S/S treatment is the speciation of metals in the raw waste. Chromium, arsenic, selenium, and some other metals form both soluble cationic species and soluble oxide anions, for example, chromate and arsenite. The latter form will not precipitate as hydroxides; their sorption differs from that of cationic species in a cement matrix. Although rarely performed, analyses of raw wastes and their leachates for metal oxidation state and chemical species are important in designing the most effective immobilization treatment.

# **Technology Status/Performance**

Treatability test data compiled from numerous sources indicate that the metals found as co-contaminants

at solvent sites are amenable to S/S. The particular S/S system that will perform well on a given contaminated material must be determined by site-specific screening and treatability tests. Some results are shown in Table 3-3. The chromium-containing wastes illustrate the importance of the contaminant oxidation state in stabilization. Ideally, the waste is tested for contaminant speciation so that prior experience with the same chemical form of the contaminant can assist decision makers in the selection of binders for treatability testing. Reduction of hexavalent chromium followed by precipitation as chromium hydroxide is a common water-treatment method that applies to S/S technology since the hydroxide is compatible with cement matrices and any solubilized metal exists in the less toxic form.

Multiple metals may not need to be remediated at all sites since sometimes there is need for only one or two metals. However, a process can be developed to meet cleanup criteria for multiple metals. The appearance of increased leachable metals in residuals following treatability tests is not unusual. It can result from contaminant destabilization (soluble complex formation with treatment agents), sample heterogeneity, or analytical error. Representative sampling, sample homogenization, multiple treatment, and analytical replication may be necessary to ensure useful results.

The performance of S/S technology is assessed by physical tests (compressive strength, permeability, resistance to physical weathering, etc.) by chemical tests that measure the leachability of contaminants after treatment and by total waste analysis. The Toxicity Characteristic Leaching Procedure (TCLP) is a laboratory method specified for characteristically toxic wastes regulated under RCRA. A detailed description of how to evaluate S/S technology as a remedial method for a particular waste is given in Solidification/Stabilization of CERCLA and RCRA Wastes: Physical Tests, Chemical Testing Procedures, Technology Screening and Field Activities (3).

No existing theoretical or empirical method can predict the degree of immobilization attained by applying S/S technology to a particular waste. Site-specific screening and treatability tests determine whether S/S is a suitable and cost-effective remediation method; they can also optimize the ingredient. In addition to ensuring compliance with contaminant- or site-specific leachability limits, these tests can identify the S/S mix that balances cost and volume increases in achieving immobilization. The volume increase upon S/S treatment can cause a significant impact upon disposal space, transportation, and landfill costs.

TABLE 3-3. S/S METAL TREATABILITY TEST RESULTS

Contaminant	Initial Concentration	Reduction (%)	Binders
Arsenic	420 mg/L	22 to 91 ND	Cement kiln dust; slag/lime/fly ash/ silica; silicate
Chromium (III)	33 to 3,960 mg/L	34 to 99 76 to 88 ND	Cement kiln dust; slag/lime/fly ash/silica; sulfide silicate
Chromium (VI)	ND	97 to 99	Sulfide silicate
Copper	ND	51 to 99	Cement; cement/ addi- tives; cement/ sulfide; lime/fly ash

ND = No data available

Source: U.S. EPA, RREL, Cincinnati, Ohio

# **Implementation Costs**

The cost of treatability screening (initial S/S applicability) for a specific site can range from \$10,000 to \$20,000. Treatability costs for remedy selection are higher and more variable depending on the ratio and matrix of binder types and water contents to be investigated. Associated analytical costs increase dramatically as the number of organic compounds analyzed increases. Costs of \$50,000 or more are not unusual.

Connor <sup>(4)</sup> estimated the cost of treatment, transportation, and landfill disposal for some common S/S systems: prices ranged from \$74 to \$397 per ton for landfilling on site, and from \$119 to \$517 per ton for landfilling 200 miles from the contaminated site. The cost was quite dependent on binder cost and on the solids content of the waste, since much more binder is required to solidify low-solids wastes. Locally available waste products — fly ash and kiln dust — can be inexpensive S/S agents, while manufactured treatment agents — organic polymers — can be quite expensive.

# **Data Requirements**

Some of the factors affecting S/S are shown in Table 3-4. Collecting and evaluating physical and chemical data about these factors can help determine the applicability of S/S to the contaminant and matrix.

From a remediation viewpoint, the most important consideration in binder selection is the chemical composition of the material to be treated. Numerous samples from various locations on site should be analyzed for the active solvent ingredients and other characteristically hazardous compounds. Test samples should include full extracts or digestates of the raw waste, TCLP, and any other regulation-mandated test to facilitate an estimate of the leachability of each constituent. Areas determined by site characterization data to be sources of migrating contaminants should be the targets of a more extensive sampling program.

In addition to chemically characterizing the waste, the data will locate typical and worst-case samples for treatability tests. In multi-contaminant wastes, several worst-case samples include high metals/moderate organics, moderate metals/high organics, and metals and organics in hydrophobic carrier solvents.

The remedial manager should study the chemical characterization of the waste and research the available literature and vendor treatability data to determine whether the waste is comparable to another material that has been successfully treated. With organic contaminants, only treatability data that clearly indicate no volatilization or volatile recovery during treatment are relevant.

TABLE 3-4. FACTORS AFFECTING S/S TREATMENT

Factor	Potential Effect
Cyanides content	Increases setting time by interfering with bonding of waste materials (>3,000 ppm).
Halide content	Retards setting; leaches easily.
Inorganic salts content (soluble salts of man- ganese, tin, zinc, copper, and lead)	Adversely affects product strength and curing rates. Reduces dimensional stability (swelling, cracking) of the cured matrix, thereby increasing leachability potential.
Oil and grease content	Weakens bonds between waste particles and cement by coating the particles (>10%).
Organic content	Adversely affects setting and curing of binder. Typical maximum (20 to 45 wt% total organic content). Decreases durability.
Particle size	Can delay setting and curing (insoluble material passing through a No. 200 sieve). Small particles coat larger particles, weakening bonds between particles and cement or other reagents. Particle > 1 inch in diameter not suitable.
Phenol concentrations	Lowers product strength (>5%).
Semivolatile organics	Interferes with bonding (>10,000 ppm) of waste materials.
Sodium arsenate, borate, phosphate, iodate, sulfide, carbohydrate concentrations	Retards setting and curing of cement. Reduces the ultimate strength of the product.
Sulfate	Retards the setting of concrete. Causes swelling due to the formation of calcium sulfoaluminate hydrate.
Solids content	Wastes with <15% solids requires large volumes of reagents, greatly increasing the volume and weight of the end product.
Volatile organic concentrations	Volatiles not effectively immobilized. Driven off by heat of reaction.

Source: U.S. EPA, 1988 <sup>(6)</sup>

# **DESTRUCTION TECHNOLOGIES**

Destruction technologies for remediation of contaminated soil, sludge, and sediment at solvent sites can be divided into three categories: thermal, chemical, and biological. Destruction technologies either destroy or detoxify hazardous wastes by altering the chemical structure of the constituents or breaking down the chemical structure into its basic components.

Table 3-5 lists the typical treatment combinations for destruction options. Waste preparation includes excavation and/or dredging, conveying the soil, dewatering sediment/sludge, screening to remove debris, and reducing particle size. Table 3-6 shows the applicability of destruction technologies to typical contaminant groups found at solvent sites.

TABLE 3-5. TYPICAL TREATMENT COMBINATIONS FOR DESTRUCTION TECHNOLOGIES

Pretreatment/Materials Handling	Destruction Technology	Post-Treatment/Residuals Management
Free-product pumping Soil-vapor extraction Excavation/conveying Dewatering Screening/size reduction In situ steam stripping	Incineration or Pyrolysis	Air pollution control Scrubber effluent treatment/disposal Ash treatment/disposal
Free-product pumping Soil-vapor extraction Excavation/conveying Screening/size reduction In situ steam stripping	Biodegradation (excavated soil)	Solids dewatering Solids treatment/disposal Water treatment/disposal, recycle VOC emission control
Free-product pumping Soil vapor extraction Plowing	Biodegradation (in situ)	Groundwater treatment/re-injection
Free-product pumping Soil-vapor extraction Excavation/conveying Screening/size reduction In situ steam stripping	Chemical dehalogenation	Air pollution control Solids treatment/disposal Washwater treatment/disposal

TABLE 3-6. APPLICABILITY OF DESTRUCTION TECHNOLOGIES TO CONTAMINANT CLASSIFICATIONS

		Destruction Options			
Group No.	Contaminant Group	Thermal Destruction	Chemical Dehalogenation	Bioremediation	In Situ Bioremediation
WO1	Halogenated nonpolar aromatics	•	Θ	•	· O
Wo.4	Halogenated aliphatics	•	Θ	Θ	Θ
W07	Heterocyclics and simple nonhalogenated aromatics	•	0	Θ	
W09	Other polar organic com- pounds	•	0	•	•

Demonstrated effectiveness

Source: U.S. EPA Engineering Bulletins

- Potential effectiveness

O - No expected effectiveness

# Thermal Destruction Technologies

Incineration and pyrolysis are two thermal technologies that destroy contaminants in soil, sludge, and sediment but leave noncombustible inorganics.

# Incineration

Incineration treats organic contaminants in solids, liquids, and gases by subjecting them to temperatures greater than 1,000° F in the presence of oxygen. This causes the volatilization and combustion of the organic contaminants and converts them to carbon dioxide, water, hydrogen chloride, nitrogen oxides, and sulfur oxides. Three common types of incineration systems can treat contaminated solids: the rotary kiln, the infrared incinerator, and the circulating fluidized bed units. The rotary kiln and the infrared units contain a primary chamber that usually operates in the temperature range of 1,000° F to 1,800° F. The rotary kiln is a refractory-lined, slightly-inclined, rotating cylinder that serves as a combustion chamber. Figure 3-2 is a schematic diagram of a rotary kiln incineration process. The infrared unit uses electrical resistance heating elements or indirect-fired radiant U-tubes to heat material passing through the chamber on a conveyor belt.

As material passes through the primary chamber, the unit evaporates moisture, volatilizes, and partially combusts the organic contaminants. Since conversion of the organic contaminants is inadequate in the primary chamber, the system sends the partially combusted gases to a secondary combustion chamber that usually operates between 1,600° F to 2,200° F. The gases are held at temperature for a residence time of 2 seconds to ensure adequate destruction of contaminants. These units are most commonly used for solids and sludges. The operating conditions (temperature, residence time, etc.) vary depending on contaminants and regulations as specified in 40 CFR Part 264 Subpart O and Part 265 Subpart O for RCRA-regulated units, and 40 CFR Part 270 for TSCA-regulated units.

The circulating fluidized bed (CFB) unit uses high-velocity air to circulate and suspend the waste particles in a combustion loop. The CFB is excellent for treating sludges. Operation of the CFB is sensitive to particle size and cannot tolerate feeds that slag at low temperatures. The CFB operates in the temperature range of 1,500-1,800° F and does not need a secondary combustion chamber to achieve adequate destruction of organic contaminants. It can handle liquids and gaseous waste better than other incinerators, operates at a lower temperature, and produces less emissions.

Incinerator off-gas requires treatment by an air pollution-control (APC) system to remove particulates and neutralize and remove acid gases (HCl, NO<sub>x</sub>, and SO<sub>x</sub>). Baghouses, venturi scrubbers, and wet electrostatic precipitators remove particulates; packed-bed scrubbers and spray driers remove acid gases. Limestone added to the combustor loop removes acid gases in the CFB.

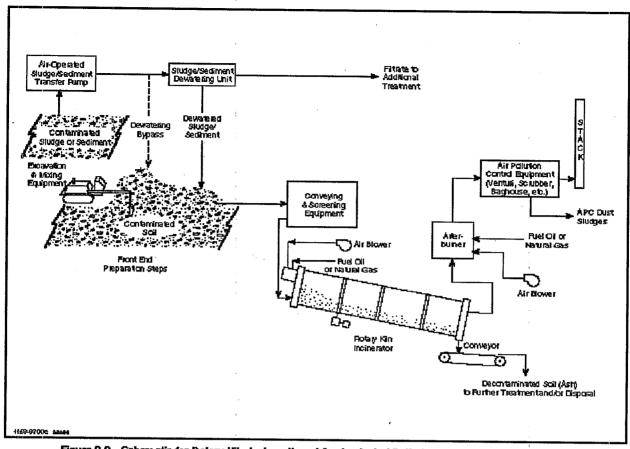


Figure 3-2 Schematic for Rotary Kiln Incineration of Contaminated Soils, Sediments, and Studges (Ex-Situ).

Typical treatment combinations: This technology may generate three residual streams: solids from the incinerator and APC system, water from the APC system, and stack and fugitive emissions from the incineration system.

Bottom ash (treated soils) from the primary chamber and fly ash from the APC system may contain toxic metal contaminants such as chromium, lead, copper, barium, silver, and arsenic. The fly ash may also contain high concentrations of volatile toxic metals such as lead, cadmium, mercury, and arsenic. If these residues fail required TCLP tests, they can be treated by another process such as S/S.

Liquid residues from the APC system may contain excess caustic or acid, high levels of chloride, dissolved and suspended heavy metals, trace organic compounds, and fine inert particulates. These residues may require further treatment—neutralization of the acids or bases; chemical precipitation and/or ion exchange to remove metals; settling, filtration, and reverse osmosis to remove particulates; and carbon adsorption to remove trace organic compounds.

Stack emissions are minimized by the APC and combustion-control system. Fugitive emissions are

controlled by equipment design (enclosed feed, ash, and dust-control systems) and operating procedures.

Technology Applicability: Incineration has effectively treated soil, sludge, sediment, and liquids containing many of the organic contaminants found at solvent sites including halogenated and nonhalogenated volatiles and semivolatiles, and other organics such as dioxins/furans, PCP, and PAHs. Incineration has treated solvent wastes at the most stringent cleanup levels. A substantial body of trial burn results and other quality-assured data verify that incineration can remove and destroy organic contaminants from a variety of waste matrices to the ppb or even the parts-per-trillion (ppt) level <sup>(7,8)</sup>. However, incineration does not destroy metals. They will be present in different residuals (bottom ash, cyclone ash, and liquid) depending on the volatility of their compounds and the incinerator operating conditions <sup>(9)</sup>.

The moisture content and heating value of the contaminated wastes are important parameters that affect the economics of the incineration process. High moisture content and low heating value increase fuel requirements. High moisture content and very high heating values reduce the incinerator's capacity. Several feasibility studies have screened out incineration due to the high moisture content of the wastes. The studies are questionable, however, since engineering solutions can improve the economics. When a waste has both high heating value and moisture content, the moisture content cools the products of combustion efficiently and permits higher throughputs (7). In addition, mechanical or thermal dewatering techniques can reduce high moisture content, and blending high heating value wastes with wastes of low heating value can reduce incineration costs.

Technology Status/Performance: Thermal destruction has been proven in commercial use. Newer techniques being studied lower temperatures in primary incineration chambers and add agents — lime, iron oxide, fly ash, proprietary inorganics — to bind and treat volatile metals in the incinerated material.

Incineration is the most regulated remediation technology and the process most frequently chosen for the destruction of organic contaminants. Of the approximately 400 RODs written for solvent-contaminated sites, 32 specified incineration as the remedial technology. These sites are listed in Table 3-7.

TABLE 3-7. INCINERATOR SELECTIONS AT SOLVENT SITES\*

Region	Site Name	Location
11	Baird & McGuire	Holbrook, MA
1	Davis Liquid Waste	Smithfield, RI
1	Cannon Engineering Corp.	Bridgewater, MA
1	Charles George Reclamation Trust	Tyngborough, MA
1	Pinette's Salvage Yard	Saco, ME
1	Wells G&H	Woburn, MA

TABLE 3-7. (Continued)

Region	Site Name	Location
1	W.R. Grace and Co., Inc.	Acton, MA
2	Hooker-Hyde Park	Niagara Falls, NY
2	Bridgeport Rental & Oil Services	Logan Township, NJ
2	Ewan Property	Shamong Township, NJ
2	Reich Farms	Dover Township, NJ
2	Bog Creek Farm	Howell Township, NJ
2	Claremont Polychemical	Old Bethpage, NY
2	SMS Instruments, Inc.	Deer Park, NY
2	FAA Technical Center	Pomona, NJ
3	Wildcat Landfill	Dover, DE
3	Drake Chemical	Lock Haven, PA
3	Greenwood Chemical Co.	Newton, VA
3	MW Manufacturing	Valley Township, PA
4	Celanese Corp.	Shelby, NC
5	Acme Solvents	Winnebago, IL
5	Big D Campground	Kingsville Township, OH
5	Cliff/Dow Dump	Marquette, MI
5	Pristine, Inc.	Reading, OH
6	Brio Refinery Co.	Friendswood, TX
6	Sikes Disposal Pit	Crosby, TX
6	Triangle Chemical	Bridge City, TX
6	North Cavalcade Street	Houston, TX
6	Motco, Inc.	La Marque, TX
7	Vogel Paint and Wax Co.	Maurice, IA
8	Woodbury Chemical Co.	Commerce City, CO
8	Sand Creek Industrial	Commerce City, CO
10	Western Processing	Kent Valley, WA

Implementation Costs: The cost of incineration includes fixed and operational costs. Fixed costs are one-time expenses including site preparation, permitting, mobilization/demobilization, trial burn, and equipment costs. Operational costs are ongoing expenses including labor, utilities, fuel, and maintenance. Fixed costs are relatively independent of site size. Operational costs vary significantly depending on the type of waste treated. Total costs vary significantly depending on the site size. Figure 3-3 shows the effect of site size on incinerator costs (10). On the average, total costs for incineration range from \$200 to \$1,500 per ton. These figures include excavation, materials handling, and disposal.

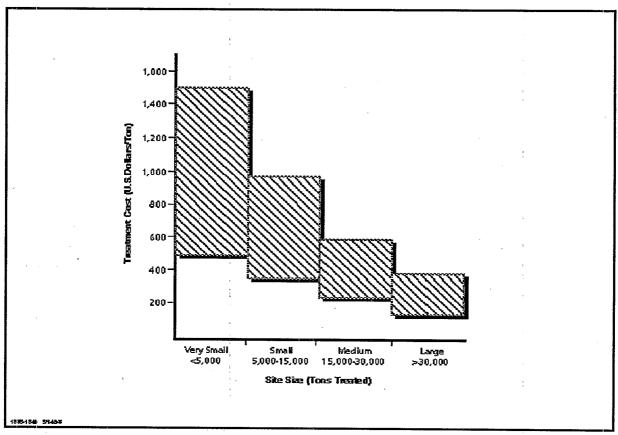


FIGURE 3-3 Effect of Site Size on Incinerator Cost [10]

Data Requirements: A summary of performance data for incineration is presented in Table 3-8. A summary of factors affecting incineration performance is given in Table 3-9. These factors determine the data requirements for incineration, i.e., the type of information (site/waste characterization, treatability study, etc.) needed to implement this technology at a solvent site.

TABLE 3-8. SUMMARY OF PERFORMANCE DATA FOR INCINERATION

Site Name	System	Initial	Performance
Lenz Oil, Lemont, IL (11)	ENSCO rotary kiln	Hydrocarbons	Reduced concentrations to <5.0 mg/kg
Sydney Mines, Brandon, FL <sup>(11)</sup>	ENSCO rotary kiln	Hydrocarbons	Treated to <5.0 mg/kg
Stockton, CA (11)	Ogden CFB	Total hydrocarbons	Treated to <1.0 mg/kg
Brio Site, Friendswood, TX <sup>(12)</sup>	Shirco Infrared System	Carbon tetrachloride	99.99% removal
McColl Superfund Site, Fulle- rton, CA <sup>(13)</sup>	Ogden circulating fluidized bed (full scale)	Carbon tetrachloride	99.99% removal

TABLE 3-9. FACTORS AFFECTING INCINERATION PERFORMANCE

Factor	Potential Effect
Ash fusion temperature	Operation of the kiln at or near the ash fusion temperature can cause melting and agglomeration of inorganic salts (slagging).
Halogenated organic compound concentration	Forms acid gases, which may attack refractory material and/or impact air emissions.
Heating value	Auxiliary fuel is required to incinerate waste with a heating value <8,000 Btu.
Metals content	
Nonvolatile heavy metals (Cr, Ag, Ba)	Ash may fail TCLP. Trivalent Cr can be oxidized to more toxic hexavalent Cr.
Volatile heavy metals (Hg, Pb, Cd, As)	Vaporize; become difficult to remove using conventional APC equipment. Ash may fail TCLP.
Alkali metals (Na, K)	Salts have low melting points; may cause slagging.
Moisture content	Higher moisture content increases feed handling and energy requirements.
Organic phosphorous content	Forms acid gas (high concentrations), which contributes to refractory attack and slagging problems.
Particle size	Oversized material requires size reduction. May hinder processing. Fines affect particulate carryover
PCBs, dioxins	Requires higher temperatures and long residence times for destruction.  May require special permits.

# **Pyrolysis**

Pyrolysis (high-temperature thermal desorption/distillation) is an innovative treatment technology that differs from incineration because it uses heat in the absence of oxygen to volatilize and decompose organic materials. Figure 3-4 depicts a schematic diagram of a pyrolysis process. It transforms hazardous organic contaminated materials into less hazardous gaseous components, liquid fractions containing concentrated contaminants, and a solid residue (coke) containing fixed carbon and ash. The soil remains in its original state. The gas product contains lower molecular weight hydrocarbons, CO, H<sub>2</sub>, and methane. Pyrolysis is an energy intensive process that can treat the same kind of contaminants as incineration.

Pyrolysis operates at temperatures between 1,000 and 2,200° F. Contaminated materials are heated indirectly in stages at temperatures which exceed the boiling points of the targeted constituents to volatilize light organics and water, hydrocarbons, and heavier organics such as PAHs, PCB, and dioxin. Clean solids are discharged and the gases are condensed or incinerated. Cracking organic contaminants produces coke by-products and gas, while desorption mechanisms concentrate the contaminants. The coke and gas can be burned to reduce external fuel requirements. Pyrolysis allows more control, permits higher throughput than incineration, and has the potential to produce fewer air pollutants and operate at lower temperatures. Chlorinated compounds can be dechlorinated using catalysts or other additives.

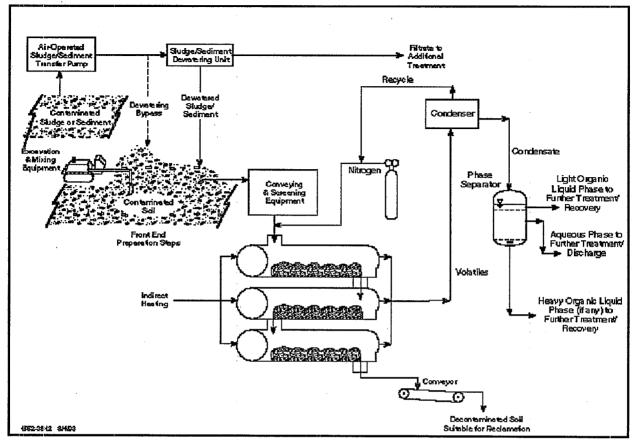


Figure 3-4 Schematic for Pyrolysis (Ex-Situ) for Contaminated Soils, Sediments, and Studges.

Typical treatment Combinations: Pyrolysis generates three process streams: solids, liquids, and gases. The solids consist of the treated soil and the coke formed from hydrocarbon decomposition. Most compounds volatilize rather than decompose, requiring incineration or condensation for further treatment. Condensed volatiles, hydrocarbons, and process water comprise the liquid streams. Condensed volatiles mainly consist of concentrated organic compounds, but may contain chlorides, volatile metals, and particulates. They can be recycled or treated off site in a permitted incinerator. The process water may contain chlorides, volatile metals, trace organics, and particulates. Standard water-treatment techniques for wastewater will suffice for treatment; APC systems will minimize dusts and remove acid gases. If necessary, S/S can treat solids generated from the process.

Technology Applicability: Pyrolysis generally applies to a wide range of organic wastes in soil and sludge, but not to inorganics and metals. Small-scale tests suggest that pyrolysis can treat soil, sediment, and sludge contaminated with nonhalogenated semivolatiles and PCBs, as well as sediment/sludge contaminated with dioxins/furans. However, pyrolysis will not treat or immobilize metals (14). Pyrolysis is best for mixed organic wastes which have PCBs or dioxin as a component because it is an energy intensive and expensive technology which

may not be appropriate for solvent-only contaminated sites.

Technology Status/Performance: Pyrolysis is an emerging technology; performance data are limited. Tests have been performed on PCBs at the Wide Beach Superfund site in Bryant, New York, and the Waukegan Harbor Superfund site outside Chicago, and on PAHs at the Pensacola Superfund site, in Pesacola, Florida. Current uses of pyrolysis technology are in the oil industry where tank bottoms, oily soil, and separator sludge are being recycled.

Implementation Costs: Pyrolysis costs are comparable to those of incineration and are a function of site size. Capital equipment, mobilization and demobilization, and energy costs are high. There are also added costs for waste stream treatment.

Data Requirements: Table 3-10 is a summary of the primary factors affecting pyrolytic performance. These factors determine the data requirements for pyrolysis — the type of information (site/waste characterization, treatability study, etc.) needed to implement this technology at a solvent site.

TABLE 3-10. FACTORS AFFECTING PYROLYSIS PERFORMANCE

Factor	Potential Effect
Temperature	Stages affect contaminant segregation and concentrations in condensate.
Residence time	Short residence time causes inadequate destruction efficiency.
Moisture content	High moisture content increases energy requirements and reduces feed rate. Low moisture content affects reactions involving halogenated organics.
pH (<5 AND >11)	Increases component corrosion.
PCBs, PCP, dioxins	Require higher temperatures and dechlorination catalysts.
Particle size	Oversized debris requires size reduction; May hinder processing; Fines increase particulate carryover.
Halogenated organic compound concentration	Forms acid gases, which may attack refractory material and/or impact air emissions.
Ash fusion temperature	Operation of the equipment at or near the ash fusion temperature can cause melting and agglomeration of inorganic salts (slagging).
Metals content	
Nonvolatile heavy metals (Cr, Ag, Ba)	Ash may fail TCLP.
Volatile metals (Hg, Pb, As, Cd)	Vaporize, become difficult to remove using conventional APC equipment. Ash may fail TCLP.
Alkali metals (Na, K)	Salts have low melting points. May cause slagging.

# **Chemical Destruction Technologies**

# **Dehalogenation**

Dehalogenation is an innovative chemical destruction technology applicable to contaminated soil, sludge, and sediment at solvent sites. A schematic diagram of a dehalogenation process is depicted in Figure 3-5.

The dehalogenation process is effective potentially in detoxifying chlorinated organic contaminants such as dioxins, PCBs, chlorobenzenes, and PCPs. This converts the more toxic compounds into less toxic, sometimes more water-soluble products and leaves compounds that are more readily separated from the soil and treated (15). In dehalogenation of halogenated aromatic compounds, a nucleophilic substitution reaction replaces a chlorine atom with an ether or hydroxyl group. Dehalogenation or dechlorination of chlorinated aliphatic compounds occurs through an elimination reaction and the formation of a double or triple carbon-carbon bond (16).

Field and laboratory tests have identified several types of solutions that can dechlorinate PCBs, dioxins, and furans. These solutions include potassium polyethylene glycolate (KPEG), sodium polyethylene glycolate (NaPEG), and methoxypolyethylene glycolate (MPEG). These are generally classified as alkali polyethylene glycolate (APEG) solutions. Base-catalyzed decomposition (BCD) process is another technology for removing chlorine molecules from contaminants such as PCBs, dioxins, and PCP. It requires the soil to be sized and screened. For the reaction to be effective, contaminated soils are combined with sodium bicarbonate and a catalyst or sodium hydroxide and sucrose and are heated at 340°C.

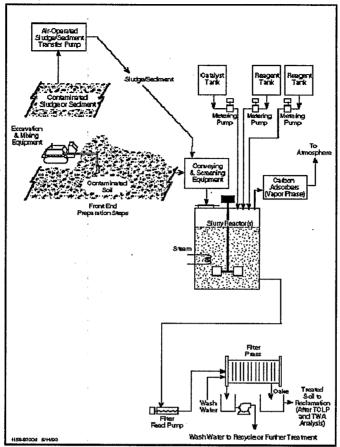


Figure 9-5 Schematic for Dehialogenation (Ex-Situ) of

Typical Treatment Combinations: Dehalogenation generates three residuals: treated soil, washwater, and air emissions. This treatment is effective for dioxin/furan, PCB, PCP, chlorobenzenes, and halogenated phenol/creosol groups. The presence of other contaminants may demand post-treatment, such as bioremediation or incineration. The washwater may require treatment prior to discharge. Volatile air emissions can be controlled by condensation and/or activated carbon adsorption.

Technology Applicability: Chemical dehalogenation is primarily for treating and destroying halogenated aromatic contaminants in a waste matrix consisting of soil, sludge, or sediment. However, this technology has achieved removal efficiencies up to 98 percent in bench-scale studies for chlorobenzene (17). Dehalogenation has been shown at laboratory-scale to be effective on halogenated aliphatic compounds such as ethylene, dibromide, carbon tetrachloride, chloroform, and methylene chloride. The presence of other contaminants may require a treatment combination that will add bioremediation, incineration, or another option.

Technology Status/Performance: Chemical dehalogenation is an innovative alternative to conventional technologies such as incineration. Bench and pilot-scale testing has been successful for treating dioxins, PCB, chlorinated pesticides, and PCP.

Implementation Costs: Chemical dehalogenation costs are estimated to range from \$200 to \$500 per ton

Data Requirements: Table 3-11 is a summary of the factors affecting dehalogenation efficiency and, thus, illustrates the important data requirements for chemical dehalogenation.

TABLE 3-11. FACTORS AFFECTING DEHALOGENATION PERFORMANCE

Factor	Potential Effect
Aliphatic organics, inorganics, metals	Achieves best results with aromatic halides—PCB, dioxins, chlorophenols, chlorobenzenes
Aluminum and other alkaline reactive metals	Requires increased use of reagent under highly alkaline conditions.
Chlorinated organics (>5%)	Requires excessive volumes of reagent.
Clay and silty soils	Increases reaction time due to binding of contaminants.
Humic content	Increases reaction time due to binding of contaminants.
Moisture content (>20%)	Requires excessive volumes of reagent because water reacts with and dilutes the reagent. Higher moisture content increases feed handling and energy requirements.
Low pH (<2)	Increases costs due to increased reagent requirements.
Particle size	Oversized material requires size reduction. May hinder processing.

Source: (19)

### **Bioremediation Technologies**

Bioremediation uses microorganisms to biochemically degrade or transform organic contaminants. It attempts to foster and optimize the natural bioremediation and biotransformation processes which occur in soils. All of the aerobic and anaerobic processes discussed in the Section 2 may be used in bioremediation processes.

Complete degradation of organic contaminants to carbon dioxide, water, and inorganic products may be achievable in some cases. In other situations, transformation of the original contaminants to other organic products occurs. The fate and effects of these products should be considered in developing bioremediation alternatives. While transformation products are often less toxic than the original contaminant, this is not always the case. In addition, the mobility of the transformation product may differ from that of the original contaminant.

Both bacteria and fungi are involved in bioremediation processes. Most research has centered on bacteria, but some investigators have found that fungi can play an important role, especially with halogenated compounds (20).

Bioremediation relies on the combined activity of a variety of microorganisms, rather than one or a few, to degrade organic contaminants. Transformation of contaminants is optimized by choosing and maintaining appropriate conditions for activity of the microorganisms. If biodegradable contamination in the soil has endured for more than a few months and the microorganisms have grown and reproduced in the contaminated soil, native microorganisms generally can transform the wastes. Management techniques can optimize the biological transformation. Little or no evidence is available to indicate that augmentation with cultured microorganisms enhances the natural bioremediation process.

Incomplete bioremediation may also result in secondary products which are more mobile due to increased solubility resulting from the introduction of oxygen into the molecular structure during the initial microbial attack of the contaminant(s), for example, reductive dechlorination of PCE, TCE, and the dichloroethylenes (DCE) results in production of VC, which is more toxic and more mobile than its parent compounds.

In terms of degree of contaminant removal and final residual levels, the extent of treatment achievable in bioremediation depends upon various factors including the types of contaminants present, and bioremediation process used, and site-specific environmental conditions. In general, bioremediation does not achieve contaminant destruction efficiencies comparable to incineration. Performance comparisons with other contaminant removal or destruction processes should be made on a case-by-case basis. Even when lower contaminant removal or destruction is achieved, as long as remedial action goals are met, bioremediation may be a favored alternative based upon factors such as cost, implementability, and public acceptability. Three principal bioremediation processes generally apply to soils at solvent sites: solid-phase, slurry-phase, and in situ bioremediation.

### **Solid-Phase Bioremediation**

Solid-phase bioremediation places contaminated soil in a thin layer, (typically 12- to 18-inches deep) in a lined treatment bed. A schematic diagram of a solid-phase bioremediation process is illustrated in Figure 3-6. Generally nutrients such as nitrogen and phosphorous are added. The bed is usually lined with clay or plastic liners, furnished with irrigation, drainage, and soil-water monitoring systems, and surrounded by a berm. Aeration, temperature control, and a leachate collection system may increase efficiency. This process is one of the older and more widely used technologies for hazardous waste treatment. It has been particularly successful in the United States, especially at petroleum refinery sites treated under RCRA. Solid-phase treatment is relatively simple and inexpensive to implement and may prove effective for a wide range of contaminants. Where greater process control is required to achieve particular performance or operating criteria, other bioremediation approaches may be necessary. Solid-phase treatment is also relatively land intensive due to the thin layer of soil required for aerobic treatment.

Several variations of conventional solid-phase treatment may also be considered. Soil heap bioremediation is conducted by piling the soil to be treated in deeper piles (typically several feet thick) shaped into rows. Containment requirements are similar to those used for solid-phase treatment. Perforated piping entails blowing air through the piping system with a mechanical blower. Nutrients and other supplements may also be added through the piping system as liquids. As compared to conventional solid-phase treatment, soil heap treatment may provide a higher level of process control and requires less space due to the deeper soil layer. Cost may be somewhat higher due to the mechanical components required, and mixing to improve treatment efficiency is not possible.

Composting is a variation of solid-phase bioremediation. The composting process can treat highly contaminated soil by adding a bulking agent (straw, bark, manure, wood chips) and organic amendments to the soil. The soil/amendment mixture is formed into piles and aerated (natural convection or forced air) in a contained system or by mechanically turning the pile. Bulking agents are added to the compost to improve texture, workability, and aeration; carbon additives provide a source of metabolic heat. Waste decomposition occurs at higher temperatures resulting from the increased biological activity within the bed. One potential disadvantage of composting is the increased volume of treated material due to the addition of bulking agents. Irrigation techniques can optimize moisture, pH, and nutrient control, and an enclosed system can achieve volatile emissions control.

As conventionally applied, all of these processes are aerobic bioremediation processes. However, anaerobic treatment may be possible by modifying operating conditions. Deleting aeration systems and covering the soil piles will foster oxygen depletion by the microorganisms and result in development of effective anoxic (low oxygen) or anaerobic conditions.

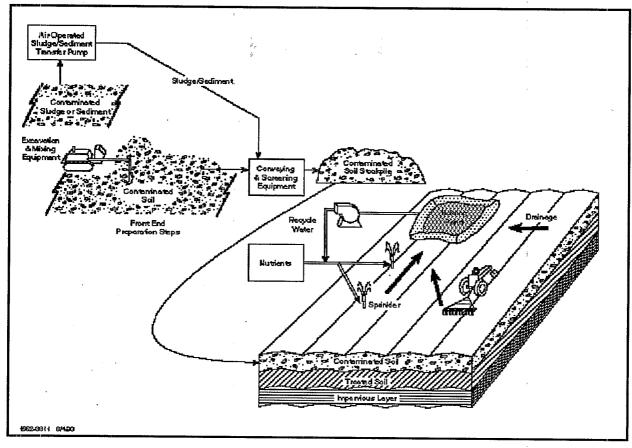


Figure 3-6 Schematic for Solid-Phase Bioremediation

# Slurry-phase Bioremediation

During slurry-phase bioremediation, excavated soil or sludge is mixed with water in a tank or lagoon to create a slurry, which is then mechanically agitated <sup>(21)</sup>. A schematic of a slurry-phase bioremediation process is depicted in Figure 3-7. The procedure adds appropriate nutrients and controls the levels of oxygen, pH, and temperature. Potential advantages of slurry-phase treatment as compared to solid-phase bioremediation include the possibility for more effective treatment due to the high degree of mixing, and the effective contact between contaminated soils and nutrients. These possible advantages should be weighed against the higher capital and operating costs for a slurry reactor system. The majority of slurry phase treatment to date has focused upon aerobic biodegradation and has been conducted at bench or pilot scale.

This process is suitable for high concentrations of organic contaminants in soil and sludge. Following treatment in the reactor, the soil is separated from the slurry by gravity settling and/or mechanical dewatering for redisposal. The water from the slurry may be recycled and/or treated and disposed. However, the presence of heavy metals can inhibit microbial metabolism.

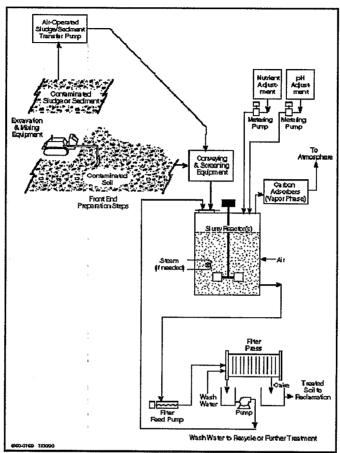


Figure 3-7 Schematic for Sturry-Phase Bioremediation (Ex-Situ) for Contaminated Soils, Sediments, and Studges.

# In Situ Bioremediation

In situ bioremediation promotes and accelerates natural processes in undisturbed soil. Figure 3-8 presents a schematic diagram of in situ bioremediation for soil. It can involve recirculation of extracted groundwater that is supplemented above ground with nutrients and oxygen. Vacuum or injection methods can supply oxygen to the subsurface soil. Under appropriate conditions, this technology can destroy organic contaminants in place without the high costs of excavation and materials handling. Also, it can minimize the release of volatile contaminants into the air. In situ bioremediation requires that nutrients and (for aerobic bioremediation) oxygen be transported through the contaminated zone. Adequate oxygen transfer is often the most difficult to achieve, due in part to the relatively low solubility of gaseous oxygen in water. In some cases and for certain types of wastes, chemical oxygen sources such as hydrogen peroxide, or alternative electron acceptors such as nitrate (22, 23) (see Section 2) can be used.

Currently, significant attention is focused on developing in situ bioremediation for chlorinated organics. This attention derives from the wide use of chlorinated solvents, with TCE being one of the most commonly observed contaminants at CERCLA sites. Recent research has evaluated both anaerobic in situ treatment and methanotrophic in situ treatment for chlorinated organics <sup>(24)</sup>.

A variation on in situ bioremediation for unsaturated soils combines SVE with enhancement of biological activity. This process, termed bioventing, is discussed in the following section.

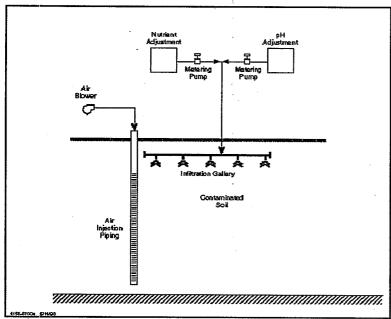


Figure 3-8 Schematic for In-Situ Bioremediation for Contaminated Soils

### **Bioventing**

Bioventing is an emerging technology that also takes advantage of aerobic biodegradation of organics. Figure 3-9 is a schematic diagram of a bioventing process. Bioventing uses forced air to carry an adequate supply of oxygen to the subsurface soils to enhance microbial degradation. The term bioventing was coined to describe in situ biodegradation occurring simultaneously with SVE, which is a widely applied in-place treatment for permeable soils contaminated with volatiles and semivolatiles, including gasoline and solvents. The SVE process discussed in detail on pages 3-46 to 3-52 involves applying a vacuum to the vadose zone to collect vapor-phase contaminants and enhance their removal from the soil by stimulating volatilization (25,26). The SVE technique is an efficient and cost-effective process the for removal of volatile compounds existing as residual saturation in permeable soils. Bioventing attempts to enhance SVE by fostering the in situ biodegradation of semivolatile and nonvolatile contaminants.

Semivolatile components of contamination are not removed by SVE alone, but may be amenable to biodegradation if sufficient oxygen is provided. The bioventing system, which incorporates small-diameter vertical wells connected to a blower or vacuum pump through a piping network, is easy to install and uses standard, readily available equipment. The system can be installed with a minimum of site disturbance and frequently allows

continuation of normal site operations. Although the system is cost efficient to install and maintain, treatment of the extracted vapors can increase total costs greatly. During bioventing, SVE operating conditions are modified to enhance biodegradation. Specifically, operating flow rates and flow configuration are changed and moisture, and/or nutrient plus moisture are added (25).

Bioventing overcomes limitations due to oxygen concentration that affect biodegradation in groundwater. At normal groundwater temperatures, oxygen concentrations range from 5 to 8 ppm in the water. Although hydrogen peroxide and pure oxygen added to water can greatly increase oxygen concentrations, they do not approach the oxygen concentrations present in the atmosphere. Bioventing can be a valuable remediation tool for vadose-zone contaminants that are readily degraded aerobically. A list of factors affecting bioventing performance is contained in Table 3-12.

A successful field demonstration of bioventing has been demonstrated by Du Pont et al. (25). The site was the scene of a January 1985 JP-4 jet-fuel spill at Hill Air Force Base in Utah which resulted from the release of approximately 27,000 gallons of fuel from an underground storage tank. Unrecovered fuel migrated away from the tank area and contaminated an area of approximately 1 acre and to a depth of 50 feet. Initial remediation involved the recovery of 2,000 gallons of free product and installation of a venting system that came on-line in December 1988. Measurement of total petroleum hydrocarbon (TPH) in soil before and after the bioventing treatment demonstrated maximum removals from 970 mg/kg to 5.6 mg/kg at the 15-feet depth interval. This field effort demonstrated enhanced biodegradation of JP-4-contaminated soils compared to removals seen with traditional soil-vacuum extraction. It is estimated that 44 percent of the contaminants were biodegraded and 56 percent were volatilized. Another bioventing project involving JP-4 jet fuel was performed at Tyndall AFB in Florida.

TABLE 3-12. FACTORS AFFECTING BOIVENTING PERFORMANCE\*

Factor	Potential Effect
Moisture Content	Moisture depleted by SVE (<40%) may inhibit aerobic degradation.
Nutrients (C-N-P)	C:N:P of 120:10:1 is necessary for optimum degradation.
SVE Flow Rate	High flow rates increase volatilization, thus decreasing the amount to be degraded.

<sup>\*</sup> Other factors are noted in the SVE and bioremediation sections.

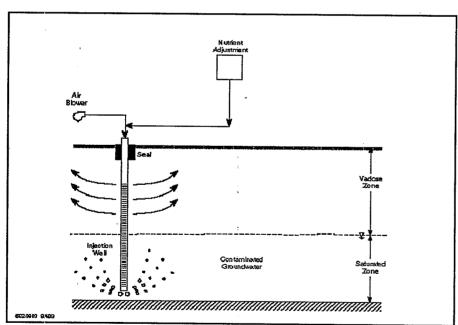


Figure 3-9 Schematic for Bioventing (In-Situ) of Contaminated Soil

# **Typical Treatment Combinations**

Performance is highly dependent on contaminant types and concentrations as well as site conditions. In case of high molecular weight contaminants, the treated and dewatered solids may contain residual organic contaminants, and these media may require further treatment. When the solids are contaminated with heavy metals, stabilization to immobilize the metals following bioremediation may be necessary. High concentrations of toxic metals may inhibit the bioremediation process. The process water also may require on-site treatment prior to discharge. Depending on the waste characteristics, air pollution-control measures, such as adsorption by activated carbon, may be necessary. Surface treatment of recovered groundwater may accompany the in situ bioremediation process.

# **Technology Applicability**

Bioremediation can treat soil, sludge, and sediment contaminated with organic contaminants such as nonhalogenated aromatics, other polar organic compounds (including many solvents), and PAHs. The type of bioremediation process (aerobic or anaerobic) and its implementation (solid, slurry, or in situ) will depend upon the type of contaminant and site-specific factors. Bioremediation of nonhalogenated aromatics, heterocyclics, and other polar compounds have exhibited an average removal efficiency of 99 percent based on pilot and full-scale tests (17). Halogenated aliphatic compounds were also successfully treated; however, the average of 99 percent removal from the available data may be a result of volatilization in addition to bioremediation (17). Bioremediation has been less successful with halogenated compounds. However, research and technology developed for chlorinated organics is ongoing, and recent advances have been made.

### **Technology Status/Performance**

Solid-phase treatment is one of the oldest and most widely used technologies for hazardous waste treatment. Slurry-phase treatment currently exists at the pilot stage, with full scale equipment available for near-term implementation. In situ bioremediation holds promise for cost-effective treatment of contaminated soil and groundwater. Table 3-13 presents a summary of CERCLA, RCRA, and state solvent-contaminated sites considering bioremediation. Results of additional in situ bioremediation efforts are presented in Table 3-14.

TABLE 3-13. SUMMARY OF PERFORMANCE DATA FOR BIOREMEDIATION

Site Name	System	initial	Performance
BRIO/DOP Site, Friendswo- od, TX [27]	ECOVA Corporation's solid-phase biore- mediation pilot scale	Methylene chloride: 15 to 17,000 ppb 1,2,-Dichloroethane: 25 to 195,000 ppb 1,1,1-Trichloroethane: 25 to 195,000 ppb Phenanthrene: 1,392 to 15,083 ppb Anthracene: 440 ppb Fluorene: 563 ppb	More than 99% removal of VOCs within 21 days due to air stripping. Biodegradation of SVOCs was much slower.
Whitehouse Waste Oil Pits Site, Jacksonville, FL [28]	ReTec soil washing followed by bioremediation	Total petroleum hydrocarbons, PAHs	Treated below detection limit

TABLE 3-14. IN SITU BIOREMEDIATION OF CONTAMINATION FROM SOLVENT CHEMICALS

	Contaminants	Treatment Description	Dofor
oform -Trichloroethane		Withdrawal and treatment by an activated-sludge process and recharge of aerated nutrient-laden water: 90% reduction of contaminated plume after 3 years operation; biodegradation based on monitoring well data, some coring data, and increased CO <sub>2</sub> in contaminated compared to uncontaminated areas.	(30)
hydrofuran -Trichloroethane	Carbon tetrachloride	Denitrifying conditions with acetate as a carbon source; confined sand gravel aquifer: 95 to 97% removal; removal rates faster when nitrate depleted, suggesting biodegradation by a population other than denitrifiers.	(31)
hydrofuran -Trichloroethane	Chloroform	Activated sludge bioreactor with the bacteria inoculated into the subsurface.	
hydrofuran -Trichloroethane	MC	Withdrawal and treatment by air stripping followed by treatment in an activated-sludge unit and recharge: treatment success measured by concentrations in monitoring wells.	(32)
hydrofuran -Trichloroethane	MEK	Tanker spill of 5,000 gallons into fractured bedrock; maximum groundwater contamination 1,000 ppm: two closed-loop groundwater recovery systems were installed with activated sludge treatment and subsequent recharge into a groundwater recharge pond; groundwater free of contamination at end of 4 months as measured by monitoring well data.	(33)
-Trichloroethane	Tetrahydrofuran	Treatment in an aboveground reactor with addition of acclimated microbes to the aquifer along with nutrients; treatment measured by monitoring well data.	(34)
	1,1,1-Trichloroethane	Denitrifying conditions with acetate as a carbon source; confined sand and gravel aquifer: present as a background contaminant; tracer and modeling accounted for dilution.	
	TCE	Confined sand and gravel aquifer; cometabolic oxidation by methanotrophic microorganisms controlled by pulsed applications of $O_2$ and CH <sub>4</sub> : 40% cometabolized; bromide tracer and modeling corrected for dilution.	(24)
	TCE	TCE-degrading bacteria, organic and inorganic nutrients, and oxygen were introduced to groundwater; sodium chloride tracer was used; theoretical dilution of TCE concentrations calculated based on ratios between rate of injection and flowrate of receiving zone. Measurable dilution effects only observed in downgradient well: TCE concentrations reduced from high of 3,000 μg/L to a mean concentration of 135 μg/L by day 3.	(32)
	втех	Spill of 25,000 gallons aviation gasoline; sandy water-table aquifer: addition of hydrogen peroxide, nutrients, conservative tracer added at depth of contaminated interval; treatment determined by modeling, oxygen breakthrough in contaminated wells, and chemical analysis of cores.	(36)
	втех	Spill of JP-4 jet fuel; sandy water-table aquifer: addition of nitrate and nutrients; conservative tracer; recirculated through infiltration gallery; modeling separated lowered concentrations due to dilution and biodegradation.	(22)

# TABLE 3-14. (Continued)

Contaminants	Treatment Description	Reference
втех	Spill of 25,000 gallons aviation gasoline; sandy water-table aquifer: research study site, used portion of contaminated subsurface; bioventing used in unsaturated zone for removal of residual contamination; treatment determined by coring analyses.	(25)
втех	JP-4 jet fuel; contamination only in unsaturated zone: bioventing used for remediation; biodegradation and volatilization enhanced.	(38)
втех	Soil vacuum extraction: dewatered because of shallow, fluctuating water table; biodegrada- tion and volatilization enhanced through reduction of flow rates	(26)
Diesel fuel	Spill of 1,000 gallons of diesel fuel: addition of nutrients and hydrogen peroxide; hydrocarbon concentrations reduced from 1500 mg/kg to <1mg/kg on solids; bioremediation confirmed by soil corings and analysis.	(38)

# **Implementation Costs**

One vendor estimates the cost of a full-scale, slurry-phase biodegradation operation ranges from \$80 to \$150 per cubic yard of soil or sludge, depending on the initial concentration and the treatment volume. The cost to use slurry-phase bioremediation varies depending upon the need for additional pretreatment, post-treatment, and air emission-control equipment (21).

Costs for solid-phase land treatment range between \$50 and \$80 per cubic yard, according to the need for a liner and the extent of excavation required. Composting costs approximately \$100 per cubic yard. Costs of in situ treatment range from \$8 to \$15 per pound of contaminant (29).

# In Situ Biotransformation of Chlorinated Aliphatic Hydrocarbons

Although chlorinated solvent compounds are among the most widespread contaminants found in groundwater and soils at Superfund sites, few reports of in situ bioremediation for these chemicals have been published. Chlorinated solvents such as TCE or PCE are persistent in oxygenated environments. Reductive dechlorination of these compounds occurs in anaerobic systems.

Complete dechlorination of TCE and/or PCE to ethylene has been observed at field scale (40, 41). Final dechlorination from VC to ethylene is the limiting step in completion of dechlorination. If further dechlorination of VC is not achieved, the transport and effects of this contaminant must be considered and may prevent the use of bioremediation. Knowledge of reductive dechlorination is not yet adequate to predict whether dechlorination will go to completion at a particular site.

Recent studies have attempted to enhance bioremediation of the chlorinated solvents. Various chlorinated compounds can be oxidized aerobically by cometabolism using low-molecular weight alkanes, such as methane, propane, or butane, as primary substrates for carbon and energy. Solvents such as PCE and carbon tetrachloride (CT) are not amenable to co-oxidation, but TCE, the DCEs, and VC are cometabolized to oxygenated secondary products. A second cometabolism involves microbial growth on aromatics such as toluene or phenol (42). The potential of using methane-oxidizing microorganisms has been evaluated at pilot scale, and initial results are promising for remediation of TCE, DCE, and VC (24). Pilot-scale evaluation of microorganisms that oxidize aromatic compounds is comparable to the methane oxidizing process. Use of methane to remediate volatile chlorinated compounds in the vadose zone may be quite feasible due to the ease of moving methane and air in the unsaturated subsurface. These innovative systems are in the initial stages of evaluation. Though they are promising, more engineering development is needed to provide a practical alternative to current pump-and-treat technology, and much research remains to be accomplished before widespread implementation at field scale.

Chlorinated solvents transformation also has been observed in denitrifying environments (bacteria that use nitrate as the terminal electron acceptor during respiration). Because denitrifying conditions are less reducing than methanogenic or sulfate-reducing environments, using denitrification in remediation activities is advantageous. For example, reductive dechlorination of carbon tetrachloride (CT) has been observed under denitrifying conditions. In batch-fed mixed denitrifying cultures, CT was observed to degrade with the production of cell mass and carbon dioxide (43). The production of cellular mass during the degradation suggests that microorganisms are growing and reproducing on the waste rather than simply transforming the wastes. Chloroform was identified as a transformation intermediate, demonstrating that reductive dechlorination occurred to some degree. In other studies, biotransformation of CT was observed in both methanogenic and denitrifying conditions in anoxic biofilms (44). Under denitrifying conditions, 41 percent of CT was mineralized to carbon dioxide, 14 percent was converted to chloroform, and 45 percent was transformed to an unknown nonvolatile product.

Denitrifying conditions are less reducing than methanogenic or sulfate-reducing environments. Subsequently, production of dissolved iron or manganese, sulfides, or other odor-causing compounds (found in more reducing environments) may be avoided in aquifers. Denitrifying bacteria also grow more rapidly and probably are distributed more widely in subsurface environments than sulfate-reducing or methanogenic bacteria.

Under both field and laboratory conditions, indigenous denitrifying bacteria were tested for their ability to biotransform CT when given an appropriate environment for growth <sup>(31)</sup>. Assessment of biotransformation was made by controlled addition, frequent sampling, quantitative analysis, and mass-balance comparisons. In addition, fate of background contaminants (TCA, freon-11, and freon-113) under denitrifying conditions were observed. This study demonstrated in situ biotransformation of CT and TCA by indigenous microorganisms. Rapid rates were observed with half-lives on the order of hours to days in the absence of oxygen, with the addition of acetate in the presence of nitrate and sulfate. Chloroform was formed as an intermediate in the transformation of CT and may pose an impediment to implementing this process. Nitrate was removed readily by denitrifying organisms in the subsurface upon addition of acetate as a growth substrate. Over 90 percent biotransformation of CT was measured at the field site with 30 to 60 percent transformed to chloroform. Transformation of CT was more rapid following nitrate depletion with a lower fraction transformed to chloroform. Rates of biotransformation of the background contamination were slower than that of CT, with extent of transformation for CT at 95 to 97 percent, and TCA at 11 to 19 percent.

# **Data Requirements**

The factors that may restrict bioremediation and its various effects are summarized in Table 3-15. A remedial manager can derive data requirements for biological destruction from this list. The data requirements include site factors and waste characteristics.

TABLE 3-15. FACTORS AFFECTING BIOREMEDIATION PERFORMANCE

Factor	Potential Effect
Contaminant solubility	Contaminants with low solubility are harder to biodegrade because the waste must be solubilized to enable organisms to use the waste as a food source.
Presence of elevated levels of heavy metals, highly chlorinated organics, some pesticides, inorganic salts	Can be highly toxic to microorganisms. Low concentrations of some metals are needed for biological activity (Fe, Mn, Mg, Ca).
Moisture content	May inhibit solid-phase aerobic remediation (land farming) of soils if >80% residual saturation. Soil remediation inhibited if <40% residual saturation. Soil-slurry reactors may have 80-90% moisture content. Liquid-phase reactors may have >99% moisture content.
Nutrients (C-N-P)	Microbial growth limited if lacking nutrients (suggested C:N:P ratio of 120:10:1). Nutrients can be added if necessary.
Oil and grease concentrations	Inhibit soil remediation at concentrations >5% by weight.
Oxygen	Sustains aerobic activity (>0.2 mg/l dissolved), inhibits anaerobic activity (>1%).
рН	Optimal in a range of 6-8, may work in a range of 4.5 to 8.5.
Soil permeability	Affects movement of water and nutrients for in situ treatment.
Suspended solids concentration	Should be <1% (can vary greatly in different types of bioremediation).
Temperature	Inhibits microbial activity. (Optimal in the range 15-35°C.) However, in some cases, can be conducted at temperatures to freezing and over 100° F.
Variable waste composition	Large variations affect biological activity, especially where continuous flow liquid bioreactors are used. Inconsistent biodegradation.
Redox potential	Inhibits microbes. Optimal >50 millivolts aerobes, <50 millivolts anaerobes.

# SEPARATION/CONCENTRATION TECHNOLOGIES

Separation/concentration technologies remove contaminants from soils by thermal, physical, or chemical means to form a concentration which can be treated more easily by other means. These technologies can be used either for excavated or in situ soil. Several such technologies include:

In Situ Soil Technologies

**Excavated Soil** 

SVE

Thermal desorption

Steam extraction

Soil washing

Radio frequency (RF) heating

Soil flushing

Solvent extraction

Typical remedial combinations for separation/concentration technologies are listed in Table 3-16. Table 3-17 is a summary of the applicability of these technologies on contaminant groups and media. For these ratings, "demonstrated effectiveness" means that at some scale (e.g., bench-scale for innovative technologies), treatability tests showed that the technology was effective. "Potential effectiveness" means that the technology requires further development, and "no expected effectiveness" means this technology does not work.

TABLE 3-16. TYPICAL TREATMENT COMBINATIONS FOR SEPARATION/CONCENTRATION TECHNOLOGIES

Pretreatment/Materials Handling	Separation/Concentration Technology	Post-Treatment Residuals Management
Free-product pumping	SVE	Groundwater air stripping Condensate air stripping Carbon regeneration Solvent disposal Catalytic oxidation
Free-product pumping SVE	Steam extraction	Groundwater air stripping Carbon regeneration Solvent disposal Catalytic oxidation
Free-product pumping	RF heating	Groundwater air stripping Carbon regeneration Solvent disposal
Free-product pumping	Soil flushing	Groundwater air stripping Carbon regeneration Solvent disposal

# TABLE 3-16. (Continued)

Free-product pumping SVE Excavation Screening/size reduction	Soil washing	Solids disposal Water treatment VOC emission control
Free-product pumping SVE Excavation Dewatering Screening/size reduction	Solvent extraction	Solids dewatering Solids disposal Solvent disposal Water treatment VOC emission control
Free-product pumping SVE Excavation Screening/size reduction Dewatering	Thermal desorption	Solids disposal GAC regeneration Water treatment Solvent disposal Catalytic oxidation

TABLE 3-17. APPLICABILITY OF SEPARATION/CONCENTRATION TECHNOLOGIES

				Separation/C	Separation/Concentration Technologies	echnologies		
			In Situ Soil	Soil			Excavated Soil	
Group No.	Contaminant Group	Soil Vapor Extraction	Steam Extraction	Radio Frequency	Soil Flushing	Thermal Desorption	Soil Washing	Solvent Extraction
W01	Halogenated nonpolar aromatics	•	Ф	Ō	, (D)		(E)	
W04	Halogenated aliphatics	•	•	•	•	•	•	Ф
W07	Heterocyclics and simple nonhalogenated aromatics	9	•	•	Ф	•	•	•
W09	Other polar organic compounds	•	Ф	Ф	•	•	Ф	•

Demonstrated effectiveness

 $\hfill \hfill  

O - No expected effectiveness

Source: U.S. EPA Engineering Bulletins

SVE

Soil vapor extraction physically separates and concentrates volatile organic compounds (VOCs) dispersed in contaminated soil. A schematic diagram of a vapor extraction process, an in situ technology that applies a vacuum to withdraw vapors from soil, is depicted in Figure 3-10. Another mode of operation injects air into the soil. An enhancement to the technology injects hot air as it applies a vacuum to remove contaminated vapors. Following removal of contaminants from the soil, equipment either condenses the vapors, collects them on activated carbon, or destroys them by catalytic oxidation. Condensed vapors are disposed of off site or destroyed by a suitable technology.

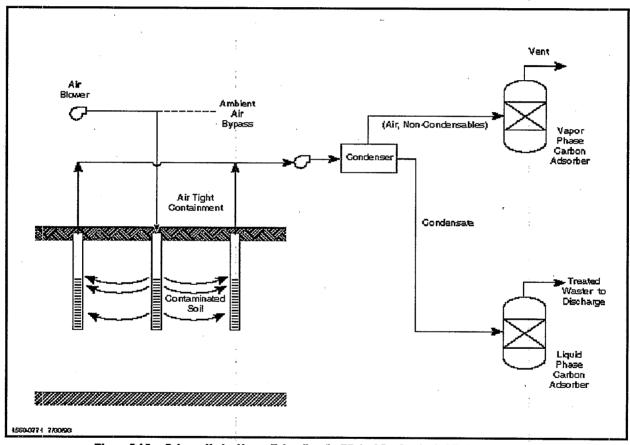


Figure 3-10 Schematic for Vapor Extraction (In-Situ) of Contaminated Soils

Typical Treatment Combinations: SVE generates the following waste streams: vapor and liquid residuals, contaminated groundwater, and soil tailings from well drilling. The usual vapor treatments are carbon adsorption and thermal destruction. Other (less common) treatments include condensation, biological degradation, and ultraviolet oxidation. Contaminated groundwater can be treated and discharged. Highly contaminated soil tailings must be collected for treatment by another technology, such as incineration.

Technology Applicability: SVE effectively processes VOCs at sites where the soils are well drained, contain low levels of organic carbon, and present a relatively high pneumatic permeability. Site heterogeneities may impede implementation of SVE. The design and proper location of SVE wells, however, can sometimes overcome the problem of site heterogeneities. Soil vapor extraction is feasible when a compound has vapor pressure of at least 0.5 Torr at ambient temperatures. The limit for site pneumatic permeability is 1 X 10<sup>-10</sup> cm<sup>2</sup>. Any site with values below this level should not be considered for SVE application. Unless site soils are arid, SVE is less effective for removing solvents that are highly soluble in water.

Technology Status/Performance: SVE is an accepted technology that has operated commercially for several years. It is a frequently selected remedial alternative for VOC-contaminated sites; more than 30 RODs have specified SVE as a remedial action. The technology has remediated many underground storage tank (UST) and RCRA sites as well. Growing experience in technology performance indicates that a properly designed system based on results from pilot-scale operations may produce a system capable of meeting performance goals and site-cleanup objectives. Table 3-18 shows sites where SVE has been selected as a remedial option. Table 3-19 presents a summary of typical SVE performance data.

TABLE 3-18. SVE SELECTIONS AT SOLVENT SITES

Region	Site Name	Location	
11	Groveland Wells	Groveland, MA	
11	Wells G&H	Woburn, MA	
11	Kellogg-Deering Well Field	Norwalk, CT	
11	South Municipal Water Supply Well	Peterborough, NH	
1	Tinkham's Garage	Londonderry, NH	
22	FAA Technical Center	Pomona, NJ	
2	Upjohn Facility	Barceloneta, PR	
3	Bendix Flight Systems Division	Bridgewater Twp., PA	
3	Henderson Road	Upper Merion Twp., PA	
3	Tysons Dump	Upper Merion Twp., PA	
4	Martin Marietta Sodyeco Div.	Mt. Holly, NC	

# TABLE 3-18. (Continued)

Region	Site Name	Location
4	Stauffer Chemical Co. Cold Creek Plant	Cold Creek, AL
4	Stauffer Chemical Co. Axis Plant	Lemoyne, AL
5	Kysor Industrial Corporation	Cadillac, MI
5	Long Prairie Long Prairie, MN	
5	MIDCO 1	Gary, IN
5	Seymour Recycling	Seymour, IN
5	Miami County Incinerator	Troy, OH
5	Pristine, Inc.	Reading, OH
5	Verona Well Field	Battle Creek, MI
5	Wausau Groundwater Contamination	Wausau, WI
6	South Valley	Albuquerque, NM
6	Hardage/Criner	Criner, OK
ブ	Hastings Groundwater Contamination	Hastings, NE
8	Sand Creek Industrial	Commerce City, CO
9	Motorola, Inc. (52nd St. Plant)	Phoenix, AZ
9	Litchfield Airport Area	Goodyear, AZ
9	Fairchild Semiconductor Corp.	San Jose, CA
9	Fairchild Semiconductor Corp.	Mountain View, CA
9	Intel Corp. (Santa Clara III)	Santa Clara, CA
9	Intersil, Inc./Siemens Components	Cupertino, CA
9	Raytheon Corp.	Mountain View, CA
9	Spectra-Physics, Inc.	Mountain View, CA

TABLE 3-19. SUMMARY OF PERFORMANCE DATA FOR IN SITU SVE

Site	Equipment	Initial	Performance
Industrial, CA	NA	TCE 0.53 mg/kg	0.06 mg/kg TCE after treatment <sup>(46)</sup>
Custom Products, Stevensville, MI	NA	PCE 5,600 mg/kg	0.70 mg/kg PCE after treatment (46)
Prison Construction Site, MI	NA	TCA 3.7 mg/kg	0.01 mg/kg TCA after treatment <sup>(46)</sup>
Sherwin-Williams Site, OH	Midwest Water Resources - Vaportech (full scale)	Paint solvents 38 mg/kg	0.04 mg/kg <sup>(46)</sup>
Upjohn Site, Barceloneta, PR	Terra Vac Corp. (full scale)	CCl <sub>4</sub> 2,200 mg/kg	<0.005 mg/kg <sup>(45,46)</sup>
UST Bellview Site, FL	Terra Vac Corp. (pilot scale)	BTEX 97 mg/kg	<0.006 mg/kg <sup>(45,48)</sup>
Verona Wellfield Site, Battle Creek, Ml	Terra Vac Corp. (pilot scale)	TCE, PCE, TCA 1,380 mg/kg	Ongoing (45,46)
Valley Manufactured Products Co., Groveland, MA	Terra Vac Corp. SITE Program	TCE 96.1 mg/kg PCE, DCE	4.19 mg/kg <sup>(45,46)</sup>
San Fernando Valley Superfund Site, Area, 1, Burbank, CA	AWD Technologies SITE Program	VOCs: TCE, PCE	98 to 99% removal <sup>(46)</sup>
Ponders Corner, Lakewood, WA	ECOVA	PCE 3.88 mg/kg TCE 3.6 mg/kg	97.97% removal 99.76% removal
Twin Cities Army Ammunitions Plant, Mi	. NA	TCE 2060 mg/kg	0.0085 mg/kg
Hinson Chemical, SC	OHM Remediation Services Corp.	BZ, TCE, PCE, DCA, MEK	<10 ppm total VOCs (47)

NA = Not available

Implementation Costs: Typical costs for SVE treatment range from \$10 to \$150 per ton (45). Capital costs cover well construction, vacuum blowers, vapor and liquid treatment systems, pipes, fittings, and instrumentation. Operations and maintenance costs include labor, power, maintenance, and monitoring activities. Costs also vary according to site, soil, and contaminant characteristics.

Data Requirements: The factors affecting SVE performance are listed in Table 3-20. From these factors, which are noted in the following, the remedial manager can begin to develop the data necessary to evaluate the technology.

• Vapor pressure is a measure of a substance's tendency to evaporate or give off vapor. A vapor pressure greater than 0.5 Torr indicates potential for removal by SVE.

- Henry's constant is a constant of proportionality that relates the partial pressure of a compound to its
  concentration in a dilute aqueous solution. A Henry's constant greater than 0.01 indicates potential for
  removal by SVE.
- The saturation zone is that region of the soil where the pores are filled with water. Soil vapor extraction cannot be applied effectively below the water table. However, SVE can sometimes be used in combination with air sparging to handle contamination below the water table. Additionally, it can be applied if a site can be dewatered economically.
- Soil permeability is a measure of a soil's ability to permit fluid flow. Soil vapor extraction is most applicable to soils of moderate to high permeability.
- Soil water content is expressed as percent residual saturation. A completely saturated soil has 100 percent residual saturation. The presence of water decreases the soil's ability to permit air flow (decreases air permeability). A soil with greater than 50 percent residual saturation has very low air permeability.
- The soil gas relative humidity is the moisture concentration in the soil/vapor phase divided by the moisture concentration of saturated vapor multiplied by 100 percent. High soil humidity reduces the tendency of contaminants to adsorb on the soil particles.
- Soil organic carbon consists of humus, peat, and other naturally occurring materials which adsorb and hold organic compounds. Thus, high levels of organic carbon adversely affect the applicability of SVE.

TABLE 3-20. FACTORS AFFECTING SVE PERFORMANCE

Factor	Potential Effect
Vapor pressure	Affects removal (>0.5 torr indicates good removal) if less, consider steam strip or thermal desorption.
Henry's constant	Affects removal (>0.01 at ambient temperature suggests good removal). Relates partial pressure to water solubility.
Saturation zone/high water table	SVE not cost-effective below water table or when water table is <5 ft. Dewatering or air sparging is necessary.
Soil permeability	Permits solvent removal if permeable (gravel, sand); efficiency decreases for low permeability soils < 10-4 cm/s (silt, clay).
Soil water content	Impedes air permeability; severely when residual saturation >50%. Diminishes air carrying capacity.
Soil relative humidity	Affects absorption; best results at 94 to 98.5%.
Subsurface temperature	Low temperatures decrease vapor pressures, thus decreasing volatilization.
Water Solubility	High water solubility decreases effectiveness of treatment.
Soil organic carbon	VOCs are adsorbed/absorbed by organic carbon. Removal becomes difficult.

Source: U.S. EPA, 1991 (49).

Ex Situ Uses: Although SVE is basically an in situ technology, it has been applied to excavated materials. Systems have been installed in stockpiled soils, and stockpiles have been constructed around SVE systems. Successful applications of ex situ SVE include remediation of excavated soil from underground storage tanks (USTs) and remediation of soil tailings from well drilling activities (50). Ex situ systems may be more effective than in situ systems because of the greater permeability and homogeneity of the soils.

At the Basket Creek site in Douglasville, Georgia, an ex situ SVE system was utilized to remove toluene, MEK, and MIBK from excavated soils. To complete the treament train, the extracted vapors from the pile were thermally destroyed. Ex situ SVE was performed also at the Hill AFB in Utah. Levels of JP-4 jet fuel in the soil were reduced from 410 to 3.8 mg/kg.

Steam Extraction: Steam extraction (steam injection) physically separates volatile and semivolatile organics from soil, sediment, and sludge. Figure 3-11 is a schematic diagram of a steam extraction process. The process uses a combination of thermal and mechanical energies generated by steam, hot air, infrared elements, and electrical systems to volatilize and transport the contaminants in the vapor phase.

Steam extraction is an emerging technology that appears promising, particularly if used in conjunction with SVE. Due to the heating of the soil, steam extraction can remove more of the less volatile compounds than SVE.

Compounds boiling at or below 350° F (51) (e.g., aniline, chlorobenzene, 1,3-dichlorobenzene, chlorophenol) can be removed by steam extraction.

Steam extraction systems may be mobile or stationary. A mobile system injects steam through rotating cutter blades that disperse it through the contaminated medium. This system is potentially applicable in low permeability soils because the steam has good access to the contaminants. In a stationary system, steam flows through individual valves from the manifold to the injection wells. Recovery wells are used to remove gases and liquids from the soil. The system then recovers the contaminants as condensed organics or activated carbon.

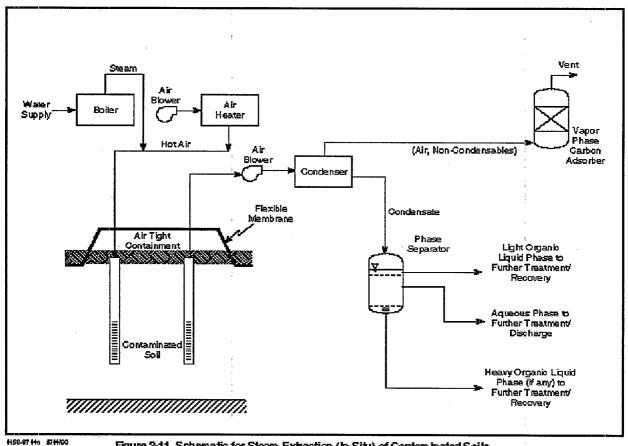


Figure 3-11 Schematic for Steam Extraction (In-Situ) of Contaminated Soils.

Typical Treatment Combinations: Steam extraction generates vapor and liquid residuals and contaminated water. Stationary systems also generate soil tailings for drilling wells. The vapor treatment usually consists of contaminant condensation followed by removal of trace contaminants with carbon adsorption. The condensed contaminants are sent off site for further treatment or disposal.

The contaminated water is treated to remove residual contaminants before disposal or reuse; the activated carbon can be regenerated or disposed. Contaminated soil tailings are sent off site for treatment or disposal.

Technology Applicability: Steam extraction has been shown effective in removing VOCs, halogenated solvents, and petroleum wastes. It should be effective in removing low-boiling-point semivolatile compounds such as aniline and dichlorobenzene. It may be effective for halogenated nonpolar aromatics and other polar organic compounds.

During a Superfund Innovative Technology Evaluation (SITE) program demonstration at the GATX Annex Terminal site in San Pedro, California, a mobile steam extraction system by Novaterra, Inc. reduced average volatile concentrations from 466 mg/kg to 71 mg/kg, achieving an 85 percent average removal efficiency for volatile contaminants (52, 53). The primary VOCs were trichloroethene, tetrachloroethene, ethylene, and chlorobenzene.

A mobile unit using cutter blades in concert with steam and hot-air injection is applicable to shallow (<30 ft) unconsolidated soils. The surface must be relatively flat (<1 percent slope), and the soil must be capable of supporting the weight of the rig. There must be ample vertical clearance (>35 ft) to overhead obstacles and unimpeded site access must be available. Underground utilities and solid obstacles (rocks larger than approximately 6 in) limit application of this process. Since the cutter blades reduce the low permeability materials to sizes of three-eights of an inch, silts and clays can be effectively treated, but an increase in treatment time and cost should be expected. Past field experience in treating medium- to high-permeability soils have demonstrated 50 percent removal of semivolatile compounds (53). Results of bench-scale tests prior to the field demonstration showed 45 to 85 percent removal of semivolatile compounds (53).

Stationary steam extraction techniques require the installation of steam injection and fluid extraction wells in a pattern that most effectively recovers the contaminants without dispersing them further. Soils of medium to high permeability can be treated with this technique, and application below and/or above the water table is possible. Low permeability soils are difficult to treat because steam flows through zones of higher permeability, and heat must be transferred across a longer path to reach contaminants in the stagnant areas. The mobilized wastes are pumped out of the fluid extraction wells to recover the contaminated aqueous- and separate-phase liquid contaminant. This technique is particularly applicable to deep contamination since deeper injection allows greater well spacing, and it lowers costs. Limited field experience has demonstrated 90 percent removal of volatile and semivolatile compounds, with better recovery in higher permeability zones and lower recoveries of high aqueous-phase solubility compounds in lower permeability regions.

Technology Status/Performance: In situ steam extraction is an emerging technology for remediation of low vapor-pressure VOCs and semivolatiles. Novaterra, Inc. mobile technology has been demonstrated under the SITE Program at the GATX Annex Terminal site in the Port of Los Angeles, California. It is being considered as a component of the selected remedy for the San Fernando Valley site in Burbank, CA. A full-scale stationary system is planned by Solvent Service, Inc. for soil contaminated by various solvents. Table 3-21 is a summary of typical performance data for steam extraction.

TABLE 3-21. SUMMARY OF PERFORMANCE DATA FOR STEAM EXTRACTION

Site	Equipment	Initial	Performance
GATX Annex Terminal, San Pedro, CA	Novaterra, Inc. (formerly Toxic Treatments USA) mobile detoxifier SITE Program (full scale)	VOCs: trichloroethene, tetrachloroethene, chlor- obenzene	Average removal rate of 85% VOCs, 50% SVOCs (63)
GATX Annex Terminal, San Pedro, CA	Novaterra, Inc. (formerly Toxic Treatments USA) mobile detoxifier (bench scale)	VOCs: trichloroethene, tetrachloroethene, chlor- obenzene	Average removal of 97% VOCs, 86% SVOCs <sup>(53)</sup> (Vendor's claim)
Lockheed Burbank, CA	AQUADETOX moderate vacuum steam stripper	Soil gas 6000 ppm VOCs	<100 ppm VOCs (ongoing)
Solvent Services, Inc., San Jose, CA	Solvent services steam injection/vapor extraction stationary unit (pilot scale)	VOCs 1,200 mg/kg	Reduced contaminant concentration to <22 mg/kg in high permeability zones (64)

Implementation Costs: According to site-to-site characteristics, estimates place costs for a stationary steam extraction system at about \$50 to \$300 per cubic yard (52). For a mobile technology, a SITE demonstration reported costs of \$111 to \$317 per cubic yard for 10-cubic-yard-per-hour and 3-cubic-yard-per-hour treatment rates, respectively (70 percent on-line operating factor). Cost estimates for this technology strongly depend on the treatment rate (a function of the soil type) the contaminant, and the on-line operating factor (53).

Data Requirements: Table 3-22 illustrates important performance factors for steam extraction. Data for these factors should be collected.

TABLE 3-22. FACTORS AFFECTING STEAM EXTRACTION PERFORMANCE

Factor .	Potential Effect
Constituent vapor pressure	Low vapor pressure decreases removal efficiencies; vapor pressure curve required for each pollutant.
Variable soil composition/ consistency	Inconsistent removal rates. Silt and clay may become unstable and increase treatment time.
Infiltration rate	Excessive rate hinders removal of organics.
Soil moisture content	High moisture increases energy requirements.
Soil Temperature	Low temperatures inhibit volatilization; increase treatment time.

# Radio Frequency (RF) Heating

RF an innovative treatment technology for rapid and uniform in situ heating of large volumes of soil. Figure 3-12 is a schematic of a radio frequency heating process. The process uses electromagnetic wave energy to heat the soil evenly to the point where volatile and semivolatile contaminants are vaporized in the soil matrix. Vented electrodes recover the gases formed in the soil matrix. The concentrated extracted gas and particulate streams can be incinerated or subjected to other treatment methods such as carbon absorption (55). Full implementation of an RF heating system at a contaminated hazardous site requires four major systems:

- RF energy deposition array
- RF power generating, transmitting, monitoring, and controlling
- Vapor barrier and containment
- Gas and liquid condensate handling and treatment

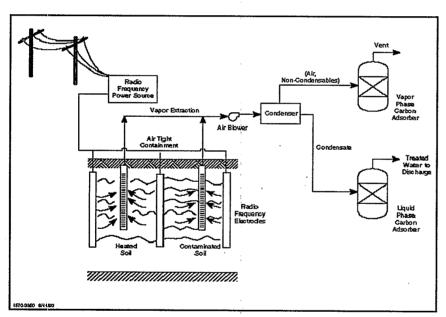


Figure 3-1.2 Schematic for Radio Frequency Heating of Contam insted Soils.

Technology Applicability: Heating by RF is applicable to materials that typically volatilize in the temperature range of 80° to 300°C such as aliphatic and aromatic fractions of jet fuels and gasoline, chlorobenzene, TCE, DCA, and PCE. This technology is applicable to predominantly sandy soils.

Technology Status/Performance: RF heating is a new technology for the cleanup of hazardous waste sites. It had previously been used in the petroleum industry for oil recovery. It is currently in the pilot- and field-scale demonstration stage and has been tested at the Volk Field ANGB, Wisconsin. On the average, 94.3 percent of the semivolatile aliphatics and 99.1 percent of the semivolatile aromatics were removed from the treated soil. Table 3-23 shows the summary of performance data for RF heating.

TABLE 3-23. SUMMARY OF PERFORMANCE DATA FOR RF HEATING

Site	Equipment	Initial	Performance
An Abandoned Fire Training Area at Volk Air National Guard Base, Camp Douglas, Wiscon- sin	ITT Research Institute field demonstration	Volatile aromatics and aliphatics; semivolatile aromatics and aliphatics	99.1% removal of volatile aromatics, aliphatics, and semivolatile aromatics; 94.3% of semivolatile aliphatics
Sandy soil	Pilot scale	Chlorobenzene 10 to 1,000 ppm Tetrachloroethylene 10 to 1000 ppm	94 to 98% removal was achieved.

Source: (55).

Implementation Costs: The estimated treatment cost varies between \$50 to \$90 per ton of treated soil, depending on the amount of native moisture present in the soil and the exact temperature of treatment.

Data Requirements: Table 3-24 shows the factors that affect RF heating.

TABLE 3-24. FACTORS AFFECTING RF HEATING PERFORMANCE

Factor	Potential Effect
Type of soil	Low permeable soils increase costs and decrease contaminant recovery.
Presence of metal drums; metallic debris	Disrupts current flow. May increase treatment costs.
Type of contaminants	Must be supplemented with other treatment methods if nonvolatile contaminants (boiling point greater than 300° C) are present.
Moisture content	High moisture increases energy requirements.

#### Soil Flushing

Soil flushing technology extracts contaminants from soil with water or other suitable aqueous solutions. Figure 3-13 is a schematic diagram of a soil flushing process. Soil flushing introduces extraction fluids into soil using an in situ injection or infiltration process. This method may apply to all types of soil contaminants. Soil flushing accomplishes permanent removal of contaminants from the soil; it proves most effective in permeable soils. The process must have an effective collection system to prevent contaminants and potentially toxic extraction fluids from migrating into uncontaminated areas of the aquifer. Soil flushing introduces potential toxins (flushing solution) into the soil system; the physical/chemical properties of the system may be altered because of the introduction of the flushing solution.

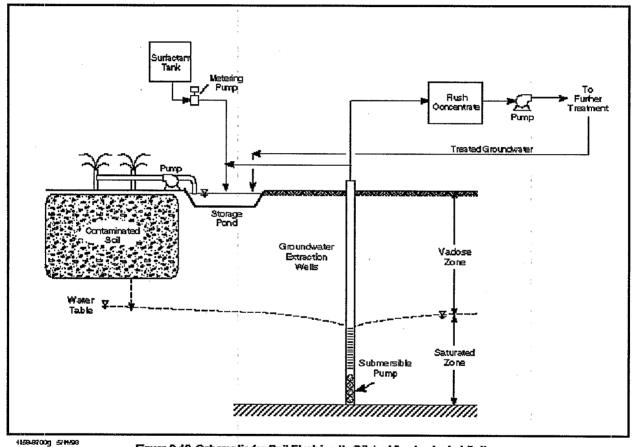


Figure 3-13 Schematic for Soil Flushing (In-Silu) of Contaminated Soils.

Typical Treatment Combinations: Typically, soil flushing is used in series with other treatments that destroy contaminants or remove them from the extraction fluid and groundwater. Soil flushing in conjunction with bioremediation may be a cost-effective means of soil remediation at sites contaminated with organic constituents such as solvents, creosote, etc. For soils contaminated with both inorganic and organic constituents, a combination of pretreatment that reduces or eliminates the metal constituents in the elutriate by precipitation followed by activated

carbon or air stripping may be a feasible cost-effective method of treatment. Wherever possible, treated water should recycle to the front end of the soil-flushing process. The wastewater sludge and solids (such as spent carbon) require appropriate treatment before disposal.

Technology Applicability: Depending on the type of flushing additive [acidic solutions for metals and organic constituents (including amines, ethers, and anilines), basic solutions for metals (zinc, lead, and tin), and surfactants for hydrophobic organics], in situ soil flushing can treat contaminants such as halogenated aliphatics, simple nonhalogenated aromatics, other polar organic compounds, and nonvolatile and volatile metals (56).

Technology Status/Performance: Soil flushing is an innovative technology. Its performance depends upon the contact between the flushing solution and the contaminants. The U.S. EPA has selected it as one of the source control remedies for 10 Superfund sites. In situ soil flushing has been demonstrated on a limited basis at a few sites contaminated by petroleum hydrocarbons and TCE. In Germany, soil flushing was used to cleanup a TCE spill, and a 50 percent decrease in TCE over an 18-month period was achieved (57). At the Lipari Landfill in Gloucester, New Jersey, a successful treatability test for in situ soil flushing was conducted, and an operational full-scale unit is being used for VOC removal.

Implementation Costs: Soil flushing costs lie in the range of \$50 to \$120 per cubic yard (58).

Data Requirements: Table 3-25 illustrates some important parameters affecting in situ soil flushing performance. These factors can provide a basis for determining data needs.

TABLE 3-25. FACTORS AFFECTING IN SITU SOIL FLUSHING PERFORMANCE

Factor	Potential Effect
pH buffering capacity	High buffering capacity increases reagent requirements, especially acids.
Heavy metals	May require pH adjustment (leaching) for removal.
Total organic carbon content	Inhibits desorption of contaminants.
Solubility data	Determines formula of suitable washing fluid.
Cation exchange capacity (CEC)	High CEC (>100 meq) interferes with metals removal.
Hydraulic conductivity (permeability)	Low permeability ( $k < 10^{-5}$ cm/s) reduces percolation and decreases effectiveness.
Site hydrogeology	Affects flow patterns that permit flushed contaminants recapture.
Complex mixtures of waste types (e.g., metals with organics)	Formulation of suitable flushing fluids difficult.
Variable soil conditions	Inconsistent flushing.
Soil pH	Affects the speciation of metal compounds.
Moisture content	High moisture decreases flushing fluid transfer.

# Separation/Concentration Technologies for Treatment of Excavated Soil

# **Thermal Desorption**

Thermal desorption technology physically separates volatile and some semivolatile contaminants with low boiling points from excavated soil, sediment, and sludge. A schematic diagram of a thermal desorption process is shown in Figure 3-14. Thermal desorption uses indirect or direct heat exchange to volatilize contaminants and water from soil into a carrier gas stream for further treatment. The carrier gas stream may be either air or an inert gas. Depending on the process selected, this technology heats contaminated media to temperatures between 200° and 1,000° F. Off-gases may be burned in an afterburner, catalytically oxidized, condensed for disposal, or captured by carbon adsorption beds (59).

Typical Treatment Combinations: Thermal desorption systems create up to seven residual streams: treated media, oversized contaminated rejects, condensed contaminants, water, particulates, clean off-gas, and/or spent carbon. Debris and oversized rejects may be suitable for on-site disposal. Solidification may be necessary, depending on the residual content of nonvolatile heavy metals in the treated medium. Condensed contaminants require further treatment.

Technology Applicability: Thermal desorption can successfully treat most of the contaminants found at solvent sites. It cannot separate metals (arsenic, cadmium, lead, zinc, chromium) or PAHs with boiling points above 1,000° F effectively. Mercury, a volatile metal, can be treated with some thermal desorption units. Bench, pilot-, and full-scale studies have demonstrated that thermal desorption achieves treatment efficiencies of 99 percent or greater for VOCs and semivolatile organic compounds (SVOCs). Some higher temperature units can treat PCBs, pesticides, and dioxins/furans (60, 61).

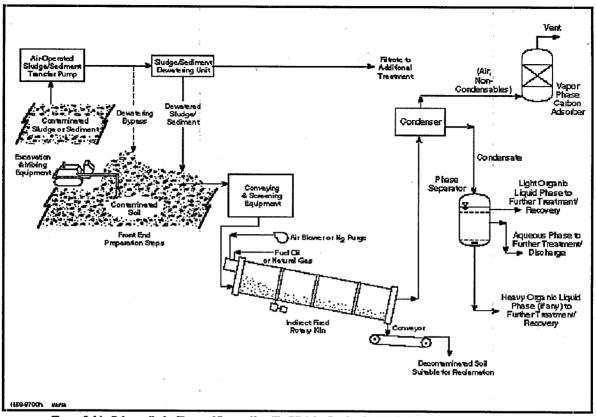


Figure 3-14 Schematic for Thermal Description (Ex-Situ) for Contaminated Soils, Sediments, and Studges.

Technology status/performance: Commercial-scale, thermal-desorption units are already in operation. Thermal desorption has been selected in one or more operable units at 14 Superfund sites. It is one of the technologies of choice for the cleanup of VOCs, semivolatiles, PAHs, and PCBs. The following companies have units: Roy F. Weston, Inc., Chemical Waste Management, Canonie Environmental, TDI Services, and Remediation Technologies, Inc. Table 3-26 contains the results of a full-scale performance test for the Roy F. Weston, Inc. LT<sup>3</sup> System. Table 3-27 is a summary of typical performance data for thermal desorption.

TABLE 3-26. FULL-SCALE PERFORMANCE RESULTS FOR LT<sup>3</sup> SYSTEM (59)

Contaminant	Soil Range (ppb)	Treated Range (ppb)	Removal Efficiency (%)
Benzene	1,000	5.20	99.5
Toluene	24,000	5.20	99.9
Xylene	110,000	<1.00	>99.9
Ethyl benzene	20,000	4.80	99.9
Naphthalene	4,900	<330	>99.3
Carcinogenic	,		
Priority PNAs	<6,000	<330 to 590	<90.2 to 94.5
Noncarcinogenic		;	
Priority PNAs	890 to 6,000	<330 to 450	<62.9 to 94.5

TABLE 3-27. SUMMARY OF PERFORMANCE DATA FOR THERMAL DESORPTION

Site	Equipment	Initial	Performance
USATHAMA Letterken- ney Army Depot, Cham- bersburg, PA	Weston Low Tempera- ture Thermal Treatment System (LT3) (pilot	Benzene, trichloroethylene, tetra- chloroethylene, xylene	>99% removal
	scale)	Total VOCs: 32,000 ppm	4,480 ppb
Cannon Bridgewater Superfund Site, Bridge- water, MA	Weston Low Tempera- ture Thermal Treatment System (LT <sup>3</sup> ) (full scale)	TCE, DCE, PCE toluene, xylene, vinyl chloride 500 to 3,000 ppm total VOCs	<0.25 ppm total VOCs
Cannon Bridgewater Site, Bridgewater, MA	Canonie Low Tempera- ture Direct Desorber	Total VOCs	Reduced to <0.1 mg/kg
Ottati & Goss Superfu- nd, Kingston, NH	Thermal desorption, Canonie Engineering	TCE, PCE, DCA, benzene up to 2,000 ppm total VOCs	<1 ppm total VOCs (48, 57,
USATHAMA Tinker Air Force Base, Oklahoma City, OK	Weston Low Tempera- ture Thermal Treatment System (LT <sup>3</sup> ) (full scale)	Up to 6,100 ppm TCE	Met required cleanup levels <sup>(68)</sup>
TP Industrial, Inc., South Kearney, NJ	Canonie Environmental Services (full scale)	Up to 10,000 ppm VOCs	Average reduction in concentration to 0.3 ppm VOCs (65)

TABLE 3-27. (Continued)

Site	Equipment	Initial	Performance
Confidential Site in Illinois	Weston Low Tempera- ture Thermal Treatment System (LT³) (full scale)	Benzene 1,000 ppb Toluene 24,000 ppb Xylene 110,000 ppb Ethyl benzene 20,000 ppb	Benzene 5.2 ppb Toluene 5.2 ppb Xylene <1.0 ppb Ethyl benzene 4.8 ppb
Privately-funded site, South Kearney, NJ	Canonie Environmental Low Temperature Ther- mal Aeration LTTA <sup>™</sup> (full scale)	VOCs 177.0 ppm (avg.) PAHs 35.31 ppm (avg.)	VOCs 0.87 ppm (avg.) PAHs 10.1 ppm (avg.)
McKin, Maine	Canonie Environmental Low Temperature Ther- mal Aeration LTTA <sup>™</sup> (full scale)	VOCs ND-3,310 ppm Up to 1,000 ppm TCE	VOCs ND to 0.04 ppm 0.1 ppm TCE <sup>(48, 85)</sup>
Coal and Tar Contami- nated Soils	Remediation Technologies, Inc. (ReTEC) (pilot scale)	Benzene 1.7 ppm Toluene 2.3 ppm Xylene 6.3 ppm Ethyl benzene 1.6 ppm	Benzene <0.1 ppm Toluene <0.1 ppm Xylene <0.3 ppm Ethyl benzene <0.1 ppm
Gas Station, Cocoa, FL	OHM Low Temperature Direct Desorber	Benzene, toluene, xylene	Treated to <0.1 mg/kg

Implementation costs: Several vendors have documented processing costs that range from \$80 to \$350 per ton of feed processed <sup>(62, 63, 64)</sup>. Cost must be considered in context, because the base year of the estimates varies. Costs also differ due to the quantity of waste to be processed, the term of the remediation contract, the moisture content, the organic constituency of the contaminated medium, and the cleanup standards to be achieved.

Data Requirements: Table 3-28 describes the factors affecting thermal desorption performance. Data requirements can be derived from these factors.

TABLE 3-28. FACTORS AFFECTING THERMAL DESORPTION PERFORMANCE

Factor	Potential Effect
Clay or tightly aggregated particles	Incomplete volatilization of contaminants due to caking.
Mercury (Hg) content	Increased temperatures to treat and air pollution control costs.
Metals, inorganics, nonvolatile organics	Not likely to be effectively treated.
Metals (As, Cd, Pb, Cr)	Residue may fail TCLP.
Moisture content	High moisture content (> 20%) increases energy requirements. Dewatering or pretreatment may be required.
pH	Causes corrosion of system components (outside 5 to 11 range).
Particle size	Oversized (>1 in) debris material requires size reductions; fines generate fugitive dusts and a greater dust loading will be placed on the downstream air pollution-control equipment.
Constituent vapor pressure	Low vapor pressure decreases removal efficiencies; Requires vapor pressure curve for each pollutant.
Volatile organic concentrations	Equipment limits: Rotary Dryer up to 10%; Thermal Screw 50 to 60% (68).

Source: (67, 68).

# Soil Washing

Soil washing technology is a water-based process for mechanically scrubbing excavated soil to remove contaminants. Figure 3-15 depicts a schematic diagram of a soil washing process, which removes contaminants in two ways: by dissolving or suspending them in the wash solution, or by concentrating them into a smaller volume of soil through particle size separation techniques. Soil washing systems that incorporate both techniques yield the greatest success for soils contaminated with heavy-metal and organic contaminants. Contaminants tend to bind chemically and physically to clay and silt particles. The silt and clay, in turn, tend to attach physically to sand and gravel. The particle size separation aspect of soil washing first scours and separates the silts and clays from the clean sand and gravel particles. The process then scrubs the soluble contaminants from the particle surfaces and dissolves them in the liquid phase.

The soil-washing process uses various additives (surfactants, acids, chelating agents) to increase separation efficiencies. After successful testing, the washed soil can be returned to the site or reclaimed. The aqueous phase and the clay/silt/sludge fraction contain high concentrations of contaminants. These two streams become waste feed for other on- or off-site treatment

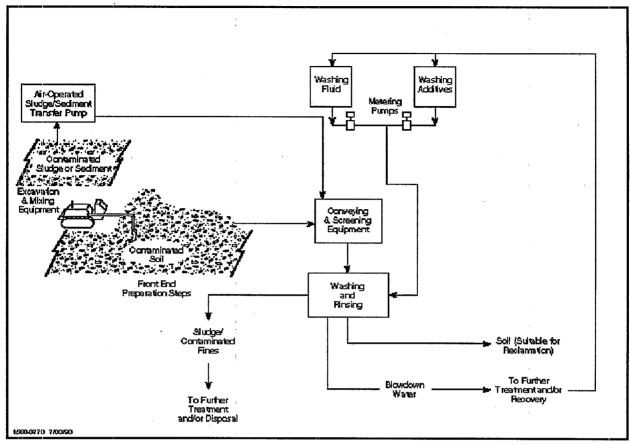


Figure 3-15 Schematic for Soil Washing of Contaminated Soils, Sediments, and Studges.

Typical Treatment Combinations: Soil washing generates four main waste streams: contaminated solids, washwater, washwater treatment sludge, and air emissions. Contaminated clay fines and sludge may require further treatment with technologies such as incineration, thermal desorption, solidification/stabilization, or bioremediation. Discharge standards may mandate washwater treatment prior to discharge. Permits may be required for collection/treatment of air emissions from the preparation area or the washing unit.

Technology Applicability: Soil washing effectively treats waste-containing halogenated phenols and creosols, nonhalogenated aromatics, and nonvolatile and volatile metals. The parocess is best suited for sandy and sandy loam soils that are low in soil organic matter and clay content. Removal efficiencies for soil washing depend on the type of contaminant and washing fluid. Soil washing can be used as a relatively cost effective way to reduce the volume of material needed to be disposed of or treated by a more energy intensive process. Water alone may easily remove volatile organics. Semivolatile organics, pesticides, and hydrophobic contaminants may require the addition of a surfactant; metals may require pH adjustment with acids or bases or the addition of chelating agents. Complex contaminant matrix systems, which contain a mixture of metals, nonvolatile organics, and semivolatile organics, may require sequential washing steps with variations in the wash formulation and operating parameters. Site-

specific, bench, or pilot-scale treatability tests determines the best operating conditions and wash fluid compositions. Soil washing has attained a removal efficiency greater than 99 percent for nonhalogenated aromatics. Bench-scale studies for nonvolatile and volatile metals achieved 99 percent. However, only 72 percent removal was achieved for halogenated phenols and creosols (56).

Technology Status/Performance: Soil washing is widely accepted in Europe but has had limited use in the United States; now it is becoming popular. A number of vendors provide soil washing processes. Information from treatability studies at solvent sites indicates possible applications (Table 3-29). However, sufficient data are not available at this time.

TABLE 3-29. SUMMARY OF PERFORMANCE DATA FOR SOIL WASHING AT SUPERFUND SITES

Equipment	Initial		Performance
MTARRI (bench	1,1-Dichloroethane	43 ppm	99.9% + removal
scale)	Chloroform	99 ppm	99.9% + removal
	1,2-Dichloroethane	4,500 ppm	99.8% + removal
	1,1,1-Trichloroethane	5 ppm	99.9% + removal
	1,1,2-Trichloroethane	3,700 ppm	99.7% + removal
	Benzene	8 ppm	99.9% + removal
	Toluene	30 ppm	99.9% + removal
	Chlorobenzene	79 ppm	98.9% + removal
	Ethylbenzene	453 ppm	98.7% + removal
	Styrene	280 ppm	97.5% + removal
	Acetone	61 ppm	75.4% + removal*
Heijman	Chlorobenzene		99.97%
	Extractable organic halo-		95%
	gens		90-99%
	Mineral oil		

<sup>\*</sup>Possible laboratory contamination (69).

Implementation costs: Vendor-supplied treatment costs for soil washing processes range from \$50 to \$205 per ton of feed soil. Treatment of the residuals may be significant for this process depending on the type and concentration of the contaminants.

Data requirements: Data requirements for soil washing can be derived from the performance factors in Table 3-30.

TABLE 3-30. FACTORS AFFECTING SOIL-WASHING PERFORMANCE

Factor	Potential Effect
Silt and clay content	Increases difficulty to remove contaminants because of strong adsorption to particles.
Complex waste mixtures	May require multiple process steps and wash fluid formulations.
Humic content	Inhibits contaminant removal if high.
Metals concentration	Resist solubilization (insoluble metals). However, some metals can be solubilized and removed.
Particle size distribution	Affect removal from wash fluid (particles < 0.063 mm); oversize debris > 0.25 IN requires removal).
Partition coefficient	High coefficient requires excessive volumes of leaching liquid (highly-bound contaminant).
Cation exchange capacity	High CEC may affect treatment of metallic compounds.
Wash solution	Large volumes become expensive to treat.

Source: (67)

# **Solvent Extraction**

Solvent extraction is a physical separation process that removes contaminants from soil, sludge, or sediment; it uses organic solvents to isolate contaminants, unlike soil washing, which uses water or water-based solutions. Figure 3-16 is a schematic diagram of a solvent extraction process. Solvent extraction is more appropriate for organic contaminants than inorganics and metals; it reduces contaminant volume by concentrating them in the extract phase. The three broad categories of the solvent extraction process are conventional solvent extraction, critical solution temperature fluid, and supercritical fluid extraction (70).

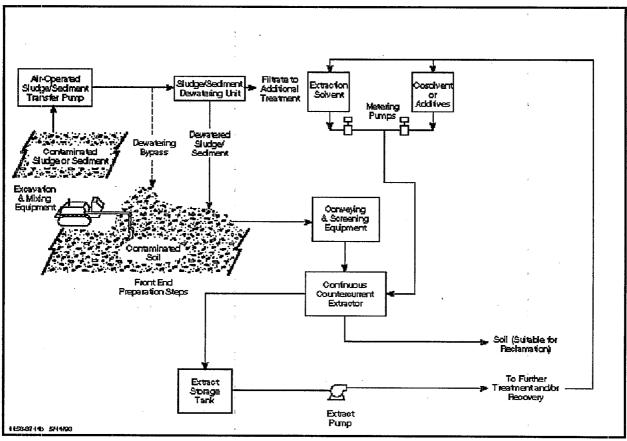


Figure 3-16 Schematic for Solvent Extraction (Ex-Situ) of Contaminated Soils, Sediments, and Studges.

Conventional solvent extraction uses organic solvents to selectively extract the contaminants of concern. The process may require several passes to reduce contamination to the desired level. The extracted solvent can be stripped of the contaminants, condensed, recycled, and reused, therefore reducing contaminant volume and providing optimum extraction efficiency.

Critical solution temperature fluid extraction uses solvents (aliphatic amines) that are miscible with water at one temperature and insoluble with water at another temperature; triethylamine is an example. These solvents can be recycled from the recovered liquid phases by steam stripping because of their high vapor pressure and low boiling point azeotrope formation.

Supercritical fluid extraction uses highly compressed gases, e.g., carbon dioxide, butane or propane, raised above their critical temperatures to extract contaminants that generally resist extraction by conventional solvents. The highly compressed gaseous fluid provides the additional diffusive/solvating power that is required to extract contaminants from spaces and particle surfaces of an environmental medium because of irregularities in soil. Supercritical fluid extraction uses higher pressure and

temperature than conventional solvent extraction. The process also can recycle and reuse the fluid.

Typical Treatment Combinations: Solvent extraction generates three streams: concentrated contaminants, treated soil or sludge, and separated solvent. Concentrated contaminants may receive further treatment or disposal; the treated soil or sludge may require further drying. Depending on the metal content or other inorganic contaminants remaining, treatment of the cleaned solids by some other technique such as S/S or soil washing may be necessary. Analysis of the liquid component determines whether further treatment is necessary before disposal.

Technology Applicability: Solvent extraction is effective in treating excavated sediment, sludge, and soil containing contaminants similar to those at solvent sites. This technology generally is not used for extracting inorganics (i.e., heavy metals). Sometimes inorganics that pass through the process experience a beneficial effect by changing the chemical compound to a less toxic or leachable form.

Technology Status/Performance: Resources Conservation Company (B.E.S.T. Process) and CF Systems have tested solvent-extraction systems at two Superfund sites under the SITE Program. Solvent extraction would be specified for a solvent-contaminated site if there were other, more difficult to remediate compounds (such as PCBs) which could not be handled by SVE or in situ bioremediation. Solvent-extraction technology was used as the remedial action for the Pinette Salvage Superfund site in Washburn, Maine, which is contaminated with PCBs and organics (chlorobenzenes, dichlorobenzene, and trichlorobenzene). Other solvent-extraction systems under consideration at hazardous waste sites include the Extraksol Process by Sanivan International, Inc.; the Low Energy Extraction Process (LEEP), a joint venture by Harmon Environmental Services and Acurex Corporation; and the Carver-Greenfield process by DeHydro Tech. Information from treatability studies at solvent sites indicate possible application (Table 3-31).

TABLE 3-31. SUMMARY OF PERFORMANCE DATA FOR SOLVENT EXTRACTION

Site	Equipment	Initial	Performance
Star Enterprise Refinery Port Arthur, TX [71]	CF Systems full-scale 50 tpd commercial unit	Benzene 30.2 mg/kg Toluene 16.6 mg/kg Ethylbenzene 30.4 mg/kg Xylenes 13.2 mg/kg Anthracene 28.3 mg/kg Naphthalene 42.2 mg/kg Phenanthrene 28.6 mg/kg	Meets or exceeds BDAT standards Benzene 0.18 mg/kg Toluene 0.18 mg/kg Ethylbenzene 0.23 mg/k g Xylenes 0.98 mg/kg Anthracene 0.12 mg/kg Naphthalene 0.66 mg/kg Phenanthrene 1.01 mg/kg
Two Petroleum Refiner-	LEEP (bench scale)	Volatiles and semivolatiles	Reduced to levels below detection limits
Bayou Bonfouca Superfund, Slidell, LA [73]	B.E.S.T. Process (pilot scale)	Semivolatiles	Greater than 99% was achieved. Total semivolatiles concentration was reduced from 6,688 mg/kg to 34 mg/kg
Jennison-Wright Corporation, Granite City, IL	B.E.S.T. Process (pilot scale)	Semivolatiles	Greater than 98% was achieved for total semivola- tiles

Implementation costs: Cost estimates for solvent extraction range from \$100 to \$500 per ton <sup>(71)</sup>. The most significant factors influencing costs are the waste volume, the number of extraction stages, and the operating parameters such as labor, maintenance, setup, decontamination, demobilization, and time lost during equipment operating delays. The cost of solvent-extraction treatment is currently higher than that for thermal desorption.

Data requirements: The data needed to evaluate system performance is presented in Table 3-32.

TABLE 3-32. FACTORS AFFECTING SOLVENT-EXTRACTION PERFORMANCE

Factor	Potential Effect
Complex waste mixtures	May be combination of solvents needed.
Metals (e.g., aluminum)	Strong reactions may occur during B.E.S.T. treatment process because of caustic addition.
Particle size	Particle size requirements vary with system from >1/8" to 2" diameter.
pH .	Must be in range compatible with extracting solvent (pH > 10 for B.E.S.T. process).
Partition coefficient	High coefficient requires additional extraction steps (highly bound) contaminants.
Volatiles	Volatiles may combine with process solvent, requiring additional extraction steps (high concentrations) or fractional distillation to separate solvents from the contaminant for reuse - increases cost if cannot recycle solvent.
Moisture content (>30%)	Water may impede some extraction processes. It may require use of a hydrophilic solvent to remove water so that contact between hydrophobic solvent and contaminant will improve.
Heavy metals	Not suitable for solvent extraction.

Source: (67)

#### WATER-TREATMENT TECHNOLOGIES

Water treatment must address three media types at solvent sites: process wastewater, surface water, and groundwater.

Based on the site-specific contaminants and the selected remedies, the wastewater can require a range of treatment. Treatment of process wastewater is part of the treatment train. The treatment of any surface water and remediation of groundwater may occur at the beginning, throughout, or after the other remedial actions. Site-specific data affects the selection of treatment options.

Also, the future use of the site dictates the remedial methods to be selected for water treatment. Two treatment categories are destruction technologies and separation/concentration technologies. Destruction technologies apply only to organic contaminants, whereas separation/concentration technologies treat both organic and inorganic contaminants.

The technologies that treat wastewater, surface water, and groundwater at solvent sites are also appropriate to other types of sites; a brief overview follows. Groundwater treatment can be performed by both in situ and ex situ technologies. The effectiveness of ex situ technology is dependent upon removing contaminants along with the groundwater. This process usually is referred to as pump and treat. If it proves too difficult, other technologies such as steam extraction or surfactant flushing can be used to improve contaminant removal with the groundwater. Groundwater technologies are discussed in more detail in other EPA documents (see Bibliography).

Destruction Technologies	Separation/Concentr	ration Technologies
Chemical oxidation	Adsorption	Membrane separation
Biological treatment	Filtration	Precipitation
	Ion exchange	Oil/water separation
	Air stripping	Air sparging
	Reverse osmosis	

Table 3-33 summarizes the water treatment technologies applicable to various contaminant groups found at solvent sites.

TABLE 3-33. EFFECTIVENESS OF GROUNDWATER-TREATMENT TECHNOLOGIES ON SOLVENT CABLE 3-33.

						1			
		,				Groundwater-Treatment Options	ent Options		
Group No.	Contaminant Group	Air Stripping	Granular- Activated Carbon Treatment	Membrane Filtration	lon Exchange	Chemical Oxidation	Precipitation	In Situ Bioremediation	Fixed-Film Biological Treatment
W01	Halogenated nonpolar aromatics	Ф	•	•	0	•	0	Ф	Ф
W04	Halogenated aliphatics	•	•	Θ	0	•	0	•	•
W07	Heterocyclic and simple nonhalogena- ted aromatics	•	•	•	0	•	0	•	•
W09	Other polar organics	•	•	•	0	•	0	•	•

Demonstrated effectiveness

Potential effectiveness
 No expected effectiveness

# **Destruction Technologies for Water Treatment**

#### **Chemical Oxidation**

Chemical oxidation primarily treats halogenated and nonhalogenated solvents (VOCs and SVOCs), phenolics, pesticides, PCBs, and nonvolatile and volatile metals. Figure 3-17 is a schematic diagram of a chemical oxidation process. This process oxidizes ions or compounds to render them nonhazardous or to make them more amenable to subsequent removal or destruction processes. Chemical oxidants are relatively nonselective; they may oxidize other compounds as they destroy accompanying contaminants of concern. Due to the cost of chemicals, this process has limited application to waters with large amounts of oxidizable components or heavily contaminated water. Chemical oxidation is most useful as a polishing step for dilute, relatively clean, aqueous wastes.

Ultraviolet (UV) radiation/oxidation uses UV radiation, ozone and hydrogen peroxide to destroy organic compounds in water. Other oxidants are chlorine dioxide, hypochlorites, and chlorine <sup>(74)</sup>. The process is a well-established disinfection technology for drinking water and wastewater. UV radiation/oxidation has been demonstrated as part of the SITE Program <sup>(74, 75)</sup>.

# **Biological Treatment**

Biological treatment of water, like soil biotreatment, detoxifies wastestream organic matter through microbial degradation. The most prevalent type is aerobic. A schematic diagram of the aerobic bioremediation of groundwater is shown in Figure 3-18. A number of biological treatment processes can treat water from solvent sites. These include conventional activated sludge techniques; various modifications of activated sludge techniques, i.e., those using pure-oxygen activated sludge, extended aeration, and contact stabilization; fixed-film systems (rotating biological discs); and in situ biological treatment.

- The activated sludge process introduces aqueous waste into a reactor containing a suspension of aerobic bacterial cells. The bacteria transform organics into cell constituents, other organics, carbon dioxide and water. It also produces new bacterial cells.
- In the pure-oxygen activated sludge process, oxygen or oxygen-enriched air replaces ambient air and increases the transfer of oxygen.
- Extended aeration uses longer residence times and a higher population of microorganisms.
- Contact stabilization requires a short contact of the aqueous wastes and suspended microbial solids, subsequent settling, and further treatment to remove sorbed organics.

- Fixed-film systems use contact of the aqueous waste stream with microorganisms attached to some inert medium, such as rock or specially designed plastic material (76).
- Rotating biological contractors consist of a series of rotating discs connected by a shaft set in a basin or trough. The contaminated water passes through the basin where the microorganisms, which are attached to the discs, metabolize the organics in the water.
- In situ bioremediation of groundwater is becoming a frequently selected treatment for low to intermediate concentrations of organic contaminants. The addition of nutrients into an impacted aquifer enhances the natural degradation of chemical compounds by indigenous microorganisms.

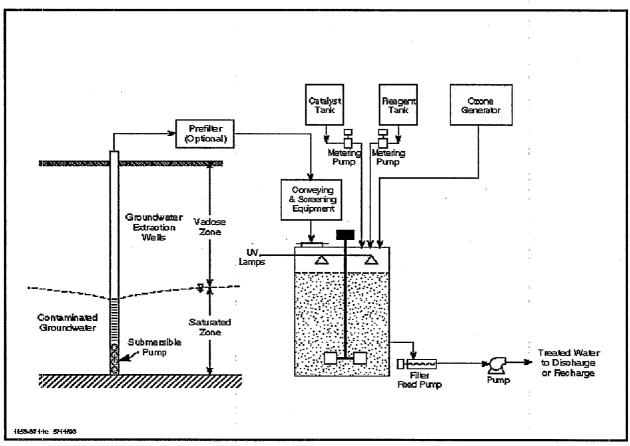


Figure 3-17 Schematic for Chemical Oxidation of Contaminated Groundwater

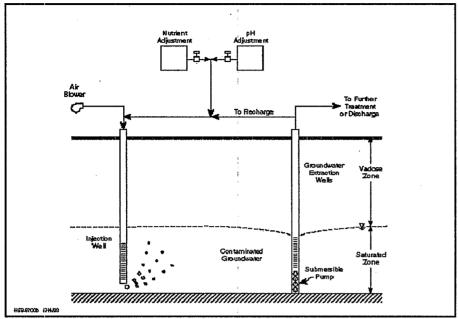


Figure 9-18 Schematic for Bioremediation (in-Situ) of Contaminated Groundwater.

# Separation/Concentration Technologies for Water Treatment

# Adsorption

In adsorption, one substance binds to the surface of another by physical and/or chemical means. In the adsorption process, contaminants transfer to the adsorbents, the most common of which are activated carbon and resins. A schematic diagram of a carbon adsorption process is shown in Figure-19. The imbalance of forces in the pore walls of the adsorbent allow the contaminants to attach and concentrate. Once adsorption has occurred, the molecular forces in the pore walls stabilize. For further adsorption, regeneration of the adsorbent is necessary. Adsorption effectively can separate various contaminants from aqueous streams.

Adsorption treatment, especially granular activated carbon (GAC), has removed halogenated and nonhalogenated solvents (VOCs and SVOCs), phenolics, pesticides, PCBs, PAHs, other polar organic compounds, dioxins, furans, some nonvolatile and volatile metals from water.

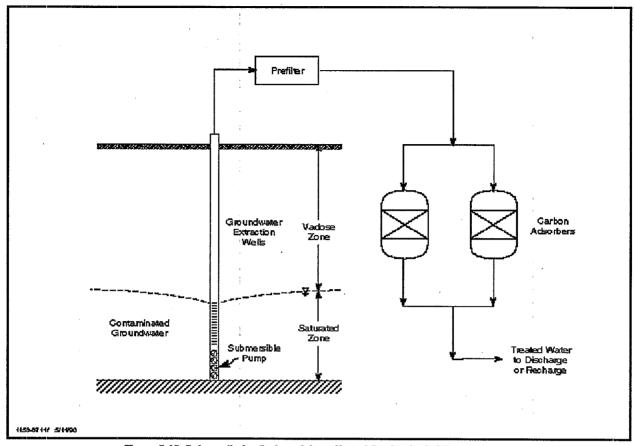


Figure 3-19 Schematic for Carbon Adsorption of Contaminated Groundwater.

# **Filtration**

Filtration isolates solid particles by running a fluid stream through a porous medium. Figure 3-20 is a schematic diagram of a filtration process. The driving force is either gravity or a pressure differential across the filtration medium. Filtration techniques include separation by centrifugal force, vacuum, or high pressure. Therefore, filtration can separate various contaminant particulates from an aqueous stream.

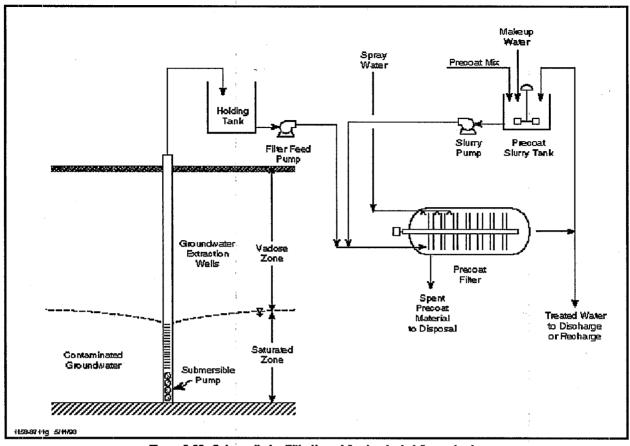


Figure 3-20 Schematic for Filtration of Contaminated Groundwater

# Ion Exchange

Ion exchange removes ions from the aqueous phase by the exchange of electrical charges between the contaminants and the exchange medium. Ion exchange materials may consist of resins made from synthetic organic materials that contain ionic functional groups to which exchangeable ions are attached. They also may be inorganic and natural polymeric materials. Ion exchange removes nonvolatile and volatile metals. This should be considered only if metals co-exist with solvents at solvent-contaminated sites. After the toxic materials have been removed, the resins can be regenerated for re-use.

# **Membrane Filtration**

Membrane filtration technologies, such as reverse osmosis and ultrafiltration, separate chemical constituents from water. Reverse osmosis (RO) is a pressure-driven, membrane-separation process. The chemicals are not destroyed; they are merely concentrated, making reclamation possible. A low-energy process, RO requires no phase change for separation of the dissolved materials, nor latent heat of vaporization, fusion, or sublimation. However, RO and ultrafiltration are sensitive to the presence of fines, which can clog the membranes. Membranes are fragile

and often rupture from over pressure. Ultrafiltration and RO can treat groundwater contaminated with heterocyclics and simple nonhalogenated aromatics, polar organic compounds, some nonvolatile and volatile metals (77).

### **Precipitation**

This physical/chemical process transforms dissolved contaminant into an insoluble solid, facilitating the contaminant's subsequent removal from the liquid phase by sedimentation or filtration. The process usually uses pH adjustment, addition of a chemical precipitant, and flocculation. Typically, metals precipitate from the solution as hydroxides, sulfides, or carbonates. The solubilities of the specific metal contaminants and the required cleanup standards will dictate the process used. Precipitation is used mainly for metals; this should be considered only if metals co-exist with solvents.

### Oil/Water Separation

Oil/water separation removes oil from water by providing surface contact for de-emulsifying oil particles from the water phase. It is a frequent pretreatment for other processes.

### Air Stripping

Air stripping is a common technique for the removal of VOCs from groundwater. Dissolved VOCs in water contact air, usually in a packed column. Spray towers and other alternative forms of aeration are sometimes used. These devices bring the contaminated water into countercurrent contact with air supplied by a blower. The columns or towers may contain a variety of packing materials, such as recently designed plastic products: polypropylene pall rings or flexi-rings, saddles, and tellerettes (circular plastic coils). The tower is constructed with stainless steel, lined carbon steels, or fiberglass.

### Air Sparging

In situ air sparging is a relatively new technique for the removal of VOCs from aquifers. Although there is substantially less experience with air sparging than with SVE, its potential advantages over conventional techniques such as excavation and groundwater pump-and-treat operations include remediation of the overlying vadose zone, shorter remediation times, reduced environmental impact, destruction or capture of the contaminant, and potentially reduced costs. The history of in situ air sparging is limited; therefore, cost estimates are uncertain.

Air sparging involves the injection of compressed air into the lower portion of the contaminated aquifer. The air percolates up through the contaminated region of the zone of saturation, generates local turbulence in the groundwater, and strips VOCs from the aqueous phase into the vapor phase. The increased local turbulence can be expected to increase the rate of the solution of DNAPL residual droplets trapped in the aquifer. After the gas leaves the saturation zone, it may be recovered by an SVE system in concert with the sparging operation to remediate the vadose zone and prevent the vapors from escaping into the atmosphere. If the VOCs are readily biodegradable, the organic vapors may be destroyed biologically as the moist, oxygen-rich soil gas rises through

the vadose zone.

Factors affecting the applicability and performance of in situ air sparging include the following.

- The vapor pressure of the VOC at the ambient temperature must be sufficient to permit its removal at a reasonable rate. The criterion for SVE, 0.5 Torr, is reasonable for air sparging.
- The dimensionless Henry's Law Constant of the VOC at ambient temperature must permit efficient stripping; values of K<sub>H</sub> less than approximately 0.01 are probably too small.

Most common organic solvents are suitable candidates for sparging (hydrocarbons, chlorinated solvents). Some oxygenated VOCs (i.e., acetone and alcohols) are soluble in water, so they have unacceptably small Henry's Law Constants. Oxygenated VOCs, however, are biodegradable.

For air sparging to be feasible, air must come in contact with all of the contaminated water. If DNAPL residual droplets are present, the circulation of groundwater induced by the injected air must be sufficient to dissolve them in an acceptable period of time. These considerations appropriate the following requirements.

- The natural rate of groundwater flow must be sufficiently slow to permit adequate contact of the contaminated groundwater in the air-stripping region around the sparging well.
- The aquifer medium must be sufficiently permeable to permit an adequate flow of air and to allow the injected air to generate the circulation and turbulence in the groundwater necessary to permit mass transport of the VOC from the DNAPL and/or aqueous phases into the vapor phase.
- Low-permeability structures (such as clay lenses) may interfere with the movement of air and water in the
  vicinity of the well, thereby preventing VOC removal from some domains.
- If molecular diffusion of the VOC in the liquid phase is the only mechanism of mass transport over distances of even a few centimeters (cm), remediation will be extremely slow, which is expected in porous fractured rock and in aquifers having highly heterogenous permeabilities.
- The greater the depth of the contaminated zone below the water table, the higher the pressure required to operate the sparging well, which will affect costs.
- Air sparging is possible underneath buildings and other overlying impermeable structures.

• The removal of residual DNAPL, lying on the underlying aquifer, can be substantially slower than the removal of the dissolved VOC. The removal of pooled DNAPL can be expected to be slow unless the air-sparging well injects air into the DNAPL pool.

Table 3-34 contains a summary of performance data for in situ air sparging. Factors affecting in situ air sparging performance are listed in Table 3-35.

TABLE 3-34. SUMMARY OF PERFORMANCE DATA FOR IN SITU AIR SPARGING

Site	Initial	Performance
Gasoline service station, RI	BTX up to 21 mg/l	<1.0 mg/l
Dry cleaning facility	VOCs 41 mg/l PCE, TCE, DCE	0.897 mg/l
Savannah River	PCE 85 to 184 ug/l TCE 500 to 1,810 ug/l	3 to 124 ug/l 10 to 1,031 ug/l
Conservancy site, Belen, NM	втх	49 to 60 % reduction

TABLE 3-35. FACTORS AFFECTING IN SITU AIR SPARGING PERFORMANCE

Factor	Potential Effect
Groundwater depth	Very deep >150 ft - increased costs.  Very shallow <5 ft - difficult vapor recovery.
Water solubility	The more soluble the contaminant, the more difficult the treatment.
Volatility	Henry's Law Constant < 10 <sup>5</sup> , the more difficult the treatment.
Permeability	Hydraulic conductivity < 0.001 cm/s, the more difficult the treatment.

### **Typical Treatment Combinations**

Typical treatment combinations for the remediation of water contaminated with solvents are presented in Table 3-36. It includes pretreatment requirements and post-treatment/residuals management.

Depending on the wastestream characteristics and the primary technology selected, the remedial combination may include pretreatment to remove free oils using an oil/water separator; pH adjustment; addition of a chemical agent to enhance coagulation, flocculation, sedimentation; and removal of suspended solids by filtration. In biological treatment, the water may require heating to reach an optimum temperature and the addition of inorganic nutrients.

The main process residual of an adsorption system is the spent sorbent holding the hazardous contaminants, which requires treatment or regeneration. The primary process residual streams created with air stripping systems are the off-gas and liquid effluent. The off-gas is released to the atmosphere after treatment; activated carbon is the treatment most frequently applied to the off-gas stream. Effluent water containing nonvolatile contaminants may need additional treatment. Other water-treatment technologies, such as filtration, ion exchange, chemical oxidation, precipitation, etc., produce contaminated sludge, which also requires treatment prior to disposal (Table 3-36). Depending on the contaminant, the treated water may need polishing by activated carbon, or biological treatment.

Residuals produced from chemical oxidation systems include partially oxidized products which may require further treatment. Depending on the oxidizing agent used and the chlorine content of the contaminant, oxidation of organic compounds may result in the formation of hydrogen chloride (HCl) and nitrogen dioxide. Acid-gas control is required for reactions that produce HCl.

TABLE 3-36. TYPICAL GROUNDWATER TREATMENT COMBINATIONS

Pretreatment/Materials Handling	Groundwater-Treatment Technology	Post-Treatment/Residuals Management
Pumping Oil/water separation pH adjustment Filtration	Air stripping	Sludge treatment/disposal  Spent carbon disposal/regeneration
Pumping Oil/water separation pH adjustment Filtration	Granular-activated carbon (GAC) treatment	Spent carbon disposal/regeneration Polishing treatment
Pumping Oil/water separation pH adjustment Flocculation/sedimentation	Membrane filtration	Sludge treatment/disposal

## TABLE 3-36. (Continued)

Pretreatment/Materials Handling	Groundwater-Treatment Technology	Post-Treatment/Residuals  Management
Pumping Oil/water separation pH adjustment Flocculation/sedimentation Filtration	Precipitation	Sludge treatment/disposal
Pumping Oil/water separation pH adjustment Flocculation/sedimentation Filtration	Chemical/UV oxidation	Sludge treatment/disposal Oxidized products treatment/disposal
Injection well/extraction  Well installation  Soil flushing  Oil/water separation  Nutrient addition  pH adjustment	In situ bioremediation	
Pumping, flow equalization Oil/water separation pH adjustment Flocculation/sedimentation	Fixed-film biological treatment	Sludge treatment/disposal Polishing wastewater treatment
Pumping Oil/water separation pH adjustment Filtration	lon exchange	Sludge treatment/disposal

### **Technology Status/Performance**

To date, more than 100 RODs have specified air stripping as a remedy for VOC-contaminated groundwater. The performance of the technology is a direct result of the design of the system used for air stripping. Air stripping commonly achieves nearly 100 percent removal efficiency for VOCs. The Rockaway Township air stripper in Rockaway Twp., New Jersey, achieved 99.99 percent removal of the VOCs in the groundwater using an air-to-water ratio of 200, and a 3-inch tellerette packing in a 9-feet diameter column. The compound with the lowest Henry's Law Constant was chloroform. Reported removal efficiencies at the Brewster Well Field site in New York were 98.5, 93.33, and 95.59 percent for PCE, TCE, and 1,2-DCE, respectively. A removal efficiency of 98.41 percent

for MEK was reported at the Hicksville spill site in New York. At Wurthsmith Air Force Base in Oscoda, Michigan, air stripping removed 99.9 percent of the TCE.

Granular-activated carbon (GAC) treatment is a specific groundwater treatment remedy for hundreds of Superfund sites. Operating data from many installations indicate that activated carbon will be completely effective on solvent site constituents. However, activated carbon is not cost effective when handling a groundwater stream with high VOC concentrations. In such an instance, air stripping is more economical, followed by GAC treatment to polish the aqueous effluent.

UV radiation/oxidation is a well-established technology for disinfecting drinking water and wastewater. Chemical oxidation is effective in treating liquids that contain oxidizable contaminants. Performance of full-scale chemical oxidation systems has been reported by several sources. Chemical oxidation was listed in the RODs for several sites. Destruction efficiencies of more than 90, 80, and 60 percent were achieved for TCE; 1,1,1-TCE; and 1,1-DCA, respectively, at Lorentz Barrel and Drum Superfund site in San Jose, California, by Ultrox International's Ultrox System. Peroxidation Systems' Perox-Pure<sup>ru</sup> has been used at a number of sites to reduce contaminants up to 90 percent. The Punis, Inc. enhanced oxidation system was demonstrated on groundwater at Lawrence Livermore National Laboratory (LLNL) where BTEX levels were reduced from 5 ppm to as little as 5 ppb.

Membrane filtration has been demonstrated at the laboratory and pilot- and full-scale stages.

In situ biodegradation has been chosen as a groundwater remedy at four Superfund sites. However, the solvent contamination is incidental to the PAH contaminants at the sites. Several fixed-film, biological treatment processes have treated wastewater commercially.

### **Implementation Costs**

Table 3-37 is a summary of the estimated treatment costs for water-treatment technologies. The base years of the estimates vary. Wastestream flow rates, types of contaminant, toxic concentrations, and the desired cleanup standards make costs variable.

**TABLE 3-37. WATER-TREATMENT COSTS** 

Water Treatment	Cost (\$)/1000 Gallon Treated	Reference
Granular activated-carbon	0.10 to 1.50 at 100 mgd flowrate 1.20 to 6.30 at 0.1 mgd	(78) (79)
Membrane filtration	1.38 to 4.56	(80)
lon exchange	0.30 to 0.80°	(80)
Chemical/ultraviolet oxidation	70 to 150	(75)
Precipitation	0.07 to 0.28 <sup>b</sup>	(80)
Fixed-film biological treatment	50 to 90	
Air stripping	0.07 to 0.7 when $K_h = 0.01$ to 1.0 7 when $K_h = 0.005$	(81)

<sup>\* 1987</sup> dollars

# **Data Requirements**

Table 3-38 is a summary of the data requirements and factors affecting the various for water-treatment technology options. These requirements provide a basic guideline for the types of information required to remediate solvent sites.

<sup>&</sup>lt;sup>b</sup> 1982 dollars

 $K_h = Henry's Law Constant$ 

TABLE 3-38. DATA REQUIREMENTS FOR WATER-TREATMENT TECHNOLOGIES

Technology	Data Needs	Potential Effects
. GAC	Molecular weight	Low molecular weight compounds are removed with less efficiency.
	Polarity	Highly polar compounds not amendable to GAC.
	Suspended solids	Can foul carbon (high suspended solids <u>&gt;</u> 50 mg/L).
	Oil and Grease	May cause carbon fouling (≥10 mg/L).
	Organic matter	Rapidly exhaust GAC (high levels of organic matter, e.g. 1,000 mg/L.
	Humic and Fulvic Acids	Rapid carbon exhaustion.
	Biological organisms	May cause fouling
Air stripping	Iron, Manganese, or carbonate	Elevated levels may reduce removal efficiencies due to scaling and the resultant channeling effects.
	рН	5 < pH > 11 may corrode system components and auxiliary equipment.
	Volatile or semivolatile organic concentration	Greater than 0.01% generally cannot be treated by air stripping.
	Volatility	Henry's Law Constant < 0.003 reduces efficiencies.
Membrane Filtration	Size of particles	May interfere with operation size depends on membrane.
	Oil and grease	May interfere with the system by decreasing flow rate.
	Contaminants	Successful only with contaminant-specific membranes.
lon exchange	Oil and grease	May clog resin.
	Suspended solids	May cause resin blinding (preferable limits <u>&lt;</u> 50 mg-/L).
	Metals and inorganic ions	Must be present as soluble species.
	pH Oxidants	May affect ion exchange varies with resin.
	CAMAINO	May damage resins
Chemical oxidation	Oil and grease	Optimize the system efficiency (low levels).
	Concentration of contaminants	Proves too expensive for highly concentrated wastes.
Precipitation	рН	Adjustment must be made for optimum precipitation.
	Oil and grease	Can interfere with process.

# TABLE 3-38. (Continued)

Technology	Data Needs	Potential Effects
In-situ biological treatment	Moisture content	Inhibits bacterial activity (contents outside 40 to 80%).
	Water solubility	Loses effectiveness beyond 4.5 to 8.5.
	Oxygen availability	Low solubility compounds are difficult to biodegrade.
	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Low oxygen inhibits aerobic activity, sustains anaerobic activity.
	Temperature	Effectiveness outside temperature range 15 to 70°C
•	Variable waste composition	slows down.
	i	Vary biological activity and cause inconsistent biodegradation.
	Heavy metals, highly chlorinated organics, some pesticides, inorganic salts	Can be highly toxic to microorganisms.
	Nutrients (C,N,P)	
,	Plada wadabilia	Low concentrations can limit activity. Addition of nutrients may enhance activity.
	Biodegradability	Certain contaminants are not or only partially biodegradable (e.e., dioxins).
	Permeability	Allows movement of water and nutrients through contaminated area.
	Soil conditions and heterogeneity	Vary biological activity and cause inconsistent biodeg-
•	Soil pH	radation.
	Organic content	Inhibit biological growth (pH < 5.5).
	Moisture content	Low concentrations can limit biological growth.
	Site hydrology	Limit biological growth (content <10%).
	Discount of the second	Determine flow patterns that permit pumping for extraction and re-injection.
	Dissolved oxygen	Low oxygen content inhibits aerobic activity and sustains anaerobic activity.
	pH ·	Very high or low pH inhibits activity. Optimal range pH 6 to 8.

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# APENDIX A

Treatment Comparisons at Selected Solvent Sites
Contaminants and Remedial Options at Solvent-Contaminated Sites
October 1993

TABLE A-1. TREATMENT COMPARISONS AT SELECTED SOLVENT SITES

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Region I						
Keefe Environmental Services Site (KES), Epping, NH	м	Remedial design	Lagoon sludge	Toluene, methanol, acetone, MEK, glycols, waste oils, waste alcohols, cyanide, heavy metals	NA	Off-site disposal
McKin Site, Gray, ME	1	Initial remedial measure	Sludge	Volatile organics	NA	Off-site disposal
			Tank liquids	DCE, freon, TCE, xylene	N/A	Off-site disposal
Davis Liquid Waste, Smithfield, RI	m	Incineration design to be completed by December 1995	Soil	Volatile organics, inorganics, TCE, 1,1- DCE, arsenic, benzene	Total VOCs to 2 ppm	Excavate, on-site incineration, on-site disposal
,		Treatment system to be completed by January 1995	Groundwater	VOCs, inorganics, oily wastes, pesticides	MCLs	Pump and treat
Auburn Road Landfill, Londonderry, NH	က	Arsenic contamination monitoring	Groundwater	TCE, PCE, benzene, toluene, arsenic, lead	Meet compliance boundaries of MCLs	Close wells, monitor
Industri-Plex, Woburn, MA	м	NA	Soil, sediment	Arsenic, chromium, lead, benzene, toluene	NA	Сар
			Groundwater		NA	Pump and treat
Kellogg-Deering, Norwalk, CT	-	Remedial design stage	Groundwater	TCE, PCE, benzene, toluene	Meet drinking water standards	Pump and treat

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Re-Solve, Dartmouth, MA	2	Operable Unit 1: Remedial action phase, source control Operable Unit 2: Remedial design phase	Soil, sludge	PCBs, VOCs	Operable Unit 1: PCBs to 25 ppm Operable Unit 2: VOCs to MCLs	Excavate, off-site disposal, cap
Yaworski Waste Lagoon, Cantebeury, CT	es	Capping completed in 1992, quarterly monitoring	Groundwater, sediment/sludge	Benzene, toluene, xylenes, organic PAHs, chromium, lead	Meet ACL (around lagoon) and MCLs (drinking water)	Cap, monitor
Region II						40) 0
Ocean Wellfield, Olean, NY	<del>-</del>	Remedial design	Groundwater	ТСЕ	g ppb	Close wells, activate surface water filtration plant
Helen Kramer, Mantua Township, NJ	m	Remedial design	Groundwater	TCA, benzene, toluene, phenols, arsenio, iron	NA	Collection, pretreatment, discharge to POTW
			Pond and lagoon, sediments and water	Magnesium	NA	Dewater, excavate, fill, cap
GE Moreau, South Glenn Falls, NY	8	Remedial action completed	Groundwater	TCE, DCE, organics	MCLs	Slurry wall, air stripping
			Soil	PCBs	Containment	Cap
Haviland Complex, Hyde Park, NY	က	Remediation design stage	Groundwater	TCE, PCE	MCLs	Pump and treat
		Remediation completed	Sediments and soil	PCE, organics, metals	PCE to 15 ppm	Excavate, off-site treatment

The same

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup doals	Technology
Williams Property, Swainton Middle, NJ	7	NA	Groundwater	PCE, MC, xylene, bis(2ethylhexyl)phthalate	NA	Pump and treat
			Soil		AN	Excavate, off-site incineration
Volney Landfill, Volney, NY	ო	Field work to be completed by 1994, pre-remedial site study in 1994	Soil	VC, benzene, arsenic, metals	Containment	Сар
	,		Groundwater		Pending results of study to determine onsite and off-site MCL standards	Slurry wall, pump and treat
Sharkey Landfill, Parsippany∕Troy Hills, NJ	ო	NA	Soil	NA	NA	Cap, grade
			Groundwater	VOCs, organics, TCE inorganics, heavy metals	NA	Pump and treat
Vestal Well 1-1, Vestal, NY	-	Operable Unit 1: Remediation completed	Groundwater	Chlorinated solvents, VOCs	Based on risk assessment	Pump and treat
		Operable Unit 2: Remediation in progress				
Caldwell Trucking, Fairfield, NJ	ო	Remedial action	Soil	VOCs, TCE, PCBs, PAHs, inorganics, lead	NA	Excavate, treat via heat addition, on-site disposal
4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			Groundwater	VOCs, TCE	NA	Pump and treat

15%

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Kentucky Ave. Well Field, Horseheads, NY		Operable Unit 1: Completion of public water supply system by January 1994	Groundwater	TCE, VOCs, chlorinated solvents	MCLs	Close wells
		Operable Unit 2: Containment phase, source RI/FS		·		
Combe Fill South,	<b>(</b>	NA	Soil	Vocs, TCE, PCE,	NA	Cap
Chester 1 Wp., No			Groundwater	toluene, benzene, MC	:	Pump and treat
·Hyde Park, Niagara Falls, NY	7	Overburden system is installed and operating, bedrock system currently being installed, containment and collection phase	Groundwater	VOCs, chlorinated organics, BTX, phenol	Performance criteria set in court decision	Pump and treat, incineration
Rockaway Borough, Rockaway, NJ	<b>-</b>	Remedial investigation	Groundwater	VOCs, TCE, PCE	NA	Pump and treat
Price Landfill, Pleasantville, NJ	м	NA	Groundwater	VOCs, organics, inorganics, TCE	NA	Pump and treat
Syncon Resins, Kearny, NJ	ო	AN	Soil, sludge	Organics, pesticides, metals	NA	Excavate, off-site disposal
	·		Groundwater		NA	Pump and treat
Lone Pine Landfill, Freehold, NJ	-	AN	Groundwater	Benzene, chlorobenzene, MC,-VC, toluene	NA	Slurry wall, pump and treat
Bridgeport Rental, Logan Twp., NJ	7	Remedial action	Sediment, sludge	PCBs, benzene, MC, toluene, acetone,	NA	On-site incineration
			Groundwater	organics	NA	Pump and treat

# TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Montgomery Twp., Montgomery Twp., NJ	<u>, -</u>	NA	Groundwater	TCE, VOCs	NA	Abandon wells
Cooper Road Site, Voorhees Twp., NJ	7	No action	Soil	Benzene, ethylbenzene, xylene, naphthalene	N/A	N/A
Vega Alta Public Supply Wells, Vega Alta, PR	-	NA	Groundwater	1,1,1-TCE, PCE, 1,1-DCE, 1,2-DCE	NA	Well treatment
Katonah Municipal Well, Bedford, NY	<b>-</b> -	NA	Groundwater	PCE	AN A	Abandon wells, new well treatment
American Thermostat Site, South Cairo, NY		Construction RFP is approved and will advertise	Groundwater	TCE, PCE	MCLs	Close wells
Old Bethpage Landfill, Oyster Bay, NY	_	Completed	Groundwater	TCE, PCE	TCE to 2 ppm, MCLs	Pump and treat
Brewster Wellfield, Brewster, NY	2	Source removed	Sediment, sludge, soil	VOCs, PCE, TCE, PCBs	PCBs to 1 ppm VOCs to 1 ppm	Excavate, off-site incineration
Region III						
Fischer & Porter, Warminster, PA	-	RI/FS in progress	Groundwater	TCE, PCE	Not established	Well treatment
Drake Chemical, Lock Haven, PA	m	Awarded contract for soil incineration to be completed within a 5 year period	Sediment, soil	TCE, toluene, benzene, xylene, inorganics, organics	Beta-naphthalene to 55 ppb	Excavate, on-site rotary kiln incinerator
			Sludge (lagoon)			Off-site disposal

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
			Stored chemicals		N/A	Off-site incineration
Blosenski Landfill, Wagontown, PA	ო	Drum removal completed March 1993	Drums	Benzene, toluene, TCE, lead, cadmium, chromium, mercury	Disposal	Excavate, off-site disposal
		Expanded RI/FS completed 1991, installation of cap in progress	Soil		Containment	Cap
		Pump and treat system in progress	Groundwater	,	To background	Pump and treat
Delaware Sand and Gravel	ო	ROD amended	Drums	VOCs, PCBs, semi- volatiles, metals	Disposal	Drum removal and off-site disposal
			Soil		Contaminant specific performance standard w/ 10- <sup>8</sup> risk range	Slurry wall, cap, SVE, bioventing
Tybouts Corner, Wilmington, DE	ო	Remedial action in progress, slurry wall is near completion	Soil	VOCs, TCE, VC, 1,2- DCA, benzene, inorganics	Containment	Excavate, consolidate, cap
-			Groundwater		100 ppb total VOC's	Slurry wall, pump and treat
Delaware City PVC, Delaware City, DE	-	ROD of 1986 has been fully implemented, new RI/FS is being developed	Soil, sludge	VC 1,2-DCA PCE	250 ppb 500 ppb 500 ppb	Excavate, recycle,
:			Groundwater	VC 1,2-DCA PCE	1 ppb 0.94 ppb 2.7 ppb	Pump and treat, air stripping
McAdoo Associates, McAdoo, PA	ო	Operable Unit 1: remediation completed	Soil	Paint sludges, spent solvents, metallic sludges, toluene, oil,	Containment	Excavate, off-site disposal, cap

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Tyson's Dump, Upper Merion Twp., PA	. 2	5th year of remediation process, new RI/FS	Soil, sediments	VOCs, benzene, PCE, TCE, trichloropropane	Trichloropropane to 50 ppb	Excavate, off-site disposal, vacuum extraction, soil cover
Kane and Lombard St. Drums, Baltimore, MD	က	Removal completed 1984, source control completed 1990, currently initiating Phase 2 for Operable Unit 2	Soil, drums	Benzene, toluene, xylene, PAHs, PCBs, heavy metals	Containment	Remove, contain, cap
-Westline Site, Westline, PA	1	- No action	Groundwater	Benzene	N/A	N/A · ·
Middletown Air Field Site, Middletown, PA	1	Supplemental study is being reviewed	Groundwater	VOCs, TCE, PCE	MCLs at the wellheads	Pump and treat
Region IV						
Varsol Spill, Miami, FL	2	No action	Groundwater	Mineral spirits	N/A	N/A
Distler Brickyard, West Point, KY	ო	Long term remedial action in progress	Soil	TCE, 1,2-DCE, benzene, toluene, naphthalene,	MCLs	Excavate, off-site disposal
			Groundwater	neavy metais		Pump and treat
Geiger (C&M Oil) Site, Rantowles, SC	m	Remedial action	Groundwater	benzo(a)pyrene benzo(a)anthracene benzo(b)fluoranthene benzo(k)fluoranthene PCB	0.2 ppb 0.1 ppb 0.2 ppb 0.5 ppb 0.5 ppb	Pump and treat
:	:		Soil	trans-1,2-DCE chromium lead toluene 1,2-dichlorobenzene 1,1-DCA	100 ppb 100 ppb 15 ppb 1000 ppb 75 ppb 5 ppb	In-situ S/S

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Martin Marietta - Soydeco Division, Charlotte, NC	7	Remedial action	Groundwater	TCE, PAHs, Volatile organics	Groundwater and soil leachate to meet the following standards:	Extraction, on-site treatment
			Soil Area B	Vocs	TCE to 2.7 ppb PCE to 0.8 ppb chlorobenzene to 60 ppb ethylbenzene to 680	Cap
:	:		Area C	TCE, PAHs	ppb 1,2-dichlorobenzene to 400 ppb toluene to 2000 ppb	Excavate, on-site treatment to be determined
			Area D	Volatile Organics	xylene to 440 ppb anthracene to 2.8 ng/l fluorene to 2.8 ng/l phenanthrene to 2.8 ng/l	Excavate, off-site incineration
Hipps Road, Jacksonville, FL		Remedial action, completed construction of air stripping tower	Groundwater	VOCs, benzene, VC	MCLs	Pump and treat (air stripping)
Lees Lane Landfill, Louisville, KY	ဗ	Completed, operations and maintenance phase	Drums	Phenolic resins, benzene, copper, chromium, lead, cadmium	Removal	Removal
·			Soil	Benzene, lead, arsenic, chromium, inorganics	Containment	Сар
Pioneer Sand, Pensacola, FL	m	PCBs removed in 1988, capped in 1989, removed	Soil	VOCs, xylene, chromium, cadmium, PCBs	Containment	S/S, trench, cap, monitor
		TYOU WAT	Groundwater	VOCs, xylene, chromium, cadmium, PCBs, LNAPLs	MCLs	Air injection wells
Hollingsworth Solderless, Fort Lauderdale, FL	m	AN.	Soil	TCE, VC, trans-1,2-DCE, copper, nickel, tin	NA	Excavate, aeration, on-site disposal

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
			Groundwater		NA	Pump and treat
			4			
Distler Farm, Louisville, KY	ო	Remedial action	Soil	VOCs, chromium, lead	MCLs	Excavate, off-site disposal
			Groundwater			Pump and treat
Northwest 58th St. Landfill, Miami, FL	ဇ	AN	Groundwater, soil	Arsenic, chromium, zinc, benzene, chlorobenzene, TCE, VC, 1,1,2,2-PCE	NA	Close wells, cap
				:	* * * * * * * * * * * * * * * * * * * *	
Gold Coast Oil Corp., Miami, FL	ю	Soil removal completed	Soil, sludge	TCE, PCE, VOCs, lead, heavy metals	Lead to 100 ppb	Excavate, off-site disposal
			Metal contaminated soil	Heavy metals		S/S, cap
		Groundwater remediation in process, pumping since 1990	Groundwater	1,1-DCA, TCE, trans- 1,2- DCE, PCE, MC, toluene, VOCs, lead, heavy metals	1,1-DCA to 5 ppb TCE to 3 ppb trans-1,2-DCE to 70 ppb MC to 5 ppb PCE to 0.7 ppb toluene to 340 ppb	Pump and treat
Region V						

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
New Brighton, Arden Hills, MN	м	Operable Unit 1: Groundwater remediation completed 9/93 Operable Unit 2: Feasability stage Operable Unit 3: Groundwater remediation completed 1992	Groundwater	Organic solvents, TCE, chlorinated solvents, lead	Meet all applicable federal and state standards, MCLs, site specific risk assessment number for lead	Pump and treat
Lehillier, Mankato, MN	2	NA	Groundwater	TCE, volatile halo- genated hydrocarbons	TCE to 2.7 ppb (risk based number)	Pump and treat
Seymour Recycling, Seymour, IN	8	NA	Groundwater	1,2-DCA, benzene, VC, 1,1,1-TCA	MCLs	Pump and treat
			Soil	VOCs, organics, TCE,	Containment	SVE, cap
			Sediment	toluene, heavy metals		Consolidate, cap
Marion (Bragg) Landfill, Marion, IN	ო	Final remediation pending	Soil	1,2-DCE, TCE, VC, bis(2- ethylhexyl)phthalates, heavy metals	Pending evaluation	Cap

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Rose Township Dump, Rose Township, MI	n	Conducted PCB contaminated soil incineration from 9/92 to 10/93, treatment of VOCs contaminated subsurface soil projected for Spring 1994	Soil	VOCs, VC, PAHs, PCBs,organics, inorganics, TCE, PCE, MC, lead, arsenic, benzene, chlorobenzene, xylene, ethyl benzene, toluene	Health based clean-up standards:  VC to 10 ppm benzene to 0.1 ppb TCE to 0.6 ppb MC to 0.9 ppb lead to 50 ppb arsenic to 50 ppb	Excavate, on-site thermal destruction
		Pump and treat of northern plume completed 3/92, expected completion of western plume pump and treat by 1994	Groundwater		chlorobenzene to 60 ppb xylene to 440 ppb ethylbenzene to 680 ppb toluene to 2 ppm	Pump and treat
Enviro-Chem Corp., Zionsville, IN	en .	Remedial design	Soil, sediment	NA	NA	Excavate, dewater, on-site disposal, cap
			Groundwater	NA	. AN	Pump and treat
Metamora Landfill, Metamora, Ml	က	Evaluation stage of incineration and excavation	Soil	VOCs, PCE, TCE, heavy metals	Meet ARAR's	Excavate, off-site incineration
Byron Johnson Salvage, Byron, IL	м	NA	Groundwater	Cyanide, heavy metals, VOCs, TCE	A N	Carbon filtration in homes
Fields Brook, Ashtabula, OH	ო	RI/FS	Sediments	TCE, PCE, chlorobenzene, VC, arsenic, zinc, mercury,	Risk assessment number	Excavate, dewater, thermal treatment, or
	:	:		chromium, hexachlorethane, toluene, diamine, toluene diisocyanate, PCBs		excavate, dewater, S/S, on- site disposal

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Spiegelberg Landfill, Brighton, MN	ო	Pump and treat design 75% completed , remediation activities completed	Soil, sludge, liquid	VOCs, organics, inorganics, base/neutral compounds, TCE, toluene, xylene, metals	Risk assessment number	Pump and treat, excavate:1/2 offsite incineration, 1/2 off-site disposal
Main Street Wellfield, Elkhard, IN	<del>.</del>	Remedial design	Groundwater	TCE, 1,2-DCE, 1,1,1- TCA, 1,1-DCA	NA	Pump and treat
Cross Brothers, Pembroke Twp., IL	, 2	Remedial action phase	Soil	Dyes, paints, inks, solvents	MCLs	Excavate, off-site disposal
Verona Well Field, Battle Creek, MI		On-going remedialaction	Groundwater	acetone benzene chlorobenzene chloroform 1,1-DCA 1,1-DCA 1,1-DCE cis-1,1-DCE trans-1,2-DCE ethylbenzene MC PCE toluene 1,1,1-TCA 1,1,2-TCA 1,1,2-TCA TCE VC	700 ppb 1 ppb 6 ppb 6 ppb 1 ppb 1 ppb 1 ppb 70 ppb 70 ppb 5 ppb 1 ppb 200 ppb 200 ppb 1 ppb 3 ppb 1 ppb	Pump and treat

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Verona Well Field, Battle Creek, MI (continued)			Soil	benzene carbon tetrachloride 1,1-DCA 1,1-DCE 1,2-DCA cis-1,2-DCE trans-1,2-DCE trans-1,2-DCE trollene MC PCE toluene 1,1,1-TCA TCE xvilenes	20 ppb 10 ppb 20 ppb 10 ppb 20 ppb 1400 ppb 10 ppb 1600 ppb 1600 ppb 60 ppb 60 ppb 60 ppb	SVE
New Lyme Landfill, New Lyme, OH	α	Remedial action completed in operations and maintenance stage	Soil .	Acetone, xylene, toluene, naphthalene, benzene, 2,4-D, asbestos, fuel oil,	NA	Cap
			Groundwater	linseed oil	Meet Clean Water Act requirements	Pump and treat
			Sediment		NA	Excavate, incinerate
Acme Solvents, Winnebago, IL	7	NA	Soil	Volatile organics, semi- volatile organics, PCBs	NA	Excavate, incinerate
Charlevoix, Charlevoix, MI	<del></del>	No action	Groundwater	TCE, PCE	N/A	Monitor
Northern Engraving Corp., Sparta, Wi	ო :	Operation and maintenance stage, with a 5 year review in fiscal year 1994	Soil, sludge	Phosphorous, aluminum, cadmium, copper, nickel, iron, fluoride	Source control, developed ACL	Excavate, S/S, cap
FMC Corp., Minneapolis, MN		Remediation completed 1987, 5 year review completed in 1992	Groundwater	TCE, PCE, benzene, toluene, xylene, other VOCs	MCLs	Pump and treat

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Eau Claire Municipal Well Field, Eau Claire, WI	1	NA	Groundwater	VOCs, PCE, TCE, 1,1- DCE, 1,1-DCA, 1,1,1- TCA	NA	Pump and treat
Pristine, Inc., Reading, OH	8	Demolition completed, thermal desorption in progress, expected	Soil, sludge	PCE, TCE, benzene, organics, metals, dioxin	Lower than MCLs	Excavate, consolidate, thermal desorption, SVE
		completion of SVE and pump and treat by late 1994	Groundwater			Pump and treat
South Andover Sites, Andover, MN	8	Work plans under review by U.S. EPA	Groundwater	Arsenic, chromium, lead, VOCs, PCE. TCE.	MCLs	Pump and treat
		and MPCA	Soil	toluene, organics, PCBs, antimony, PAHs	PCBs to 2 ppm antimony to 25 ppm PAHs to 4 ppm	
Long Prairie Site, Long Prairie, MN	-	Remedial design completed and bidding in progress	Groundwater	VOCs, 1,2-DCE, PCE, TCE	NA	Pump and treat
Mason County Landfill, Pere Marquette Twp.,	-	NA	Groundwater	VOCs, benzene, PCE, TCE, xylene	NA	Cap
U.S. Aviex, Niles, MI	8	Construction completed in fiscal year 1993, remedial action operation and function demonstration in fiscal year 1994	Groundwater	Ethyl ether	Meet site specific standards based on state regulations	Pump and treat
			Soil	TCA, TCE, PCE	NA	Soil flushing

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
A&F Materials, Greenup, IL	ო	Remedial action completed, continued monitoring	Groundwater	Sulfates, inorganics, TCE, metals	Meet drinking water MCLs	Monitor
Region VI						
Petro-Chemicals, Liberty, TX	2	Remedial design	Soil	VOCs, PAHs, benzene, naphthalene	PAHs < 100 ppm	Excavate, on-site storage
Geneva Industries, Houston, TX	2	NA	Soil	VOCs, PAHs, TCE, PCBs, phenols, fuel oils	PAHs to 100 ppm	Excavate, off-site disposal, cap
			Groundwater		NA	Slurry wall, pump and treat
Sikes Disposal Pit, Crosby, TX	7	NA	Soil, sludge	Organics, toluene, creosote, benzene, DCA, phenolics, halides, VC,	NA	Excavate, on-site incineration, on-site ash disposal
			Groundwater	xylene	NA -	Ban use
Sand Springs Petro- Chemical Complex, Sand Springs, OK	က	NA .	Soli, sludge	Organic solvents, heavy metals	NA	Excavate, on-site thermal destruction, or off-site thermal destruction
		No action	Groundwater	NA	N/A	N/A
Brio Refinery Co., Inc., Friendswood, TX	7	Remedial action	Soil, sludge	DCA, MC, 1,1,2-TCA, phenanthrene, fluoranthene	NA	Excavate, incineration, or biological
	i					treatment
Region VII						

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
Des Moines TCE, Des Moines, IA	· <del>-</del>	On-going remedial action (6th year)	Groundwater	TCE, PCE, DCE, VC	MCLS, TCE to 0.5 ppb	Pump and treat, air stripping
Big River Sand Co., Wichita, KS	8	No action	Soil	VOCs, toluene	N/A	N/A
		No action, 5 year review	Groundwater	Arsenic, lead, selenium, toluene	N/A	Monitor
Region VIII						
Rocky Mountain Arsenal, Commerce City, CO		Remedial action	- Groundwater	Organic solvents, TCE, PCE, TCA, DCA, 1,1- DCE, trans-1,2-DCE, VC	"NA	Well treatment
Marshall Landfill, Boulder, CO	က	NA	Groundwater	1,2-DCE, cadmium, TCE, PCE, 1,1-DCE, trans-1,2- DCE	NA	Pump and treat
Region IX						
Stringfellow Acid Pits, Riverside, CA	က	Remedial action	Groundwater	VOCs, TCE, organics, inorganics, metals	Not established	Slurry wall, extraction wells
			Sludge, soil			Excavate, off-site disposal, cap
Phoenix-Goodyear Airport Area, Goodyear, AZ		Remedial action	Groundwater	DCE TCE chromium MEK acetone	7 ppb 5 ppb 50 ppb 350 ppb 700 ppb	Pump and treat
San Fernando Valley - Area 1, Los Angeles, CA	-	Interim groundwater action	Groundwater	TCE, PCE	Not established	Pump and treat

TABLE A-1. (Continued)

Site name	Category*	Status	Matrix	Contaminants	Cleanup goals	Technology
San Gabriel Valley - Area 1, El Monte, CA	<b>-</b>	Interim RODs, source remediation	Groundwater	TCE, PCE, chlorinated hydrocarbons, TCA, carbon tetrachloride	Not established	Well treatment, air stripping or carbon absorption
Region X		,				
Colbert Landfill, Colbert, WA	-	Final phase, construction of air stripper expected to be completed by January 1994	Groundwater	Organic solvents, MC, VOCs, 1,1-TCA, 1,1- DCE, DCA, TCE, PCE	MCLs	Pump and treat
Ponders Corner, Lakewood, WA	-	Operation and maintenance phase	Groundwater	TCE PCE 1,2-DCE	5 ppb 5 ppb 70 ppb	Well treatment
			Soil	PCE	500 ppb	Excavate, treat, SVE
Western Processing, Kent, WA	ო	Extracting and treating groundwater	Drummed liquids and waste piles	1,2-DCE, chloroform, benzene, 1,2-DCA, TCE, phenol, arsenic, cadmium, cyanides	1,2-DCE to 70 ppb	Off-site disposal or incineration

Category Codes:

1 = Solvents
2 = Solvents and organics
3 = Solvents, organics, and inorganics

N/A = Not applicable NA = Not available

Acronym list can be found on page ix of document.

### REFERENCES

- ATTIC On-line System--Alternative Treatment Technology Information Center, Computerized Database and Electronic Bulletin Board on Treatment of Contaminated Materials. Information: J.Perdek, U.S. EPA, (908) 321-4380; Modem Access: (301) 670-3808.
- CERCLIS On-line System--Comprehensive Environmental Response, Compensation, and Liability Information System, Computerized Database. Information: M.Cullen, U.S. EPA, (703) 603-8730; Modem Access for U.S. EPA staff only.
- 3. RODS On-line System--Records of Decision System, Computerized Database and Electronic Bulletin Board. Information: M.Cullen, U.S. EPA, (703) 603-8730; Modern Access for U.S. EPA staff only.